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# Inorganic Reactions and Methods

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Volume 4

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# Inorganic Reactions and Methods

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# Inorganic Reactions and Methods

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## Volume 4

**The Formation of Bonds to  
Halogens (Part 2)**

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**J.J. Zuckerman**

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# How to Use this Book

## 1. Organization of Subject Matter

### 1.1. Logic of Subdivision and Add-On Chapters

This volume is part of a series that describes all of inorganic reaction chemistry. The contents are subdivided systematically and so are the contents of the entire series: Using the periodic system as a correlative device, it is shown how bonds between pairs of elements can be made. Treatment begins with hydrogen making a bond to itself in  $H_2$  and proceeds according to the periodic table with the bonds formed by hydrogen to the halogens, the groups headed by oxygen, nitrogen, carbon, boron, beryllium and lithium, to the transition and inner-transition metals and to the members of group zero. Next it is considered how the halogens form bonds among themselves and then to the elements of the main groups VI to I, the transition and inner-transition metals and the zero-group gases. The process repeats itself with descriptions of the members of each successive periodic group making bonds to all the remaining elements not yet treated until group zero is reached. At this point all actual as well as possible combinations have been covered.

The focus is on the primary formation of bonds, not on subsequent reactions of the products to form other bonds. These latter reactions are covered at the places where the formation of those bonds is described. Reactions in which atoms merely change their oxidation states are not included, nor are reactions in which the same pairs of elements come together again in the product (for example, in metatheses or redistributions). Physical and spectroscopic properties or structural details of the products are not covered by the reaction volumes which are concerned with synthetic utility based on yield, economy of ingredients, purity of product, specificity, etc. The preparation of short-lived transient species is not described.

While in principle the systematization described above could suffice to deal with all the relevant material, there are other topics that inorganic chemists customarily identify as being useful in organizing reaction information and that do not fit into the scheme. These topics are the subject of eight additional chapters constituting the last four books of the series. These chapters are systematic only within their own confines. Their inclusion is based on the best judgment of the Editorial Advisory Board as to what would be most useful currently as well as effective in guiding the future of inorganic reaction chemistry.

## **1.2. Use of Decimal Section Numbers**

The organization of the material is readily apparent through the use of numbers and headings. Chapters are broken down into divisions, sections and subsections, which have short descriptive headings and are numbered according to the following scheme:

- 1. Major Heading
- 1.1. Chapter Heading
- 1.1.1. Division Heading
- 1.1.1.1. Section Heading
- 1.1.1.1.1. Subsection Heading

Further subdivision of a five-digit “slice” utilizes lower-case Roman numerals in parentheses: (i), (ii), (iii), etc. It is often found that as a consequence of the organization, cognate material is located in different chapters but in similarly numbered pieces, i.e., in parallel sections. Section numbers, rather than page numbers, are the key by which the material is accessed through the various indexes.

## **1.3. Building of Headings**

### **1.3.1. Headings Forming Part of a Sentence**

Most headings are sentence-fragment phrases which constitute sentences when combined. Usually a period signifies the end of a combined sentence. In order to reconstitute the context in which a heading is to be read, superior-rank titles are printed as running heads on each page. When the sentences are put together from their constituent parts, they describe the contents of the piece at hand. For an example, see 2.3 below.

### **1.3.2. Headings Forming Part of an Enumeration**

For some material it is not useful to construct title sentences as described above. In these cases hierarchical lists, in which the topics are enumerated, are more appropriate. To inform the reader fully about the nature of the material being described, the headings of connected sections that are superior in hierarchy always occur as running heads at the top of each page.

## **2. Access and Reference Tools**

### **2.1. Plan of the Entire Series (Front Endpaper)**

Printed on the inside of the front cover is a list, compiled from all 18 reaction volumes, of the major and chapter headings, that is, all headings that

are preceded by a one- or two-digit decimal section number. This list shows in which volumes the headings occur and highlights the contents of the volume that is at hand by means of a gray tint.

## 2.2. Contents of the Volume at Hand

All the headings, down to the title of the smallest decimal-numbered subsection, are listed in the detailed table of contents of each volume. For each heading the table of contents shows the decimal section number by which it is preceded and the number of the page on which it is found. Beside the decimal section numbers, successive indentations reveal the hierarchy of the sections and thereby facilitate the comprehension of the phrase (or of the enumerative sequence) to which the headings of hierarchically successive sections combine. To reconstitute the context in which the heading of a section must be read to become meaningful, relevant headings of sections superior in hierarchy are repeated at the top of every page of the table of contents. The repetitive occurrences of these headings is indicated by the fact that position and page numbers are omitted.

## 2.3. Running Heads

In order to indicate the hierarchical position of a section, the top of every page of text shows the headings of up to three connected sections that are superior in hierarchy. These running heads provide the context within which the title of the section under discussion becomes meaningful. As an example, the page of Volume 1 on which section 1.4.9.1.3 “in the Production of Methanol” starts, carries the running heads:

- 1.4. The Formation of Bonds between Hydrogen and O,S,Se,Te,Po
- 1.4.9. by Industrial Processes
- 1.4.9.1. Involving Oxygen Compounds

whereby the phrase “in the Production of Methanol” is put into its proper perspective.

## 2.4. List of Abbreviations

Preceding the indexes there is a list of those abbreviations that are frequently used in the text of the volume at hand or in companion volumes. This list varies somewhat in length from volume to volume; that is, it becomes more comprehensive as new volumes are published.

Abbreviations that are used incidentally or have no general applicability are not included in the list but are explained at the place of occurrence in the text.

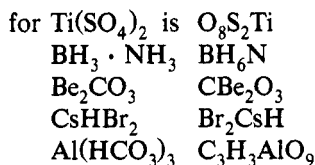
## 2.5. Author Index

The author index is compiled by computer from the lists of references. Thus it tells whose publications are cited and in that respect is comprehensive. It is not a list of authors, beyond those cited in the references, whose results are reported in the text. However, as the references cited are leading ones, consulting them, along with the use of appropriate works of the secondary literature, will rapidly lead to the complete literature related to any particular subject covered.

Each entry in the author index refers the user to the appropriate section number.

## 2.6. Compound Index

The compound index lists individual, fully specified compositions of matter that are mentioned in the text. It is an index of empirical formulas, ordered according to the following system: the elements within a given formula occur in alphabetical sequence except for C, or C and H if present, which always come first. Thus, the empirical formula



The formulas themselves are ordered alphanumerically without exception; that is, the formulas listed above follow each other in the sequence  $\text{BH}_6\text{N}$ ,  $\text{Br}_2\text{CsH}$ ,  $\text{CBe}_2\text{O}_3$ ,  $\text{C}_3\text{H}_3\text{AlO}_9$ ,  $\text{O}_8\text{S}_2\text{Ti}$ .

A compound index constructed by these principles tells whether a given compound is present. It cannot provide information about compound classes, for example, all aluminum derivatives or all compounds containing phosphorus.

In order to open this route of access as well, the compound index is augmented by successively permuted versions of all empirical formulas. Thus the number of appearances that an empirical formula makes in the compound index is equal to the number of elements it contains. As an example,  $\text{C}_3\text{H}_3\text{AlO}_9$ , mentioned above, will appear as such and, at the appropriate positions in the alphanumeric sequence, as  $\text{H}_3\text{AlO}_9^*\text{C}_3$ ,  $\text{AlO}_9^*\text{C}_3\text{H}_3$  and  $\text{O}_9^*\text{C}_3\text{H}_3\text{Al}$ . The asterisk identifies a permuted formula and allows the original formula to be reconstructed by shifting to the front the elements that follow the asterisk.

Each nonpermuted formula is followed by linerarized structural formulas that indicate how the elements are combined in groups. They reveal the connectivity of the compounds underlying each empirical formula and serve to

distinguish substances which are identical in composition but differ in the arrangement of elements (isomers). As an example, the empirical formula  $C_4H_{10}O$  might be followed by the linearized structural formulas  $(CH_3CH_2)_2O$ ,  $CH_3(CH_2)_2OCH_3$ ,  $(CH_3)_2CHOCH_3$ ,  $CH_3(CH_2)_3OH$ ,  $(CH_3)_2CHCH_2OH$  and  $CH_3CH_2(CH_3)CHOH$  to identify the various ethers and alcohols that have the element count  $C_4H_{10}O$ .

Each linearized structural formula is followed in a third column by keywords describing the context in which it is discussed and by the number(s) of the section(s) in which it occurs.

## 2.7. Subject Index

The subject index provides access to the text by way of methods, techniques, reaction types, apparatus, effects and other phenomena. Also, it lists compound classes such as organotin compounds or rare-earth hydrides which cannot be expressed by the empirical formulas of the compound index.

For multiple entries, additional keywords indicate contexts and thereby avoid the retrieval of information that is irrelevant to the user's need.

Again, section numbers are used to direct the reader to those positions in the book where substantial information is to be found.

## 2.8. Periodic Table (Back Endpaper)

Reference to periodic groups avoids cumbersome enumerations. Section headings in the series employ the nomenclature.

Unfortunately, however, there is at the present time no general agreement on group designations. In fact, the scheme that is most widely used (combining a group number with the letters A and B) is accompanied by two mutually contradictory interpretations. Thus, titanium may be a group IVA or group IVB element depending on the school to which one adheres or the part of the world in which one resides.

In order to clarify the situation for the purposes of the series, a suitable labeled periodic table is printed on the inside back cover of each volume. All references to periodic group designations in the series refer to this scheme.

## Preface to the Series

**Inorganic Reactions and Methods** constitutes a closed-end series of books designed to present the state of the art of synthetic inorganic chemistry in an unprecedented manner. So far, access to knowledge in inorganic chemistry has been provided almost exclusively using the elements or classes of compounds as starting points. In the first 18 volumes of **Inorganic Reactions and Methods**, it is bond formation and type of reaction that form the basis of classification.

This new route of access has required new approaches. Rather than sewing together a collection of review articles, a framework has had to be designed that reflects the creative potential of the science and is hoped to stimulate its further development by identifying areas of research that are most likely to be fruitful.

The reaction volumes describe methods by which bonds between the elements can be formed. The work opens with hydrogen making a bond to itself in  $H_2$  and proceeds through the formation of bonds between hydrogen and the halogens, the groups headed by oxygen, nitrogen, carbon, boron, beryllium and lithium to the formation of bonds between hydrogen and the transition and inner-transition metals and elements of group zero. This pattern is repeated across the periodic system until all possible combinations of the elements have been treated. This plan allows most reaction topics to be included in the sequence where appropriate. Reaction types that do not arise from the systematics of the plan are brought together in the concluding chapters on oxidative addition and reductive elimination, insertions and their reverse, electron transfer and electrochemistry, photochemical and other energized reactions, oligomerization and polymerization, inorganic and bioinorganic catalysis and the formation of intercalation compounds and ceramics.

The project has engaged a large number of the most able inorganic chemists as Editorial Advisors creating overall policy, as Editorial Consultants designing detailed plans for the subsections of the work, and as authors whose expertise has been crucial for the quality of the treatment. The conception of the series and the details of its technical realization were the subject of careful planning for several years. The distinguished chemists who form the Editorial Advisory Board have devoted themselves to this exercise, reflecting the great importance of the project.

It was a consequence of the systematics of the overall plan that publication of a volume had to await delivery of its very last contribution. Thus was the defect side of the genius of the system revealed, as the excruciating process of extracting the rate-limiting manuscripts began. Intense editorial effort was

required in order to bring forth the work in a timely way. The production process had to be designed so that the insertion of new material was possible up to the very last stage, enabling authors to update their pieces with the latest developments. The publisher supported the cost of a computerized bibliographic search of the literature and a second one for updating.

Each contribution has been subjected to an intensive process of scientific and linguistic editing in order to homogenize the numerous individual pieces, as well as to provide the highest practicable density of information. This had several important consequences. First, virtually all semblances of the authors' individual styles have been excised. Second, it was learned during the editorial process that greater economy of language could be achieved by dropping conventionally employed modifiers (such as *very*) and eliminating italics used for emphasis, quotation marks around nonquoted words, or parentheses around phrases, the result being a gain in clarity and readability. Because the series focuses on the chemistry rather than the chemical literature, the need to tell who has reported what, how and when can be considered of secondary importance. This has made it possible to bring all sentences describing experiments into the present tense. Information on who published what is still to be found in the reference lists. A further consequence is that authors have been burdened neither with identifying leading practitioners, nor with attributing priority for discovery, a job that taxes even the talents of professional historians of science. The authors' task then devolved to one of describing inorganic chemical reactions, with emphasis on synthetic utility, yield, economy, availability of starting materials, purity of product, specificity, side reactions, etc.

The elimination of the names of people from the text is by far the most controversial feature. Chemistry is plagued by the use of nondescriptive names in place of more expository terms. We have everything from Abegg's rule, Adkin's catalyst, Admiralty brass, Alfven number, the Amadori rearrangement and Adurssov oxidation to the Zdanovskii law, Zeeman effect, Zincke cleavage and Zinin reduction. Even well-practiced chemists cannot define these terms precisely except for their own areas of specialty, and no single source exists to serve as a guide. Despite these arguments, the attempt to replace names of people by more descriptive phrases was met in many cases by a warmly negative reaction by our colleague authors, notwithstanding the obvious improvements wrought in terms of lucidity, freedom from obscurity and obfuscation and, especially, ease of access to information by the outsider or student.

Further steps toward universality are taken by the replacement of element and compound names wherever possible by symbols and formulas, and by adding to data in older units their recalculated SI equivalents. The usefulness of the reference sections has been increased by giving journal-title abbreviations according to the *Chemical Abstracts Service Source Index*, by listing in each reference all of its authors and by accompanying references to patents and journals that may be difficult to access by their *Chemical Abstracts* cita-



tions. Mathematical signs and common abbreviations are employed to help condense prose and a glossary of the latter is provided in each volume. Dangerous or potentially dangerous procedures are highlighted in safety notes printed in boldface type.

The organization of the material should become readily apparent from an examination of the headings listed in the table of contents. Combining the words constituting the headings, starting with the major heading (one digit) and continuing through the major chapter heading (two digits), division heading (three digits), section heading (four digits) to the subsection heading (five digits), reveals at once the subject of a "slice" of the plan. Each slice is a self-contained unit. It includes its own list of references and provides definitions of unusual terms that may be used in it. The reader, therefore, through the table of contents alone, can in most instances quickly reach the desired material and derive the information wanted.

In addition there is for each volume an author index (derived from the lists of references) and a subject index that lists compound classes, methods, techniques, apparatus, effects and other phenomena. An index of empirical formulas is also provided. Here in each formula the element symbols are arranged in alphabetical order except that C, or C and H if present, always come first. Moreover, each empirical formula is permuted successively. Each permuted formula is placed in its alphabetical position and cross referenced to the original formula. Therefore, the number of appearances that an empirical formula makes in the index equals the number of its elements. By this procedure all compounds containing a given element come together in one place in the index. Each original empirical formula is followed by a linearized structural formula and keywords describing the context in which the compound is discussed. All indexes refer the user to subsection rather than page number.

Because the choice of designations of groups in the periodic table is currently in a state of flux, it was decided to conform to the practice of several leading inorganic texts. To avoid confusion an appropriately labeled periodic table is printed on the back endpaper.

From the nature of the work it is obvious that probably not more than two persons will ever read it entire: myself and the publisher's copy editor, Dr. Lindsay S. Ardwin. She, as well as Ms. Mary C. Stradner, Production Manager of VCH Publishers, are to be thanked for their unflagging devotion to the highest editorial standards. The original conception for this series was the brainchild of Dr. Hans F. Ebel, Director of the Editorial Department of VCH Verlagsgesellschaft in Weinheim, Federal Republic of Germany, who also played midwife at the birth of the plan of these reaction volumes with my former mentor, Professor Alan G. MacDiarmid of the University of Pennsylvania, and me in attendance, during the Anaheim, California, American Chemical Society Meeting in the Spring of 1978. Much of what has finally emerged is the product of the inventiveness and imagination of Professor Helmut Gr newald, President of VCH Verlagsgesellschaft. It is a pleasure to

acknowledge that I have learned much from him during the course of our association. Ms. Nancy L. Burnett is to be thanked for typing everything that had to do with the series from its inception to this time. Directing an operation of this magnitude without her help would have been unimaginable. My wife Rose stood by with good cheer while two rooms of our home filled up with 10,000 manuscript pages, their copies and attendant correspondence.

Finally, and most important, an enormous debt of gratitude toward all our authors is to be recorded. These experts were asked to prepare brief summaries of their knowledge, ordered in logical sequence by our plan. In addition, they often involved themselves in improving the original conception by recommending further refinements and elaborations. The plan of the work as it is being published can truly be said to be the product of the labors of the advisors and consultants on the editorial side as well as the many, many authors who were able to augment more general knowledge with their own detailed information and ideas. Because of the unusually strict requirements of the series, authors had not only to compose their pieces to fit within narrowly constrained limits of space, format and scope, but after delivery to a short deadline were expected to stand by while an intrusive editorial process homogenized their own prose styles out of existence and shrank the length of their expositions. These long-suffering colleagues had then to endure the wait for the very last manuscript scheduled for their volume to be delivered so that their work could be published, often after a further diligent search of the literature to insure that the latest discoveries were being cited and that claims for facts now proved false were eliminated. To these co-workers (270 for the reaction volumes alone), from whom so much was demanded but who continued to place their knowledge and talents unstintingly at the disposal of the project, we dedicate this series.

J. J. ZUCKERMAN  
Norman, Oklahoma  
July 4, 1985

The scientific community is appreciative of the JJZ vision for a systematic inorganic chemistry. Many of the contributions had been edited prior to his death; therefore, his precise syntax will remain an important part of the series.

A.P. HAGEN  
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August 10, 1990

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## **2.0. The Formation of Bonds to Halogens (Part 2)**

## Abbreviations

abs	absolute
a.c.	alternating current
Ac	acetyl, $\text{CH}_3\text{CO}$
acac	acetylacetonate anion
acacH	acetylacetone, $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CH}_3$
AcO	acetate anion, $\text{CH}_3\text{C}(\text{O})\text{O}$
Ad	adamantyl
ads	adsorbed
AIBN	2,2'-azobis(isobutyronitrile), $2,2'-[(\text{CH}_3)_2\text{CCN}]_2\text{N}_2$
Alk	alkyl
am	amine
amt	amount
Am	amyl, $\text{C}_5\text{H}_{11}$
amu	atomic mass unit
anhyd	anhydrous
aq	aqueous
Ar	aryl
asym	asymmetrical, asymmetric
at	atom (not atomic, except in atomic weight)
atm	atmosphere (not atmospheric)
av	average
BBN	9-Borabicyclo[3.3.1]nonane
bcc	body-centered cubic
BD	butadiene
bipy	2,2'-bipyridyl
bipyH	protonated 2,2'-bipyridyl
bp	boiling point
Bu	butyl, $\text{C}_4\text{H}_9$
Bz	benzyl, $\text{C}_6\text{H}_5\text{CH}_2$
c-	cyclo (used in formulas)
ca.	circa, about, approximately
catal	catalyst (not catalyzing, catalysis, catalyzed, etc.)
CDT	cyclododecatriene
cf.	compare
Ch.	chapter
CHD	1,3-cycloheptadiene
Chx	cyclohexyl
ChxD	1,3-cyclohexadiene
CI	configuration interaction
Cob	cobalamine
COD	cyclooctadiene
COE	cyclooctene
conc	concentrated (not concentration)
const.	constant
COT	cyclooctatriene
COTe	cyclooctatetraene
Cp	cyclopentadienyl, $\text{C}_5\text{H}_5$
CPE	controlled-potential electrolysis

cpm	counts per minute
CT	charge-transfer
CV	cyclic voltammetry
CVD	chemical vapor deposition
CW	continuous wave
d	day, days
DABIP	N,N'-diisopropyl-1,4-diazabutadiene
DBA	dibenzylideneacetone
d.c.	direct current
DCM	dicyclopentadienylmethane
DCME	$\text{Cl}_2\text{CHC}(\text{O})\text{CH}_3$
DCP	1,3-dicyclopentadienylpropane
DDT	dichlorodiphenyltrichloroethane, 1,1,1',-trichloro-2,2-bis-(4-chlorophenyl)ethane
dec	decomposed
DED	1,1-bis(ethoxycarbonyl)ethene-2,2-dithiolate, $[(\text{H}_5\text{C}_2\text{OC}(\text{O}))_2\text{C}=\text{CS}_2]^2$
depe	1,2-bis(diphenylphosphino)ethene, $(\text{C}_6\text{H}_5)_2\text{PCH}=\text{CHP}(\text{C}_6\text{H}_5)_2$
DIAD	diindenylanthracenyl
diars	1,2-bis(dimethylarsino)benzene, o-phenylenebis(dimethylarsino), 1,2-( $\text{CH}_3$ ) <sub>2</sub> AsC <sub>6</sub> H <sub>4</sub> As( $\text{CH}_3$ ) <sub>2</sub>
dien	diethylenetriamine, $[\text{H}_2\text{N}(\text{CH}_2)_2]_2\text{NH}$
diglyme	diethyleneglycol dimethylether, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})\text{CH}_2$
dil	dilute
diop	2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane, $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}[\text{OCH}(\text{CH}_3)=\text{CH}_2]\text{CH}$ $[\text{OCH}(\text{CH}_3)=\text{CH}_2]\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$
dipda	p-i-PrC <sub>6</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>4</sub> -c-p
diphos	1,2-bis(diphenylphosphino)benzene, 1,2-( $\text{C}_6\text{H}_5$ ) <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> P( $\text{C}_6\text{H}_5$ ) <sub>2</sub>
Div.	division
DMA	dimethylacetamide
dme	dropping mercury electrode
DME	1,2-dimethoxyethane, glyme, $\text{CH}_3\text{O}(\text{CH}_2)_2\text{OCH}_3$
DMF	N,N-dimethylformamide, $\text{HC}(\text{O})\text{N}(\text{CH}_3)_2$
DMG	dimethylglyoxime, $\text{CH}_3\text{C}(=\text{NOH})\text{C}(=\text{NOH})\text{CH}_3$
DMP	1,2-dimethoxybenzene, 1,2-( $\text{CH}_3\text{O}$ ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>
dmpe	1,2-bis(dimethylphosphino)ethane, $(\text{CH}_3)_2\text{P}(\text{CH}_2)_2\text{P}(\text{CH}_3)_2$
DMSO	dimethylsulfoxide, $(\text{CH}_3)_2\text{SO}$
dpam	bis(diphenylarsino)methane, $[(\text{C}_6\text{H}_5)_2\text{As}]_2\text{CH}_2$
dpic	dipicolinate ion
DPP	differential pulse polarography
dppb	1,4-bis(diphenylphosphino)butane, 1,4-( $\text{C}_6\text{H}_5$ ) <sub>2</sub> P( $\text{CH}_2$ ) <sub>4</sub> P( $\text{C}_6\text{H}_5$ ) <sub>2</sub>
dppe	1,2-bis(diphenylphosphino)ethane, 1,2-( $\text{C}_6\text{H}_5$ ) <sub>2</sub> P( $\text{CH}_2$ ) <sub>2</sub> P( $\text{C}_6\text{H}_5$ ) <sub>2</sub>
dppm	bis(diphenylphosphino)methane, $[(\text{C}_6\text{H}_5)_2\text{P}]_2\text{CH}_2$
dppoe	bis(diphenylphosphoryl)ethane
dppp	1,3-bis(diphenylphosphino)propane, 1,3-( $\text{C}_6\text{H}_5$ ) <sub>2</sub> P( $\text{CH}_2$ ) <sub>3</sub> P( $\text{C}_6\text{H}_5$ ) <sub>2</sub>



dptpe	1,2-bis(di-p-tolylphosphino)ethane, 1,2-(4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> P (C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> -4) <sub>2</sub>
DTA	differential thermal analysis
DTBQ	3,5-di-t-butyl-o-benzoquinone
DTH	1,6-dithiahexane, butane-1,4-dithiol, 1,4-HS(CH <sub>2</sub> ) <sub>4</sub> SH
DTS	dithiosquarate
ed.	edition, editor
eds.	editors
EDTA	ethylenediaminetetraacetic acid, [HOC(O)] <sub>2</sub> N(CH <sub>2</sub> ) <sub>2</sub> N[C(O)OH] <sub>2</sub>
e.g.	exempli gratia, for example
EHMO	extended Hückel molecular orbital
emf	electromotive force
en	ethylenediamine, H <sub>2</sub> N(CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub>
enH	protonated ethylenediamine
EPR	electron paramagnetic resonance
equimol	equimolar
equiv	equivalent
EPR	electron paramagnetic resonance
Eq.	equation
ERF	effective reduction factor
ES	excited state
ESR	electron-spin resonance
esu	electrostatic unit
Et	ethyl, CH <sub>3</sub> CH <sub>2</sub>
etc.	et cetera, and so forth
Et <sub>2</sub> O	diethyl ether, (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O
EtOH	ethanol, C <sub>2</sub> H <sub>5</sub> OH
et seq.	et sequentes, and the following
eu	entropy unit
fac	facial
Fc	ferrocenyl
fcc	face-centered cubic
ff.	following
Fig	figure
Fl	fluorenyl
Fp	$\eta^5$ -C <sub>5</sub> H <sub>5</sub> Fe(CO) <sub>2</sub>
fp	freezing point
g	gas
g-at	gram-atom
GLC	gas-liquid chromatography
glyme	1,2-dimethoxyethane, CH <sub>3</sub> O(CH <sub>2</sub> ) <sub>2</sub> OCH <sub>3</sub>
graph	graphite
GS	ground state
h	hour, hours
H-Cob	cobalamine
HD	1,5-hexadiene
hept	heptyl
Hex	hexyl
HMDB	hexamethyl(Dewar benzene)
hmde	hanging mercury drop electrode
MHI	heptamethylindenyl

HMPA	hexamethylphosphoramide, $[(CH_3)_2N]_3PO$
HOMO	highest occupied molecular orbital
HPLC	high-pressure liquid chromatography
i.e.	id est, that is
Im	imidazole
inter alia	among other things
IPC	isopinocampylborane
IR	infrared
irrev	irreversible
ISC	intersystem crossing
isn	isonicotinamide
l	liquid
L	ligand
LC	ligand centered
LF	ligand field
LFER	linear free-energy relationship
liq	liquid
LMCT	ligand-to-metal charge transfer
Ln	lanthanides, rare earths
LSV	linear-scan voltammetry
LUMO	lowest unoccupied molecular orbital
m	meta
max	maximum
M	metal
MC	metal centered
Me	methyl, $CH_3$
Men	menthyl
mes	mesitylene, 1,3,5-trimethylbenzene derivative
MeOH	methanol, $CH_3OH$
mer	meridional; the repeating unit of an oligomer or polymer
mhp	2-hydroxy-6-methylpyridine, 2-HO, 6- $CH_3C_5H_3N$
min	minimum, minute, minutes
MLCT	metal-to-ligand charge transfer
MO	molecular orbital
mol	molar
mp	melting point
MV	methyl viologen, 1,1'-dimethyl-4,4'-bipyridinium dichloride
n.a.	not available
napy	naphthyridine
NBD	norbornadiene, [2.2.1]bicyclohepta-2,5-diene
neg	negative
nhe	normal hydrogen electrode
NMR	nuclear magnetic resonance
No.	number
np	tris-[2-(diphenylphosphino)ethyl]amine, $N[CH_2CH_2P(C_6H_5)_2]_3$
Np	naphthyl
Nuc	nucleophile
NPP	normal pulse polarography
NQR	nuclear quadrupole resonance
NTA	nitritotriacetate
o	ortho
obs	observed

Oct	octyl
ocp	octaethylporphyrin
O <sub>F</sub>	oxidation factor
O <sub>h</sub>	octahedral
Oq	oxyquinolate
ox.	oxidation
p	para
p.	page
P	pressure
Pat.	patent
pet.	petroleum
Ph	phenyl, C <sub>6</sub> H <sub>5</sub>
phen	1,10-phenanthroline
Ph <sub>2</sub> PPy	2-(diphenylphosphino)pyridine, 2-(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PC <sub>5</sub> H <sub>4</sub> N
pip	piperidine, C <sub>5</sub> H <sub>10</sub> N
PMDT	pentamethyldiethylenetriamine, (CH <sub>3</sub> ) <sub>2</sub> N(CH <sub>2</sub> ) <sub>2</sub> N(CH <sub>3</sub> )(CH <sub>2</sub> ) <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub>
PMR	proton magnetic resonance
pn	propylene-1,3-diamine, 1,3-H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>
pos	positive
Po-tol <sub>3</sub>	tri-o-tolylphosphine
pp.	pages
ppb	parts per billion
ppm	parts per million
ppn	bis(diphenylphosphino)amine, [(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P] <sub>2</sub> NH
ppt	precipitate
Pr	propyl, C <sub>3</sub> H <sub>7</sub>
PSS	photostationary state
PVC	poly(vinyl chloride)
py	pyridine, C <sub>5</sub> H <sub>5</sub> N
pyr	pyrazine
pz	pyrazolyl
PZE	potential of zero charge
rac	racemic mixture, racemate
R	organic group; universal gas constant
RDE	rotated disk electrode
RE	rare earths, lanthanides
red.	reduction
Redox	reduction-oxidation reactions
ref.	reference
rev	reversible
rf	radiofrequency
RF	reduction factor
R <sub>F</sub>	R group with substituted F
rh	rhombohedral
rms	root mean square
rpm	revolutions per minute
RT	room temperature
s	second, seconds; solid
sce	saturated calomel electrode
SCE	standard calomel electrode
sec	secondary
Sep	sepulcrate, 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]heicosane

Sia	Diisamyl
SMAD	solvated metal-atom dispersed
soln	solution
solv	solvated
sp	specific
STP	standard temperature and pressure
subl	sublimes
Suppl.	supplement
sym	symmetrical, symmetric
t	time; tertiary
T	temperature
T <sub>d</sub>	tetrahedral
TCNE	tetracyanoethylene
TEA	tetraethylammonium ion, [(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N] <sup>+</sup>
terpy	2,2',2''-terpyridyl
tetraphos	Ph <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> PPhCH <sub>2</sub> CH <sub>2</sub> PPhCH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub>
TGA	thermogravimetric analysis
TGL	triethyleneglycol dimethylether
THF	tetrahydrofuran
THP	tetrahydropyran
THT	tetrahydrothiophene
Thx	thexyl
TLC	thin-layer chromatography
TMED	N,N,N',N'-tetramethylethylenediamine, (CH <sub>3</sub> ) <sub>2</sub> N(CH <sub>2</sub> ) <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub>
tmen	N,N,N',N'-tetramethylethylenediamine
TMP	2,2,6,6-tetramethylpiperidyl
TMPH	2,2,6,6-tetramethylpiperidine, 2,2,6,6-(CH <sub>3</sub> ) <sub>4</sub> C <sub>5</sub> H <sub>7</sub> N
Tol	tolyl, C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> , p-tolyl
Tos	tosyl, tolylsulfonyl, 4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub>
TPA	tetraphenylarsonium ion, [(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> As] <sup>+</sup>
TPPO	triphenylphosphineoxide
triars	bis-[-(dimethylarsino)phenyl]methylarsine, [2-(CH <sub>3</sub> ) <sub>2</sub> AsC <sub>6</sub> H <sub>4</sub> ] <sub>2</sub> AsCH <sub>3</sub>
triphos	1,1,1-tris(diphenylphosphinomethyl)ethane, [(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PCH <sub>2</sub> ] <sub>3</sub> CCH <sub>3</sub>
trien	triethylenetetraamine, H <sub>2</sub> N(CH <sub>2</sub> ) <sub>2</sub> NH(CH <sub>2</sub> ) <sub>2</sub> NH(CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub>
UV	ultraviolet
v	vicinal
Vi	(E)-[2-(CH <sub>3</sub> ) <sub>2</sub> NCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ] <sub>2</sub> C=C(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> -4
viz.	videlical, that is to say, namely
vol., Vol.	volume
VPE	vapor-phase epitaxy
vs.	versus
wk.	week
wt	weight
X	halogen or pseudohalogen
xs	excess
Y	often used for S, Se
yr.	year
§	section
η	hapto designator

## 2.6. The Formation of the Halogen–Group-IIIB Element (B, Al, Ga, In, Tl) Bond

### 2.6.1. Introduction

Group-IIIB halides are a common starting material for many group-IIIB compounds. These bonds can be formed from the elements or from other bonds.

(A. P. HAGEN)

### 2.6.2. from the Elements.

The powerful oxidizing ability of the elemental halogens, coupled with the relatively strong element–halogen bonds that form (see Table 1), results in a general method for the formation of group-IIIB halides.

The dissociation energy of  $F_2$  is low ( $158.8 \text{ kJ mol}^{-1}$ ; cf.  $Cl_2$ , 242.6) but the E–F bond energies are large. Thus, fluorinations of the elements occur generally and, in theory,  $F_2$  may be employed to prepare any binary fluoride. The preparation of  $AlF_3$ , e.g., dates back to the turn of the century, when it was found that while there was slight attack of the metal by the halogen in the cold, complete reaction occurred on heating. When fluorine reacts with Tl the metal becomes incandescent<sup>1</sup>.

The preference of occurrence in the reactions between the group-IIIB element and the halogen is exemplified by the reactions of boron. Even though there may be uncertainties in the purity and crystallinity of the boron employed, it is clear that  $F_2$  attacks at ordinary T in an exothermic reaction, while  $Cl_2$ ,  $Br_2$  and  $I_2$  require 700, 1000 and 1500 K. respectively. The direct synthesis is used<sup>2</sup> to produce  $BBr_3$ . While this procedure has been developed more for the purification of commercial boron,  $BBr_3$  may be trapped and distilled, a preparation that is feasible and convenient for relatively large quantities<sup>3</sup>. The halides  $BX_3$  ( $X = Cl, Br, I$ ) may be prepared via this direct interaction at high T and these syntheses may be extended to include the use of metal borides, boron nitride or boron carbide as the source of elemental boron in specialist applications (e.g., boron recovery from alloys, manufacture of electronic components)<sup>3</sup>.

TABLE 1. BOND ENERGIES FOR GROUP-IIIB HALIDES ( $\text{kJ mol}^{-1}$ )<sup>a</sup>

E	E–F	E–Cl	E–Br	E–I
B	646	444	368	267
Al	582	427	360	285
Ga		473	339?	
In		427	176?	
Tl		377	326	

<sup>a</sup> Refs. 7–10.

TABLE 2. ELEMENTAL COMBINATIONS FOR Al, Ga AND In HALIDES

Product	Reaction conditions	Ref.
AlCl <sub>3</sub>	Al turnings. Heat in Cl <sub>2</sub> stream	4
AlBr <sub>3</sub>	Excess of dry Al turnings. Add Br <sub>2</sub> ; 370 K	11
AlI <sub>3</sub>	Al turnings; 770-870 K; I <sub>2</sub> sublimed over Al	5
GaCl <sub>3</sub>	Molten Ga, controlled addn. of Cl <sub>2</sub>	2, 15
GaBr <sub>3</sub>	Molten Ga, Br <sub>2</sub> passed through with N <sub>2</sub>	12
GaI <sub>3</sub>	Slight xs molten Ga + I <sub>2</sub> , sealed tube; 630 K	13
InCl <sub>3</sub>	Molten In, Cl <sub>2</sub> in N <sub>2</sub> carrier; ca. 410 K	14
InBr <sub>3</sub>	Similar to InCl <sub>3</sub> , but longer reaction time	14
InI <sub>3</sub>	Stoichiometric In + I <sub>2</sub> , sealed tube; 450 K, or in ether, 12 h	14, 16

Even though gaseous F<sub>2</sub> is available, its direct interaction is not a favored method for preparing group-IIIB fluorides, probably because of the difficulty in controlling the reactions. The other elemental halogens, however, are much more easily controlled in direct combinations and enable the halides of Al, Ga and In to be prepared in high purity and good yields. For example, AlCl<sub>3</sub> may be prepared in this manner. The reaction must be initiated by brief application of heat, but its exothermic nature carries it to completion<sup>2</sup>. On an industrial scale cooling is required. The use of Cl<sub>2</sub> from an electrolytic cell assists in the production of a purer product. The reactions between Al and Br<sub>2</sub> or I<sub>2</sub> also are markedly exothermic<sup>4</sup> and similar combinations of the elements are used to produce AlBr<sub>3</sub> and AlI<sub>3</sub>. The latter may also be produced conveniently in solution<sup>2</sup>. Since decomposition of AlI<sub>3</sub> occurs at relatively low T, the slow sublimation of I<sub>2</sub> over the heated metal is found to yield the purest product<sup>5</sup>. With GaI<sub>3</sub>, however, xs I<sub>2</sub> remains bound to the product and careful procedures are required to obtain the pure solid<sup>6</sup>.

Reaction conditions for the preparation of Al, Ga and In halides via direct combination are given in Table 2.

The Tl(III) halides are best prepared by oxidation from Tl(I). For example, pure Tl is only slowly attacked (weeks) by Br<sub>2</sub>.

(B.D. JAMES)

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## 2.6.3. by Halogenation of the Elements

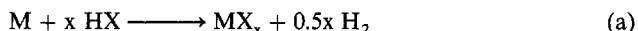
## 2.6.3.1. with Hydrogen Halides.

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## 2.6.3. by Halogenation of the Elements

### 2.6.3.1. with Hydrogen Halides.

Anhydrous hydrogen halides are versatile and vigorous reagents for halogenation of metals:



Since  $\Delta G_f^\circ$  for the hydrogen halides are approximately  $-273$ ,  $-95$ ,  $-53$  and  $+1.7 \text{ kJ mol}^{-1}$  (at 298 K) for HF, HCl, HBr and HI, respectively, the group-IIIB element thermodynamically is capable of being oxidized to  $\text{MX}_3$  if  $\Delta G_f^\circ$  for these compounds is lower than three times these values. In many cases, these occur readily and are exothermic. For example, high-purity  $\text{AlCl}_3$  has been synthesized<sup>1</sup> by passing xs anhyd HCl over good-quality Al metal at 870 K. Similarly, anhyd  $\text{GaF}_3$  is produced<sup>2</sup> when HF in a stream of  $\text{N}_2$  is passed over Ga metal at 825 K. After several hours, the metal becomes coated with a white crystalline crust and the sublimate is the  $\text{GaF}_3$ . This type of reaction is claimed to be the best method<sup>3</sup> for producing  $\text{GaCl}_3$ . Certainly, the reaction of HCl with pure Ga metal proceeds at T as low as 350 K and sublimation to separate the product quantitatively from the reaction zone at higher T makes the method most convenient<sup>4,5</sup>.

While attack on boron by HX has been noted<sup>6</sup> (HF does not attack below dull red heat, HCl attacks at bright red heat and HI requires temperatures  $> 1500 \text{ K}$ ), these reactions are not generally of any synthetic importance, even though the use of borides as an alternative source of boron may offer some advantages under special circumstances<sup>7</sup>. However, atomic vapors (vapor synthesis) have been employed to examine the reactions of boron cocondensed with a number of molecules<sup>8</sup>. At 2800–3000 K and  $10^{-6} \text{ mbar}$  the boron vapor is believed to be largely  $\text{B}_1$  in a  $^2\text{P}$  state. When cocondensed with HX ( $\text{X} = \text{Cl, Br}$ ) the products are  $\text{H}_2$ ,  $\text{BX}_3$ ,  $\text{BHX}_2$  and some  $\text{X}_2$ . This reaction seems to be a free-radical process, involving  $\text{HBX}$ .

With In and Tl metals, attack of HX tends to produce the lower valent metal halides. For example,  $\text{InCl}_2$  and  $\text{TlCl}$  can be formed, respectively, by heating the metals in a stream of dry HCl. Although both  $\text{InBr}_3$  and  $\text{InI}_3$  have been prepared via this type of reaction, it is less convenient than direct interaction of the elements<sup>9</sup>.

Solutions of HX in water are well-known attacking reagents and hydrochloric acid has long been known to attack Al metal. The hexahydrate of  $\text{AlCl}_3$  is obtained by evaporating the solution and the bromide analog may be produced similarly<sup>10</sup>. On the other hand,  $\text{InBr}_3$  is reported to crystallize in the anhydrous state from a solution obtained by dissolving the metal in aq HBr. This preparation is recommended only if large quantities of In are available<sup>11</sup>.

2.6. The Formation of the Halogen (B, Al, Ga, In, Tl) Bond  
 2.6.3. by Halogenation of the Elements  
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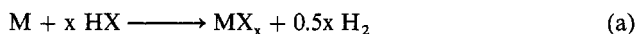
3

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Thallium dissolves in 9% HF to form a TlF soln (which is water soluble), but the metal is attacked only slightly by the other acids because of the formation of a layer of the insoluble Tl(I) halide<sup>12</sup>.

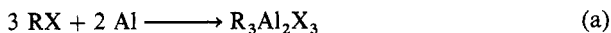
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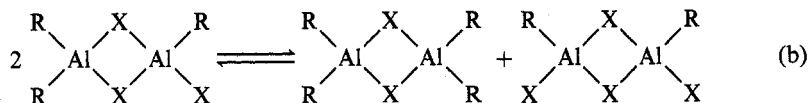
### 2.6.3.2. with Carbon-Halogen Compounds.

The direct interaction of a group-IIIB element with organic halides is important for the synthesis of organoaluminum compounds.

Aluminum metal interacts with organic halides (RX) generally to produce the sesquihalide:



Only a limited number of halides may be prepared in this fashion and the reaction probably does not follow (a) but appears to yield an equilibrium mixture:



with the equilibrium favoring the sesquihalide in many cases. For example,  $\text{C}_2\text{H}_5\text{I}$  reacts with Al metal at 345 K to give liq  $(\text{C}_2\text{H}_5)_3\text{Al}_2\text{I}_3$  from which  $(\text{C}_2\text{H}_5)_2\text{AlI}$  and  $\text{C}_2\text{H}_5\text{AlI}_2$  may be separated by fractional distillation. With iodobenzene, the reaction takes longer<sup>1</sup>.

Activation of the metal may be necessary for this reaction and is even more critical for reactions with RCl and RBr. These reactions are important for preparing Al alkyls on a small scale. Initiation is slow, but **the process is exothermic so a good deal of care is required**. For example, an autoclave is recommended to confine  $\text{C}_2\text{H}_5\text{Cl}$  and  $\text{CH}_3\text{Cl}$  reactions.

For higher alkyl halides, there is a tendency for electron-pair acceptor acid-catalyzed HX elimination reactions to compete, with the HX which is formed cleaving the Al—R bond. Despite this, Al reacts successfully with RX (R = *n*-C<sub>3</sub>H<sub>7</sub>, *n*-C<sub>4</sub>H<sub>9</sub> and *i*-C<sub>4</sub>H<sub>9</sub>;

## 2.6. The Formation of the Halogen (B, Al, Ga, In, Tl) Bond

## 2.6.3. by Halogenation of the Elements

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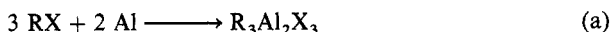
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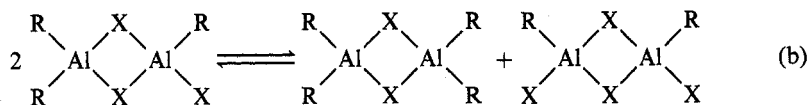
## 2.6.3.2. with Carbon-Halogen Compounds.

The direct interaction of a group-IIIB element with organic halides is important for the synthesis of organoaluminum compounds.

Aluminum metal interacts with organic halides (RX) generally to produce the sesquihalide:



Only a limited number of halides may be prepared in this fashion and the reaction probably does not follow (a) but appears to yield an equilibrium mixture:



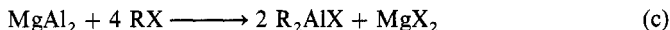
with the equilibrium favoring the sesquihalide in many cases. For example,  $\text{C}_2\text{H}_5\text{I}$  reacts with Al metal at 345 K to give liq  $(\text{C}_2\text{H}_5)_3\text{Al}_2\text{I}_3$  from which  $(\text{C}_2\text{H}_5)_2\text{AlI}$  and  $\text{C}_2\text{H}_5\text{AlI}_2$  may be separated by fractional distillation. With iodobenzene, the reaction takes longer<sup>1</sup>.

Activation of the metal may be necessary for this reaction and is even more critical for reactions with RCl and RBr. These reactions are important for preparing Al alkyls on a small scale. Initiation is slow, but **the process is exothermic so a good deal of care is required**. For example, an autoclave is recommended to confine  $\text{C}_2\text{H}_5\text{Cl}$  and  $\text{CH}_3\text{Cl}$  reactions.

For higher alkyl halides, there is a tendency for electron-pair acceptor acid-catalyzed HX elimination reactions to compete, with the HX which is formed cleaving the Al—R bond. Despite this, Al reacts successfully with RX (R = n-C<sub>3</sub>H<sub>7</sub>, n-C<sub>4</sub>H<sub>9</sub> and i-C<sub>4</sub>H<sub>9</sub>;

X = halide) especially when an ether solvent is employed. Such solvents are especially recommended when R = allyl, benzyl, crotyl and propargyl and X = Br.

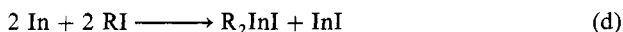
A useful variation is to employ instead an Al alloy. For example, a 70:30 Al:Mg alloy provides the metal in the correct ratio required for the reaction:



Again, activation of the metal seems to be important as also is the use of ether solvents in critical cases with alkyl halides<sup>1</sup>.

More recently, activation of metals has been achieved by means of the reduction of a salt in an ether or hydrocarbon solution using an alkali metal. This method yields a finely divided, highly reactive powder<sup>2</sup>. With Al, the reaction with PhBr is able to take place quantitatively within 5 min at 410 K, whereas with the previous activation method (using AlCl<sub>3</sub> in a ball mill) the conversion to the sesquihalide requires a number of hours. Using similar procedures, highly active In and Tl powders may be obtained.

Activated In reacts with PhI at 420 K over 2 h to give (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>InI almost quantitatively, whereas commercial In powder yields only 30% conversion over 25 h. Other aryl iodides also react at moderate T, giving high yields of organoindium iodides<sup>3</sup>:



Metallic Ga, alkyl iodides and elemental I<sub>2</sub> combine at RT over 1–2 weeks to give RGaI<sub>2</sub> directly. This is a convenient method because "GaI" need not be prepared first<sup>4</sup>.

Another useful technique for inducing the metal to react with formation of a M–X bond is to employ it as an anode in a cell of the type Pt | RX + CH<sub>3</sub>CN | In<sub>+</sub>. Employing voltages in the range 4–30 V and currents 7–35 mA, a range of organoindium compounds may be prepared<sup>5</sup>. If a complexing agent (e.g., 2,2'-bipyridyl) is also present in the solvent, products such as RInX<sub>2</sub>(bipy) may be obtained. With a tetraalkylammonium halide in place of bipy, compounds of the type [R'<sub>4</sub>N][RInX<sub>3</sub>] are obtained. This method appears to have great scope for preparations on the laboratory scale. First, it does not require separate activation of the metal and, second, other useful variations may be introduced by changing the solution phase employed. For example, electrolysis of a benzene-methanol solution of [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]Cl containing a low concentration of Cl<sub>2</sub> produces gram quantities of [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>2</sub>InCl<sub>5</sub><sup>6</sup>.

Elemental boron, benzene and bromine combine to give C<sub>6</sub>H<sub>5</sub>BBr<sub>2</sub> in the presence of a Ni catalyst<sup>7</sup>. In studies of the reactivity of boron, it has been shown that while CCl<sub>4</sub> yields BCl<sub>3</sub> on reaction with the element at 470–520 K, C<sub>2</sub>Cl<sub>4</sub> reacts less readily and hexachlorobenzene not at all<sup>8</sup>. Dibromoethane and tribromohydrin react with boron in sealed tubes to form a good deal of BBr<sub>3</sub>. The vapor synthesis method<sup>9</sup> appears to offer scope for small-scale investigations of more reactions of this type. Despite its surface oxide layer, Al is also attacked by CCl<sub>4</sub> at a significant rate, yielding AlCl<sub>3</sub> via a radical process<sup>10</sup>.

(B.D. JAMES)

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### 2.6.3.3. with Other Halides.

The exchange of a group that is bonded to a relatively electronegative element onto another of lower electronegativity is a reaction of great utility, especially on the laboratory scale, and many important compounds may be prepared conveniently via this procedure. Halogen may be transferred this way and the electronegativities of the lighter group-IIIB elements lend themselves to this method for the preparation of their halides.

Thus, anhyd  $\text{ZnCl}_2$  reacts quantitatively with Al ( $\chi_{\text{Zn}} = 1.6$ ,  $\chi_{\text{Al}} = 1.5$ ) while anhyd  $\text{MgCl}_2$  does not react ( $\chi_{\text{Mg}} = 1.2$ ). Reaction of Al with  $\text{HgCl}_2$  is so energetic that excess of Al melts<sup>1</sup>. Heating  $\text{PbCl}_2$ ,  $\text{Cu}_2\text{Cl}_2$  or  $\text{AgCl}$  with an xs Al in a glass tube causes  $\text{AlCl}_3$  to volatilize. This appears to be a very convenient route for obtaining small amounts of electron-pair acceptor catalyst because the fresh  $\text{AlCl}_3$  may be distilled directly into the reaction vessel<sup>2</sup>. Similarly, the method is applicable<sup>3</sup> to Ga. The metal, warmed with  $\text{AgBr}$  or  $\text{PbBr}_2$ , yields  $\text{GaBr}_3$ . While the use of the solid heavy-metal halide reagents is a convenient procedure, the vapors of the perhaps less conveniently employed halides of phosphorus or sulfur, for example, may also be employed<sup>1</sup>.

Despite its generally inert character, solid boron will react with silver or copper(I) halides on heating (720–970 K) under vacuum to give good yields of the boron halides. Optimum yields (ca. 70%) for  $\text{BCl}_3$  may be obtained from stoichiometric quantities of the reagents at 920 K. This method is useful for preparing small amounts of radioactively labeled volatile halides with high specific activities<sup>4,5</sup>. **Silver fluoride and boron, however, are reported to detonate on contact.** The reaction of boron with  $\text{GeCl}_4$  has been studied between 820 and 1370 K, but largely in the context of producing low-valent species. Boron trichloride and Ge,  $\text{GeCl}_2$  or  $\text{GeCl}$  are formed, depending on the temperature employed<sup>6</sup>. The vapor synthesis technique shows some promise for studying unusual reactions. Boron atoms and  $\text{PCl}_3$  yield some  $\text{BCl}_3$  and  $\text{P}_2\text{Cl}_4$  in this type of experiment, although it is noted that the cocondensation technique is essential for the reaction of boron atoms<sup>7</sup>.

Nitrosyl chloride attacks aluminum quite vigorously but the reaction with Al strip is more easily controlled and after some hours a red syrup is formed. On removing xs  $\text{ONCl}$ , the yellow  $[\text{NO}][\text{AlCl}_4]$  is obtained. Similarly,  $\text{ONCl}$  reacts vigorously with Ga metal, but in both cases this preparation of the salt is not the most convenient one. As expected, the attack on In and Tl becomes progressively slower, thallium being attacked only sluggishly over 5 d at 383 K.

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6            2.6. The Formation of the Halogen (B, Al, Ga, In, Tl) Bond  
               2.6.3. by Halogenation of the Elements  
               2.6.3.3. with Other Halides.

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## 2.6.4. from Halogenation of Anionic Group-IIIB Clusters

### 2.6.4.1. by Elemental Halogens.

Direct halogenation of anionic cluster compounds is a proven method for introducing halogens into boron hydride ions<sup>1</sup>. Most work has been performed on the easily prepared  $[\text{B}_{10}\text{H}_{10}]^{2-}$  and  $[\text{B}_{12}\text{H}_{12}]^{2-}$  anions, with significantly fewer studies on the other anions. These dianions react smoothly in aqueous or alcoholic solution with elemental  $\text{X}_2$  to give a range of products in which from one to all the hydrogen atoms may be replaced. For both anions, these reactions are extremely rapid in the initial stages, but the rates decrease as halogenation is continued. These halogenations are assumed to be electrophilic in nature,  $[\text{B}_{12}\text{H}_{12}]^{2-}$  being more resistant to perhalogenation than  $[\text{B}_{10}\text{H}_{10}]^{2-}$ . The reactivity order for the halogens is  $\text{Cl} > \text{Br} > \text{I}$ .

The very rapid initial rates lead to difficulties in isolating some species, especially those with low degrees of substitution, but details for the preparation of a number of well-characterized species are presented in Tables 1 and 2. Preparation of the more highly halogenated species naturally requires larger quantities of added halogen and somewhat more forcing conditions. By means of similar reactions, other halogeno derivatives such as  $[\text{B}_{10}\text{H}_6\text{Br}_4]^{2-}$  and  $[\text{B}_{10}\text{H}_5\text{I}_5]^{2-}$  have been claimed<sup>2</sup> and the preparations of species containing mixed halogen substituents are also described<sup>1</sup>.

By this general route,  $[\text{B}_{11}\text{H}_7\text{Br}_4]^{2-}$  also may be obtained<sup>3</sup> by adding  $\text{Br}_2$  to  $[\text{B}_{11}\text{H}_{11}]^{2-}$  at 275 K, while  $[\text{B}_{11}\text{H}_2\text{Br}_9]^{2-}$  is obtained via bromination using sodium

TABLE 1. HALOGENATED DERIVATIVES OF  $[\text{B}_{10}\text{H}_{10}]^{2-}$  (FROM REF. 12)

Product	Reaction conditions
$[\text{B}_{10}\text{H}_2\text{Cl}_8]^{2-}$	$[\text{B}_{10}\text{H}_{10}]_{\text{aq}}^{2-}$ , 273–278 K; $\text{Cl}_2$ passed in until exothermic reaction ceases
$[\text{B}_{10}\text{Cl}_{10}]^{2-}$	$[\text{B}_{10}\text{H}_{10}]_{\text{aq}}^{2-}$ , 288–293 K; $\text{Cl}_2$ passed in until exothermic reaction ceases, then continued
$[\text{B}_{10}\text{H}_3\text{Br}_7]^{2-}$	$[\text{B}_{10}\text{H}_{10}]_{\text{aq}}^{2-}$ , 273 K; $\text{Br}_2$ added until color persists
$[\text{B}_{10}\text{Br}_{10}]^{2-}$	$[\text{B}_{10}\text{H}_{10}]^{2-}$ in 1:1 $\text{MeOH-H}_2\text{O}$ ; $\text{Br}_2$ (18.5 mol per mole $\text{B}_{10}\text{H}_{10}^{2-}$ ) in $\text{EtOH}$ ; mixture refluxed
$[\text{B}_{10}\text{H}_9\text{I}]^{2-}$	$[\text{B}_{10}\text{H}_{10}]_{\text{aq}}^{2-} + \text{I}_2$ (1 mol) in $\text{KI}$ . Separate products via fractional cryst. of
$[\text{B}_{10}\text{H}_8\text{I}_2]^{2-}$	$\text{Cs}^+$ , $\text{NMe}_4^+$ salt
$[\text{B}_{10}\text{H}_7\text{I}_3]^{2-}$	$[\text{B}_{10}\text{H}_{10}]^{2-}$ in $\text{EtOH-H}_2\text{O}$ ; 278–283 K; $\text{I}_2$ (2.62 mol) added, soln warmed, stirred until colorless. Ppt as $\text{Cs}^+$ salt $\rightarrow \text{I}_3$ product. Reflux with more
$[\text{B}_{10}\text{H}_4\text{I}_6]^{2-}$	$\text{I}_2 \rightarrow \text{I}_6$ product
$[\text{B}_{10}\text{H}_6\text{I}_4]^{2-}$	$[\text{B}_{10}\text{H}_{10}]^{2-}$ in $\text{MeOH}$ ; add $\text{I}_2$ (3.39 mol per mole of $[\text{B}_{10}\text{H}_{10}]^{2-}$ )
$[\text{B}_{10}\text{I}_{10}]^{2-}$	$[\text{B}_{10}\text{H}_{10}]^{2-}$ in $\text{MeOH}$ ; add $\text{I}_2$ until no further reaction; reflux; add $\text{ICl}$ , heat to 350 K, extract product with $\text{CCl}_4$ , then $\text{CS}_2$

## 2.6. The Formation of the Halogen (B, Al, Ga, In, Tl) Bond

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## 2.6.4. from Halogenation of Anionic Group-IIIB Clusters

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$[\text{B}_{10}\text{H}_9\text{I}]^{2-}$	$[\text{B}_{10}\text{H}_{10}]_{\text{aq}}^{2-} + \text{I}_2$ (1 mol) in KI. Separate products via fractional cryst. of $\text{Cs}^+$ , $\text{NMe}_4^+$ salt
$[\text{B}_{10}\text{H}_8\text{I}_2]^{2-}$	$[\text{B}_{10}\text{H}_{10}]^{2-}$ in EtOH– $\text{H}_2\text{O}$ ; 278–283 K; $\text{I}_2$ (2.62 mol) added, soln warmed, stirred until colorless. Ppt as $\text{Cs}^+$ salt $\rightarrow \text{I}_3$ product. Reflux with more $\text{I}_2 \rightarrow \text{I}_6$ product
$[\text{B}_{10}\text{H}_7\text{I}_3]^{2-}$	
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$[\text{B}_{10}\text{H}_6\text{I}_4]^{2-}$	$[\text{B}_{10}\text{H}_{10}]^{2-}$ in MeOH; add $\text{I}_2$ (3.39 mol per mole of $[\text{B}_{10}\text{H}_{10}]^{2-}$ )
$[\text{B}_{10}\text{I}_{10}]^{2-}$	$[\text{B}_{10}\text{H}_{10}]^{2-}$ in MeOH; add $\text{I}_2$ until no further reaction; reflux; add $\text{ICl}$ , heat to 350 K, extract product with $\text{CCl}_4$ , then $\text{CS}_2$

TABLE 2. HALOGENATED DERIVATIVES OF  $B_{12}H_{12}^{2-}$  (FROM REF. 12)

Product	Reaction conditions
$[B_{12}F_{11}OH]^{2-}$	$[B_{12}H_{12}]_{aq}^{2-}$ , 273 K; $F_2:N_2$ mixture (1:5) passed in, 50 h; $KBF_4$ ppt removed; neutralize, 7M KOH
$[B_{12}H_6Cl_6]^{2-}$	$[B_{12}H_{12}]_{aq}^{2-}$ , 273 K; $Cl_2$ added until color retained
$[B_{12}Cl_{12}]^{2-}$	$[B_{12}H_{12}]_{aq}^{2-}$ , ambient T + $Cl_2$ ; further attack with xs $Cl_2$ at 420 K
$[B_{12}H_6Br_6]^{2-}$	$[B_{12}H_{12}]^{2-}$ -1:1 MeOH- $H_2O$ , 278 K; $Br_2$ (6.33 mol per mole $[B_{12}H_{12}^{2-}]$ added
$[B_{12}H_2Br_{10}]^{2-}$	$[B_{12}H_{12}]_{aq}^{2-}$ ; $Br_2$ (11.9 mol) added and T raised (350 K), then more $Br_2$ added at this T.
$[B_{12}Br_{12}]^{2-}$	$[B_{12}H_{12}]^{2-}$ -1:1 MeOH- $H_2O$ , 283 K; $Br_2$ (6.4 mol) added; further 2.1 mol $Br_2$ added and $Cl_2$ passed in
$[B_{12}H_{11}I]^{2-}$	$[B_{12}H_{12}]^{2-}$ in $H_2O$ -MeOH; $I_2$ (1 mol) added slowly
$[B_{12}H_{10}I_2]^{2-}$	As in $[B_{12}H_{11}I]^{2-}$ , except 2 mol $I_2$ added
$[B_{12}I_{12}]^{2-}$	$[B_{12}H_{12}]^{2-}$ in $Cl_2HCCHCl_2$ , $I_2$ (2.2 mol) added; $ICl$ (14 mol) added, reflux 40 h.

hypobromite<sup>4</sup>. Halogenation of  $[B_{11}H_{11}]^{2-}$  in acidic media leads to degradation, and derivatives of  $[B_{10}H_{10}]^{2-}$  are obtained instead. The hypobromite reagent also may be employed<sup>5</sup> to yield  $[B_8H_8Br_6]^{2-}$  from  $[B_8H_8]^{2-}$  and  $[B_9H_9Br_6]^{2-}$  from  $[B_9H_9]^{2-}$ .

A similar pattern of electrophilic substitution reactions is evident from halogenation studies on carborane anions. For example, addition of  $Br_2$  in MeOH to the monocarbon ion  $[B_{10}H_{12}CH]^-$  causes the color to be discharged rapidly, yielding  $[B_{10}H_{10}Br_2CH]^-$ . Reaction with  $Cl_2$ , even at 273 K, causes extensive degradation, however. Initial halogenation occurs at boron in the 4 position, well removed from the carbon atom<sup>6</sup>. Similarly, stirring  $K[B_9C_2H_{12}]$  in EtOH with equimolar  $I_2$  or  $Br_2$  gives high yields of  $[B_9C_2H_{11}X]^-$  ( $X = Br, I$ )<sup>7</sup>. This ion, in common with many other carborane anions, is easily protonated to give the neutral halogenocarborane  $B_9C_2H_{12}X$ . A direct conversion of a carborane anion to the neutral halogenocarborane is observed when the C,C'-dimethyl nido derivative  $[C_2(CH_3)_2B_4H_5]^-$  is treated with  $ICl$ <sup>8</sup>. A 3:1 mixture of 2- $ClC_2(CH_3)_2B_4H_5$  and 3- $ClC_2(CH_3)_2B_4H_5$  is obtained, while reaction of the anion with  $Br_2$  gives 3- $BrC_2(CH_3)_2B_4H_5$ .

Halogenation of carborane anions complexed with transition metals has also been studied. The Co(III) complex  $[(C_2B_9H_{11})_2Co]^-$  is also subject to electrophilic bromination in glacial acetic acid. Three Br atoms are substituted on each carborane anion in the 8, 9 and 12 positions—those boron atoms which are furthest from the C atoms<sup>9</sup>. Similar substitution reactions are reported for the cyclopentadienyl cobalt derivatives of  $[1,2-B_9C_2H_{11}]^{2-}$  and  $[1,6-B_7C_2H_9]^{2-}$ . In these cases, brominations again occurred at the cage boron atoms and attack was not observed on the hydrocarbon ring<sup>10,11</sup>. Generally, the cobalt complexes of the carborane anions behave in an analogous manner to the carboranes themselves under the conditions of electrophilic bromination. In addition, bromination of the  $\pi$ -complexes occurs in glacial acetic acid, whereas carboranes are inert in this medium<sup>13</sup>. On the other hand, the heterocarboranes  $CH_3MC_2B_4H_6$  ( $M = Ga, In$ ) do not survive electron-pair acceptor acid-catalysed conditions. Both carboranes consume  $Br_2$  very rapidly at 298 K in  $CS_2$  with destruction of the cage structure<sup>14</sup>.

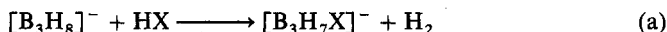


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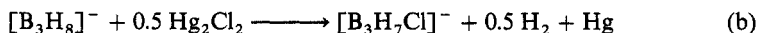
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The acidity of a number of the boron hydrides precludes the use of HX reagents for substitutions. For example, the anion  $[\text{1-XB}_5\text{H}_7]^-$  is prepared via hydride attack on  $\text{1-XB}_5\text{H}_8$ . Conversely, then, many hydroboron ions are reprotonated by HX and return to the parent hydride<sup>3</sup>. In those cases in which reprotonation is not a problem, HX may effect substitutions. Thus, the  $[\text{Bu}_4\text{N}][\text{B}_3\text{H}_8]$  forms the halide derivatives when treated with stoichiometric quantities of HX (X = Cl, Br, I) at 195 K in  $\text{CH}_2\text{Cl}_2$  or ether<sup>4</sup>:



A more appealing method, which has been reported for the  $[\text{B}_3\text{H}_8]^-$  anion but not apparently more generally applied, involves treatment with mercury halides in a non-coordinating solvent<sup>5</sup>. Thus, with  $\text{Hg}_2\text{Cl}_2$ , the reaction proceeds stepwise forming  $\text{B}_3\text{H}_7\text{Cl}^-$  and some  $\text{B}_3\text{H}_6\text{Cl}_2^-$  at RT:



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## 2.6. The Formation of the Halogen (B, Al, Ga, In, Tl) Bond

9

## 2.6.4. from Halogenation of Anionic Group-III B Clusters

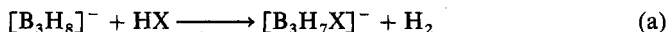
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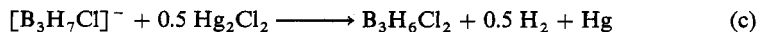
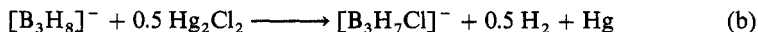
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Product	Conditions: HX, T(K)	Ref.
$[B_{12}H_{11}F]^{2-}$	HF, 273 K	6
$[B_{12}H_{10}F_2]^{2-}$	HF, ca. 273 K	7
$[B_{12}H_8F_4]^{2-}$	HF, 373 K; 330–360 K	6, 8
$[B_{12}H_7F_5]^{2-}$	HF, 420 K	6
$[B_{12}H_6F_6]^{2-}$	HF, 473 K; 420–450 K	6, 8
$[B_{12}H_{11}Cl]^{2-}$	HCl, 360 K	6
$[B_{12}H_{11}Br]^{2-}$	HBr, 373 K	6

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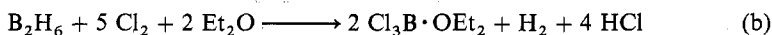
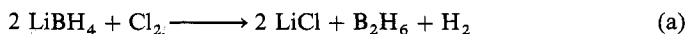
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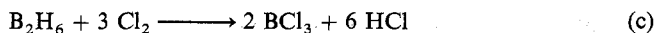
## 2.6.5. from Cleavage of Group-IIIB–Hydrogen Bonds

### 2.6.5.1. by Halogens.

The relatively weak E–H bonds (B–H, ca. 385 kJ mol<sup>-1</sup>; Al–H, ca. 272; Ga–H, ca. 272; Tl–H, ca. 209) are generally susceptible to replacement by stronger E–halogen bonds. There is a steady decrease in the stability of the tetrahydrido complexes in the sequence  $LiBH_4 > LiAlH_4 > LiGaH_4 > LiInH_4 > LiTlH_4$ , with substantial information being available only for the first two. Chlorine reacts with  $LiBH_4$  in ether at T as low as 210 K, but  $H_2$  and  $B_2H_6$  are the main volatile products and only limited amounts of  $BCl_3$  (etherate) are obtained:



Diborane reacts violently with  $Cl_2$  at RT (and  $F_2$  reacts at low T), but at lower T, the reaction may be controlled to proceed quantitatively<sup>1</sup>:



Liquid  $Br_2$  reacts vigorously with  $K[BH_4]$  at RT but yields only a small amount of  $BBr_3$ . The reaction of  $[BH_4]^-$  with  $I_2$  gives  $BI_3$  as the predominant product, with  $LiBH_4$

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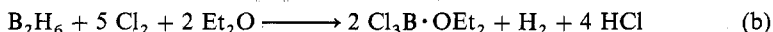
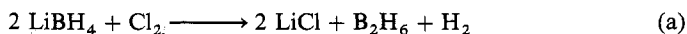
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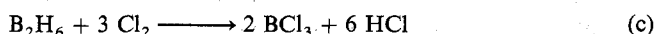
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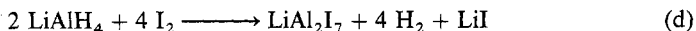


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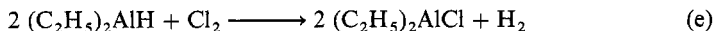


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providing the highest yield<sup>2</sup>. This reaction may be controlled to give a convenient preparation of  $\text{BI}_3$ <sup>3</sup>. As expected,  $\text{LiAlH}_4$  reacts rapidly with  $\text{I}_2$  in ether at 173 K, apparently yielding  $\text{LiAlI}_4$  as a white solid. At 77 K, the product is reported to yield  $\text{LiAl}_2\text{I}_7$ , according to:



A similar reaction is reported between  $\text{LiAlH}_4$  and  $\text{Br}_2$ <sup>4</sup>. A deficit of  $\text{Cl}_2$  gas at 293 K cleaves  $(\text{C}_2\text{H}_5)_2\text{AlH}$ <sup>5</sup>:



A powerful method for direct fluorinations, involving a very low initial  $\text{F}_2$  concentrations has been described<sup>6</sup>. This technique gives essentially quantitative yields of fluoride derivatives at RT, starting from complex hydrides, e.g.,  $\text{M}_3[\text{AlH}_6]$  is converted to  $\text{M}_3[\text{AlF}_6]$  ( $\text{M} = \text{Li, Na}$ ).

Reactions of  $\text{X}_2$  with higher boranes and carboranes, in contrast with those of  $\text{B}_2\text{H}_6$ , are more controlled and occur as electrophilic substitution reactions (similar to those in §2.6.4.1). Attack of the halogen is mainly at the B atom which has the greatest negative charge. Thus, aluminium halide catalyzed halogenation of  $\text{B}_{10}\text{H}_{14}$  readily yields the monohalogeno compound, with the major attack (65%) being at the 2-position, the remainder being at the 1-position. Prolonged action of  $\text{Br}_2$  and  $\text{I}_2$  on  $\text{B}_{10}\text{H}_{14}$  yields dihalo derivatives<sup>7</sup>. Similarly, electrophilic halogenation of  $\text{B}_5\text{H}_9$  occurs in the apical position. If  $\text{AlCl}_3$  is not employed as a catalyst, attack is favored in the 2 position when chlorination is attempted, although bromination and iodination still occur in the 1 position;  $\text{B}_4\text{H}_{10}$  is attacked by  $\text{Br}_2$  at 258 K over 12–18 h to yield 2- $\text{BrB}_4\text{H}_9$ , while attack of  $\text{F}_2$  or  $\text{Cl}_2$  is extremely violent<sup>8</sup>. Detailed methods for the preparation of halogenated boranes may be found<sup>9</sup>.

Electrophilic halogenations are very stereospecific in the carboranes in which the negative charge is usually greatest on the boron atoms farthest away from the skeletal carbon atoms. Thus, in the electron-pair acceptor acid-catalyzed chlorination, bromination and iodination of closo-1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$  and its C-methyl derivatives, substitution occurs first at the 9 and 12 positions and then on boron atoms 8 and 10. Principal halogenation in closo-1,7- $\text{C}_2\text{B}_{10}\text{H}_{12}$  occurs in the 9 and 10 positions. Electrophilic bromination and iodination of 1,12- $\text{C}_2\text{B}_{10}\text{H}_{12}$  yields both mono- and dihalogen compounds, while chlorination yields the tetrachloro derivative<sup>10</sup>. Fluorination, however, appears to be quite nonselective and all 10 boron atoms of 1,2-, 1,7- and 1,12- $\text{C}_2\text{B}_{10}\text{H}_{12}$  have been fluorinated by direct reaction with  $\text{F}_2$  in liq HF<sup>11</sup>. Direct fluorination methods<sup>6</sup> completely fluorinates the B atoms in 1,2-carborane over 4–8 h at RT. The carbon atoms may be fluorinated under more forcing conditions. The electron-pair acceptor acid-catalyzed halogenation of 1-Phl-1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$  is an interesting reaction because it is possible to quench it before any halogenation of the phenyl ring has occurred. The electron-withdrawing properties of the carborane cage thus passivate the aromatic ring<sup>12</sup>. Although the order of electrophilic substitution on the 1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$  cage appears almost invariant, there is evidence that the choice of catalyst may alter the course of the reaction. Thus, chlorination or bromination in the presence of Fe metal appears to be less selective than with aluminum halide catalysts<sup>13,14</sup>.

Similar selectivity is observed for photochemical chlorination and bromination, although chlorination proceeds easily to the B-decachloro derivatives. The reaction takes place in stages, with substitution occurring at the most negative boron atoms first—until

finally the 3,6 boron atoms are attacked. With 1,7-carborane, two monochloro isomers may be obtained, but chlorination of 1,12-carborane appears to be fairly random. Both 1,2- and 1,7-carboranes resist photochemical bromination, yielding only the monobromo derivatives in the absence of a catalyst<sup>15,16</sup>.

The smaller closo-carboranes undergo similar reactions, with substitution on the boron atoms farthest away from the skeletal carbons. Thus, chlorination of 2,4-C<sub>2</sub>B<sub>5</sub>H<sub>7</sub> in the presence of AlCl<sub>3</sub> yields mostly the 5-chloro derivative and bromination of 1,6-C<sub>2</sub>B<sub>7</sub>H<sub>9</sub> occurs in the 8 position. Direct chlorination of 1,10-C<sub>2</sub>B<sub>8</sub>H<sub>10</sub> in CCl<sub>4</sub> generates the B-octachloro derivative and complete chlorination of the 1,10-dimethyl derivative occurs under the influence of UV light. Other examples are cited in refs. 14–17.

Attack on the B—H bonds of borazines by halogen appears, on the other hand, to be a nucleophilic process. This is shown by the fact that H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>R<sub>3</sub> reacts with Br<sub>2</sub> to give Br<sub>6</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub>R<sub>3</sub> which eliminates HBr on heating to produce Br<sub>3</sub>B<sub>3</sub>N<sub>3</sub>R<sub>3</sub>. There is, however, no reaction between Br<sub>2</sub> and Cl<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub> or (CH<sub>3</sub>)<sub>3</sub>B<sub>3</sub>N<sub>3</sub>(CH<sub>3</sub>)<sub>3</sub>. Chlorine produces Cl<sub>3</sub>B<sub>3</sub>N<sub>3</sub>R<sub>3</sub>, but only with UV radiation, while iodination proceeds stepwise<sup>18</sup>, giving I<sub>n</sub>H<sub>3-n</sub>B<sub>3</sub>N<sub>3</sub>R<sub>3</sub>.

Halogen-substituted pyrayaboles can be prepared by treating β-hydropyrayabole in halogenated methane with Cl<sub>2</sub> or Br<sub>2</sub> (elemental) until the halogen color persists<sup>19</sup>.

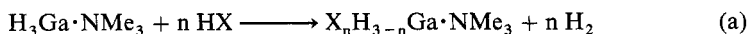
(B.D. JAMES)

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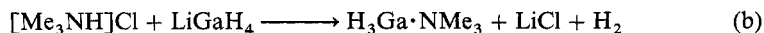
2.6. The Formation of the Halogen (B, Al, Ga, In, Tl) Bond 13  
 2.6.5. from Cleavage of Group-IIIB-Hydrogen Bonds  
 2.6.5.2. by Hydrogen Halogens.

### 2.6.5.2. by Hydrogen Halides.

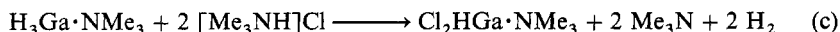
The generally hydridic ( $H^{\delta-}$ ) character of the group-IIIB hydrides and the protonic ( $H^{\delta+}$ ) nature of the HX leads to **very vigorous** reactions between the two. Thus, the  $[BH_4]^-$ ,  $[AlH_4]^-$  and  $[GaH_4]^-$  species are decomposed by these reagents. As expected, the trimethylamine adducts of halogenogallanes can be prepared<sup>1</sup> by the treatment of solid  $H_3Ga \cdot NMe_3$  with stoichiometric quantities of HX gas at low T:



where  $n = 1, 2$ ;  $X = Cl, Br$ . Reliable, high-yield syntheses for the production of adducts of haloboranes via similar procedures have been developed<sup>2</sup>. The method is easily modified for large-scale preparations and no special precautions for the exclusion of air or water are required<sup>3,4</sup>. On the other hand, complexed HX, such as in the salts  $[Me_3NH]Cl$  or  $[C_5H_5NH]Cl$ , provides a most useful synthetic reagent also causing cleavage of a hydridic linkage under mild conditions. For example,  $H_3Ga \cdot NMe_3$  may be prepared via the reaction of  $Me_3N \cdot HCl$  on  $LiGaH_4$  in ether below 273 K:



Excess  $[Me_3NH]Cl$  then causes cleavage of other Ga—H bonds, producing the amine adduct of  $GaHCl_2$  directly without isolation of the  $GaH_3$  adduct:



The reaction does not appear to go to completion, however, when the analogous bromide system is employed<sup>1</sup>. Similar reactions are known for  $AlH_3$  and its  $Me_3N$  adduct, yielding chloroalanes<sup>5</sup>. With HF,  $AlF_3$  is formed because its large enthalpy of formation drives the reaction toward complete substitution.

$[B_3H_8]^-$  and its substituted derivatives  $[B_3H_9Y]^-$  ( $Y = NCO, NCS$  or  $NCBH_3$ ) undergo substitution with HCl. By contrast, CN-bridged  $[B_3H_7(NC)B_3H_7]^-$  undergoes substitution only in the B cage that is bonded to the N<sup>6</sup>.

Bromine substitution of a terminal hydrogen atom in  $B_2H_6$  may be achieved using HBr in the presence of  $AlBr_3$ , but other monohalogenodiboranes are more easily prepared via other reactions<sup>7</sup>. In the presence of  $AlCl_3$ ,  $B_4H_{10}$  is degraded slowly by HCl to give  $BCl_3$ . With the higher boranes, the H atoms tend to become protonic, and while hydrogen halides interact (especially in the presence of  $AlCl_3$ ) to exchange protons, there is not generally any halogen substitution at the B—H bonds.

Controlled addition of HX permits the preparation of organoaluminum halides from the corresponding hydrides. Addition of 1 mol of HCl gas above the surface of a 4:1  $(C_2H_5)_2AlH-(C_2H_5)_3Al$  mixture at 298 K gives  $(C_2H_5)_2AlCl$  with the Al—H bond being cleaved selectively. The bromide and iodide may be prepared by similar methods<sup>8</sup>. The compound reported to be  $(CH_3)_2GaH$  is unstable and has not been authenticated<sup>9</sup>, so an analogous reaction for Ga appears unlikely on these grounds.

Indium and Tl hydrides, whether in the +I or +III oxidation states also seem to be either very unstable or poorly characterized species (apart from the  $[MH_4]^-$  ions) and their reactions have not been investigated<sup>10,11</sup>.

(B.D. JAMES)

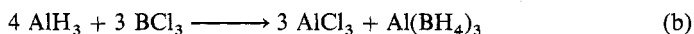
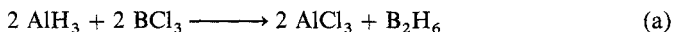
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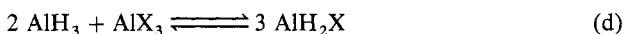
### 2.6.5.3. with Other Halides.

The high enthalpies of formation of  $\text{AlX}_3$  ( $\text{AlF}_3$ ,  $-1302 \text{ kJ mol}^{-1}$ ;  $\text{AlCl}_3$ ,  $-695$ ;  $\text{AlBr}_3$ ,  $-526.6$ ;  $\text{AlI}_3$ ,  $-314.8$ ) together with the reducing ability of  $\text{AlH}_3$  make it probable that nonmetal and many metal halides undergo hydrogen-halogen exchange reactions<sup>1</sup>. Depending on the stability and reactivity of the intermediate steps, partial or complete hydride transfer to the halide or elimination of  $\text{H}_2$  or  $\text{HX}$  from that hydrided compound may follow.

Thus,  $\text{PCl}_3$  reacts with xs  $\text{AlH}_3$  in ether to give  $\text{H}_2$ , some  $\text{PH}_3$  [but mostly  $(\text{PH})_x$  polymer] and  $\text{AlCl}_3$  etherate. This interesting reaction, however, was studied with a view to optimizing the yields of either  $\text{PH}_3$  or the  $(\text{PH})_x$  polymer<sup>2</sup>. Similarly, boron halides are converted to diborane and the reaction may proceed through to the formation of  $\text{Al}(\text{BH}_4)_3$ :



Stoichiometric redistribution reactions of this type between  $\text{BCl}_3$  and  $\text{BH}_3$  in THF may be employed to prepare  $\text{BHCl}_2$  and  $\text{BH}_2\text{Cl}$ , but fluoroboranes cannot be prepared by such means<sup>3</sup>, although F substitution on  $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$  is possible. Halogen derivatives of the larger boron hydrides may be prepared by reactions of this type<sup>4</sup>. For example,  $\text{B}_6\text{H}_9\text{X}$  ( $\text{X} = \text{Br}, \text{I}$ ) is produced in good yield from  $\text{B}_6\text{H}_{10}$  with xs  $\text{BX}_3$ . Similar redistribution reactions also have been reported for aluminum<sup>5,6</sup>:



where  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ . A very good preparation for monohalogenodiboranes also involves cocondensing  $\text{B}_2\text{H}_6$  and  $\text{BX}_3$  ( $\text{X} = \text{Br}, \text{I}$ ) and allowing the mixture to warm. The mixture is then fractionated by passing through cold traps successively at 195, 147 and 77 K. The product collects in the middle trap and excess reagents in the other two. If these are then condensed back into the reaction flask another crop of product may be obtained. For  $\text{IB}_2\text{H}_5$ , the reaction should be performed in the absence of light and  $\text{Hg}$  vapor<sup>7</sup>.



## 2.6. The Formation of the Halogen (B, Al, Ga, In, Tl) Bond

2.6.5. from Cleavage of Group-III<sub>B</sub>-Hydrogen Bonds

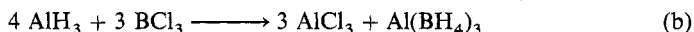
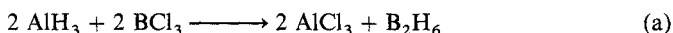
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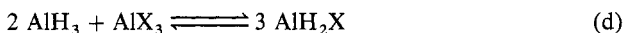
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Thus, PCl<sub>3</sub> reacts with xs AlH<sub>3</sub> in ether to give H<sub>2</sub>, some PH<sub>3</sub> [but mostly (PH)<sub>x</sub> polymer] and AlCl<sub>3</sub> etherate. This interesting reaction, however, was studied with a view to optimizing the yields of either PH<sub>3</sub> or the (PH)<sub>x</sub> polymer<sup>2</sup>. Similarly, boron halides are converted to diborane and the reaction may proceed through to the formation of Al(BH<sub>4</sub>)<sub>3</sub>:



Stoichiometric redistribution reactions of this type between BCl<sub>3</sub> and BH<sub>3</sub> in THF may be employed to prepare BHCl<sub>2</sub> and BH<sub>2</sub>Cl, but fluoroboranes cannot be prepared by such means<sup>3</sup>, although F substitution on 1,2-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> is possible. Halogen derivatives of the larger boron hydrides may be prepared by reactions of this type<sup>4</sup>. For example, B<sub>6</sub>H<sub>9</sub>X (X = Br, I) is produced in good yield from B<sub>6</sub>H<sub>10</sub> with xs BX<sub>3</sub>. Similar redistribution reactions also have been reported for aluminum<sup>5,6</sup>:



where X = Cl, Br, I. A very good preparation for monohalogenodiboranes also involves cocondensing B<sub>2</sub>H<sub>6</sub> and BX<sub>3</sub> (X = Br, I) and allowing the mixture to warm. The mixture is then fractionated by passing through cold traps successively at 195, 147 and 77 K. The product collects in the middle trap and excess reagents in the other two. If these are then condensed back into the reaction flask another crop of product may be obtained. For IB<sub>2</sub>H<sub>5</sub>, the reaction should be performed in the absence of light and Hg vapor<sup>7</sup>.

For reactions with the more saltlike halides, electron-pair acid-base interactions of the type  $X: \rightarrow AlH_3 \cdots X_n^-$  may occur. Such interactions probably are responsible for stabilizing  $AlH_3$  solutions whenever  $AlH_3$  and lithium halides are obtained together. Complexes such as  $Li[H_3AlX]$  are formed<sup>1</sup>.

A convenient method for the chlorination in good yield of the stable amine-boranes employs  $NaOCl$  in a manner reminiscent of the halogenation of clusters (§2.6.4.1). Thus, N-methylmorpholine chloroborane may be obtained in 84% yield at RT from the  $BH_3$  adduct<sup>8</sup>.

A useful reaction for halogen exchange is to interact a hydride with a halide of a metal that is easily reduced. This reaction was foreshadowed earlier in the reactions of  $[B_3H_8]^-$  with  $HgX_2$ <sup>9</sup> but is of more general utility. For example, borazine and  $HgCl_2$  react in ether or pentane:



This is a good method for producing unsymmetrically halogen-substituted borazines. The chlorides of Cu(II), Pb(II) and Ag(I) however, do not react in this system<sup>10</sup>. Other less desirable reagents such as  $COCl_2$  and  $SOCl_2$  also may be employed to effect chlorination at the B atom<sup>11</sup>. Stannic halides ( $X = Cl, Br$ ) may be used in this type of reaction, but separation of the product mixtures may be difficult. For example,  $SnCl_4$  reacts immediately with N,N',N''-trimethylborazine at 250 K giving  $(CH_3)_3N_3B_3H_2Cl$  and  $(CH_3)_3N_3B_3HCl_2$  with a small amount of  $(CH_3)_3N_3B_3Cl_3$ . The  $HCl$  byproduct reacts with some of the borazine starting material to give an adduct<sup>12</sup>.

Finally, many hydrides can also be halogenated by reaction with halogenated hydrocarbons, although it is not always easy to control the reaction. Chloroform, dichloromethane and 1,2-dichloroethane all react with  $[AlH_4]^-$  to replace H with chlorine, although no recommendation is made for this as a synthetic method in this case<sup>13</sup>. Useful derivatives of amine-boranes may be prepared by this reaction; the halocarbons may be  $CCl_4$ ,  $CCl_3Br$ ,  $ClCH_2CH_2Cl$  and  $(C_6H_5)_3CCl$ . The ease of reaction depends on the ligating amine; the reaction appears to be free radical, being initiated with benzoyl peroxide<sup>14</sup>. Similarly, the useful hydroborating agent  $H_2CIB \cdot S(CH_3)_2$  may be prepared quantitatively<sup>15</sup> by refluxing dimethylsulfide-borane with equimolar  $CCl_4$ . These reactions are of use in halogenating more stable compounds since 1,2- $C_2B_{10}H_{12}$  can be chlorinated by refluxing it with  $CCl_4$  or  $CHCl_3$  over  $AlCl_3$ . The 9,12-dichloro derivative is obtained in high yield. Also, reaction of the 1,2-carborane with iodobenzene at 570 K yields the 9- and 8-iodo derivatives<sup>16</sup>.

(B.D. JAMES)

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4. *Gmelin's Handbuch der Anorganischen Chemie*, 8 Aufl., Syst. 13, Boron Compounds, New Supplement Series, Part 14, Springer-Verlag, Berlin, 1977.
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6. Redistributions in systems such as  $[AlH_4]^- + [AlCl_4]^-$  have been studied and the various  $AlH_nCl_{4-n}$  species shown to predominate under different conditions. See L. V. Titov, V. D. Sasnovskaya, V. Y. Rosolovskii, *Bull. Acad. Sci. USSR*, **29**, 675 (1980); L. A. Gavrilova, L. V. Tirov, V. Y. Rosolovskii, *Russ. J. Inorg. Chem.*, **26**, 1116 (1981).

7. J. E. Drake, B. Rapp, C. Riddle, J. Simpson, *Inorg. Synth.*, **18**, 145 (1978).
8. H. C. Kelly, S. C. Yasui, A. B. Twiss-Brooks, *Inorg. Chem.*, **23**, 2220 (1984).
9. G. B. Jacobson, J. H. Morris, *Inorg. Chim. Acta*, **59**, 207 (1982).
10. R. Maruca, O. T. Beachley, A. W. Laubengayer, *Inorg. Chem.*, **6**, 575 (1967).
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12. G. A. Anderson, J. J. Lagowski, *Chem. Commun.*, 649 (1966).
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## 2.6.6. from Cleavage of Group-IIIB–Oxygen Bonds

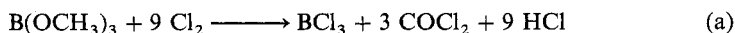
### 2.6.6.1. by Halogens.

Fluorination of metal oxides is one of the oldest known methods of preparing inorganic fluorides. Thermodynamically, all metal oxides should react with fluorine to liberate oxygen and form the fluoride (usually in the highest oxidation state). Frequently, however, this is not achieved for one of two reasons. Either a layer of fluoride product on the oxide surface prevents further reaction or the activation energy for the reaction is too high. Group IIIB illustrates the extremes very well. Fluorination of  $\text{Tl}_2\text{O}_3$  begins even at RT and is an example of a good preparation<sup>1</sup>. In practice the fluorination should proceed slowly, otherwise fusion of the product prevents complete reaction<sup>2</sup>. On the other hand, the high lattice energy of  $\text{Al}_2\text{O}_3$  causes the activation energy for fluorination to be very large and the reaction to be inhibited. Activated alumina is quite easily converted to the trifluoride with only gentle warming in a  $\text{F}_2$  atmosphere, while the sintered  $\text{Al}_2\text{O}_3$  resists  $\text{F}_2$  so strongly that it may be employed as a fluorine container<sup>1</sup>.

Reaction of  $\text{F}_2$  with  $\text{In}_2\text{O}_3$  is a recommended method for  $\text{InF}_3$ . Initial gentle heating starts the reaction, which then proceeds exothermically. The reaction remains incomplete, however, unless the product is heated further for several hours in a  $\text{F}_2$  stream<sup>3</sup>. Reaction of  $\text{F}_2$  with  $\text{Ga}_2\text{O}_3$  is incomplete even at high T, with about 5% of the oxide remaining. The extent of reaction is markedly dependent on the T at which the oxide is calcined<sup>4</sup>.

Extension of these reactions to the less reactive  $\text{Cl}_2$  leads inevitably to lower yields. The reaction of  $\text{Cl}_2$  on  $\text{Al}_2\text{O}_3$  is endothermic<sup>5</sup>, and there does not appear to be appreciable reaction with  $\text{Ga}_2\text{O}_3$  up to 1000 K. In any event, other methods for producing the metal halides are more convenient.

Other group-IIIB-oxygen species are also susceptible to reaction with halogens. Trimethoxyborane interacts rapidly with  $\text{Cl}_2$  gas at RT:



but with fluorinated compounds of the type  $(\text{R}_\text{F}\text{CH}_2\text{O})_3\text{B}$  chlorination occurs initially at the  $-\text{CH}_2-$  carbon atom before cleaving the B–O bond to yield  $(\text{R}_\text{F}\text{CHClO})_2\text{BCl}$ <sup>6</sup>. Halogen attack on metal alkoxides is a general reaction<sup>7</sup>. The propensity for Tl to adopt either the +III or the +I oxidation state tends to complicate the reactions of its carboxylates with  $\text{Br}_2$ . Thallous acetate is oxidized to  $\text{Tl}(\text{O}_2\text{CCH}_3)\text{Br}_2$ , but with the

16      2.6. The Formation of the Halogen (B, Al, Ga, In, Tl) Bond  
           2.6.6. from Cleavage of Group-IIIB–Oxygen Bonds  
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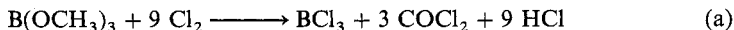
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Reaction of  $F_2$  with  $In_2O_3$  is a recommended method for  $InF_3$ . Initial gentle heating starts the reaction, which then proceeds exothermically. The reaction remains incomplete, however, unless the product is heated further for several hours in a  $F_2$  stream<sup>3</sup>. Reaction of  $F_2$  with  $Ga_2O_3$  is incomplete even at high T, with about 5% of the oxide remaining. The extent of reaction is markedly dependent on the T at which the oxide is calcined<sup>4</sup>.

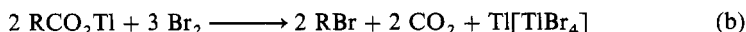
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higher carboxylates there is Tl—O bond cleavage and partial oxidation to give Tl[TlBr<sub>4</sub>], according to<sup>8</sup>:

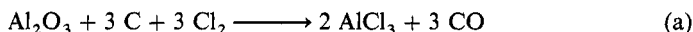


(B.D. JAMES)

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5. J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 5, Longmans, Green, London, 1961.
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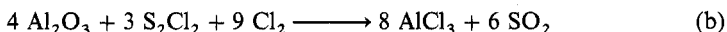
### 2.6.6.2. by Halogens with Reducing Agents.

Because the action of Cl<sub>2</sub> alone on Al<sub>2</sub>O<sub>3</sub> is incomplete, the assistance of reductants has been invoked. Aluminum chloride may be produced by means of the reaction of Cl<sub>2</sub> on a mixture of alumina and coke at 1100 K, the formation of CO causing the reaction to be exothermic<sup>1</sup>:



The extension to the preparation of other group-IIIB halides (e.g., AlBr<sub>3</sub>) is a general procedure. Likewise, InCl<sub>3</sub> may be prepared by heating In<sub>2</sub>O<sub>3</sub> with powdered carbon in a dry Cl<sub>2</sub> stream<sup>2</sup>.

Other reductants may also be employed. For example, S<sub>2</sub>Cl<sub>2</sub> in a reaction to produce AlCl<sub>3</sub>:



Passing S<sub>2</sub>Cl<sub>2</sub> and Cl<sub>2</sub> over a heated mixture of Al<sub>2</sub>O<sub>3</sub> and carbon yields as the first product the addition compound Cl<sub>3</sub>Al·S<sub>2</sub>Cl<sub>2</sub>, the components of which may be separated by distillation<sup>1</sup>. It is mainly carbon compounds, however, that have been recommended for these reactions: petroleum vapor, CCl<sub>4</sub>, COCl<sub>2</sub> or chloronaphthalene are reported<sup>1,3</sup>. Similarly, the use of a mixture of CCl<sub>4</sub> and Cl<sub>2</sub> is recommended to produce GaCl<sub>3</sub> from Ga<sub>2</sub>O<sub>3</sub> because Cl<sub>2</sub> alone does not react appreciably<sup>4</sup>.

These reduction reactions, however, are not now generally employed for the production of Al, Ga and In halides because they are neither clean nor convenient. **Phosgene is a likely byproduct and contaminant.** These halides are much more easily prepared via direct halogenation. On the other hand, BCl<sub>3</sub> is prepared on an industrial scale by this type of process starting from either boric oxide or a metal borate<sup>5</sup>; BBr<sub>3</sub> has also been prepared in this fashion.

(B.D. JAMES)

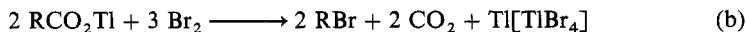
## 2.6. The Formation of the Halogen (B, Al, Ga, In, Tl) Bond

17

## 2.6.6. from Cleavage of Group-IIIB–Oxygen Bonds

## 2.6.6.2. by Halogens with Reducing Agents.

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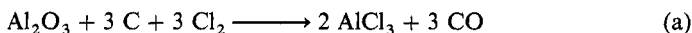


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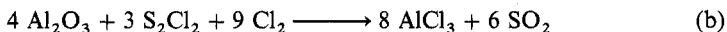
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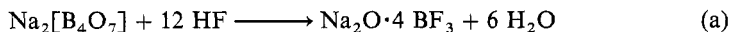
### 2.6.6.3. with Hydrogen Halides.

The interaction of HX with metal oxides is a long-established method for the production of group-IIIB metal halides. Frequently, these reactions are performed using the aqueous solutions of HX: the important aluminum halide hydrates may be obtained conveniently by dissolving the hydrated oxide in concentrated acid<sup>1</sup>. Similarly, Ga<sub>2</sub>O<sub>3</sub> dissolves on warming in conc HCl. Anhydrous InCl<sub>3</sub> and GaCl<sub>3</sub> may be obtained from interaction of the heated oxide and gaseous HCl. The details of the Ga<sub>2</sub>O<sub>3</sub> reaction have been examined. The β-form of Ga<sub>2</sub>O<sub>3</sub> contained in a quartz dish was maintained in a vertical oven and attached to a torsion balance by a quartz thread. The measurements show that chlorination occurs even at RT in a stream of dry HCl. The optimal T range seems to be between 610 and 870 K where the reaction is very rapid and the GaCl<sub>3</sub> product distills off easily<sup>2</sup>.

When HCl gas is passed into suspensions of Ti<sub>2</sub>O<sub>3</sub> either in water or alcohol, the oxide dissolves and chlorothallate derivatives may be obtained by adding suitable counteranions. The reactions seem to proceed through chlorothallic acid as an intermediate. This acid HTiCl<sub>4</sub>·3 OH<sub>2</sub> may be isolated from water, while a [TiCl<sub>5</sub>]<sup>2-</sup> derivative was obtained from ethanol<sup>3</sup>.

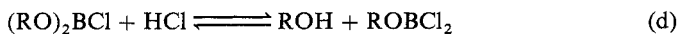
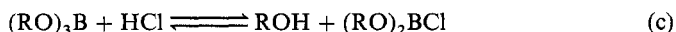
Other oxy species, such as carbonates, are useful in reactions of this type. Thallous fluoride, for example, is formed easily from the carbonate and either aq or anhyd HF<sup>1</sup>. Thallous oxide interacts with HF (either as 40% aqueous solution or as the gas at 373 K) to yield TlOF, the metal surprisingly remaining in the +III oxidation state<sup>4</sup>. Other thallium oxyhalides are not prepared this way because of the tendency for thallium to reduce to the +I state.

Hydrogen fluoride attacks borates quite aggressively. The modern two-step, high-yield process for the preparation of BF<sub>3</sub> involves the synthesis from Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> of an intermediate that is then dissociated by H<sub>2</sub>SO<sub>4</sub> attack<sup>5</sup>:



Further, boric acid is converted exothermically to fluoroboric acid (and its metal derivatives) by interaction with hydrogen fluoride<sup>6,7</sup>.

The breaking of the B—O bond in boron esters and its replacement with a B—Cl bond is a reaction of considerable significance<sup>8</sup>. If a trialkylborate contains an alkyl group of ordinary reactivity (e.g., n-C<sub>4</sub>H<sub>9</sub>) electron density at the oxygen is low, while that on boron is quite high due to the π back bonding. The rate of reaction with HX then is fairly slow according to the equilibria<sup>9</sup>:



## 2.6. The Formation of the Halogen (B, Al, Ga, In, Tl) Bond

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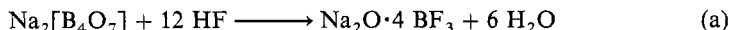
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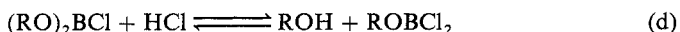
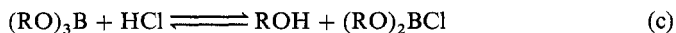
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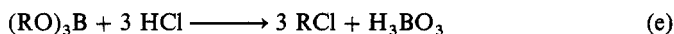
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but increases in the order  $\text{HCl} < \text{HBr} < \text{HI}$ . When the alkyl group is markedly reactive (e.g.,  $\text{t-C}_4\text{H}_9$ ) formation of alkyl halide occurs:

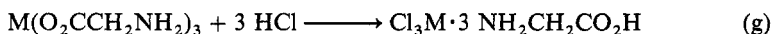


The lower trialkoxyboranes react with HF at 300 K to give  $\text{BF}_3$  alcoholates<sup>8</sup>:



Tributoxyboroxine, however, does not appear to react with HCl or HBr at 293 K.

In metal-oxygen compounds in which the synthesis has been effected by removal of a proton from a weak acid (e.g., metal alkoxides, acetylacetonates) cleavage of the metal-oxygen bond is caused by addition of the acidic hydrogen halide. For example, tris(glycinato) derivatives of gallium or thallium interact with gaseous HCl<sup>10,11</sup>:



Similarly, stoichiometric amounts of dry hydrogen halides added to solutions of aluminum alkoxides may be employed to produce compounds such as  $(\text{RO})_2\text{AlCl}$  ( $\text{R} = \text{i-C}_3\text{H}_7$ ,  $\text{C}_6\text{H}_5\text{CH}_2$ , etc.)<sup>12</sup>, while Ga isopropoxide produces the propanol adduct of  $\text{GaCl}_3$ <sup>13</sup>.

(B.D. JAMES)

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#### 2.6.6.4. by Other Halides.

Oxygen is liberated quantitatively from  $\text{B}_2\text{O}_3$  and  $\text{Ti}_2\text{O}_3$  when the oxides are reacted with  $\text{BrF}_3$  between 348 and 398 K, while oxygen replacement is incomplete for alumina<sup>1</sup>. When  $\text{Al}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$  or  $\text{In}_2\text{O}_3$  react with their respective fluorides at high T, however, the metal oxyfluorides are obtained<sup>2</sup> (although the Al compound is only identified in the vapor phase) and this procedure is regarded as the best preparation for  $\text{InOF}$ <sup>3</sup>.

Sulfur tetrafluoride is an attractive fluorinating agent because it is easily prepared and not difficult to handle<sup>4</sup>. When boric oxide is treated with this reagent in the presence of other fluorides, tetrafluoroborate salts are obtained<sup>1</sup>. Fluorination of such compounds as boron monoxide, diboron tetraethoxide or diboric acid to produce good yields of  $\text{B}_2\text{F}_4$  can also be carried out with  $\text{SF}_4$ <sup>5</sup>.

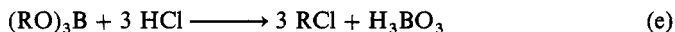
## 2.6. The Formation of the Halogen (B, Al, Ga, In, Tl) Bond

19

## 2.6.6. from Cleavage of Group-IIIB–Oxygen Bonds

## 2.6.6.4. by Other Halides.

but increases in the order  $\text{HCl} < \text{HBr} < \text{HI}$ . When the alkyl group is markedly reactive (e.g.,  $t\text{-C}_4\text{H}_9$ ) formation of alkyl halide occurs:

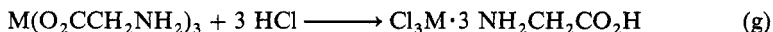


The lower trialkoxyboranes react with HF at 300 K to give  $\text{BF}_3$  alcoholates<sup>8</sup>:



Tributoxyboroxine, however, does not appear to react with HCl or HBr at 293 K.

In metal-oxygen compounds in which the synthesis has been effected by removal of a proton from a weak acid (e.g., metal alkoxides, acetylacetonates) cleavage of the metal-oxygen bond is caused by addition of the acidic hydrogen halide. For example, tris(glycinato) derivatives of gallium or thallium interact with gaseous HCl<sup>10,11</sup>:



Similarly, stoichiometric amounts of dry hydrogen halides added to solutions of aluminum alkoxides may be employed to produce compounds such as  $(\text{RO})_2\text{AlCl}$  ( $\text{R} = i\text{-C}_3\text{H}_7$ ,  $\text{C}_6\text{H}_5\text{CH}_2$ -, etc.)<sup>12</sup>, while Ga isopropoxide produces the propanol adduct of  $\text{GaCl}_3$ <sup>13</sup>.

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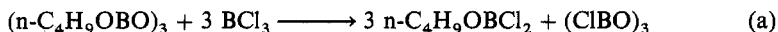
## 2.6.6.4. by Other Halides.

Oxygen is liberated quantitatively from  $\text{B}_2\text{O}_3$  and  $\text{Tl}_2\text{O}_3$  when the oxides are reacted with  $\text{BrF}_3$  between 348 and 398 K, while oxygen replacement is incomplete for alumina<sup>1</sup>. When  $\text{Al}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$  or  $\text{In}_2\text{O}_3$  react with their respective fluorides at high T, however, the metal oxyfluorides are obtained<sup>2</sup> (although the Al compound is only identified in the vapor phase) and this procedure is regarded as the best preparation for  $\text{InOF}$ <sup>3</sup>.

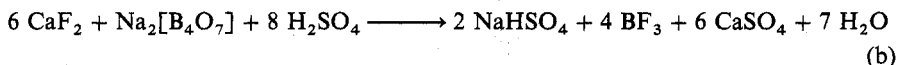
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The reaction of  $\text{CCl}_4$  with metal oxides is an old method for producing chlorides. Generally, only nonmetal oxides do not undergo conversion to the chloride (e.g.,  $\text{B}_2\text{O}_3$ ). Thus, good quality crystals of anhyd  $\text{AlCl}_3$  can be obtained by heating  $\text{Al}_2\text{O}_3$  with  $\text{CCl}_4$  at ca. 670 K in a sealed tube for a few hours<sup>6</sup> and it is reported that  $\text{GaCl}_3$  can be obtained via a similar reaction<sup>7</sup>.

Trialkoxyboroxines undergo redistribution reactions with  $\text{BCl}_3$ , e.g.:

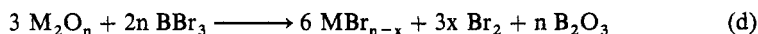


Trialkylboroxines and trialkoxyboranes also react with halides such as  $\text{AlCl}_3$ ,  $\text{PCl}_5$  and  $\text{SOCl}_2$ , but B—Cl bonds are not generally present in the products<sup>8</sup>. On the other hand, boric acid and boric oxide react with  $\text{PCl}_5$  or  $\text{PBr}_5$  to form boron halides<sup>7</sup>. Such attack of  $\text{B}_2\text{O}_3$  however, is not, regarded as a particularly good laboratory preparation, but a common commercial method for  $\text{BF}_3$  involves the treatment of  $\text{B}_2\text{O}_3$  (or a metal borate) mixed with fluorospar with concentrated sulfuric acid<sup>9</sup>:



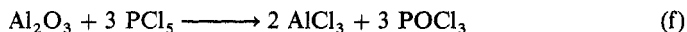
The attack of boric oxide with other fluoroborates is also recommended as an alternative in this reaction and the procedure is thoroughly documented<sup>10</sup>.

Boron trihalides,  $\text{BX}_3$  ( $\text{X} = \text{Br}, \text{I}$ ) may be employed to form metal-halogen bonds in reactions with metal oxides<sup>11</sup>. Three types of reaction are found across a broad range of oxides, summarized as follows:



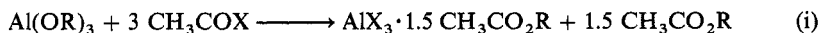
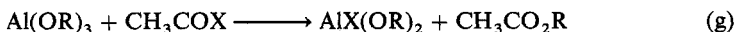
With  $\text{Ga}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$ , Eq. (c) operates, while with  $\text{Tl}_2\text{O}_3$ ,  $\text{TlBr}$  is formed in accordance with Eq. (d). Good yields are obtained and the reactions are easily performed, using quite mild conditions<sup>11</sup>.

Alumina reacts with  $\text{PCl}_5$  at 373 K:



At higher T, with increased molar ratio of  $\text{PCl}_5$  and longer reaction times,  $[\text{PCl}_4][\text{AlCl}_4]$  is formed. With  $\text{S}_2\text{Cl}_2$  and  $\text{Cl}_2$ , chlorination of  $\gamma\text{-Al}_2\text{O}_3$  forms<sup>12</sup>  $\text{AlCl}_3$  or finally  $[\text{SCl}_3][\text{AlCl}_4]$ .

Acetyl halides attack Al and Ga alkoxides to form metal-halogen bonds<sup>13</sup>, the reaction occurring in stages and involving ester adducts:



Dimethylthallium ethoxide reacts with  $\text{CHCl}_3$  to yield  $(\text{CH}_3)_2\text{TlCl}$ , in contrast to other heavy-metal alkoxides, which tend to form  $-\text{CCl}_3$  derivatives<sup>14</sup>.

The adventitious so-called "Al—O—Cl" impurity always found in chloroaluminate

ionic liquids can be removed by treating with  $\text{COCl}_2$ . The safer  $\text{SOCl}_2$  is less satisfactory<sup>15</sup>.

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## 2.6.7. from Cleavage of Group-IIIB–Other Group-VIB Element Bonds

The group-IIIB elements with their relatively low electronegativities are excellent candidates to bond with the more electronegative first-row elements. As a result, the strong bonds to oxygen make the compounds that contain them the more generally accessible ones, while those with bonds to the heavier chalcogens are in the realm of synthetic compounds. The average B—O bond dissociation energy is ca.  $500 \text{ kJ mol}^{-1}$  while it is around  $375 \text{ kJ mol}^{-1}$  for B—S bonds<sup>1</sup>. Thus, while transformations involving group-IIIB–chalcogen bonds are expected to be more facile than those involving bonds to oxygen, they need to offer practical advantages or interesting and novel possibilities in order to justify any extensive utility.

The reactivity of boron–chalcogen bonds is influenced by the bond order. There still appears to be a significant amount of  $2p\text{--}3p$   $\pi$  bonding between boron and sulfur, at least in thioboranes  $(\text{MeS})_n\text{BMe}_{3-n}$ , but relatively long B—Se distances (ca. 193 pm) argue against a significant  $\pi$  contribution to the bonding. On the other hand, triselenadiborolanes display an unexpectedly high thermal stability, which suggests particularly favorable orbital overlap<sup>2</sup>. Boron–tellurium compounds in which the B is  $\text{sp}^2$  hybridized do not appear to be stable and even in salts such as  $\text{Li}[\text{Al}(\text{TeMe})_4]$  the Al—Te bond is so weak that disproportionation occurs in reactions. Even though compounds such as  $\text{R}_2\text{GaER}'$  ( $\text{E} = \text{S}, \text{Se}$ ) are dimeric, the group-IIIB metal is still very susceptible to attack by electron-pair donors<sup>3</sup>. On the other hand, the thermal and relatively high hydrolytic stability of the Tl analogs has invited the suggestion that some  $\pi$ -character is still present in the group-IIIB–chalcogen bonds<sup>4</sup>.

(B.D. JAMES)

## 2.6. The Formation of the Halogen (B, Al, Ga, In, Tl) Bond

### 2.6.7. from Cleavage of Group-IIIB–Other Group-VIB Element Bonds

21

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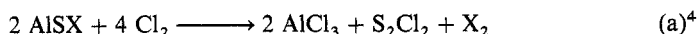
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### 2.6.7.1. by Halogens.

The formation of  $\text{GaF}_3$  via interaction of elemental  $\text{F}_2$  with a  $\text{Ga}_2\text{S}_3$  prepared at 1070 K has the advantage of proceeding more rapidly and completely than that with the corresponding oxide, reflecting the lower relative bond strength<sup>1</sup>. This reaction is quantitative between 570 and 670 K, but proceeds more slowly if the  $\text{Ga}_2\text{S}_3$  is previously heated at 1170–1270 K. Corresponding preparation of  $\text{BBr}_3$  by interaction of  $\text{B}_2\text{S}_3$  with  $\text{Br}_2$  offers no advantage. Similarly,  $\text{B}_2\text{S}_3$  burns in  $\text{Cl}_2$  yielding the  $\text{Cl}_3\text{B} \cdot \text{SCl}_4$  adduct<sup>2</sup>. As expected, the required reaction T increases as  $\text{Cl} < \text{Br} < \text{I}$ . Gallium sulfide is reported to react with  $\text{Br}_2$ <sup>1</sup>. While these sulfides are not difficult to prepare ( $\text{Al}_2\text{S}_3$ , for example, from Al and  $\text{H}_2\text{S}$ <sup>3</sup>) they decompose quite rapidly in the air and create a storage problem. The mixed halides,  $\text{AlSX}$ , are susceptible to attack by halogens, with  $\text{Cl}_2$  acting at RT to release  $\text{X}_2$  as in:



Similar degradations also are observed with the selenium and tellurium analogs, yielding  $\text{SeCl}_4$  and  $\text{TeCl}_2$ , respectively. Elemental bromine also attacks  $\text{AlSeI}$  and  $\text{AlTeI}$ , but iodine does not react<sup>5,6</sup>. Halogen attack in this fashion is in contrast with the corresponding  $\text{AlOX}$  derivatives in which substitution rather than degradation takes place<sup>4</sup>.

On the other hand, B–S bond cleavage in thiolato compounds is an excellent synthesis that makes dialkylboron bromides readily available. Since the dealkylation reaction of  $\text{Bu}_3\text{B}$  with  $\text{HBr}$  remains incomplete even after 75 min at 330 K, it is useful to have an alternative procedure. The  $\text{R}_2\text{BSR}'$  derivatives are easily prepared (quantitative yield) from readily available  $\text{R}_3\text{B}$  materials and thiols. For reactions to yield the bromides, the  $-\text{SMe}$  derivatives are employed because the  $\text{MeSSMe}$  by-product is easily removed and reaction occurs with bromine:



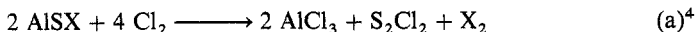
Thus, di-*n*-hexylboron methane thiolate reacts with a stoichiometric quantity of  $\text{Br}_2$  at 273 K in a markedly exothermic process to give  $(\text{Hex})_2\text{BBr}$  in 70% yield<sup>7</sup>. However, if the addition is made at ca. 210 K in the dark, followed by warming to RT, the yield is quantitative. With xs  $\text{Br}_2$ , in the presence of THF or light, the yield is reduced. It is possible that THF is cleaved by the bromoborane product and light may encourage bromination at the  $\alpha$ -C atoms, inducing some dealkylation. For reactions of  $\text{R}_2\text{BSMe}$  in the absence of solvent, yields of  $\text{R}_2\text{BB}$  are very high (e.g., 97% for  $\text{R} = \text{n-C}_5\text{H}_{11}$ ) but are slightly lower when R is a secondary alkyl. The lower yield also possibly arises because of a competing  $\alpha$ -bromination. The yields do, however, remain extremely useful (generally > 75%) and the extension of this procedure to the preparation of various dialkylboron bromides from alkenes via an initial hydroboration step is obviously attractive. Iodine does not react with these thiol derivatives because its oxidizing ability is insufficient to produce the disulfide byproduct<sup>8</sup>.

22      2.6. The Formation of the Halogen (B, Al, Ga, In, Tl) Bond  
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**2.6.7.1. by Halogens.**

The formation of  $\text{GaF}_3$  via interaction of elemental  $\text{F}_2$  with a  $\text{Ga}_2\text{S}_3$  prepared at 1070 K has the advantage of proceeding more rapidly and completely than that with the corresponding oxide, reflecting the lower relative bond strength<sup>1</sup>. This reaction is quantitative between 570 and 670 K, but proceeds more slowly if the  $\text{Ga}_2\text{S}_3$  is previously heated at 1170–1270 K. Corresponding preparation of  $\text{BBr}_3$  by interaction of  $\text{B}_2\text{S}_3$  with  $\text{Br}_2$  offers no advantage. Similarly,  $\text{B}_2\text{S}_3$  burns in  $\text{Cl}_2$  yielding the  $\text{Cl}_3\text{B} \cdot \text{SCl}_4$  adduct<sup>2</sup>. As expected, the required reaction T increases as  $\text{Cl} < \text{Br} < \text{I}$ . Gallium sulfide is reported to react with  $\text{Br}_2$ <sup>1</sup>. While these sulfides are not difficult to prepare ( $\text{Al}_2\text{S}_3$ , for example, from Al and  $\text{H}_2\text{S}$ <sup>3</sup>) they decompose quite rapidly in the air and create a storage problem. The mixed halides,  $\text{AlSX}$ , are susceptible to attack by halogens, with  $\text{Cl}_2$  acting at RT to release  $\text{X}_2$  as in:



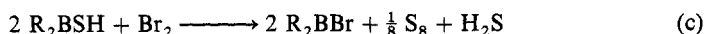
Similar degradations also are observed with the selenium and tellurium analogs, yielding  $\text{SeCl}_4$  and  $\text{TeCl}_2$ , respectively. Elemental bromine also attacks  $\text{AlSeI}$  and  $\text{AlTeI}$ , but iodine does not react<sup>5,6</sup>. Halogen attack in this fashion is in contrast with the corresponding  $\text{AlOX}$  derivatives in which substitution rather than degradation takes place<sup>4</sup>.

On the other hand, B—S bond cleavage in thiolato compounds is an excellent synthesis that makes dialkylboron bromides readily available. Since the dealkylation reaction of  $\text{Bu}_3\text{B}$  with  $\text{HBr}$  remains incomplete even after 75 min at 330 K, it is useful to have an alternative procedure. The  $\text{R}_2\text{BSR}'$  derivatives are easily prepared (quantitative yield) from readily available  $\text{R}_3\text{B}$  materials and thiols. For reactions to yield the bromides, the —SMe derivatives are employed because the  $\text{MeSSMe}$  by-product is easily removed and reaction occurs with bromine:

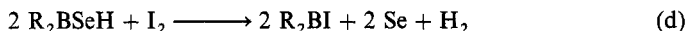


Thus, di-n-hexylboron methane thiolate reacts with a stoichiometric quantity of  $\text{Br}_2$  at 273 K in a markedly exothermic process to give  $(\text{Hex})_2\text{BBr}$  in 70% yield<sup>7</sup>. However, if the addition is made at ca. 210 K in the dark, followed by warming to RT, the yield is quantitative. With xs  $\text{Br}_2$ , in the presence of THF or light, the yield is reduced. It is possible that THF is cleaved by the bromoborane product and light may encourage bromination at the  $\alpha$ -C atoms, inducing some dealkylation. For reactions of  $\text{R}_2\text{BSMe}$  in the absence of solvent, yields of  $\text{R}_2\text{BB}$  are very high (e.g., 97% for  $\text{R} = \text{n-C}_5\text{H}_{11}$ ) but are slightly lower when R is a secondary alkyl. The lower yield also possibly arises because of a competing  $\alpha$ -bromination. The yields do, however, remain extremely useful (generally > 75%) and the extension of this procedure to the preparation of various dialkylboron bromides from alkenes via an initial hydroboration step is obviously attractive. Iodine does not react with these thiol derivatives because its oxidizing ability is insufficient to produce the disulfide byproduct<sup>8</sup>.

Attack of the halogens  $\text{Cl}_2$  or  $\text{Br}_2$  on dialkylthioboric acids  $\text{R}_2\text{BSH}$  in  $\text{CS}_2$  is exothermic and also gives the dialkyl boron halides in good yield:



The selenium analogs also react with  $\text{I}_2$  to yield the expected iodoborane derivatives but produce  $\text{H}_2$  as the gaseous product:



The weaker B—Se bonding (compared to B—S) makes these derivatives now susceptible to attack by the weaker oxidant.

With  $\text{PhGa}(\text{SR})_2$  ( $\text{R} = \text{Et}, \text{n-Pr}$ ),  $\text{I}_2$  cleaves the Ga—C bond in preference to that with S.

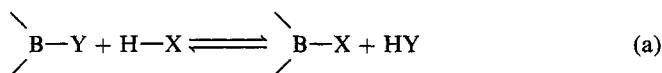
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### 2.6.7.2. by Hydrogen Halides.

Acidic species react easily with group-IIIB sulfides and selenides. Gaseous  $\text{HCl}$  reacts with  $\text{B}_2\text{S}_3$  at ca. 670 K, yielding  $\text{BCl}_3$  and  $\text{H}_2\text{S}$ , although gaseous  $\text{HI}$  does not react<sup>1</sup>. It seems likely  $\text{B}_2\text{Se}_3$  is just as suitable as  $\text{B}_2\text{S}_3$  for reactions with nucleophilic reagents ( $\text{HX}$ ) for yielding a B—X bond (and  $\text{H}_2\text{Se}$ ), despite the doubts about the precise composition of the compound<sup>2</sup>. The presence of an  $\text{sp}^2$ -hybridized B atom in B—S or B—Se compounds assists in making them susceptible to attack. Increased reactivity in the Se systems stems from the progressive diminution of the boron–chalcogen  $\pi$  interactions, as expected<sup>3</sup>. Not surprisingly, then,  $\text{AlCl}_3$  form readily by the interaction of  $\text{Al}_2\text{S}_3$  and  $\text{HCl}$ <sup>4</sup>.

Generally, displacement reactions on boron compounds of the type indicated by the equation<sup>5</sup>:

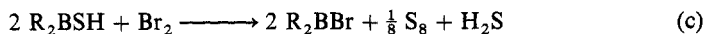


are in the order  $\text{Y} = \text{OH} < \text{OR} < \text{NR}_2 \sim \text{SR}$  which not only reflects the relative bond strengths but also suggests particularly facile reactivity with the chalcogens provided that these compounds are easily manipulated. Reactions of this kind are typified by  $\text{B}(\text{SeR})_3$  ( $\text{R} = \text{Ph}, \text{n-Bu}$ ) which with prolonged treatment with anhyd  $\text{HCl}$  in cyclohexane (for

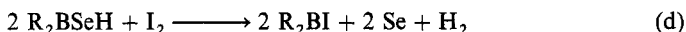


2.6. The Formation of the Halogen (B, Al, Ga, In, Tl) Bond 23  
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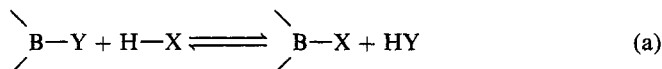
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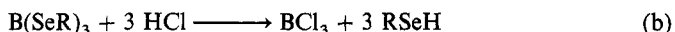
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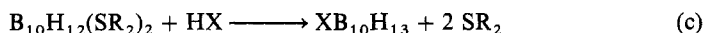
R = Ph) or CS<sub>2</sub> (R = n-Bu) produce BCl<sub>3</sub> and the appropriate selenol, this mixture being separated via trap-to-trap distillation<sup>6</sup>:



The first representative of the thiogallanes, CH<sub>3</sub>Ga(SR)Cl, has only recently been obtained, but with its reported electron-pair acceptor acidity and extreme moisture sensitivity, it will doubtless react with hydrogen halides<sup>7</sup>.

The five-membered ring system of the trithiadiborolanes, however, is a relatively stable one. The dibromotrithiadiborolane, for example, undergoes halogen exchange to yield the dichloro derivative rather than cleaving the B—S bonds in the ring. Anhydrous HBr does not react<sup>8</sup>. This high ring stability seems to be at least partly due to the lack of strain in the ring system. That electron-pair acceptor acidity at boron also has a marked influence may be seen by the inability to prepare either the parent (HB)<sub>2</sub>S<sub>3</sub> or (FB)<sub>2</sub>S<sub>3</sub> five-membered rings or the six-membered borathiin analogs<sup>3</sup>. The sp<sup>2</sup>-hybridized B atom in the selenodiborolane, however, favors attack by nucleophilic agents, which may lead to cleavage of the ring by some reagents having oxidizing ability<sup>9</sup>.

A particularly useful B—S system is that formed by the reaction of decaborane with dialkylsulfides. Hydrogen gas is eliminated and the reactive adduct (R<sub>2</sub>S)<sub>2</sub>B<sub>10</sub>H<sub>12</sub> is obtained. Anhydrous hydrogen halides react easily with these adducts at ambient temperature to produce reasonable yields of the 5- or 6-halogeno decaborane derivatives:



The 5-F, 5-Br, 5-I and 6-Cl derivatives may be obtained by this method, whereas halogenation of B<sub>10</sub>H<sub>14</sub> under electrophilic conditions normally causes substitution in the 2,4 or 1,3 positions (§2.6.5). A useful yield (55%) of the 5-FB<sub>10</sub>H<sub>13</sub> derivative is obtained by reaction over several hours in benzene. It is stated explicitly that very pure starting materials and a strict adherence to the recommended concentrations are necessary in the synthesis; otherwise **vigorous decomposition** may result<sup>10</sup>. Yields of the other derivatives similarly are around 50%, except for the 5-I compound which is much poorer (15%).

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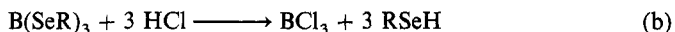
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### 2.6.7.3. by Other Halides.

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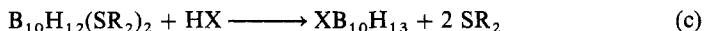
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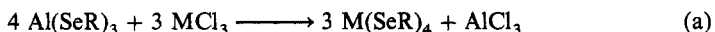
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### 2.6.7.3. by Other Halides.

The relatively weak group-IIIB–group-VA element bonds permit facile exchange reactions with a wide variety of halides. Thus, tetravalent transition-metal chlorides

undergo simple exchange with  $\text{Al}(\text{SeR})_3$  in refluxing ether-benzene mixture in a short time:



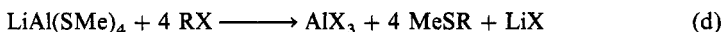
where  $\text{M} = \text{Ti, Zr}$ ;  $\text{R} = \text{Ph, naphthyl}$ . Chromium chloride (as the THF adduct) reacts similarly, while analogous reactions with niobium or tantalum pentachloride in ether- $\text{CS}_2$  cause the metal to reduce and form the concomitant diselenide<sup>1</sup>:



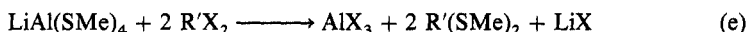
The aluminate salts are similarly reactive. For example, the tetrakis(phenylseleno) derivative interacts in ether with the chlorosilane,  $\text{Me}_2\text{Si}(\text{H})\text{Cl}$ , on warming to RT from 77 K, giving a 95 % yield of the volatile seleno-substituted silane<sup>2</sup>:



In like fashion, Si, Ge and Sn halides react with the thio analogs:



where  $\text{X} = \text{Cl, Br}$ ;  $\text{R} = \text{Me}_3\text{M, SiH}_3, \text{GeH}_3, \text{Si}_2\text{H}_5$ ;  $\text{M} = \text{Si, Ge, Sn}$  and

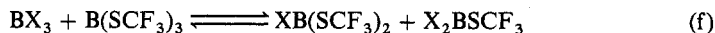


where  $\text{X} = \text{Cl, Br}$ ;  $\text{R}' = \text{Me}_2\text{M, SiH}_2$ ;  $\text{M} = \text{Si, Ge, Sn}$ . Readily available  $\text{F}_3\text{B} \cdot \text{OEt}_2$  also undergoes exchange reactions with these thio- and selenoaluminate salts<sup>3</sup>. The yields are excellent in these reactions: it is greater than 70 %, even with the  $\text{Me}_2\text{Sn}$  derivative. They are much worse, however, when  $\text{LiAl}(\text{TeMe})_4$  is employed because elemental tellurium is deposited and the products disproportionate, giving  $\text{Me}_2\text{Te}$  and the group IVB telluride<sup>4</sup>. These aluminate salts are particularly useful reagents, not only because they are able to transfer the appropriate functional group quite readily, but also because they are easily prepared in situ in ether from recrystallized  $\text{LiAlH}_4$ .

Electrophilic reagents cleave the B—S bond in  $\text{Me}_2\text{BSMe}$ , as expected. Thus, a mixture of this compound and  $\text{BCl}_3$  in the absence of a solvent reacts in a few minutes at 273 K, giving  $\text{Me}_2\text{BCl}$  and  $(\text{Cl}_2\text{B-SMe})_2$ . Similarly,  $\text{BBr}_3$  will react to give  $(\text{Br}_2\text{B-SMe})_2$ . When  $\text{Me}_2\text{BSMe}$  reacts with  $\text{SbCl}_5$ , a dark precipitate is obtained immediately, which then decomposes and evolves  $\text{Me}_2\text{BCl}$  at RT. Also, reaction with  $\text{FeCl}_3$  produces a black precipitate and  $\text{Me}_2\text{BCl}$ . In both these cases, there is no evidence for the formation of sulfonium salts of the type  $[(\text{Me}_2\text{B})_2\text{SMe}]\text{X}$ , presumably because the electron pair basicity at S is insufficient. With  $\text{MeI}$ , however, if the reaction is allowed to proceed in the dark, a small amount of  $[\text{Me}_3\text{S}]\text{I}$  salt is produced over about 3 w<sup>5</sup>. On the other hand,  $\text{PhB}(\text{SBu})_2$  does not react with  $\text{MeI}$  or  $\text{BuBr}$  under normal conditions<sup>6</sup>. The salt  $[\text{Me}_3\text{S}][\text{GaI}_4]$  forms on the extended reaction of  $\text{I}_2\text{GaSMe}$  with  $\text{MeI}$ <sup>7</sup>.

The combination of a relatively weak B—S bond and the ease of separation of the volatile boron halide byproduct enables boron trisulfide to function as a useful sulfur transfer agent toward metal halides. Thus,  $\text{WSCl}_4$  may be prepared by interaction of the hexachloride with  $\text{B}_2\text{S}_3$  at 373–393 K. Similarly, reactions of stoichiometric amounts of  $\text{MCl}_5$  and  $\text{B}_2\text{S}_3$  at 363 K ( $\text{M} = \text{Nb}$ ), 353 K ( $\text{M} = \text{Ta}$ ) or 464 K ( $\text{M} = \text{Mo}$ ) produce the corresponding  $\text{MSCl}_3$  derivatives. The ease and potential utility of this type of reaction is shown because liq  $\text{BCl}_3$  forms in the  $\text{NbCl}_5$ — $\text{B}_2\text{S}_3$  reaction even at RT<sup>8</sup>. Both  $\text{Al}_2\text{S}_3$  and  $\text{Al}_2\text{Se}_3$  react readily with  $\text{Se}_2\text{Cl}_2$ , producing  $\text{AlCl}_3$ . The reaction with the sulfide

precipitates sulfur and selenium<sup>9</sup>. Little  $\text{AlCl}_3$  appears to be obtained by heating  $\text{Al}_2\text{S}_3$  with the more ionic halides ( $\text{NaCl}$ ,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ), although  $\text{KCl}$  appears to produce a volatile,  $\text{AlCl}_3$ -containing product<sup>10</sup>. Potassium fluoride interacts at 383 K with the somewhat thermally unstable  $\text{B}(\text{SCF}_3)_3$  in an apparently catalytic reaction, giving  $\text{BF}_3$  and  $\text{F}_2\text{CSe}$ , but the expected redistributions with boron halides are more facile:



The mono- and dihalogeno compounds ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ) in this case may be obtained, however, at lower  $T$  (ca. 220 K) in sealed vessels<sup>3</sup>.

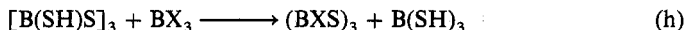
The aluminum chalcogen halides may be obtained by similar disproportionation reactions in sealed tubes:



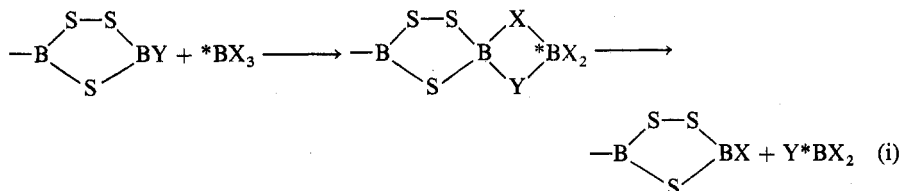
( $\text{Y} = \text{S}$ ,  $\text{Se}$ ,  $\text{Te}$ ;  $\text{X} = \text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ). The single  $\text{AlYX}$  compound is formed as a stable phase, so that if  $x\text{s AlX}_3$  is employed it may be sublimed away from the product. All the iodides, however, are more conveniently prepared from direct combination of the elements. The seleno derivative is particularly difficult because not only are  $\text{AlI}_3$  and  $\text{Al}_2\text{Se}_3$  very sensitive reagents, but also the desired reaction is very slow at 620 K while the product becomes thermally unstable at  $T$  that would otherwise accelerate its formation<sup>11,12</sup>.

In view of the ability of  $\text{HgCl}_2$  to form covalent bonds with thiols and thioethers, this halide can be expected also to react with compounds containing  $\text{B}-\text{SR}$  bonds. In agreement with this, it is found that  $\text{R}_2\text{B}(\text{SR}')$  compounds ( $\text{R} = n\text{-Pr}$ ) react readily (ca. 1 h) in toluene at 353 K, giving good yields (ca. 60%) of  $\text{R}_2\text{BCl}$  which may be separated by distillation. The compound with  $\text{R}' = n\text{-Bu}$  reacts more readily than that where  $\text{R}' = t\text{-Bu}$ . A four-center transition state containing an electrophilic  $\text{Hg}$  and a nucleophilic  $\text{Cl}$  possibly is involved in these reactions which are favored by the strong  $\text{Hg}-\text{S}$  bond<sup>13</sup>. Mercuric chloride also reacts smoothly (but slowly) with the decaborane-sulfido adducts, to produce the 6-chloro derivative in about 60% yield. This is a simple route to this isomer. Unfortunately, the analogous reaction with  $\text{HgBr}_2$  does not occur<sup>14</sup>.

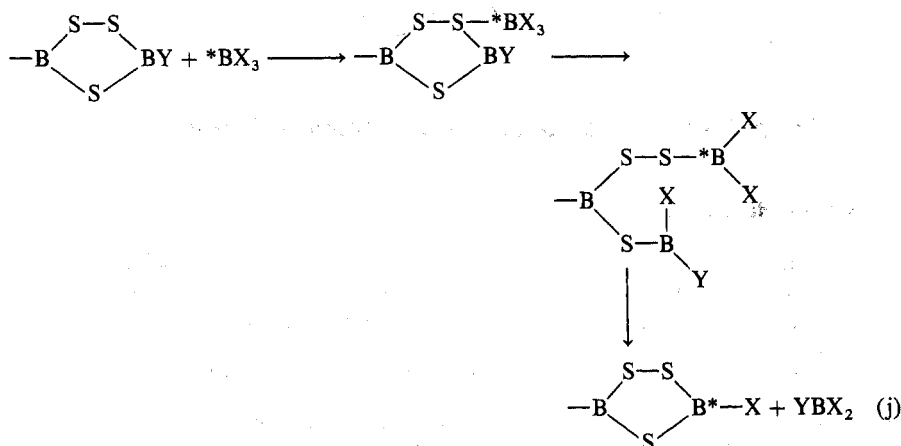
In cyclic boron systems, the  $\text{B}-\text{SH}$  group is reactive and the thio group may be replaced easily. For example, with metathioboric acid, exchange reactions, e.g.:



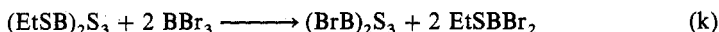
occur not only for  $\text{X} = \text{Cl}$ ,  $\text{Br}$  but also for other groups such as  $\text{CH}_3$ ,  $\text{NMe}_2$  and  $\text{SR}$ . Such reactions appear to take place via an intermediate addition compound<sup>15</sup>. In the dialkylthioboric acid derivative  $\text{Bu}_2\text{BSH}$ , the  $\text{B}-\text{S}$  bond is easily ruptured by  $\text{S}_2\text{Cl}_2$  (in  $\text{CS}_2$  sol), giving  $\text{Bu}_2\text{BCl}$  in high yield<sup>15</sup>. Even in the ionic species  $\text{X}_3\text{BSH}^-$  ( $\text{X} = \text{F}$ ,  $\text{Cl}$ ) replacement of  $\text{SH}$  by halide occurs quite readily on addition of excess boron halide<sup>17</sup>. Exchange in the five-membered ring system of the trithiadiborolanes may occur by an exocyclic substituent exchange such as:



or by an endocyclic process proceeding via ring opening followed by X–Y exchange according to:



The endocyclic process dominates if the substituents at the ring carry no lone pairs of electrons (e.g., CH<sub>3</sub>), while the exocyclic mechanism is favored when the substituents on the trithiadiborolane are more basic than the ring S atoms (which are only weakly basic anyway). Thus, both of the opposite types of exchange reactions:



and



occur by virtually 100% exocyclic processes<sup>18</sup>. The AsF<sub>3</sub> reagent, however, causes destruction of the ring system (producing BF<sub>3</sub>) in its reaction with (BrB)<sub>2</sub>S<sub>3</sub>, in part because it is an aggressive reagent, but also because of the instability of the (FB)<sub>2</sub>S<sub>3</sub> product as a ring system<sup>19</sup>.

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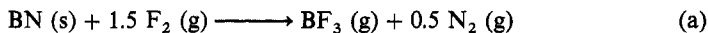
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## 2.6.8. from Cleavage of Group-IIIB–Nitrogen Bonds

### 2.6.8.1. by Halogens.

The strong group-IIIB–halogen bonds facilitate the formation of halides from the nitrides and the BN–F<sub>2</sub> reaction is the most studied system. With the assistance of the weak F–F bond, BN burns spontaneously in F<sub>2</sub> at RT when the pressure is ca. 13 kPa:



At higher pressures, pellets of BN burn white hot and combustion appears to be essentially complete ( $\Delta H_{298}^\circ = -885 \text{ kJ mol}^{-1}$ ). Virtually no nitrogen fluorides appear in the products<sup>1–4</sup>. Reaction is dependent on the state of the solid material, evidenced by the fact that no reaction is observed between F<sub>2</sub> and dense, hot-pressed BN at RT, although rapid conversion occurs if the gas is dissociated by a microwave discharge. Under nonequilibrium conditions, it is also possible to produce BF (g) or BF<sub>2</sub> (g). Also in this conversion, the reaction-induced temperature rise may increase the reaction rate. If the limiting BN consumption is <0.5% of the specimen and the T is maintained below 500 K, this conversion may be employed as an accurate gravimetric determination of F-atom concentration<sup>5</sup>.

A similar situation obtains for the AlN–Cl<sub>2</sub> reaction. The agglomerated material is not attacked until relatively high T (1030 K), yielding AlCl<sub>3</sub> and N<sub>2</sub>, although traces of moisture (which lead to the presence of HCl) result in a very lively reaction. Dry bromine reacts less readily<sup>6,7</sup>. Crystalline nitrides<sup>8</sup> are extremely resistant to chemical attack, although the BN still reacts with chlorine<sup>9</sup>.

For dialkylamido compounds of the type L<sub>2</sub>M–NR<sub>2</sub> (M = group-IIIB element), reactions with elemental halogens do not appear to have been reported<sup>9</sup>. Such compounds, however, are highly reactive and even though there appears to be little tendency to form a nitrogen–halogen bond, it is possible that controlled reactions with halogens may prove useful in cleaving the M–N bond and permitting the synthesis of substituted hydrazines.

Addition of Br<sub>2</sub> to B≡N in iminoboranes RB≡NBu-t gives the N-bromoamino-boranes, BrB(B)=NBrBu-t. The thermal stability of the product depends on the R group (R = alkyl, C<sub>6</sub>F<sub>5</sub> and Me<sub>3</sub>SiNBu-t)<sup>11</sup>.

(B.D. JAMES)

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## 2.6. The Formation of the Halogen (B, Al, Ga, In, Tl) Bond

## 2.6.8. from Cleavage of Group-IIIB–Nitrogen Bonds

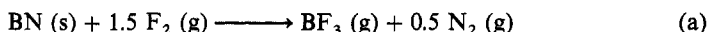
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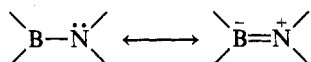
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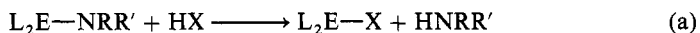
### 2.6.8.2. with Hydrogen Halides.

If one or more B—N bonds occur in BXYZ (e.g., in aminoboranes) the electron pair on nitrogen is free to participate in  $\pi$ -bonding and the system is often represented as:



However, the assigned charges on the atoms seem to have little reality because the  $\pi$  charge transfer from N to B largely compensates for the B—N electronegativity difference in the  $\sigma$  bonding. Thus, the B—N bond order may be strongly influenced by substituents on the two atoms and the chemistry is often subject to steric influences<sup>1</sup>.

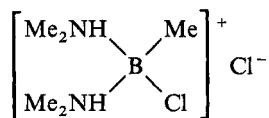
Amido compounds generally are subject to reactions with protic species (HX) according to a schematic equation of the type<sup>2</sup>:



The electron-pair acceptor acidity of group-IIIB compounds facilitates attack by such reagents. The course of the reaction of bis(amino)boranes,  $(\text{R}_2\text{N})_2\text{BR}'$ , with HX at RT depends on the nature of the group R'. If R' = alkoxy, alkyl (other than Me), SiR<sub>3</sub> or NMe<sub>2</sub>, then cleavage of the B—N bond occurs:



This type of reaction proceeds easily, e.g., with  $\text{PrB}(\text{NMe}_2)_2$  and HX (X = Cl, Br, I) in ether or pentane, but with  $\text{MeB}(\text{NMe}_2)_2$  reaction occurs to form a boronium salt<sup>3</sup>:



Similarly,  $\text{B}(\text{NMe}_2)_3$  reacts with HCl at 273 K in ether initially to yield  $(\text{Me}_2\text{N})_2\text{BCl}$  and  $\text{Me}_2\text{HN} \cdot \text{HCl}$ , but with 3 or 4 mol equiv HCl the boronium salt  $[\text{Cl}_2\text{B}(\text{HNMe}_2)_2]\text{Cl}$  is obtained:



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On the other hand, the compound  $\text{B}(\text{NEt}_2)_3$  reacts quite differently from its dimethylamino analog. With 4 mol equiv of HCl, the dichloroborane derivative is obtained and a further mole is required to cleave the remaining B—N bond<sup>4</sup>:



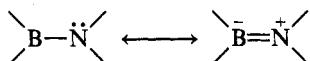
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 2.6.8.2. with Hydrogen Halides.

29

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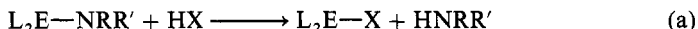
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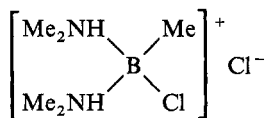
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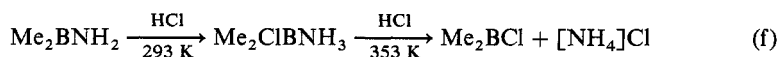


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Monoaminoboranes,  $R_2NBR'_2$ , and even those with mixed substituents on the boron atom are quite easily available so that if the volatile  $Me_2NH$  can be evolved this method may hold some advantages for synthesis<sup>5</sup>. The compound  $Me_2BNH_2$  does not react with HCl unless the dimer is first dissociated to the monomer, which then reacts vigorously at RT. A further mole of HCl reacts on heating<sup>6</sup>:



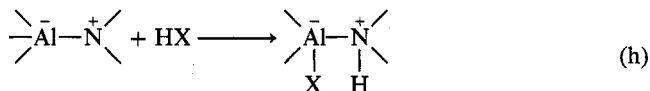
Similarly, the compounds  $(R_2N)_2BH$  ( $R = Et, Pr, Bu$ ) in their monomeric forms react with HCl to give  $R_2NH:BHCl_2$ , but in contrast, if  $R = Me$ , the compound reacts to form the boronium salt  $[Cl(H)B(NHMe)_2]Cl$ . This salt is not as stable as others and decomposes on heating to give  $Me_2NBHCl$  and the amine hydrochloride<sup>7</sup>.

Tetrakis(dialkylamino)diboranes (4) initially form adducts with hydrogen halides, but the tetra-substituted product is obtained (as the amine adduct) with higher mole ratios<sup>2,8</sup>. Excess HCl also converts a B-bonded dibutylamino group in a borazine into the B-chloro derivative<sup>9</sup> but the general reaction of hydrogen halides with borazenes is one of addition<sup>1,10</sup>. After addition, however, cleavage of the ring can occur, especially on heating and in the presence of excess hydrogen halide. Hexamethylborazene, e.g., is cleaved with xs HCl above 420 K, giving methyldichloroborane<sup>10</sup>.

Aluminium derivatives likewise are susceptible to attack with hydrogen halides. Excess HCl may be employed to completely decompose the  $Me_2AlNMe_2$  dimer<sup>11</sup>:



The more associated anilino derivative  $[EtAlNPh]_4$  is also subject to attack by hydrogen halides at RT:



yielding an Al—halogen bond in an aniline adduct. Excess HCl finally cleaves the Al—C bond, showing that the Al—N bond is more readily attacked<sup>12</sup>.

Nitrides are attacked by hydrogen halides, although the presence of small amounts of moisture may have an effect on the reaction temperature. Aluminum nitride is completely converted into  $AlCl_3$  and  $NH_3$  quite quickly by gaseous HCl at 1170 K, while dissolution in aqueous solutions of HCl are reported for both the Al and In compounds<sup>13</sup>. Likewise, BN is converted to  $[NH_4]BF_4$  by HF treatment<sup>14</sup>.

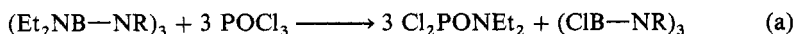
(B.D. JAMES)

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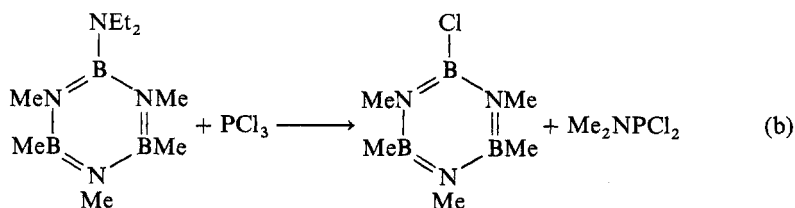
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### 2.6.8.3. with Other Halides.

Many reactions of group-IIIB–nitrogen bonds with various halides have been reported. Typical of these are the reactions of  $\text{—NR}_2$  substituted derivatives of borazine with boron or phosphoryl halides, halogenating at boron. Thus, B-tris(di-n-butylamino)-borazine and  $\text{BCl}_3$  in  $\text{CH}_2\text{Cl}_2$  gives B-trichloroborazine in 57% yield. A similar reaction with  $(\text{Et}_2\text{NB—NH})_3$  gives over 90% yield of  $\text{Et}_2\text{NBCl}_2$ , but although some B-trichloroborazine presumably is produced it is not reported. With  $\text{POCl}_3$ , a 96% yield is reported<sup>1</sup>:



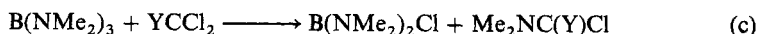
When  $\text{PCl}_3$  is allowed the opportunity to cleave either a B—N or B—C bond in substituted borazines, the B—N bond is attacked preferentially:



Similarly, both  $\text{PCl}_3$  and  $\text{BCl}_3$  cleave the B—N bonds in the diborane (4) derivative  $(\text{Bu})(\text{Me}_2\text{N})\text{B—B}(\text{NMe}_2)(\text{Bu})$  and  $\text{TiCl}_4$  exchanges halogen for the  $\text{NMe}_2$  group in  $(\text{Me}_2\text{N})_2\text{BCH}_3$ . For the latter reaction product,  $\text{Me}_2\text{NBCH}_3$ , this procedure provides an excellent, straightforward preparation<sup>2,3</sup>. The  $\text{Me}_2\text{N}$  group in the  $\mu$ -boranedi-thiolato-bridged binuclear metal complex,  $\text{Me}_2\text{NBS}_2\text{Fe}_2(\text{CO})_6$  also can be exchanged for Cl or Br using the respective B halides<sup>4</sup>.

In reactions of  $\text{B}(\text{NEt}_2)_3$  with  $\text{PCl}_3$  or  $\text{YPCl}_3$  ( $\text{Y} = \text{O}, \text{S}$ ) cleavage of the B—N bonds occur to give mixed species,  $\text{Cl}_{3-n}\text{E}(\text{NEt}_2)_n$ , [where  $\text{E} = \text{B}$  or  $\text{P}$ ]. These mixed species, however, show distributions that are not in accord with a completely random mechanism. In the  $\text{B}(\text{NEt}_2)_3\text{—PCl}_3$  mixture, the chloride substituent prefers P over B, while the reverse is true in the case of 4-coordinate phosphorus. Thus, it appears that the more effective  $\pi$  donor  $(\text{NEt}_2)$  bonds to the better acceptor. In the case of 4-coordinate phosphorus, the presence of the oxygen or sulfur atom enhances the effective electronegativity of the P center and assists its ability to behave as an effective acceptor<sup>5</sup>.

The compound  $\text{B}(\text{NMe}_2)_3$  also has one B—N bond cleaved by either phosgene or thiophosgene<sup>6</sup>:



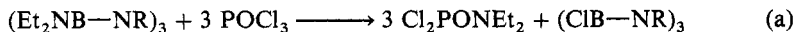
2.6. The Formation of the Halogen (B, Al, Ga, In, Tl) Bond  
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 2.6.8.3. with Other Halides.

31

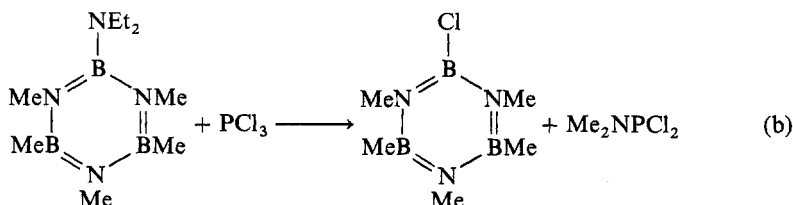
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13. *Gmelin's Handbuch der Anorganischen Chemie*, 8 Aufl., Syst. 35B, Die Verbindungen des Aluminiums, Verlag Chemie, Berlin, 1934.
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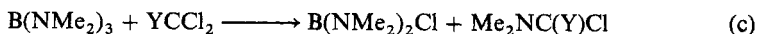
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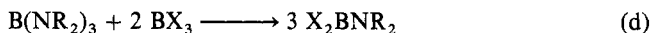
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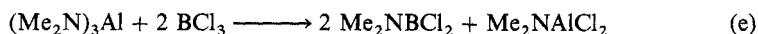


where Y = O, S. Cleavage of all the B–N bonds occurs with SF<sub>4</sub> in SO<sub>2</sub> solution yielding the sulfonium salt [(Me<sub>2</sub>N)<sub>3</sub>S][BF<sub>4</sub>], which remains after the volatile materials have been removed<sup>7</sup>. Parenthetically, this is a good synthesis for the aminosubstituted cation.

Redistribution reactions:



are common and easy to carry out<sup>8</sup>. Such a reaction is an excellent method for the preparation of Et<sub>2</sub>NBF<sub>2</sub>, and the chloro-substituted dimethylaminoalanes are likewise obtained under mild conditions<sup>9</sup>. That redistribution occurs so as to exchange the nonbridging groups in the system is shown by the reaction:



in which the first and last species are associated via NR<sub>2</sub> bridges.

A reaction occurs between Me<sub>2</sub>BNH<sub>2</sub> and BF<sub>3</sub>, yielding Me<sub>2</sub>BF which may be isolated by fractionation. Similar reactions occur between Me<sub>2</sub>BNMe<sub>2</sub> and BX<sub>3</sub> (X = F, Cl) but the products appear to be formed via decomposition of unstable adducts<sup>10</sup>.

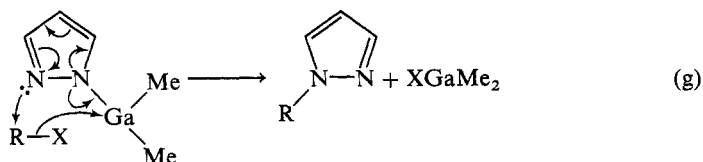
Aminoiminoboranes react with more covalent halides in two distinct ways. With BX<sub>3</sub>, there is insertion into the B–N bond to give cyclic R<sub>2</sub>N–BX–NR'–BX<sub>2</sub>. The tetramethylpiperidinoiminoboranes (with R = bulky groups such as t-Bu) insert into the Y–X bond of YX<sub>3</sub> (Y = P, As, Sb; X = Cl, Br) to yield compounds having B–X bonds. A similar reaction occurs with HgCl<sub>2</sub>, but HgBr<sub>2</sub> and HgI<sub>2</sub> yield only 1:1 adducts (no B–X bond) as is also the case with GaCl<sub>3</sub> and aluminum halides<sup>11</sup>.

Organoaminoaluminates also undergo facile cleavage of their Al–N bonds; this reaction may be exploited synthetically more in the context of the organo-containing product than for the fact that an Al–halogen bond is formed. A simple example is the reaction between BF<sub>3</sub> and LiAl(NMe<sub>2</sub>)<sub>4</sub> to produce the substituted borane<sup>12</sup>:



Similarly, silyl bromide reacts with aminoaluminates to give generally good yields of compounds containing N–Si bonds. The reactions occur at convenient rates (10–60 min) with cooling (177–230 K) in ethereal solvents providing a facile procedure for the preparation of compounds that have proved troublesome via other methods. Pyrrolidine silane, for example, may be obtained in 75% yield<sup>13</sup>.

Exchange reactions with organometallic derivatives often are much less facile. For example, Me<sub>2</sub>TiNMe<sub>2</sub> only reacts very slowly with BuBr, although a high yield of Me<sub>2</sub>TiBr eventually is obtained after refluxing in benzene. Exchange with Me<sub>3</sub>SnCl in ether, however, is much faster<sup>14</sup>. The pyrazole derivative of dimethylgallium also is attacked relatively slowly by alkyl halides in what appear to be S<sub>N</sub>2 reactions:



The reaction appears to be useful in preparing N-alkylated pyrazoles. With PrBr, a 67% yield of the alkylated derivative seems to be the highest<sup>15</sup>.

(B.D. JAMES)

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## 2.6.9. from Cleavage of the Group-IIIB–Other Group-VB Element Bond

### 2.6.9.1. by Halogens.

This type of reaction appears not to have been employed to date on a wide scale. Insofar as the compounds containing group-IIIB–group-VB element bonds are themselves prepared from group-IIIB halides, this is not too surprising. However, the relatively high bond strengths to halogen for group-VB elements other than nitrogen (Table 1) suggests that there is more scope for cleavage of bonds to phosphorus, As and Sb than for the corresponding reactions involving group-IIIB–nitrogen bonds (§2.6.8.1). The reaction is driven effectively by the formation of both the group-IIIB–halogen and group-VB–halogen bonds and may prove to be useful for the synthesis of group VB halide derivatives. Thus, the B–M bonds (M = As, Sb) in the carboranyl derivatives 9-(C<sub>2</sub>H<sub>2</sub>B<sub>10</sub>H<sub>9</sub>)MCl<sub>2</sub> are cleaved by interaction with bromine<sup>1</sup>. This reaction is employed to determine the position of the metal substitution because it yields the known bromocarborane in a "clean" reaction.

TABLE 1. GROUP-VB–HALOGEN  
 BOND STRENGTHS (in kJ mol<sup>-1</sup>)<sup>7</sup>

	F	Cl	Br	I
N	272	192		
P	527	330	263	184
As	485	288	242	180
Sb	385	309		
Bi	309	279	263	242

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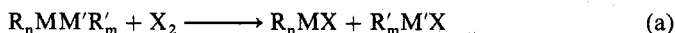
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In the binary compounds, it has been found that BP reacts rather vigorously ( $\Delta H_{rx} = 805 \text{ kJ mol}^{-1}$ ) with  $\text{Cl}_2$  at around 800 K and under a pressure of 700 kPa to form crystalline  $\text{Cl}_3\text{P}\cdot\text{BCl}_3$  (presumably  $[\text{PCl}_4][\text{BCl}_4]$ ). Such interaction with halogen may be employed to yield a low-valent intermediate, which then reconverts to BP and is thus able to form a more crystalline variety of BP via transport growth. Transported BP crystals are rather more inert than the powder<sup>2</sup>. The general susceptibility of these group-III-group-V compounds to attack in air signifies that the materials react in general in a similar manner to BP. The thallium phosphides are not well characterized<sup>3</sup>. A similar expectation is reasonable for halogenation of compounds such as  $(\text{Me}_2\text{N})_2\text{B}=\text{MR}_2$  ( $\text{M} = \text{As, Sb; R} = \text{Me, Et}$ )<sup>4</sup> or  $\text{R}_2\text{Tl}-\text{MR}'\text{Ph}$  ( $\text{R} = \text{Me, Et; M} = \text{P, As; R}' = \text{Ph, H}$ )<sup>5</sup> since the reaction:



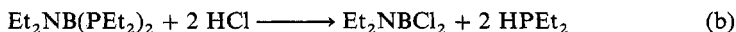
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### 2.6.9.2. by Hydrogen Halides.

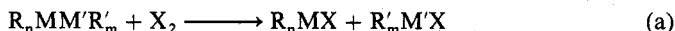
These reactions are potentially widely applicable and likely to produce high yields in view of their generally clean nature, although those reactions producing arsine and stibine derivatives may exhibit more thermal decomposition products than those releasing phosphines. The electron-pair acceptor acidity of group-IIIB compounds facilitates attack by HX and since any  $\pi$  overlap is weaker in group-IVB-phosphorus compounds than it is in their nitrogen counterparts, reactions often occur readily. Thus, in the reaction of aminobis(phosphino)boranes in which the  $\text{R}_2\text{N}$  function provides the stabilizing  $p\pi-p\pi$  overlap with boron, 1 or 2 mol equiv HCl at 223 K successively cleave the boron-phosphorus bonds in preference to the boron-nitrogen bond<sup>1</sup>. The phosphine is released and a B—Cl bond formed immediately:



Thus, no participation of the phosphorus lone pair in  $\pi$  bonding is evident. Another indication of the relative reactivities of these bonds is exemplified by  $(\text{Me}_2\text{N})_2\text{BPEt}_2$ ,

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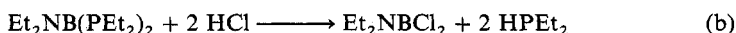
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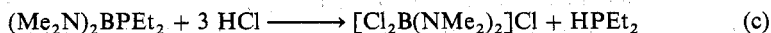
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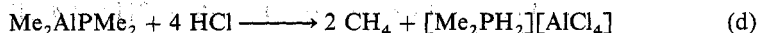
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which, when subjected to  $\geq 3$  mol equiv HCl, releases only the phosphine and forms the boronium salt<sup>2</sup>:



The arsenido and stibinido analogs probably react similarly in view of their reported sensitivity<sup>3</sup>.

The chemistry of compounds in which P, As or Sb is bonded to elements in group IIIB other than B is rather poorly developed<sup>4,5</sup>, but where examples are found, the reactions are quite unexceptionable. For example, with the dialkylthallium compound,  $\text{Me}_2\text{TlP}(\text{H})\text{Ph}$ , a 1 mol  $\text{L}^{-1}$  HCl solution releases  $\text{PhPH}_2$  very quickly and a high yield (79%) of  $\text{Me}_2\text{TiCl}$  can be obtained from the aqueous phase<sup>6</sup>. While the reactions of other phosphido and arsenido derivatives are not specifically described, the implication is that these are entirely analogous. With the more reactive diorganoaluminum derivatives, the hydrogen halide cleaves the Al—C bonds in addition to the Al—P linkage<sup>7</sup> and the chloroaluminate salt is obtained:



A number of bis(borane) salts of phosphorus and arsenic are known<sup>8</sup>, but in the reported reaction of  $\text{NaH}_2\text{P}(\text{BH}_3)_2$  with 1 mol equiv HCl at 177 K in ether, only the conversion of the anion into  $\mu\text{-H}_2\text{PB}_2\text{H}_5$  has been noted<sup>9</sup>. This protonic attack makes it appear likely that xs HCl cleaves not only the B—P bridge but also the B—H bonds (§2.6.5.2).

Most boron-phosphorus compounds are polymeric (especially trimeric) cyclic structures in which the P atoms carry formal positive charges and the B atoms are formally negative. These compounds possess significant stability, not only thermally but also toward hydrolysis reactions. With [P] hexamethylcycloborophane, for example, the reaction with dry HCl occurs only very slowly at ca. 570 K and releases hydrogen. Thus, attack occurs at the B—H bond rather than the reagent being able to disrupt the ring to any significant extent<sup>9</sup>. However, the compound  $\text{Ph}_2\text{AsBPH}_2$ , even though it is monomeric, resists dilute acids at 370 K. The high stability of the ring structure is postulated to come about because B—H bonding electrons are able to supplement the  $\text{P} \rightarrow \text{B}$  dative  $\sigma$  bond<sup>10</sup>. With compounds such as  $(\text{H}_2\text{Al—PEt}_2)_3$ , on the other hand, their trimeric nature does not lead to any special stability, and spontaneous ignition in air foreshadows particularly high reactivity<sup>11</sup>.

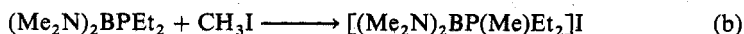
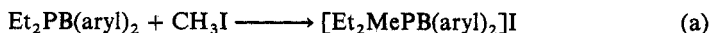
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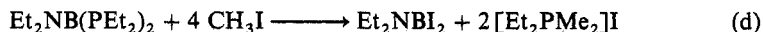
- 36 2.6. The Formation of the Halogen (B, Al, Ga, In, Tl) Bond  
 2.6.9. from Cleavage of the Group-IIIB–Other Group-VB Element Bond  
 2.6.9.3. by Other Halides.

### 2.6.9.3. by Other Halides.

Compounds that contain a group-IIIB–group VB element bond display typical inorganic and organic substitution reactions with various polar reagents. For example, compounds such as  $\text{Et}_2\text{P}-\text{B}(\text{aryl})_2$  and  $(\text{Me}_2\text{N})_2\text{B}-\text{PEt}_2$  react with limited quantities of methyl iodide in organic solvents and methylate at phosphorus, forming boronium salts<sup>1,2</sup>. This suggests that the lone pair on phosphorus is still available for complexation. The reactions are:

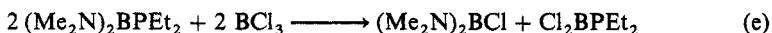


With xs  $\text{CH}_3\text{I}$  reagent, however, the B–P bond is cleaved and the phosphonium salt separates<sup>2</sup>:



In a similar way,  $\text{EtI}$  reacts with  $\text{Me}_2\text{TIP}(\text{H})\text{Ph}$  in pentane slowly (over 72 h) giving the phosphine,  $\text{HPh}(\text{Et})$  (from the filtrate) and a 35% yield of  $\text{Me}_2\text{TII}$  (from the residue)<sup>3</sup>.

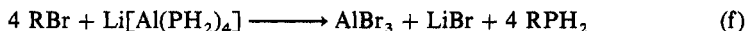
Boron trichloride and  $(\text{Me}_2\text{N})_2\text{B}-\text{PEt}_2$  participate in a kind of scrambling reaction represented by the equation:



but which appears to proceed via an unstable adduct intermediate<sup>2</sup>.

Reactions involving cleavage of group-IIIB–group-VB element bonds have a wide applicability in synthesis. For this, the easily obtained aluminate anions<sup>4</sup> generally are the reagents of choice. Thus,  $\text{Li}[\text{Al}(\text{PH}_2)_4]$  can be employed to introduce PH groups into various molecules and is a valuable reagent when the products of the reaction are volatile. The phosphinoaluminate reagent reacts with  $\text{EtI}$  in diglyme over 12 h to evolve  $\text{EtPH}_2$  (together with  $\text{PH}_3$ ), although some of the ethylphosphine becomes incorporated into the solid reaction products and is released only on hydrolysis. The reaction contrasts with that between  $\text{EtI}$  and the nitrogen analog,  $\text{Li}[\text{Al}(\text{NH}_2)_4]$ , which fails to produce any  $\text{EtNH}_2$  over 2 d at ambient temperature<sup>5</sup>.

Similar reactions with silyl and germyl halides to yield phosphino derivatives (which could only be obtained with difficulty by other methods) proceed very readily. For example,  $\text{Li}[\text{Al}(\text{PH}_2)_4]$  reacts with  $\text{H}_3\text{SiBr}$  at 228 K to give an 82% yield of silylphosphine,  $\text{H}_3\text{SiPH}_2$  [along with  $\text{SiH}_4$ ,  $\text{PH}_3$  and  $\text{H}_2\text{Si}(\text{PH}_2)_2$  side products] in only a few minutes<sup>6,7</sup>:



where  $\text{R} = \text{H}_3\text{Si}$  or  $\text{H}_3\text{Ge}$ . It is possible that the  $\text{PH}_3$ -producing side reaction involves lithium halide cleavage of  $\text{Si}-\text{P}$  (or  $\text{Ge}-\text{P}$ ) bonds. These reactions are easily and conveniently extended to the trimethylsilyl and germyl halides to produce the  $\text{Me}_3\text{MPH}_2$  derivatives in high yield from triglyme media within minutes<sup>8</sup>.

Aluminate salts produced from  $\text{LiAlH}_4$  and methylphosphines behave in a similar manner. Thus,  $\text{Li}[\text{HAl}(\text{PMe})_3]$  (which is generated from  $\text{LiAlH}_4$  and  $\text{MePH}_2$  over 12 d) and  $\text{Li}[\text{H}_2\text{Al}(\text{PMe}_2)_2]$  (from  $\text{Me}_2\text{PH}$  over 8 d) both react with  $\text{H}_3\text{SiBr}$  at 228 K within 30 min, yielding  $\text{MePH}(\text{SiH}_3)$  and  $\text{Me}_2\text{PSiH}_3$ , respectively<sup>9</sup>.

TABLE 1. SYNTHESIS OF ARSINE DERIVATIVES  $\text{RAsH}_2$  OF SILYL AND GERMYL COMPOUNDS<sup>11</sup>

R	RBr (mmol)	$\text{Li}[\text{Al}(\text{AsH}_2)_4]$ (mmol)	$\text{RAsH}_2$ (mmol)	Yield (%)	$\text{AsH}_3$ (mmol)	RH (mmol)	Others (mmol)
$\text{H}_3\text{Si}$	11.18 <sup>a</sup>	3.20 <sup>c</sup>	7.80	70	1.8	0.9	
$\text{H}_3\text{Ge}$	9.77 <sup>a</sup>	2.63 <sup>c</sup>	6.33	65	1.8	0.5	$\text{Ge}_2\text{H}_6$ (0.6)
$\text{Si}_2\text{H}_5$	7.21 <sup>a</sup>	1.91 <sup>c</sup>	4.26	59	1.9	0.3	$\text{SiH}_4$ (0.1)
$\text{Ge}_2\text{H}_5$	5.21 <sup>b</sup>	1.54 <sup>d</sup>	—	—	5.1	2.6	$\text{GeH}_4$ (3.1)
$\text{MeSiH}_2$	10.00 <sup>a</sup>	2.60 <sup>d</sup>	5.72	57	2.6	0.8	
$\text{MeGeH}_2$	6.61 <sup>b</sup>	2.12 <sup>d</sup>	3.18	48	3.1	0.5	$(\text{MeGeH}_2)_2$ (0.16)
$\text{Me}_3\text{Si}$	14.95 <sup>b</sup>	4.00 <sup>e</sup>	11.48	77	2.72	1.32	
$\text{Me}_3\text{Ge}$	12.10 <sup>b</sup>	3.51 <sup>e</sup>	8.20	68	1.90	0.10	$\text{Me}_2\text{GeH}_2$ (1.10)

<sup>a</sup> Reaction in diglyme.

<sup>b</sup> Reaction in triglyme.

<sup>c</sup> Reaction at 228 K.

<sup>d</sup> Reaction at 250 K.

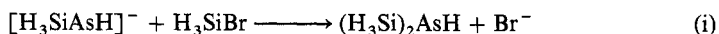
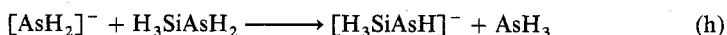
<sup>e</sup> Reaction at 273 K.

In reactions of the arseno derivative, it is found that bromide precursors are more suitable than chlorides. Thus, a low yield of  $\text{Me}_3\text{SnAsH}_2$  may be obtained from the interaction of a less than stoichiometric amount of  $\text{Me}_3\text{SnBr}$  with  $\text{Li}[\text{Al}(\text{AsH}_2)_4]$  at 228 K in monoglyme<sup>10</sup>. Reaction conditions for the synthesis of primary arsine derivatives of several silyl and germyl compounds are given in Table 1.

Disilylarsine,  $(\text{H}_3\text{Si})_2\text{AsH}$ , is obtained without any  $(\text{H}_3\text{Si})_3\text{As}$  from the reaction of an excess of  $\text{Li}[\text{Al}(\text{AsH}_2)_4]$  with  $\text{H}_3\text{SiBr}$  in  $\text{Me}_2\text{O}$  at low T. Presumably, this reaction proceeds via  $\text{H}_3\text{SiAsH}_2$  as the initial product:



The  $[\text{AsH}_2]^-$  entity, however, then acts as a base and leads to the formation of the disilyl product:



Such a scheme is in accordance with a similar one suggested for the reaction of silyl bromide with the  $[\text{PH}_2]^-$  analog<sup>12</sup>.

The recent report of chelating species of stoichiometry  $\text{Al}[(\text{Me}_2\text{P})_2\text{CY}]_3$  (with  $\text{Y} = \text{PMe}_2$  or  $\text{SiMe}_3$ ) that are obtained reasonably easily argues well for an upsurge of synthetic activity using such reagents<sup>13</sup>.

(B.D. JAMES)

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4. While these species are easily prepared, their formation tends to be rather slow and the product is also somewhat unstable in the long term. Thus, complete conversion is not achieved and syntheses involving these reagents are subject to a number of side reactions due to small amounts of hydridoaluminate species that remain.
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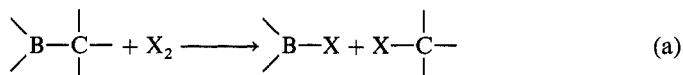
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## 2.6.10. Cleavage of Group-IIIB–Carbon Bonds

### 2.6.10.1. by Halogens.

While boron–carbon bonds are quite strong (average B–C bond enthalpy  $365 \text{ kJ mol}^{-1}$ ) there is a progressive weakening of the group IIIB–carbon bond as the group is descended. Average M–C bond enthalpies are: Al–C,  $274 \text{ kJ mol}^{-1}$ ; Ga–C, 247; In–C, 160; Tl–C, 115. This, together with the relatively low molar enthalpies of formation for alkyls of the type  $\text{M}(\text{CH}_3)_3$  means that the group-IIIB–C bonds are very susceptible to cleavage by halogens<sup>1</sup>. This leads to a general method for the preparation of group-IIIB halides. Thus, treatment of trimethylgallium with  $\text{I}_2$  in ether or benzene proceeds finally to yield  $\text{GaI}_3$ , although removal of the third methyl group is rather slow<sup>2</sup>.

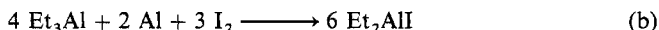
The facile cleavage of B–C bonds with  $\text{Cl}_2$  or  $\text{Br}_2$  can occur with formation of an organic halide and a boron halide according to the schematic equation:



This cleavage probably is not a simple B–C bond rupture but involves a free-radical chain and can be encouraged by irradiation with UV light. Such reactions have been studied mainly with a view to their synthetic utility for transformations on the organic groups rather than as a means of producing B–halogen bonds<sup>3</sup>. In fact, the lower trialkylboranes ignite in  $\text{Cl}_2$  or  $\text{Br}_2$ , although tripropylborane reacts smoothly with  $\text{I}_2$  at ca. 420 K. Similarly, a 91% conversion of  $(\text{C}_6\text{H}_5)_2\text{BBr}$  to  $\text{BBr}_3$  occurs<sup>4</sup> via interaction with  $\text{Br}_2$  at 470 K over 15 h.

Diorganoaluminum halides may be prepared by Al–C bond cleavage, but again the reactions tend to be violent if excess halogen is permitted. The presence of an electron-pair donor base moderates the reaction (and, incidentally, provides a route for good yields of alkyl halides to be prepared from terminal olefins). Thus, chlorination of the pyridine complexes of  $\text{R}_3\text{Al}$  (R = P, Bu, i-Bu, etc.) with 3 mol  $\text{Cl}_2$  at low T (238–253 K) gives good yields (60–70%) of the corresponding  $\text{R}_2\text{AlCl}$ . Similarly, brominations of  $\text{R}_3\text{Al}$  in ether below 273 K or reaction with  $\text{I}_2$  in refluxing ether yield  $\text{R}_2\text{AlX}$  (X = Br, I), respectively<sup>5</sup>.

Triethylaluminum is cleaved by  $< 1$  mol of  $\text{I}_2$  to yield ethyl iodide, which may then react with added Al to give the sesquiodide<sup>5</sup>. This route has been used as an economical synthesis of  $\text{Et}_2\text{AlI}$  because the sesquiodide interacts in turn with  $\text{Et}_3\text{Al}$ :



## 2.6. The Formation of the Halogen (B, Al, Ga, In, Tl) Bond

## 2.6.10. Cleavage of Group-IIIB–Carbon Bonds

## 2.6.10.1. by Halogens.

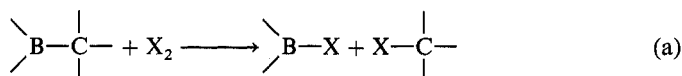
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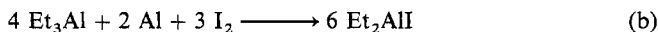
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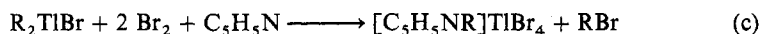
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Metal-carbon bond cleavage reactions using halogens have a relatively long history in organogallium and -indium chemistry. Triphenylindium reacts instantly with  $I_2$  in benzene solution and all three In—C bonds may be cleaved in this way to precipitate  $InI_3$  as the final product<sup>6</sup>. Addition of stoichiometric quantities of  $Br_2$  or  $I_2$  provides a simple, high-yield synthesis of compounds of the type  $PhInX_2$  and  $Ph_2InX$  (being especially good for the former<sup>7</sup>). Some side reactions occur in the reaction of  $Ph_3Ga$  with  $Br_2$  as evidenced by the appearance of benzene and p-dibromobenzene in the volatiles separated<sup>8</sup>.

Halogenation of  $R_2TlX$  compounds also cleaves the Tl—C linkages. The reaction between  $Br_2$  and several diorganothallium(III) compounds in  $C_5H_5N$  solution gives salts of alkylpyridinium cations and  $[TlX_4]^-$ . The  $[C_5H_5NR]^+$  ions seem to arise from pY and the  $R-X$  produced via cleavage<sup>9</sup>:



where  $R = Me, Et, n-Pr, n-Bu$ .

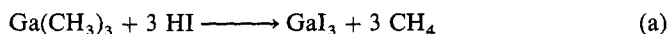
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### 2.6.10.2. by Hydrogen Halides.

Reactions of group-IIIB compounds containing element-carbon bonds with hydrogen halides are influenced not only by the element-halogen bond strength in the product but also by the polarities of the element-carbon and H-halogen bonds. This element-carbon cleavage is a generally useful method.

When HCl is passed into tributylborane at 380 K, dibutylchloroborane is obtained almost quantitatively. The separation of the butane byproduct from  $Bu_2BCl$  (bp 446 K) is easily achieved and serves to make this a useful method<sup>1</sup>. In general, cleavage reactions of this type have been investigated for  $X = F, Cl$  and  $Br$ , but frequently in the context of the synthesis of the hydrocarbon product rather than for the boron halide. Similarly,  $Me_3Ga$  and  $HI$  react<sup>2</sup>:



The separation of the highly volatile  $CH_4$  byproduct is again propitious from the manipulative viewpoint.

The addition of stoichiometric amounts of hydrogen chloride to  $Ph_3Ga$  in a vacuum system may be employed to produce  $Ph_2GaCl$  or  $PhGaCl_2$  at  $RT$ <sup>3,4</sup>.

A striking example of the ease with which such reactions proceed is given by the ammonia adduct of  $Me_3Ga$ . Addition of 1 mol equiv HCl to an ether solution of the



## 2.6. The Formation of the Halogen (B, Al, Ga, In, Tl) Bond

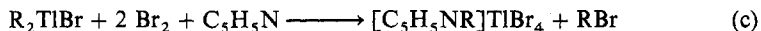
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## 2.6.10. Cleavage of Group-IIIB–Carbon Bonds

## 2.6.10.2. by Hydrogen Halides.

Metal–carbon bond cleavage reactions using halogens have a relatively long history in organogallium and -indium chemistry. Triphenylindium reacts instantly with  $I_2$  in benzene solution and all three In—C bonds may be cleaved in this way to precipitate  $InI_3$  as the final product<sup>6</sup>. Addition of stoichiometric quantities of  $Br_2$  or  $I_2$  provides a simple, high-yield synthesis of compounds of the type  $PhInX_2$  and  $Ph_2InX$  (being especially good for the former<sup>7</sup>). Some side reactions occur in the reaction of  $Ph_3Ga$  with  $Br_2$  as evidenced by the appearance of benzene and p-dibromobenzene in the volatiles separated<sup>8</sup>.

Halogenation of  $R_2TiX$  compounds also cleaves the Ti—C linkages. The reaction between  $Br_2$  and several diorganothallium(III) compounds in  $C_5H_5N$  solution gives salts of alkylpyridinium cations and  $[TiX_4]^-$ . The  $[C_5H_5NR]^+$  ions seem to arise from pY and the R—X produced via cleavage<sup>9</sup>:



where R = Me, Et, n-Pr, n-Bu.

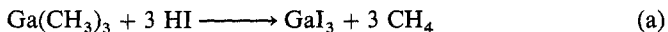
(B.D. JAMES)

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## 2.6.10.2. by Hydrogen Halides.

Reactions of group-IIIB compounds containing element–carbon bonds with hydrogen halides are influenced not only by the element–halogen bond strength in the product but also by the polarities of the element–carbon and H–halogen bonds. This element–carbon cleavage is a generally useful method.

When HCl is passed into tributylborane at 380 K, dibutylchloroborane is obtained almost quantitatively. The separation of the butane byproduct from  $Bu_2BCl$  (bp 446 K) is easily achieved and serves to make this a useful method<sup>1</sup>. In general, cleavage reactions of this type have been investigated for X = F, Cl and Br, but frequently in the context of the synthesis of the hydrocarbon product rather than for the boron halide. Similarly,  $Me_3Ga$  and HI react<sup>2</sup>:

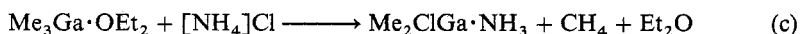
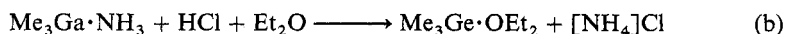


The separation of the highly volatile  $CH_4$  byproduct is again propitious from the manipulative viewpoint.

The addition of stoichiometric amounts of hydrogen chloride to  $Ph_3Ga$  in a vacuum system may be employed to produce  $Ph_2GaCl$  or  $PhGaCl_2$  at  $RT^{3,4}$ .

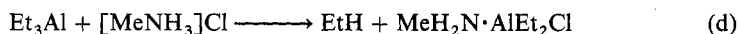
A striking example of the ease with which such reactions proceed is given by the ammonia adduct of  $Me_3Ga$ . Addition of 1 mol equiv HCl to an ether solution of the

adduct causes  $\text{NH}_4\text{Cl}$  to separate instantly<sup>5</sup>, but this is sufficiently acidic to react with the  $\text{Me}_3\text{Ga}$  ether adduct to form a  $\text{Ga}-\text{Cl}$  bond and evolve  $\text{CH}_4$ :



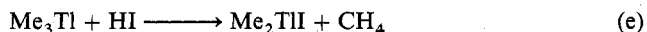
With xs  $\text{HCl}$ ,  $\text{Me}_3\text{Ge}\cdot\text{NH}_3$  forms  $[\text{NH}_4][\text{GaCl}_4]$ .

With the even more electropositive center, aluminum will likewise undergo cleavage of  $\text{Al}-\text{C}$  bonds with weak acids<sup>5</sup>. For example, with methylammonium chloride and  $\text{AlEt}_3$ :

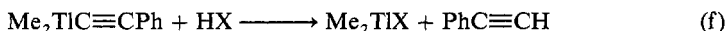


In fact, the particular sensitivity of organoaluminum compounds to protonic reagents demands that very careful control of experimental conditions be exercised<sup>6</sup>. Frequently the hydrogen halide needs to be diluted in an inert carrier gas and the organoaluminum compound be likewise kept at low concentration and cooled. An electron-pair base in the solution helps to moderate the reaction, although the product is obtained as an adduct, which may not always be desired. As a consequence, redistribution reactions that avoid the vigorous transformations are more popular procedures for producing compounds of the type  $\text{R}_2\text{MX}$  and  $\text{RMX}_2$  for  $\text{M} = \text{Al}, \text{Ga}$ .

On the other hand, dialkyl- and diarylthallium(III) compounds are particularly stable entities, with the  $[\text{Me}_2\text{Tl}]^+$  group being kinetically inert<sup>7</sup>. This property, together with the relative weakness of the  $\text{Tl}-\text{C}$  bond, causes  $\text{Me}_3\text{Tl}$  to react with protic reagents to yield the diorganothallium(III) compounds:



For another example, the dimethylthallium phenylacetylide derivative, which may be prepared because phenylacetylene has a slightly acidic proton, interacts with hydrogen halides only so far as to reprotonate the acetylenic group. A thallium-halogen bond is formed, but the inert  $\text{Tl}-\text{CH}_3$  bonds are not cleaved<sup>7</sup>.



A similar reaction occurs with  $\text{Me}_2\text{TlC}_3\text{H}_5$ .

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### 2.6.10.3. by Other Halides.

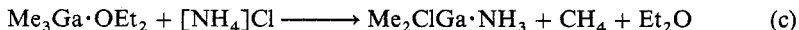
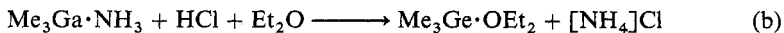
Group-IIIB alkyls are well-known alkylating agents, with those of  $\text{Al}$  being the archetypal examples. While this alkylation property is of great relevance in the study of

## 2.6. The Formation of the Halogen (B, Al, Ga, In, Tl) Bond

## 2.6.10. Cleavage of Group-IIIB–Carbon Bonds

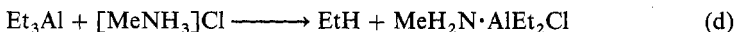
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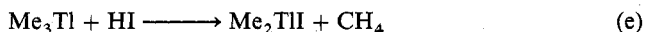
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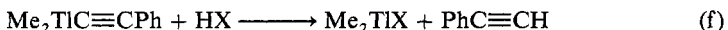


In fact, the particular sensitivity of organoaluminum compounds to protonic reagents demands that very careful control of experimental conditions be exercised<sup>6</sup>. Frequently the hydrogen halide needs to be diluted in an inert carrier gas and the organoaluminum compound be likewise kept at low concentration and cooled. An electron-pair base in the solution helps to moderate the reaction, although the product is obtained as an adduct, which may not always be desired. As a consequence, redistribution reactions that avoid the vigorous transformations are more popular procedures for producing compounds of the type  $\text{R}_2\text{MX}$  and  $\text{RMX}_2$  for  $\text{M} = \text{Al}, \text{Ga}$ .

On the other hand, dialkyl- and diarylthallium(III) compounds are particularly stable entities, with the  $[\text{Me}_2\text{Tl}]^+$  group being kinetically inert<sup>7</sup>. This property, together with the relative weakness of the  $\text{Tl}-\text{C}$  bond, causes  $\text{Me}_3\text{Tl}$  to react with protic reagents to yield the diorganothallium(III) compounds:



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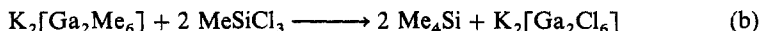
## 2.6.10.3. by Other Halides.

Group-IIIB alkyls are well-known alkylating agents, with those of Al being the archetypal examples. While this alkylation property is of great relevance in the study of

catalysis (e.g.,  $\text{Et}_3\text{Al} + \text{TiCl}_4$ ) the reaction frequently is not a practically useful method for preparing compounds with Al–halogen bonds, despite its utility in preparations for complementary compounds, such as  $\text{CH}_3\text{TiCl}_3$ . However, numerous halides may be employed in such halogen-transfer reactions. For example,  $\text{HgCl}_2$  is readily phenylated by  $\text{PhTiCl}_2$ :



and stannic halides give excellent yields of  $\text{Et}_3\text{SnX}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) via the stoichiometric reaction of  $\text{Et}_3\text{Al}$  and  $\text{SnX}_4$  in ether. Variation of the mole ratio of the reactants produces different organotin products. For example, 3 mol equiv  $\text{SnCl}_4$  react with *i*- $\text{Bu}_3\text{Al}$  in the presence of  $\text{KCl}$  to give *i*- $\text{Bu}_2\text{SnCl}_2$ . Germanium tetrachloride is alkylated quite easily, with  $\text{R}_4\text{Ge}$  being the dominant product, while the alkyl germanium halides are alkylated even more readily<sup>1</sup>. Also, the chlorosilane  $\text{MeSiCl}_3$  appears to cleave all the Ga–C bonds in  $\text{K}_2[\text{Ga}_2\text{Me}_6]$ . This latter is a good example of the power of this type of cleavage reaction because it leaves the metal–metal bond intact<sup>2</sup>:

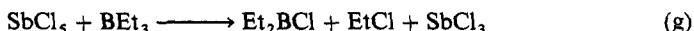
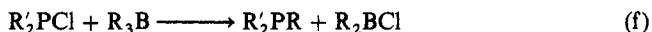
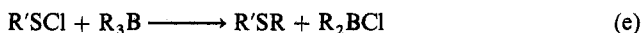


In similar vein,  $\text{Me}_3\text{SiF}$  forms an intermediate complex with  $\text{AlEt}_3$ , which on gentle heating forms  $\text{Et}_2\text{AlF}$ . While fluorosilanes do not fluorinate trialkylgallium compounds,  $\text{Me}_3\text{SnF}$  or  $\text{BF}_3$  does<sup>3</sup>:



These sorts of reactions also have been noted<sup>4</sup> for  $\text{Me}_3\text{In}$  and for trialkylaluminum compounds, although commercial  $\text{AlF}_3$  is usually too unreactive<sup>5</sup>.

In a similar manner, phosphorus and sulfur halides undergo alkylation with trialkylboranes, as does  $\text{SbCl}_5$ , according to<sup>6,7</sup>:



The dialkylindium compound  $\text{R}_2\text{InCl}$  reacts somewhat similarly<sup>8</sup> with  $\text{SbCl}_5$ :



and organoarsenic(V) and -antimony(V) halides also may be employed as halogenating agents toward the gallium and indium trialkyls<sup>4</sup>:



Boron–carbon bond cleavage reactions also occur with reagents such as  $\text{ZnCl}_2$ ,  $\text{HgCl}_2$ ,  $\text{PbCl}_2$ ,  $\text{SbF}_3$  and  $\text{NOCl}$ <sup>6</sup>. Again, many reactions with metal halides have been performed in the context of alkylation rather than for interest in the formation of B halogen bonds and, indeed, the further transformation of the alkylboron halide intermediate under oxidizing and hydrolytic conditions is a most useful procedure for organic synthesis<sup>6,9</sup>. The reaction of  $\text{Bu}_3\text{B}$  and  $\text{SbF}_3$  proves to be a convenient synthesis for  $\text{Bu}_2\text{BF}$ . The cleavage reaction in this case is unusual<sup>10</sup>. Generally,  $\text{SbF}_3$  is employed to transfer  $\text{F}^-$  ion in metatheses (§2.6.12).

Reactions of group-IIIB alkyls with halogenated hydrocarbons may sometimes be a useful reaction. While interactions with aluminum alkyls are generally uncontrollable (probably free-radical chain) reactions, trialkylindium compounds may be transformed conveniently and in high yields to the monohalides by refluxing briefly with  $\text{CHCl}_3$  or  $\text{CHBr}_3$  in hexane<sup>11</sup>. Similarly,  $\text{Me}_3\text{Tl}$  reacts with halomethanes<sup>12</sup>. While there is no reaction with  $\text{CH}_2\text{Cl}_2$  or  $\text{CCl}_4$  at RT, reaction with  $\text{CHCl}_3$  occurs over ca. 10 min, yielding  $\text{Me}_2\text{TlCl}$ . Faster reactions occur with bromo- and iodoalkanes and the reactivity of the various haloalkanes decreases as  $\text{CHX}_3 > \text{CH}_2\text{X}_2 > \text{CH}_3\text{X}$ .

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## 2.6.11. from Cleavage of the Group-IIIB–Other Group-IVB Element Bond

### 2.6.11.1. by Halogens.

In common with those processes for producing group-IIIB-halogen bonds described in §2.6.7 and 2.6.9, cleavage of bonds between group-IIIB and other group-IVB elements suffers because group-IIIB halides are generally employed as starting materials for the synthesis of these reagents; therefore, this method is seldom used for producing a group-IIIB-halogen bond.

Paralleling the carbanionic character of the alkyl groups in group-IIIB organo derivatives, the group-IVB entities in group-IIIB-group-IVB compounds appear to be slightly negatively polarized. This property is in accordance with the thermodynamic electro-negativities, for which  $\chi_M = 1.90$  (Si), 2.01 (Ge), 1.96 (Sn) and 2.33 (Pb) and a number of stable covalent compounds are available. These are generally less thermally stable, however, than the corresponding carbon (organo) derivatives, leading to problems with preparing them in high-yield syntheses and also with their storage once they have been obtained. Thus, for group-IIIB element–Sn bonds in the Li salts of the  $[\text{Me}_3\text{Sn}—\text{MMe}_3]^{2-}$  anion, the thermal stability decreases in the order  $\text{M} = \text{Tl} > \text{In} \sim \text{Ga} > \text{Al}$ , which parallels the electronegativities<sup>1</sup>. In addition, the large radii and availability of low-lying empty d atomic orbitals in the other group-IVB elements compared to carbon facilitate nucleophilic attack<sup>2</sup>.

42    2.6. The Formation of the Halogen (B, Al, Ga, In, Tl) Bond  
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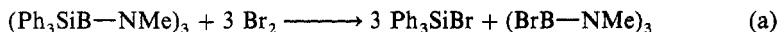
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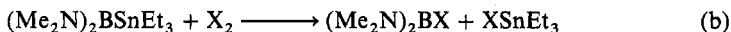
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It is evident that the reactivity of  $(\text{Me}_2\text{N})_2\text{BSiMe}_3$ , in which the electron deficiency at boron is counteracted through  $\pi$  overlap with the lone pair on the amino group nitrogen atoms, is similar to that of  $(\text{Me}_2\text{N})_2\text{BCR}_3$ , except for the higher electrophilic character of the silyl. Thus, the B—Si bond, like its B—C counterpart, is relatively easily oxidized so that  $\text{Br}_2$  in  $\text{CCl}_4$  cleaves it to yield  $\text{Me}_3\text{SiBr}$  and  $\text{BrB}(\text{NMe}_2)_2$ . Other compounds of similar type containing the B—Si bond are all attacked easily by  $\text{Br}_2$ <sup>3</sup> (and presumably by the other halogens). The relatively strong group-IVB–halogen bonds<sup>2</sup> can thus be seen to be contributing to making the reactions particularly facile. On the other hand, the reaction of B–triphenylsilyl borazines with  $\text{Br}_2$  tends to cleave the B—N ring as well as the B—Si bonds<sup>4,5</sup>. The bromine-substituted intermediate decomposes to give methylammonium bromide:



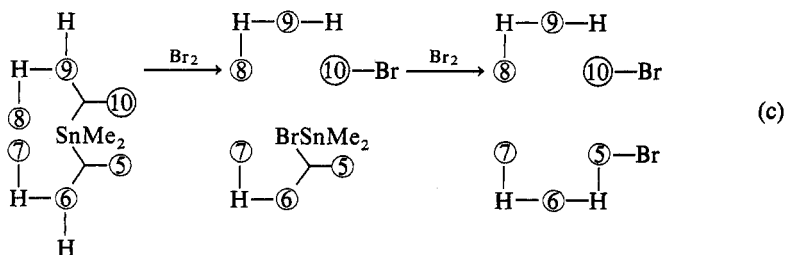
In other instances, the B—Si bond cannot be regarded as especially reactive<sup>6</sup>.

Dialkylamino groups also are effective in stabilizing analogous compounds to those cited above and which contain B—Sn and B—Pb bonds<sup>7,8</sup>. While these compounds are thermally less stable than their silicon-containing analogs, reactions with halogens occur exothermically (although  $\text{I}_2$  reacts slowly) in analogous fashion, thus:



where X = halogen.

In carborane compounds, boron–tin bonds are quite stable and cleave only in the presence of excess halogen; otherwise attack takes place only at the tin atom. The 9-carboranyl group largely behaves as an alkyl group when attached to the tin atom<sup>9</sup>. On the other hand, in  $\text{Me}_2\text{SnB}_{10}\text{H}_{12}$ , in which the  $\text{Me}_2\text{Sn}$  group is bonded to the  $\text{B}_{10}$  cage at the edge borons  $\text{B}_5$ — $\text{B}_6$  and  $\text{B}_9$ — $\text{B}_{10}$  by two three-center B—Sn—B bonds, cleavage of the  $\text{Me}_2\text{Sn}$  grouping by excess bromine occurs to yield the facially disubstituted 5,10-dibromodecaborane. The reaction appears to involve a stepwise rupture of the B—Sn—B three-center bonds in an oxidative cleavage process since  $\text{Me}_2\text{SnBrB}_{10}\text{H}_{12}\text{Br}$  may be obtained when the compound is reacted with a deficiency of bromine<sup>10</sup>. Thus, the reaction may be represented as follows:

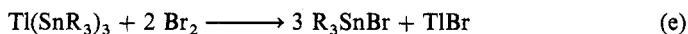


The presence of a trimethylsilyl group bridging the 2 and 3 boron atoms in pentaborane does not imbue the system with any particular reactivity. While bromination of this compound occurs rapidly at RT, the site of attack is the 1 position rather than cleavage of the B—Si—B three-center bond<sup>11</sup>.

For other compounds containing group-IIIB–group-IVB element bonds, it is clear that cleavage of the bonds according to the general equation<sup>12</sup>:



continues to take place quite readily. In those cases in which reactivity has been reported, the compounds are clearly highly reactive toward any sort of oxidative process<sup>13</sup>. Thus, tris(triethylgermyl)gallium gives high yields of GaBr<sub>3</sub> and Et<sub>3</sub>GeBr when treated with bromine<sup>14</sup> and it appears that similar reactions occur when salts of the [Ph<sub>3</sub>MBPh<sub>3</sub>]<sup>–</sup> anion (M = Si, Ge) react in chloroform, although specific product analyses are not given<sup>15</sup>. For Tl(III) compounds of the type Tl(MR<sub>3</sub>)<sub>3</sub>, reactions with Br<sub>2</sub> cleave the Tl–M bond quite readily although the Tl gives a precipitate of the lower halide<sup>16,17</sup>.



where R = Me<sub>3</sub>SiCH<sub>2</sub>. These reactions, taking place in hydrocarbon solvents, produce high yields of the Tl(I) halides.

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### 2.6.11.2. by Hydrogen Halides.

In view of the negative polarity exhibited by the R<sub>3</sub>M group when bonded to group-IIIB metals, cleavage of those group-IIIB–group-IVB element bonds by HX normally is expected to occur readily according to the general equation<sup>1</sup>:



in which R<sub>n</sub>M represents the group-IVB moiety. Thus, the salt Li[Ga(SiMe<sub>3</sub>)<sub>4</sub>] releases trimethylsilane when treated with HCl. It is presumed that GaCl<sub>3</sub> or LiGaCl<sub>4</sub> is also formed, although the product is not explicitly stated<sup>2</sup>. The extreme reactivity noted for other compounds of this type indicates the generality of their susceptibility to acidic HX



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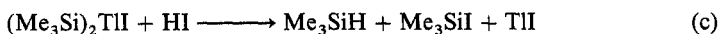
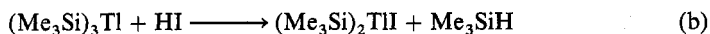
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reagents<sup>3</sup>. The phenylsilyl aluminate salt  $K[PhAl(SiPh_3)(Si_2Ph_5)Cl]$  also reacts readily with HCl, here cleaving not only both Al—Si bonds but also the Al—C bond (as expected, §2.6.10.2) releasing triphenylsilane, pentaphenyldisilane and benzene<sup>4</sup>.

With reactions of the (trimethylsilyl)thallium(III) derivatives, there is a marked tendency toward reduction of the metal center. Thus, while  $(Me_3Si)_2TlCl$  reacts readily with 2 mol equiv HCl in a few minutes to give  $TlCl_3$ , xs HCl reacting with  $(Me_3Si)_3Tl$  gives a mixture of  $Me_3SiH$ ,  $Me_3SiCl$  and hydrogen together with a white solid that decomposes within 0.5 h to Tl and  $Me_3SiCl$ . While these reactions appear to proceed in steps, the  $[(Me_3Si)_2Tl]^+$  intermediate—in marked contrast to its diorganothallium(III) analogs—is not stable. The reaction of  $(Me_3Si)_3Tl$  with xs HI proceeds readily to deposit TII:



If 1 mol equiv HI is employed, a nonvolatile solid that appears to correspond to a mixture of TII and  $(Me_3Si)_2TII$  can be produced<sup>5</sup>. Although there are relatively few group-IIIB–germanium compounds available to provide a comparison<sup>6</sup>, the reactions of  $(Et_3Ge)_3Tl$  would be expected to be similar. The reaction of the pentafluorophenyl derivative,  $(C_6F_5)_2GeTlEt$ , with xs HCl produces  $TlCl$  quantitatively; but since  $C_2H_6$ ,  $(C_6F_5)_2GeHCl$ ,  $(C_6F_5)_2GeHEt$ , substituted digermenes and other products are obtained, the mechanism of the process is certainly unclear<sup>7</sup>.

In contrast, group-IVB element bonds to boron ( $\chi_B = 2.04$ ) are not especially reactive toward hydrogen halides and tend to reflect a relatively low degree of polarity. Thus, despite a degree of thermal instability which increases with the heavier substituents, even compounds such as  $(Me_2N)_2BMR_3$  (where  $M = Si, Sn$ ) are attacked by HCl only at the B—N bond rather than cleaving the B—M bond<sup>8</sup>. Thus, with 2 mol equiv HCl, a B—Cl bond is formed together with the ammonium salt, according to:



Even with 4 mol equiv, the B—Sn bond is not cleaved, chloroborate anion formation being favored over B—Sn bond rupture<sup>9</sup>. It should be noted that cleavage of B—N bonds by HCl frequently requires heating in view of boronium salt formation (§2.6.8.2). Similarly, in carborane derivatives, the B—Sn bond is rather inert and HCl attack provokes substitution at the tin center rather than cleaving the bond<sup>10</sup>, and HCl in the presence of  $AlCl_3$  attacks  $Me_3SiB_5H_9$ , causing protonation of the borane rather than B—Cl bond formation<sup>11</sup>. In  $C_2B_4H_8$  carboranes having bridging  $Me_3M$  substituents ( $M = Si, Ge, Sn, Pb$ ), while the rate of the reaction with anhydrous HCl reflects the B—M bond polarity (with the Sn and Pb derivatives reacting fastest and the Ge derivative more sluggishly), again the electronic distribution is such as to cause the Cl to bond preferentially to the metal rather than to boron<sup>12</sup>.

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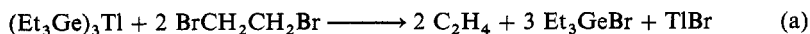
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The interactions of group-IIIB–group-IVB element bonds with electrophilic reagents also reflect the reactivities observed previously (§2.6.11.1, 2.6.11.2). Thus, the rather low reactivity of boron–silicon bonds is once again observed. It is noted that  $\text{Me}_3\text{SiCl}$ ,  $\text{MeI}$  and  $\text{PhCH}_2\text{Cl}$  all react very slowly with the tetrasilylborate complex,  $\text{Li}[\text{B}(\text{SiMe}_3)_4]$ , although reactions with  $\text{Me}_2\text{BBr}$  and  $\text{AlCl}_3$  are faster. Specific details are not known, although a variety of products occur<sup>1</sup>. On the other hand, given the extreme sensitivity of the corresponding aluminate  $\text{Li}[\text{Al}(\text{SiMe}_3)_4]$  reactions with such reagents should proceed very much more readily<sup>2</sup>. Thus, the Li and Na aluminate derivatives as well as  $\text{Al}(\text{SiMe}_3)_3 \cdot \text{OEt}_2$  react rapidly and quantitatively in pentane with  $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$  to transfer one  $-\text{SiMe}_3$  group onto the titanium center. An Al–Cl linkage presumably is generated, although such a product is not specifically described. Substitution of the second chloride attached to titanium does not occur even when a 2:1 (or greater) mole ratio of the aluminum silyl reagent is employed. A similar reaction is reported with the  $\text{Al}(\text{GeMe}_3)_3$  etherate derivative, as expected<sup>3</sup>. The second Ti–Cl linkage in the  $(\text{C}_5\text{H}_5)_2\text{TiCl}(\text{SiMe}_3)$  product also resists reaction with  $\text{Et}_2\text{AlCl}$ , with exchange of  $-\text{SiMe}_3$  and ethyl groups occurring between the two metals rather than giving rise to Al–Cl bond formation<sup>4</sup>.

The utility of the aluminum silyl reagent for the synthesis of other metal silyls is shown by the complete exchange of both chlorides in  $\text{MCl}_2$  ( $\text{M} = \text{Zn}, \text{Cd}$ ) when  $\text{Li}[\text{Al}(\text{SiMe}_3)_4]$  is reacted in ether. Once again, the Al-containing product is not specifically described<sup>5</sup>. It is expected that similar germyl and stannyl reagents could react in a similar fashion.

This relatively high reactivity is maintained as group-IIIB is descended and quite a thorough study has been made on the compound  $[(\text{Me}_3\text{SiCH}_2)_3\text{Sn}]_3\text{Tl}$  in which the large group attached to tin helps to confer a thermal stability which is greater than that of  $(\text{Et}_3\text{Ge})_3\text{Tl}$ . Excess  $\text{BrCH}_2\text{CH}_2\text{Br}$  produces thallous bromide,  $\text{C}_2\text{H}_4$  and  $(\text{Me}_3\text{SiCH}_2)_3\text{SnBr}$  in quantitative yields<sup>6</sup>. Similarly, an exothermic reaction occurs between  $\text{BrCH}_2\text{CH}_2\text{Br}$  and  $(\text{Et}_3\text{Ge})_3\text{Tl}$  in a sealed tube and is complete in 5–7 min. Again,  $\text{TlBr}$  is formed quantitatively, along with  $\text{C}_2\text{H}_4$  and  $\text{Et}_3\text{GeBr}$ :



The same reaction with  $(\text{Et}_3\text{Si})_3\text{Tl}$  is analogous<sup>7</sup>. Excess  $\text{EtBr}$  reacts in THF at RT with the tris(stannyl)thallium compound to precipitate  $\text{TlBr}$  completely in 30 min. The  $\text{Sn}(\text{IV})$  bromide is also produced in high yield together with  $(\text{Me}_3\text{SiCH}_2)_3\text{SnEt}$ . With equimolar

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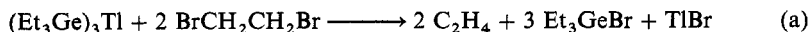
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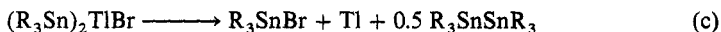
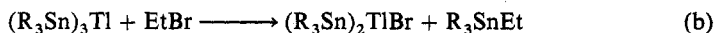
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This relatively high reactivity is maintained as group-IIIB is descended and quite a thorough study has been made on the compound  $[(\text{Me}_3\text{SiCH}_2)_3\text{Sn}]_3\text{Tl}$  in which the large group attached to tin helps to confer a thermal stability which is greater than that of  $(\text{Et}_3\text{Ge})_3\text{Tl}$ . Excess  $\text{BrCH}_2\text{CH}_2\text{Br}$  produces thallous bromide,  $\text{C}_2\text{H}_4$  and  $(\text{Me}_3\text{SiCH}_2)_3\text{SnBr}$  in quantitative yields<sup>6</sup>. Similarly, an exothermic reaction occurs between  $\text{BrCH}_2\text{CH}_2\text{Br}$  and  $(\text{Et}_3\text{Ge})_3\text{Tl}$  in a sealed tube and is complete in 5–7 min. Again,  $\text{TlBr}$  is formed quantitatively, along with  $\text{C}_2\text{H}_4$  and  $\text{Et}_3\text{GeBr}$ :



The same reaction with  $(\text{Et}_3\text{Si})_3\text{Tl}$  is analogous<sup>7</sup>. Excess  $\text{EtBr}$  reacts in THF at RT with the tris(stannyl)thallium compound to precipitate  $\text{TlBr}$  completely in 30 min. The  $\text{Sn}(\text{IV})$  bromide is also produced in high yield together with  $(\text{Me}_3\text{SiCH}_2)_3\text{SnEt}$ . With equimolar

EtBr, however, the reaction is much slower. It is believed that an unstable intermediate  $(R_3Sn)_2TlBr$ , may be involved in the reaction and that it decomposes, producing Tl metal, the Sn(IV) bromide and ethyl derivatives, together with the  $R_3SnSnR_3$  <sup>6</sup>:



In a similar fashion, dry  $CHCl_3$  and  $(Me_3Si)_3Tl$  interact in vacuo over a few minutes to give a high yield of  $(Me_3Si)_2TlCl$ . This reaction is analogous to that shown by the  $TlMe_3$  derivative. A comparison with the reactivity of the  $Tl-C$  bond is provided, however, by the interactions with  $CH_2Br_2$  and  $MeI$ . While  $TlMe_3$  also reacts with these to produce the  $[Me_2Tl]^+$  species, the corresponding  $[(Me_3Si)_2Tl]^+$  entity is not obtained from the reactions of  $(Me_3Si)_3Tl$  with these reagents<sup>8</sup>. The stability of the diorganothallium(III) species probably assists these reactions in comparison with those involving the silyl and the stannyl derivatives.

(B.D. JAMES)

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## 2.6.12. from Halide-Halide Exchange Reactions (Metathesis)

Metathesis is a reaction in which a halogen atom bonded to a group-IIIB element is replaced by a different halogen (e.g., Cl is replaced by F). Systems in which, e.g., Cl bonded to a group-IIIB element is replaced by isotopically labeled Cl are regarded as scrambling reactions and are described in §2.6.15.

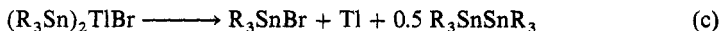
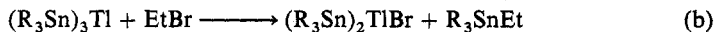
### 2.6.12.1. by Hydrogen Halides.

The most widely employed hydrogen halide is HF, especially for industrial applications because of its low price and relative ease of handling. It generally is avoided for laboratory operations even though procedures and materials for conducting experiments are described<sup>1</sup>. For exchanging a bound Cl for F, it is advantageous that byproduct HCl have very low solubility in HF (give a solution of ca.  $0.17 \text{ mol dm}^{-3}$  at 273 K), presumably because it undergoes neither protonation nor dissociation to any significant extent. Furthermore, the high volatility makes separation very easy and this combination of properties leads to a propitious general route for the preparation of anhydrous fluorides<sup>2</sup>. Any chloride is likely to decompose gradually with liq HF. Certainly,  $AlCl_3$  reacts to give a ppt of the fluoride<sup>3</sup>. Thallium and Ag appear to be exceptions, in that HX

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47

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bubbled through a solution of a Tl or Ag salt in liq HF precipitates the corresponding halide. This appears to be related to the insolubility of the latter<sup>3</sup>.

Reactions with liq HCl, carried out using sealed tubes equilibrated at RT have shown  $\text{AlI}_3$  is not solvolyzed but boron halides are, with  $\text{BBr}_3$ ,  $\text{BI}_3$  and derivatives such as  $\text{Me}_2\text{S} \cdot \text{BBr}_3$ ,  $\text{Ph}_3\text{As} \cdot \text{BBr}_3$  and  $[\text{Me}_4\text{N}][\text{BBr}_4]$  having their halogens replaced by chlorine. Similarly,  $\text{BCl}_3$  reacts in HBr to form  $\text{BBr}_3$  and both  $\text{BCl}_3$  and  $\text{BBr}_3$  will undergo this type of solvolysis to form the triiodide. On the other hand, the fluorine-containing solutes  $\text{BF}_3$  and  $\text{Et}_2\text{O} \cdot \text{BF}_3$  may be recovered unchanged from liq HCl<sup>4,5</sup>. The use of HBr and HI presents rather more practical problems because of their small liquid ranges and rather weak solvent properties, which are related to their low dielectric constants<sup>6</sup>.

(B.D. JAMES)

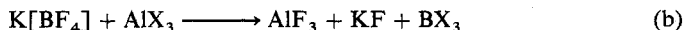
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### 2.6.12.2. by Metal and Nonmetal Halides.

The often rapid and complete halogen-radiohalogen exchange exhibited by group-IIIB halides (§2.6.15) is but one factor facilitating the broader process of metathesis. The most general reaction for converting a nonmetal fluoride into another halide is by employing the appropriate Al halide. The driving force in a reaction, e.g.:

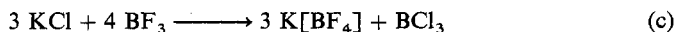


where  $\text{X} = \text{Cl}, \text{Br}$ , is the high stability of  $\text{AlF}_3$ . This is a trouble-free, high-yield procedure<sup>1</sup> for synthesizing  $\text{BBr}_3$ . This method also may be adapted to prepare the higher halides  $\text{B}_n\text{Br}_n$  ( $n = 8, 9$ )<sup>2</sup>. The volatile  $\text{BF}_3$  may be substituted by the somewhat more convenient  $\text{K}[\text{BF}_4]$ , the product being obtained by heating the mixture (420–450 K) over a few hours:



The yield of  $\text{BBr}_3$  via this route is much improved (to 80%) by preparing the  $\text{AlBr}_3$  reagent in situ and having the  $\text{K}[\text{BF}_4] : \text{AlBr}_3$  ratio around 1:10. Thus, it becomes suitable for preparing isotopically labeled boron compounds<sup>3</sup>.

Similarly,  $\text{BF}_3$  reacts readily with alkali-metal and alkaline-earth halides to exchange halogen and form tetrafluoroborate:



Passing  $\text{BCl}_3$  through pellets of the readily available  $\text{CaF}_2$  at 430–470 K yields  $\text{BF}_3$  rapidly and completely<sup>4</sup>. In most cases, however,  $\text{CaF}_2$  is a poor fluorinating agent because of its high lattice energy and low kinetic activity.

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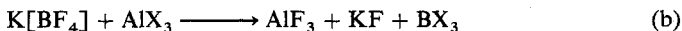
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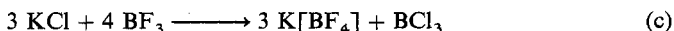


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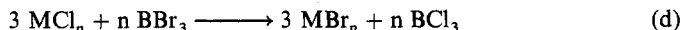
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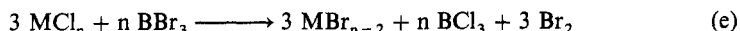
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In a useful procedure,  $\text{BBr}_3$  and  $\text{BI}_3$  may be employed as general reagents since they easily undergo exchange reactions with a variety of anhydrous metal chlorides. Most metal chlorides [ $\text{M} = \text{Al(III)}, \text{Sn(IV)}, \text{Ti(IV)}, \text{Co(II)}, \text{Cu(II)}$ ] react by an equation of the type:



whereas  $\text{SbCl}_5$ ,  $\text{VOCl}_3$  and  $\text{MoCl}_5$  convert to a lower bromide:

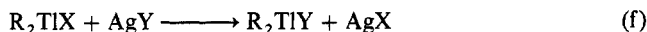


Excellent yields generally are obtained, using quite mild (ca. 370 K) conditions<sup>5</sup>. These reactions are favored by the greater volatility of  $\text{BCl}_3$ , than  $\text{BBr}_3$ , the higher electron-pair acceptor acidity of  $\text{BBr}_3$  than  $\text{BCl}_3$  and the favorable enthalpy change:



Similarly,  $\text{BI}_3$  reacts with  $\text{B}_2\text{Cl}_4$  to give  $\text{B}_2\text{I}_4$  almost quantitatively<sup>6</sup>.

Not surprisingly, metathesis has been studied as a possible means to introduce F into an accessible molecule without the use of particularly aggressive reagents. [B]trichloroborazene may be converted to the corresponding [B]trifluoro compound with a number of reagents. Conversion with KF, however, is very poor<sup>7</sup>, but NaF replaces Cl in the borazenes  $(-\text{NR}-\text{BCl}-)_3$  (where R = Ph, benzyl) reasonably conveniently in  $\text{CH}_3\text{CN}$  over several hours, although using NaI gives a poor yield of the [B]iodoborazene<sup>8</sup>. Silver salts may be widely employed for metatheses in diorganothallium chemistry, according to the general equation:

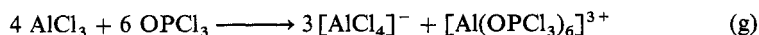


The X group is frequently I but can also be Cl or Br, while Y can be a range of anions<sup>9</sup>. Conversion takes place so as to favor the least soluble  $\text{AgX}$  product and it is preferable for the  $\text{AgY}$  reagent to be freshly prepared in order to facilitate reactivity at the solid surface. For example, a good yield of bis(perfluoroalkyl)thallium chloride starting from the bromide has been obtained by this procedure<sup>10</sup>.

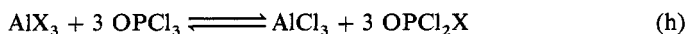
Finely divided alkali-metal fluorides convert the diorganoaluminum chlorides to the fluorides. Their high lattice energies tend to render alkali-metal fluorides relatively unreactive, except at high T, although activity may be increased by slurrying the fluoride in a polar organic liquid of relatively high dielectric constant<sup>11</sup>.

Other interesting and potentially useful halogen-transfer reactions have been reported. One example is the preparation of polyhaloalkanes such as  $\text{Cl}_4$  by heating  $\text{CCl}_4$  with  $\text{AlI}_3$ . The inert  $\text{CF}_4$  does not react with  $\text{AlCl}_3$  up to 1000 K, but reaction does occur with higher pressures. As expected,  $\text{SiF}_4$  reacts with  $\text{AlCl}_3$  much more readily and  $\text{GeF}_4$ , in turn, is even more reactive<sup>12</sup>.

In studies of the solvent properties of  $\text{POCl}_3$ ,  $[\text{Al}(\text{OPCl}_3)]^{3+}$  and  $[\text{AlCl}_4]^-$  ions may predominate in solution when  $\text{AlCl}_3$  is the solute. These possibly arise via, e.g.:

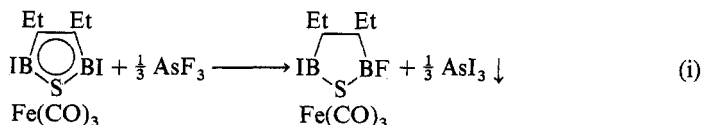


However, when  $\text{AlBr}_3$  and  $\text{AlI}_3$  are dissolved,  $[\text{AlCl}_4]^-$  is still identified in solution. Thus, halogen transfer must occur:



followed by the formation of  $[\text{AlCl}_4]^-$  as before<sup>13</sup>. It is possible that similar reactions take place with gallium halides<sup>14</sup>.

Arsenic trifluoride is an important metathetical reagent for transforming chlorides into the corresponding fluoride derivatives. Thus, over 12 h, the tricarbonyliron complex is smoothly converted into a monofluoro species<sup>15</sup>.



(B.D. JAMES)

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### 2.6.12.3. by Fluorinating Agents.

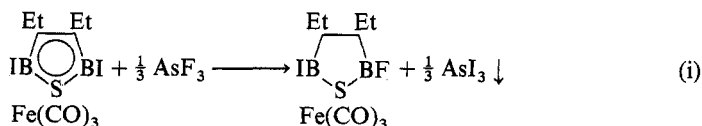
Preparations of fluorine derivatives are generally associated with more aggressive reagents and the use of special materials and techniques. This is not always the case as is illustrated by the use of  $\text{AgF}$  in metathesis (§2.6.12.2). Even though techniques for handling  $\text{HF}$  are now much more common, an alternative reagent such as  $\text{NH}_4\text{F}$  is still a more appealing alternative. Thus, the addition of freshly prepared  $\text{MBr}_3$  ( $\text{M} = \text{Al, In}$ ) in  $\text{MeOH}$  to a rapidly stirred solution of  $\text{xs NH}_4\text{F}$  gives a quantitative conversion to the fluorides. Thallium fluoride is not precipitated under these conditions<sup>1</sup>. Although  $\text{CaF}_2$  is useful for the preparation of volatile  $\text{BF}_3$  (§2.6.12.2), attempted fluorination of  $\text{AlCl}_3$  leads to the  $\text{AlF}_3$  being retained in some kind of complex<sup>2</sup>.

An approximate measure of the reactivity of various fluorides toward halogen exchange may be obtained from Table 1 of free energy differences<sup>3</sup>. Antimony trifluoride (alone, or together with  $\text{SbF}_5$ ) is an important and effective compound for replacing  $\text{Cl}$  in covalent compounds; very few halides resist exchange with this reagent. Arsenic trifluoride, although a weaker fluorinating agent than  $\text{SbF}_3$ , is preferred for preparing high-bp fluorides since the byproduct  $\text{AsCl}_3$  (bp 403 K) can be distilled off. Conversely,  $\text{SbF}_3$  is preferred for the low-boiling fluorides that can be fractionated from  $\text{SbCl}_3$  (bp 496 K)<sup>4</sup>. Thus,  $\text{PhBCl}_2$  undergoes immediate, vigorous reaction when  $\text{SbF}_3$  is added slowly to it. If the mixture is held below 318 K, a 66% yield of  $\text{PhBF}_2$  is obtained. The aggressive nature of the reagent tends to lead to  $\text{B}-\text{C}$  bond cleavage<sup>5</sup>. Thus, unless the reaction mixture is held below 300 K, the yield for the p-tolyl analog p-tolBF<sub>2</sub> is quite

2.6. The Formation of the Halogen (B, Al, Ga, In, Tl) Bond  
 2.6.12. from Halide-Halide Exchange Reactions (Metathesis)  
 2.6.12.3. by Fluorinating Agents.

followed by the formation of  $[\text{AlCl}_4]^-$  as before<sup>13</sup>. It is possible that similar reactions take place with gallium halides<sup>14</sup>.

Arsenic trifluoride is an important metathetical reagent for transforming chlorides into the corresponding fluoride derivatives. Thus, over 12 h, the tricarbonyliron complex is smoothly converted into a monofluoro species<sup>15</sup>.



(B.D. JAMES)

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### 2.6.12.3. by Fluorinating Agents.

Preparations of fluorine derivatives are generally associated with more aggressive reagents and the use of special materials and techniques. This is not always the case as is illustrated by the use of  $\text{AgF}$  in metathesis (§2.6.12.2). Even though techniques for handling  $\text{HF}$  are now much more common, an alternative reagent such as  $\text{NH}_4\text{F}$  is still a more appealing alternative. Thus, the addition of freshly prepared  $\text{MBr}_3$  ( $\text{M} = \text{Al, In}$ ) in  $\text{MeOH}$  to a rapidly stirred solution of  $\text{xs NH}_4\text{F}$  gives a quantitative conversion to the fluorides. Thallium fluoride is not precipitated under these conditions<sup>1</sup>. Although  $\text{CaF}_2$  is useful for the preparation of volatile  $\text{BF}_3$  (§2.6.12.2), attempted fluorination of  $\text{AlCl}_3$  leads to the  $\text{AlF}_3$  being retained in some kind of complex<sup>2</sup>.

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TABLE 1. FREE-ENERGY DIFFERENCES FOR CHLORIDE-FLUORIDE EXCHANGE<sup>a</sup>

Couple	$\Delta F_{\text{MCl}}^{\circ} - \Delta F_{\text{MF}}^{\circ}$ (kJ g-at <sup>-1</sup> )
AgF-AgCl	75.37
KF-KCl	129.80
NH <sub>4</sub> F-NH <sub>4</sub> Cl	145.29
NaF-NaCl	159.52
$\frac{1}{3}(\text{SbF}_3 - \text{SbCl}_3)$	169.57
HF-HCl	178.37
$\frac{1}{6}(\text{WF}_6 - \text{WCl}_6)$	194.28
$\frac{1}{4}(\text{TiF}_4 - \text{TiCl}_4)$	205.58
$\frac{1}{2}(\text{CaF}_2 - \text{CaCl}_2)$	206.00
$\frac{1}{3}(\text{BF}_3 - \text{BCl}_3)$	240.75
$\frac{1}{4}(\text{SiF}_4 - \text{SiCl}_4)$	250.80

<sup>a</sup> Ref. 3.

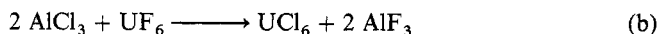
small. Not surprisingly, BCl<sub>3</sub> also is smoothly converted to BF<sub>3</sub> at 273 K and 50 kPa in the presence of SbCl<sub>5</sub> catalyst<sup>6</sup>.

Antimony fluorides also react spontaneously with [B] trichloroborazenes and partially fluorinated products may be obtained by careful control of conditions. The use of TiF<sub>4</sub>, however, appears to be a convenient method for the fluorination of such compounds because of the short reaction time and a solvent is not necessary<sup>7</sup>. In the reaction:



yields are 64% (R = Me), 89% (R = Et), 95% (R = n-Pr) and 96% (R = n-Bu).

Transition-metal fluorides generally react quite rapidly with BCl<sub>3</sub> reflecting the fact that the enthalpy of formation of BF<sub>3</sub> is more negative than that of BCl<sub>3</sub> by 722 kJ mol<sup>-1</sup>. In a number of cases redox reactions occur also. Generally, the third transition series fluoride is the least reactive and that of the first series the most reactive<sup>8</sup>. Thus, VF<sub>5</sub> condensed onto xs BCl<sub>3</sub> and allowed to warm produces BF<sub>3</sub>, VCl<sub>4</sub> and Cl<sub>2</sub>. Niobium and Ta pentafluorides also yield BF<sub>3</sub>, but without reduction of the metals. The reaction of MoF<sub>6</sub> with xs BCl<sub>3</sub> gives MoCl<sub>5</sub> together with a mixture of BF<sub>3</sub>, BClF<sub>2</sub> and BCl<sub>2</sub>F. Similarly, AlCl<sub>3</sub> is fluorinated readily by the reactive UF<sub>6</sub> compound. When AlCl<sub>3</sub> is in excess, simple metathesis occurs:



but with excess of the fluorinating agent, reduction to UF<sub>4</sub> occurs and Cl<sub>2</sub> is released along with the formation of the AlF<sub>3</sub> product<sup>9</sup>.

Sulfur tetrafluoride has been mentioned previously (§2.6.6.4) as an attractive fluorinating agent. This compound will fluorinate BCl<sub>3</sub> and undergo concomitant reduction to SCl<sub>2</sub> and chlorine<sup>10</sup>. On the other hand, SF<sub>6</sub> resists halogen transfer. Only 15% conversion of AlCl<sub>3</sub> into AlF<sub>3</sub> is observed after 24 h in a sealed tube at 450–470 K, and up to 470 K, BCl<sub>3</sub> does not react<sup>11</sup>.

Bromine trifluoride, on the other hand, has long been recognized as a typically corrosive but reasonably convenient fluorinating agent. It fluorinates any compound dissolves in it and is a useful preparative solvent, although it is sometimes difficult to remove from products<sup>12</sup>. Thus,  $\text{AlCl}_3$  is converted slowly to  $\text{AlF}_3$ , but with no evidence of  $\text{BrF}_3$  retention. Thallous chloride is converted to a mixture of  $\text{TlF}$  and  $\text{TlF}_3$ , with 80–90% of the metal being in the 3+ state<sup>13</sup>. Aluminum oxyfluoride proved more difficult to prepare than other oxyhalides but was finally obtained via  $\text{BrF}_3$  fluorination of the corresponding bromide<sup>14</sup>.

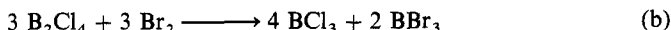
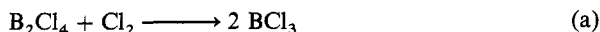
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## 2.6.13. Cleavage of Other Group-IIIB-Element Bonds

### 2.6.13.1. by Halogens.

The major remaining group-IIIB-element bonds to be considered are those between the group-IIIB elements themselves<sup>1</sup> and those between the elements and the transition metals<sup>2,3</sup>. Thus, the B—B bond in compounds such as  $\text{B}_2\text{Cl}_4$  is susceptible to attack by  $\text{Cl}_2$  and  $\text{Br}_2$  (at 228 and 250 K, respectively):



Iodine does not show any signs of reaction with  $\text{B}_2\text{Cl}_4$  under these relatively cool conditions<sup>4</sup>. Similarly, the metal-metal bond present in the  $[\text{In}_2\text{X}_6]^{2-}$  anions is ruptured by elemental halogens ( $\text{Y}_2$ ), giving  $[\text{InX}_3\text{Y}]^-$ . These reactions occur readily on heating in benzene and the tetrahaloindate compound crystallizes on cooling. The order of addition in these reactions seems to be vitally important, since if the halogen is added to a solution of  $[\text{In}_2\text{X}_6]^{2-}$ , precipitation of the  $[\text{XY}_2]^-$  salt in a competing reaction occurs more rapidly than the oxidation<sup>5</sup>.

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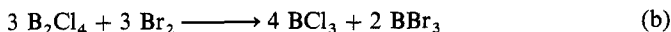
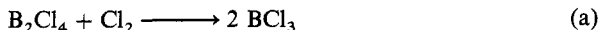
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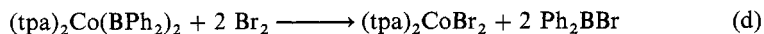


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In a similar general reaction, halogens cleave the element-transition-metal bond according to the equation<sup>6</sup>:



Thus, with tetraphenylphosphinoethane (TPA) coordinated to cobalt in the boryl complex  $(Ph_2B)_2Co(tpa)_2$ , bromine cleaves the Co—B bonds easily in a few minutes in  $CCl_4$  solvent<sup>7</sup>:



Boron bonded to other metals in complexes such as  $Ph_2BMo(CO)_3(C_5H_5-\eta^5)$ ,  $Ph_2BPtCl(PEt_3)_2$  or  $Ph_2BMn(CO)_4PPh_3$  also undergo cleavage reactions of this type<sup>6,8</sup>. Note that  $(Me_2N)_2BMn(CO)_4L$  also suffers B—Mn bond cleavage, indicating that the bond to the transition metal is broken in preference to those between boron and carbon or boron and nitrogen<sup>9</sup>. Borine-metal complexes react similarly and in steps. For example, the polymeric  $Et_2NBF_3Fe(CO)_4$  interacts first with 1 mol equiv of  $Br_2$  in  $CCl_4$ , yielding  $Et_2NB(Br)Fe(CO)_4$ , but with xs of  $Br_2$ , cleavage of the Fe—B bond is observed, giving a precipitate of  $(CO)_4FeBr_2$  and leaving  $Et_2NBBR_2$  in solution<sup>10</sup>.

When more than one group-IIIB-transition-metal bond occurs, stoichiometric quantities of halogen may successively cleave the bonds. Thus, with  $In[Mn(CO)_5]_3$ ,  $Cl_2(g)$  or  $Br_2$  in  $CCl_4$  successively yield  $XIn[Mn(CO)_5]_2$ ,  $X_2InMn(CO)_5$  and  $InX_3$  together with 1, 2 or 3 mol equiv of  $XMn(CO)_5$ <sup>11</sup>. With  $Tl[Mn(CO)_5]_3$ , a similar reaction occurs only with  $Cl_2$  (yielding  $TlCl_3$ ) but with  $Br_2$  or  $I_2$  the  $TlX$  precipitates over 0.5 h<sup>12</sup>. Thus, a 2:1 mole ratio of halogen:thallium produces  $Mn(CO)_5X$  and  $TlX$ . Iodine monochloride reacts similarly with  $R_2TlMo(CO)_3(C_5H_5-\eta^5)$  in order to attach Cl to thallium, whereas  $Br_2$  instead reacts to cleave the Tl—C bonds (to give  $RBr$ ) as well as the Tl—Mo bond<sup>13</sup>.

Boron-Hg bonds are obtained via reaction of o-, m- or p-carborane with mercury trifluoroacetate. The mercurated reagents are useful in turn for forming carborane derivatives (with boron bonded to Tl, Sn, As, Sb) via transmetallation. The position of substitution in these compounds is determined by fission of the boron-metal bond with  $Br_2$  to give known bromocarboranes<sup>14,15</sup>.

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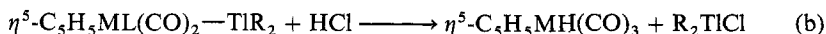
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**2.6.13.2. by Hydrogen Halides.**

Generally, reactions of group-IIIB-transition-metal bonds proceed according to<sup>1</sup>:

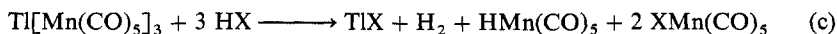


with the hydrogen being transferred to the transition element as a hydrido ligand and concomitant formation of the group-IIIB-element-halogen bond. For example<sup>2</sup>:

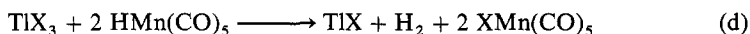


(specifically reported for M = Mo, L = CO and R = Me, but may be generalized). In  $(Me_2N)_2BMn(CO)_5$ , hydrogen chloride first splits the B—N bond, yielding  $Cl_2BMn(CO)_5$  and dimethylamine hydrochloride; then a further mole equivalent releases  $BCl_3$  and  $HMn(CO)_5$ <sup>3</sup>.

Stoichiometric equivalents of HX successively cleave the In—Mn bonds in  $In[Mn(CO)_5]_3$  yielding 1–3 mol of  $HMn(CO)_5$  and the  $InX_3$ <sup>4</sup>, but with the Tl analog reduction occurs and the Tl(I) halide precipitates in accordance with<sup>5</sup>:



where X = Cl, I. It is possible that the Tl—Mn bonds are indeed first cleaved to give  $TlX_3$  and  $HMn(CO)_5$ , but that the thallic halide then reacts further:



since this reaction does occur when X = Cl. Interactions of hydrogen halides with group-IIIB-group-IIIB bonded molecules do not appear to be well known<sup>6</sup>.

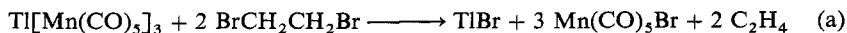
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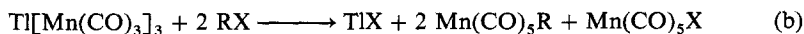
**2.6.13.3. by Other Halides.**

The interactions of thallium-transition-metal bonds with other metal and non-metal halides are illustrated in Table 1. In all cases the electronegative halogen is transferred to Tl. The reactions proceed smoothly, giving high yields of the organothallium halide after several hours<sup>1</sup>.

With 1,2-dibromoethane, the Tl—Mn compound  $Tl[Mn(CO)_5]_3$  also reacts to evolve ethene, but the thallium is reduced:



Reductions also observed in reactions with alkyl and acyl halides



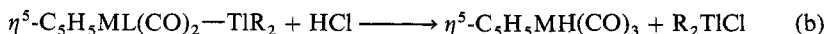


**2.6.13.2. by Hydrogen Halides.**

Generally, reactions of group-IIIB-transition-metal bonds proceed according to<sup>1</sup>:

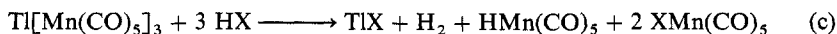


with the hydrogen being transferred to the transition element as a hydrido ligand and concomitant formation of the group-IIIB-element-halogen bond. For example<sup>2</sup>:

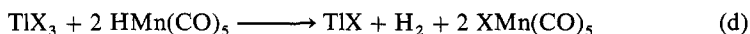


(specifically reported for M = Mo, L = CO and R = Me, but may be generalized). In  $(Me_2N)_2BMn(CO)_5$ , hydrogen chloride first splits the B—N bond, yielding  $Cl_2BMn(CO)_5$  and dimethylamine hydrochloride; then a further mole equivalent releases  $BCl_3$  and  $HMn(CO)_5$ .<sup>3</sup>

Stoichiometric equivalents of HX successively cleave the In—Mn bonds in  $In[Mn(CO)_5]_3$  yielding 1–3 mol of  $HMn(CO)_5$  and the  $InX_3$ ,<sup>4</sup> but with the Tl analog reduction occurs and the Tl(I) halide precipitates in accordance with<sup>5</sup>:



where X = Cl, I. It is possible that the Tl—Mn bonds are indeed first cleaved to give  $TlX_3$  and  $HMn(CO)_5$ , but that the thallic halide then reacts further:



since this reaction does occur when X = Cl. Interactions of hydrogen halides with group-IIIB-group-IIIB bonded molecules do not appear to be well known<sup>6</sup>.

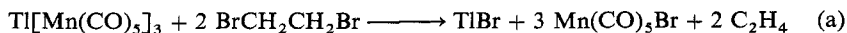
(B.D. JAMES)

1. N. S. Vyazankin, G. A. Razuvaev, O. A. Kruglaya, *Organomet. Chem. Rev.*, **A3**, 323 (1968).
2. B. Walther, H. Albert, A. Kolbe, *J. Organomet. Chem.*, **145**, 285 (1978).
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**2.6.13.3. by Other Halides.**

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Reductions also observed in reactions with alkyl and acyl halides

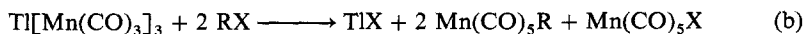
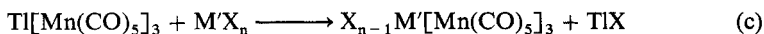


TABLE 1. REACTIONS OF THALLIUM-TRANSITION-METAL BONDS WITH HALIDES<sup>a</sup>

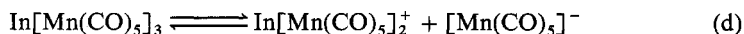
Organothallium reagent	Halide	Products
$\text{Me}_2\text{TlMo}(\text{CO})_3\text{C}_5\text{H}_5\text{-}\eta^5$	MeI	$\text{R}_2\text{TlI}$ (91 %) + $\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_3\text{Me}$
$\text{Me}_2\text{TlMo}(\text{CO})_3\text{C}_5\text{H}_5\text{-}\eta^5$ or $\text{EtTlMo}(\text{CO})_3\text{C}_5\text{H}_5\text{-}\eta^5$	$\text{ICH}_2\text{CH}_2\text{I}$	$\text{R}_2\text{TlI}$ (78 %) + $\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_3\text{I}$ + $\text{C}_2\text{H}_4$
$\text{Me}_2\text{TlMo}(\text{CO})_3\text{C}_5\text{H}_5\text{-}\eta^5$ or $\text{Me}_2\text{TlW}(\text{CO})_3\text{C}_5\text{H}_5\text{-}\eta^5$	ICl	$\text{R}_2\text{TlCl}$ (86 %) + $\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_3\text{I}$
$\text{Me}_2\text{TlMo}(\text{CO})_3\text{C}_5\text{H}_5\text{-}\eta^5$	$\text{Me}_3\text{SnCl}$	$\text{R}_2\text{TlCl}$ (88 %) + $\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_3\text{SnMe}_3$
$\text{Me}_2\text{TlMo}(\text{CO})_3\text{C}_5\text{H}_5\text{-}\eta^5$	$\text{HgCl}_2$	$\text{R}_2\text{TlCl}$ (89 %) + $\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_3\text{HgCl}$
$\text{Me}_2\text{TlMo}(\text{CO})_3\text{C}_5\text{H}_5\text{-}\eta^5$	$\frac{1}{2}\text{HgCl}_2$	$\text{R}_2\text{TlCl}$ (94 %) + $\frac{1}{2}[\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_3]_2\text{Hg}$

<sup>a</sup> Ref. 1.<sup>b</sup> Yield is 66 % using III.

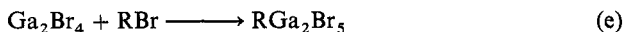
where R = Me, MeCO, PhCO. These reactions proceed easily also, probably because of a tendency for ionization in solution. The reaction with MeI, e.g., is complete<sup>2</sup> in 0.5 h. Generally,  $\text{Tl}[\text{Mn}(\text{CO})_5]_3$  reacts with low-valent metal halides,  $\text{M}'\text{X}_n$ :



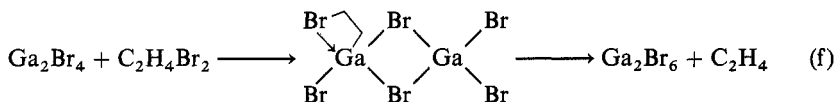
where  $\text{M}' = \text{Ga, In}$ ,  $\text{X} = \text{Cl, Br}$  and  $n = 1$ ;  $\text{M}' = \text{Ge, Sn}$ ,  $\text{X} = \text{Cl, Br}$  and  $n = 2$ ;  $\text{M}' = \text{Sb}$ ,  $\text{X} = \text{Cl}$  and  $n = 3$ . Similarly, there appears to be partial ionization of the In—Mn bonds in  $\text{In}[\text{Mn}(\text{CO})_5]_3$ , expressed as<sup>3</sup>:



The reaction of a low oxidation state metal complex with  $\text{RX}$  to yield a product in which the metal has inserted into a C—X bond is well known in transition-metal chemistry but is less so in the main-group area. However, in group IIIB, this type of reaction may be employed to synthesize organometallic halides of Ga and In using  $\text{E}^+$  or  $\text{E}_2\text{X}_4$  ( $\text{E} = \text{Ga, In}$ ):



With 1,2-dibromoethane,  $\text{GaBr}_3$  and ethene are formed:



The analogous reactions with In(II) halides do not appear to be known, but In(I) halides may be oxidized by  $\text{RX}$  to  $\text{RInX}_2$ . The reaction between  $\text{InBr}$  and  $\text{MeBr}$  is slow at RT, but the yields are very high<sup>4</sup>. A somewhat similar reaction sees the diborane (4) derivative  $\text{Ph}(\text{Me}_2\text{N})\text{B—B}(\text{NMe}_2)\text{Ph}$  cleaved by  $\text{CCl}_4$  under the influence of radiation<sup>5</sup>:

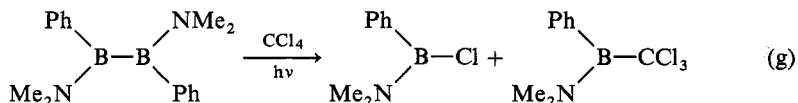


TABLE 2. REACTIONS OF THALLIUM-MERCURY COMPOUNDS (I) AND (II) WITH VARIOUS HALIDES<sup>a</sup>

Compound	Halide	Products <sup>b</sup>
I	HCl	TlCl (100%) + A + B
I	R <sub>3</sub> GeBr <sup>c</sup>	TlBr (98 %) + (C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> GeGeR <sub>3</sub> + B
I	HgCl <sub>2</sub>	TlCl (99 %) + Hg <sub>2</sub> Cl <sub>2</sub> + Hg + (C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> GeCl + B
II	HgCl <sub>2</sub>	TlCl (100%) + B (92%)
II	ZnI <sub>2</sub>	TlI (100%) + A + B + Zn(OEt) <sub>2</sub>
II	[(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Cr]I	TlI (100%) + [Cr(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ] <sub>2</sub> [(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> Ge] <sub>4</sub> Hg} (99%)
II	Ph <sub>3</sub> SbBr <sub>2</sub>	TlBr (100%) + A (96%) + B + Ph <sub>3</sub> Sb(OEt) <sub>2</sub>
II	( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> NbCl <sub>2</sub>	TlCl (97%) + A (68%) + B + ( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> NbOEt (?)
II	( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> TiCl <sub>2</sub>	TlCl (100%) + ( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Ti{[(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> Ge] <sub>3</sub> Hg} <sub>2</sub> (73%)
II	CuCl <sub>2</sub>	TlCl (85%) + Cu <sub>2</sub> Cl <sub>2</sub> (86%) + A + B + (C <sub>6</sub> F <sub>5</sub> ) <sub>6</sub> Ge <sub>2</sub> (10%)
II	MCl <sub>2</sub> <sup>d</sup>	TlCl + M{[(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> Ge] <sub>3</sub> Hg} <sub>2</sub> + A + B
II	MnCl <sub>2</sub>	TlCl (100%) + Mn{[(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> Ge] <sub>3</sub> Hg} <sub>2</sub> 1.5 DME (85%)

<sup>a</sup> Ref. 8, 9.<sup>b</sup> A = (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>GeH; B = [(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Ge]<sub>2</sub>Hg.<sup>c</sup> R = Et, C<sub>6</sub>F<sub>5</sub>.<sup>d</sup> M = Co, Ni.

In Tl(I) compounds such as Tl[Co(CO)<sub>4</sub>] or Tl[Mn(CO)<sub>5</sub>], the transition-metal group is mobile, making these reagents an excellent source of the [M(CO)<sub>n</sub>]<sup>-</sup> group. Thus, Ph<sub>3</sub>SnCl in benzene reacts with Tl[Co(CO)<sub>4</sub>], yielding Ph<sub>3</sub>SnCo(CO)<sub>4</sub>, and with BrMn(CO)<sub>5</sub> in CH<sub>2</sub>Cl<sub>2</sub> to give (CO)<sub>4</sub>CoMn(CO)<sub>5</sub>, precipitating thallous halides<sup>6</sup>. The compound Tl[Co(CO)<sub>4</sub>] does not react with organosilicon halides to an appreciable extent<sup>7</sup>.

In contrast, detailed study of the reactions of the unusual compounds (R<sub>3</sub>Ge)<sub>2</sub>Hg·TlGeR<sub>3</sub> (I) and (R<sub>3</sub>Ge)<sub>3</sub>Hg·Tl (II) (both are dimethoxyethane solvates) shows that they have distinct ionic character. Most of the reactions with halides occur readily, proceeding to completion at RT in a few minutes (Table 2). Most of the reactions of (II) occur in dimethoxyethane-ethanol but do not take place even under drastic conditions unless alcohol or water is present<sup>8,9</sup>.

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## 2.6.14. Subvalent Group-III B Halides

### 2.6.14.1. Boron, Aluminum, Gallium, Indium.

The subhalides of boron have been reviewed<sup>1</sup>. The known compounds are shown in Table 1.

## 2.6. The Formation of the Halogen (B, Al, Ga, In, Tl) Bond

## 2.6.14. Subvalent Group-IIIB Halides

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II	(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> TiCl <sub>2</sub>	TlCl (100%) + (η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Ti[(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> Ge] <sub>3</sub> Hg (73%)
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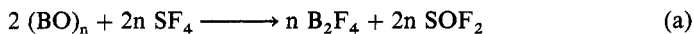
The subhalides of boron have been reviewed<sup>1</sup>. The known compounds are shown in Table 1.

TABLE 1. THE KNOWN BORON SUBHALIDES

BF	BCl	—	—
B <sub>2</sub> F <sub>4</sub>	B <sub>2</sub> Cl <sub>4</sub>	B <sub>2</sub> Br <sub>4</sub>	B <sub>2</sub> I <sub>4</sub>
B <sub>3</sub> F <sub>5</sub>	—	—	—
—	B <sub>4</sub> Cl <sub>4</sub>	—	—
—	—	B <sub>7</sub> Br <sub>7</sub>	—
—	B <sub>8</sub> Cl <sub>8</sub>	B <sub>8</sub> Br <sub>8</sub>	(B <sub>8</sub> I <sub>8</sub> ) <sup>a</sup>
B <sub>8</sub> F <sub>12</sub>	—	—	—
—	B <sub>9</sub> Cl <sub>9</sub>	B <sub>9</sub> Br <sub>9</sub>	B <sub>9</sub> I <sub>9</sub>
—	B <sub>10</sub> Cl <sub>10</sub>	(B <sub>10</sub> Br <sub>10</sub> ) <sup>a</sup>	—
—	B <sub>11</sub> Cl <sub>11</sub>	—	—
—	(B <sub>12</sub> Cl <sub>12</sub> ) <sup>a</sup>	—	—
B <sub>14</sub> F <sub>8</sub>	—	—	—

<sup>a</sup> Detected, but not isolated satisfactorily.

A central compound is B<sub>2</sub>Cl<sub>4</sub> which is prepared from BCl<sub>3</sub> by discharge methods. For example, using cells with W electrodes supplying a discharge of up to 12 kV and with Cu as a Cl abstractor, it is possible to obtain up to 0.5 g h<sup>-1</sup> of B<sub>2</sub>Cl<sub>4</sub> if several cells are operated in series<sup>2</sup>. From it, B<sub>2</sub>F<sub>4</sub> may be obtained by treatment with SbF<sub>3</sub> or TiF<sub>4</sub>. A better synthesis for B<sub>2</sub>F<sub>4</sub>, however, is the interaction of SF<sub>4</sub> and diboronoxy compounds, such as B<sub>2</sub>(OMe)<sub>4</sub> or boron monoxide at low T<sup>3</sup>:



The preparation of B<sub>2</sub>Cl<sub>4</sub> via a similar procedure using BCl<sub>3</sub> as the chlorinating agent gives a much poorer yield<sup>4</sup>, although the B<sub>2</sub>(OMe)<sub>4</sub> + BBr<sub>3</sub> reaction at RT in CH<sub>2</sub>Cl<sub>2</sub> provides a convenient (50% yield) synthesis for the bromide analog<sup>5</sup>.

A number of monochlorides, B<sub>n</sub>Cl<sub>n</sub>, are obtained by thermal decomposition of B<sub>2</sub>Cl<sub>4</sub>. By decomposition for 3 d in a sealed tube at 353 K, BCl<sub>3</sub> is formed along with B<sub>8</sub>Cl<sub>8</sub> and B<sub>9</sub>Cl<sub>9</sub> together with B<sub>10</sub>Cl<sub>10</sub>, B<sub>11</sub>Cl<sub>11</sub> and B<sub>12</sub>Cl<sub>12</sub>. These products have only slightly differing volatilities and must be separated by careful fractional sublimation<sup>6</sup>. Also, dilute solutions of B<sub>9</sub>Cl<sub>9</sub> in BCl<sub>3</sub> if decomposed over many weeks yield mostly B<sub>11</sub>Cl<sub>11</sub> with some B<sub>12</sub>Cl<sub>12</sub>. The compound B<sub>4</sub>Cl<sub>4</sub> is obtained in batches of 3–5 mg h<sup>-1</sup> by passing BCl<sub>3</sub> through a RF discharge at RT, using Hg as a Cl abstractor<sup>7</sup>. Preparations of the bromides and iodides have some parallels with the chlorides: B<sub>2</sub>Br<sub>4</sub> and B<sub>2</sub>I<sub>4</sub> are obtained from RF discharge syntheses and the compounds undergo thermal decompositions, the bromide at RT giving B<sub>7</sub>Br<sub>7</sub>, B<sub>9</sub>Br<sub>9</sub> and B<sub>10</sub>Br<sub>10</sub>, while B<sub>2</sub>I<sub>4</sub> decomposes above its melting point to give B<sub>8</sub>I<sub>8</sub> and B<sub>9</sub>I<sub>9</sub>; B<sub>8</sub>Br<sub>8</sub> is obtained from the reaction of B<sub>8</sub>Cl<sub>8</sub> with AlBr<sub>3</sub> at 373 K in BBr<sub>3</sub>.

Major advances have come to this area in recent years. Now B<sub>2</sub>Cl<sub>4</sub> may be obtained in gram quantities quite readily using a vapor synthesis method<sup>8</sup>. Typically, 10 g of Cu metal are evaporated over 1 h in a reactor while BCl<sub>3</sub> is passed in at ca 2.5 g min.<sup>-1</sup> These are condensed together using liq N<sub>2</sub>, and up to 4 g B<sub>2</sub>Cl<sub>4</sub> is obtained. The method may be scaled up.

Second, it has proved possible to oxidize [B<sub>9</sub>X<sub>9</sub>]<sup>2-</sup> ions (X = Cl, Br, I) to give good yields of the neutral B<sub>9</sub>X<sub>9</sub> species. The preparations start from the relatively easily obtained hydride anions. For example, sulfonyl chloride acts as both a chlorinating and an oxidizing agent to the [Bu<sub>4</sub>N]<sup>+</sup> salt of [B<sub>9</sub>H<sub>9</sub>]<sup>2-</sup> in CH<sub>2</sub>Cl<sub>2</sub> or the hydrides may be halogenated using N-halosuccinimides and then oxidized<sup>9</sup>.

Third, vapor synthesis methods make it possible to produce useful quantities of the reactive BF and BCl monohalides<sup>10</sup>. Cocondensation of BF and B<sub>2</sub>F<sub>4</sub> yields B<sub>3</sub>F<sub>5</sub>, in which the BF molecule has inserted itself into the B—F bond of B<sub>2</sub>F<sub>4</sub>. Other lower fluorides may be obtained from B<sub>3</sub>F<sub>5</sub>.

By way of contrast with many boron subhalides, the Al monohalides (X = F, Cl, Br, I) are known only as short-lived molecular species that are formed in gas-phase reactions between the elements. The compounds are unstable thermodynamically with respect to disproportionation into the trihalide and the metal. Gallium and In, however, form insoluble lower halides such as M<sup>I</sup>X and the mixed-valence M<sup>I</sup>[M<sup>III</sup>X<sub>4</sub>], except that the fluorides, GaF and InF, again are only observed as gas-phase species<sup>11</sup>.

When InBr<sub>3</sub> is prepared via direct union of the elements, InBr and In[InBr<sub>4</sub>] intermediates may be observed<sup>12</sup> but convenient and, more importantly, reliable procedures have been developed for compounds of these types. Gallium monohalides, GaX (X = Br, I), may be obtained by reducing the trihalide or "dihalide" with the metal in a sealed tube. Similarly, GaCl is obtained by reducing GaCl<sub>3</sub> vapor by passing it over molten metal. The chloride is the least well characterized of the compounds owing to its propensity to disproportionate. Like the other monohalides, however, it is an electron-pair acceptor acid and donor molecules stabilize the system<sup>11</sup>.

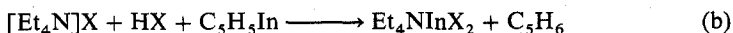
The mixed-valence "dihalides" likewise may be prepared via reduction of the trihalide<sup>13,14</sup>. Very convenient procedures for producing gallium and indium dihalides by using aromatic solvents now supersede the sealed tube methods<sup>15,16</sup>. For example, InI<sub>3</sub> reacts with xs In metal when refluxed, yielding a pure, crystalline precipitate of InI<sub>2</sub>. The reaction is slow in benzene but proceeds at a convenient rate in the higher boiling xylenes, and similar reactions occur with InBr<sub>3</sub> and InCl<sub>3</sub>. By way of bonus, InX<sub>2</sub> compounds disproportionate in ether (and other electron-pair donor bases) to give the trihalide etherate together with the monohalide which precipitates in a finely divided and particularly reactive form.

A range of subhalides exists in addition to the MX and MX<sub>2</sub> species already mentioned. The In—Cl phase diagram also shows In<sub>2</sub>Cl<sub>3</sub>, In<sub>3</sub>Cl<sub>4</sub> and In<sub>5</sub>Cl<sub>9</sub>, and In<sub>4</sub>Br<sub>7</sub> and In<sub>7</sub>Br<sub>9</sub> are known. Such compounds have been obtained via reduction of the trihalide with the metal at elevated T under anhydrous conditions.

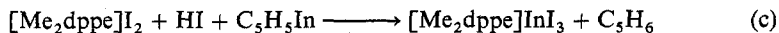
The complex anions [M<sub>2</sub>X<sub>6</sub>]<sup>2-</sup> (M = Ga, In; X = Cl, Br, I) containing the formally divalent metals also have straightforward syntheses. In the indium case, a mixture of InI<sub>2</sub> and [Bu<sub>4</sub>N]I suspended in xylene deposits a yellow oil when refluxed and finally gives a good yield of [Bu<sub>4</sub>N]<sub>2</sub>[In<sub>2</sub>I<sub>6</sub>] on cooling<sup>18</sup>. For [Ga<sub>2</sub>X<sub>6</sub>]<sup>2-</sup>, anodic dissolution of the metal in an electrolyte of 6 mol L<sup>-1</sup> HX (X = Cl, Br) at 273 K, followed by addition of [R<sub>4</sub>N]X, precipitates the solid, which contains some [GaX<sub>4</sub>]<sup>-</sup> but which is easily purified by recrystallization from CH<sub>3</sub>NO<sub>2</sub>. The complex iodide, however, is not obtained via this procedure<sup>19</sup>.

The direct union of stoichiometric quantities of the elements is the traditional, albeit not especially convenient, procedure for lower valent halides. Gallium metal and I<sub>2</sub> react at 620–770 K in a sealed tube to produce GaI over several days, but this is sufficiently unstable in the presence of xs Ga metal that a limiting phase GaI<sub>1.19</sub> is obtained. From this, the more soluble "di-iodide" may be extracted using dry benzene, and GaI remains<sup>20</sup>. Reaction of stoichiometric quantities is also useful for the preparation of compounds such as Cs<sub>2</sub>In<sup>I</sup>(In<sup>III</sup>Cl<sub>6</sub>) (from 2:1:1 CsCl, InCl and InCl<sub>3</sub>), which may also be prepared by reducing of Cs<sub>3</sub>[In<sub>2</sub>Cl<sub>9</sub>] with In metal<sup>21</sup>. A convenient alternative to direct union methods is to react the metal with stoichiometric quantities of Hg(I) or Hg(II) halides<sup>11,22,23</sup>.

Cyclopentadienylindium(I) may be a useful reagent for the preparation of indium(I) complexes. In the presence of acid, cyclopentadiene is released and halide complexes with the metal<sup>24</sup>, as in:



and



where  $[\text{Me}_2\text{dppe}]^{2+} = 1,2\text{-bis(methyldiphenylphosphonio)ethane}$  dication;  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ .

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## 2.6.14.2. Thallium.

In complete contrast with its congeners, Tl is most stable in its +I oxidation state. Rather than the +I halides tending to disproportionate to the element and the +III halide, with Tl there is almost invariably some difficulty in maintaining the metal in the higher oxidation state<sup>1</sup>. For example, while  $\text{TlCl}_3$  is conveniently prepared by oxidation of thallos chloride with chlorine in warm water, attempts to dehydrate the trichloride product thermally lead to a reversion to the  $\text{Tl(I)}$  state<sup>2</sup>. A similar reaction of thallos

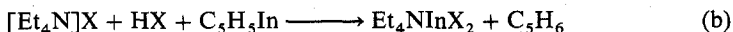
## 2.6. The Formation of the Halogen (B, Al, Ga, In, Tl) Bond

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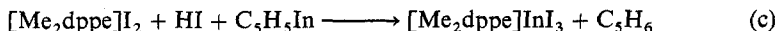
## 2.6.14. Subvalent Group-IIIb Halides

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iodide with  $I_2$  in conc HI yields  $TlI_3$ , but this is a  $Tl(I)$  derivative of the  $I_3^-$  ion<sup>3</sup>. This preference for forming the lower oxidation state is not confined to the binary halides; e.g., halide ions (except  $F^-$ ) react with alkylthallium(III) dicarboxylates to give a ppt of thallium(I) halide and form the alkyl halide. The intermediate  $RTlX_2$  undergoes the extremely facile reductive degradation prevalent in these species<sup>4</sup>. The much more stable  $R_2TlX$  species are not immune from reduction, either—especially in the presence of even mild reductants. For example, the pentafluorophenyl compounds  $(C_6F_5)_2TlX$  are decomposed by  $I^-$  in MeOH, EtOH or water, giving  $C_6F_5H$  and thallos iodide<sup>5</sup>.

Apart from the fluoride, which is quite soluble in water, the other  $Tl(I)$  halides are very easily obtained by adding the appropriate halide ion to precipitate them from any soluble thallos salt<sup>1</sup>. The compounds obtained are anhydrous, having little electron-pair acceptor acid character. This is in contrast with the Ga and In monohalides, which are stabilized by employing their electron-pair acceptor acid properties<sup>6</sup>. Despite its high water solubility,  $TlF$  also is obtained very easily from straightforward reactions, usually from the interaction of  $TlOH$  or  $Tl_2CO_3$  with aq  $HF$ <sup>7</sup>.

Other lower valent halides, e.g., compounds of empirical formula  $TlX_2$ , are easily obtained by adding  $TlX$  to  $TlX_3$ . For example,  $TlCl_2$  is obtained from a boiling, conc aq  $TlCl_3$  soln<sup>8</sup>. Similar to their Ga and In counterparts, these compounds are  $Tl(I)$ – $Tl(III)$  mixed-valence species, with the  $Tl(III)$  center acting as an acceptor for the halide ion. Other mixed-valence compounds are quite readily obtained. For example,  $Tl_2F_3$  is prepared by heating stoichiometric quantities of  $TlF$  and  $TlF_3$  at 570 K under  $Ar$ <sup>1,9</sup>, and the stable chloride analog precipitates very easily from warm, acidified  $TlCl_3$  by addition of  $TlCl$ <sup>10</sup>.

Astatine in the 1 – oxidation states coprecipitates from aqueous solution with  $TlI$ , presumably as  $TlAt$ <sup>11</sup>. Addition of  $Tl^+$  to an aq  $I_2$ – $I^-$  sol containing  $At$  precipitates  $TlI_3$ , and a large portion of the  $At$  coprecipitates, presumably as  $TlAtI_2$ <sup>12</sup>.

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### 2.6.15. from Scrambling Reactions.

Redistribution reactions are extremely common in main-group chemistry<sup>1</sup> and a number of broad principles concerning them may be offered<sup>2</sup>, as follows.

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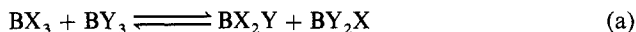
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12. E. H. Appelman, U. S. Atomic Energy Commission Report UCRL-9025 (1960).

## 2.6.15. from Scrambling Reactions.

Redistribution reactions are extremely common in main-group chemistry<sup>1</sup> and a number of broad principles concerning them may be offered<sup>2</sup>, as follows.

First, reactions proceed to place the more electronegative group onto the more electropositive metal. Thus, while  $\text{BCl}_3$  transfers halide to a diarylmercury compound,  $\text{Ph}_3\text{Al}$  receives chloride from  $\text{HgCl}_2$ .

Second, like groups (such as halogens) distribute themselves about metal centers randomly. The extremely mobile equilibria involved in boron halide mixtures<sup>3</sup> are examples of this:

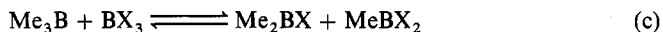


Rapid exchange occurs, possibly via a halide-bridged intermediate (although no spectroscopic evidence exists for it), and the mixed halide products are not generally isolated. However,  $\text{BF}_3$  and  $\text{BI}_3$  do not exchange, even after a day at RT in heptane. An alternative mechanism for halogen exchange may be via an ionization such as:



Again, no direct evidence has been found.

Third, unlike groups (particularly those of different electronegativity) tend to distribute themselves so as to favor proportionation products. Thus, 2 mol of  $\text{Ph}_3\text{Al}$  mixed with 1 mol of  $\text{AlCl}_3$  yield  $\text{Ph}_2\text{AlCl}$ . It is this property that renders reactions of this type among the most useful and convenient methods for preparing a large variety of compounds<sup>4</sup>. Examples are legion:



where  $\text{X} = \text{Cl}, \text{Br}$ ;



In redistribution reactions where the alkyl of one element is treated with a halide of another, the overall stoichiometry and position of equilibrium is determined by a balance of the first and third principles above. For example, only one of the three alkyl groups in  $\text{R}_3\text{Al}$  is effectively transferred onto  $\text{GaCl}_3$  or  $\text{InCl}_3$ . Addition of a complexing agent may be necessary to transform the remaining aluminum alkyl into a stable salt and so help to fix the stoichiometry<sup>5</sup>. Thus,  $\text{R}_3\text{As}$  is obtained when  $\text{R}_3\text{Al}$  reacts with  $\text{AsX}_3$  ( $\text{X} = \text{F}, \text{Cl}$ ) in the presence of  $\text{NaCl}$ . The reaction between  $\text{Et}_3\text{Al}$  and  $\text{SnCl}_4$  is a striking example. In the absence of a solvent and in the 4:3 mole ratio indicated by:



only ca 10% of  $\text{Et}_4\text{Sn}$  is obtained. If, however, the 4:3 mixture is heated briefly with xs ether,  $\text{Et}_4\text{Sn}$  is obtained in good yield<sup>6</sup>.

In reactions shown in Eq. (c), while redistributions about boron occur for all halogens, exchange is slowed by the presence of  $\text{B}-\text{F}$  bonds (presumably due to stabilization via backbonding)<sup>7</sup>. Preparation of fluorides via this route almost invariably presents a problem. With  $\text{R}_2\text{AlF}$ , the preparation is only successful if the  $\text{AlF}_3$  employed is finely divided. In organoaluminum compounds, there is a marked tendency to form those redistribution products which are most strongly associated. When the halogen-bridged dimers are labile, there is no difficulty in obtaining halides  $\text{R}_n\text{AlX}_{3-n}$  via redistribution and the products obtained are stable with respect to disproportionation<sup>2</sup>.

Preparation of the highly associated fluorides, however, demands a reactive form of  $\text{AlF}_3$ . Similarly, attempted transfer of fluoride from  $\text{K}[\text{HF}_2]$  onto  $\text{Me}_3\text{In}$  in ether gives very poor yields, but  $\text{BF}_3$  may be employed as a convenient fluorinating agent<sup>8</sup>.

As in Eq. (d), those compounds containing both primary and secondary alkyl groups and haloalkyls may be prepared almost quantitatively from stoichiometric amounts of the starting materials in low-boiling solvents<sup>9</sup>.

From Eq. (e), a high yield of  $\text{Ph}_2\text{GaCl}$  is obtained if  $\text{Ph}_3\text{Ga}$  and  $\text{GaCl}_3$  are heated (420 K) for 12 h<sup>10</sup>. An exothermic reaction occurs in the preparation of  $\text{Et}_2\text{GaCl}$ , but it is necessary to heat the mixture (373 K) in order to obtain a uniform fraction for distillation. Too high a T, however, leads to thermal decomposition<sup>11</sup>. Most combinations for  $\text{R}_n\text{MX}_{3-n}$  (R = alkyl, aryl; M = Al, Ga, In; X = Cl, Br, I) may be obtained conveniently via this route. The method is not as successful for thallium, however, where reduction to  $\text{Tl(I)}$  and the extraordinary stability of  $\text{R}_2\text{TlX}$  compounds rob the equilibria of their lability<sup>12</sup>.

The low-energy exchange pathway required for the second factor (above) is not generally available in coordinatively saturated boron compounds. Thus, the use of a donor (D) bonded to electron-pair acceptor acid boron compounds retards halogen exchange and permits mixed-halide products to be isolated<sup>13</sup>. The most general route to such mixed boron trihalides, then, is with a mixture  $\text{D} \cdot \text{BX}_3 + \text{BY}_3$ . Reactions occur readily in solution at ambient T, even with amine adducts that do not exchange halogen in the absence of free  $\text{BX}_3$ . Also, adducts that exchange halogen slowly in the absence of uncomplexed trihalide react much faster when uncomplexed trihalide is added. Similarly, mixed-halide products may be isolated by adding a donor to a previously equilibrated mixture of free boron halides.

It is also possible for adducts of different boron halides with the same donor to exchange halogens and thus form adducts of the mixed halides. The weaker the donor, generally the more rapid is the formation of the mixed adducts, which suggests that free  $\text{BX}_3$  is an active species in the exchange. Exchange between various tetrahaloborates occur in similar fashion, although that between  $[\text{BF}_4]^-$  and  $[\text{BCl}_4]^-$  is slow.

Many halogen exchange reactions have been studied with a view to their being employed to produce isotopically labeled compounds<sup>14</sup>. For example, exchange between halogen fluorides and metal fluorides is useful for producing labeled volatile fluorides. Thus, exchange between  $\text{ClF}_3$  and  $\text{BF}_3$  in the gas phase at 300 K is complete within 3 min. On the other hand, heterogeneous exchange between labeled alkali-metal chlorides and  $\text{BCl}_3$  is very slow, although more rapid exchange is observed when  $[\text{R}_4\text{N}]\text{Cl}$  is employed. Exchange reactions involving  $\text{AlCl}_3$  appear to be related to the freshness of the solid surface. With a fresh surface, detectable exchange may be observed with  $\text{HCl}$  even at 193 K and is rapid at 373 K. Partial hydrolysis of the surface drastically reduces the exchange rate, especially at lower T.

Other experiments have been performed in the context of assessing the degree of self-ionization in nonaqueous solvents such as  $\text{OPCl}_3$  and  $\text{ONCl}$ . However, the electron-pair acceptor acidity of group-IIIB halides would assist inclusion of external radiohalogen anyway. While much data on  $^{128}\text{I}$  exchange seems to be low quality, it seems certain that fused  $\text{I}_2$  exchanges quite rapidly with a number of species, including  $\text{AlI}_3$ . A summary of radiohalogen exchange reactions is presented in Table 1.

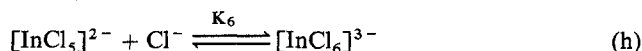
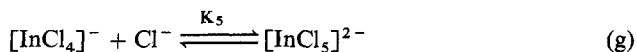
Most tetrahaloborate ions undergo halogen exchange with methylene halides giving mixed halide ions<sup>15</sup>. Similar reactions are observed with aluminum, so that mixtures of  $\text{AlI}_3$  and  $\text{Pr}_4\text{NI}$  in  $\text{CH}_2\text{X}_2$  yield not only  $[\text{AlI}_4]^-$ , but also  $[\text{AlX}_n\text{I}_{4-n}]^-$  ions<sup>15</sup>.

TABLE 1. ISOTOPIC EXCHANGE REACTIONS FOR SOME GROUP-IIIB HALIDES<sup>a</sup>

Halide	Reactant	Conditions	Exchange observed
BCl <sub>3</sub>	C <sub>5</sub> H <sub>6</sub> NCl	CHCl <sub>3</sub> , 293 K	Complete, 3 min
BCl <sub>3</sub>	[R <sub>4</sub> N]Cl	Heterogeneous, 273 K	Rapid
BCl <sub>3</sub>	HCl	Gas phase, 297 K	Rapid
BCl <sub>3</sub>	LiCl	Heterogeneous, 273 K	Slow
BCl <sub>3</sub>	Cs(Rb)Cl	Heterogeneous, 273 K	None, 46 h
AlCl <sub>3</sub>	HCl	OCCL <sub>2</sub> , 213 K	Very fast
BCl <sub>3</sub>	SiCl <sub>4</sub>	Gas phase, 303 K	None, 24 h
AlCl <sub>3</sub>	Me <sub>3</sub> SiCl	C <sub>6</sub> H <sub>6</sub> , ambient	Some observed
MCl <sub>3</sub> <sup>b</sup>	ONCl	263 K	Complete, 4 min
BCl <sub>3</sub>	OPCl <sub>3</sub>	273 K	Rapid: xs OPCl <sub>3</sub> ; None: xs BCl <sub>3</sub>
M'Cl <sub>3</sub> <sup>b</sup>	OPCl <sub>3</sub>	291 K	None
BBr <sub>3</sub>	Br <sub>2</sub>		Rapid
M'Br <sub>3</sub> <sup>b</sup>	Br <sub>2</sub>	293 K	Complete (not In?)
AlBr <sub>3</sub>	CBr <sub>4</sub>	323 K	Complete
AlBr <sub>3</sub>	SiBr <sub>4</sub>	373 K	None
AlI <sub>3</sub>	KI	Fused, 633 K	Complete, 10 min
AlI <sub>3</sub>	HI	293 K	Slow
AlI <sub>3</sub>	I <sub>2</sub>	Fused, 423 K	Complete, 1-2 h
KAlI <sub>4</sub>	HI	423-443 K	Measurable rate
TlI <sub>3</sub>	I <sub>2</sub>	MeOH, ambient	Complete, 10 min
AlF <sub>3</sub>	ClF <sub>3</sub>	Gas-solid, ambient	Some observed
BF <sub>3</sub>	ClF <sub>3</sub>	Gas, 300 K	Complete, 3 min
[BF <sub>4</sub> ] <sup>-</sup>	HF	H <sub>2</sub> O, up to 373 K	Very rapid, after hydrolysis

<sup>a</sup> From ref. 14.<sup>b</sup> M = Al, Ga, In, Tl; M' = Al, Ga, Tl.

Scrambling of ligands among mixtures of tetrahaloborates themselves is moderately rapid except for [BF<sub>4</sub>]<sup>-</sup>/[BCl<sub>4</sub>]<sup>-</sup>. Mixed ligand tetrahalometallates for Ga, In and Tl are also known<sup>16,17</sup>. Various ionic intermediates of the type suggested for aluminum halide equilibria in nonaqueous media or melts<sup>18,19</sup> are likely to contribute to the facile ligand redistributions. Also, K<sub>5</sub> and K<sub>6</sub> equilibrium constants in



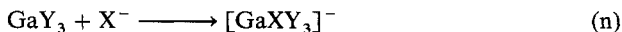
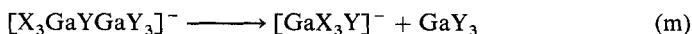
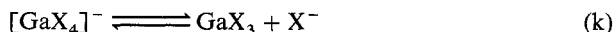
have been estimated to be  $350 \pm 100$  and  $10 \pm 3$ , respectively, making higher coordination number intermediate ions likely in some cases. The easy isolation of the mixed tetrahalothallates from MeCN via:



may be an example<sup>20</sup>.

Gallium, however, does not generally exceed a coordination number of four in its halide complexes, so that the slow halogen exchange observed, probably results instead

from an initial dissociation step to a  $\text{GaX}_3$  species followed by its association with a neighboring  $[\text{GaY}_4]^-$  anion<sup>16,17</sup>, according to:



(B.D. JAMES)

1. J. C. Lockhart, *Chem. Rev.*, **65**, 131 (1965).
2. T. Mole, in *Organometallic Reactions*, E. I. Becker and M. Tsutsui, eds., Vol. 1, Wiley-Interscience, New York, 1970 p. 1.
3. N. N. Greenwood, B. S. Thomas, in *Comprehensive Inorganic Chemistry*, J. C. Bailes Jr., H. J. Emeleus, R. Nyholm, A. F. Trolman-Dickenson, eds., Vol. 1, Ch. 11, Pergamon Press, Oxford, 1973.
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8. D. G. Tuck, in *Comprehensive Organometallic Chemistry*, G. Wilkinson, ed., Vol. 1, Ch. 7, Pergamon Press, Oxford, 1982. A lucid review.
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14. M. F. A. Dove, D. B. Sowerby, in *Halogen Chemistry*, V. Gutmann, ed., Vol. 1, Academic Press, New York, 1967, p. 41.
15. R. G. Kidd, D. R. Truax, *J. Am. Chem. Soc.*, **90**, 6867 (1968).
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17. B. R. McGarvey, C. O. Trudell, D. G. Tuck, L. Victoriano, *Inorg. Chem.*, **19**, 3432 (1980).
18. J. Deroualt, P. Granger, M. T. Forel, *Inorg. Chem.*, **16**, 3214 (1977).
19. J. L. Gray, G. E. Maciel, *J. Am. Chem. Soc.*, **103**, 7147 (1981).
20. R. W. Matthews, R. A. Walton, *J. Chem. Soc., A.*, 1639 (1968).

## 2.6.16. Miscellaneous Modes of Formation.

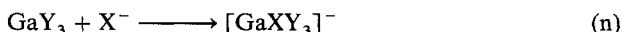
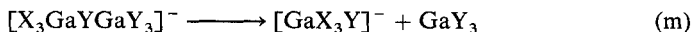
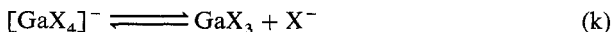
Miscellaneous methods are perhaps like beauty and lie in the mind of the beholder. One worker's occasional excursion into the unknown may be another's standard method. Thus, the techniques of vapor synthesis and electrochemical methods have been mooted previously in the context of reactions of the elements (§2.6.3.3 and 2.6.3.2) because they are accepted standard procedures.

Metal vaporization methods are now well established<sup>1</sup> and a simple metal vapor reaction vessel is commercially available<sup>2</sup>. The method, although a general one, has two major limitations. The first is the ready reversion of metal atoms to their condensed states and the second is that the substrate must be sufficiently volatile to enter the reaction vessel as a vapor. A reliable vacuum system is absolutely vital. While novel boron compounds have been obtained with this method<sup>3,4</sup>, there is much scope for its

## 2.6. The Formation of the Halogen (B, Al, Ga, In, Tl) Bond

### 2.6.16. Miscellaneous Modes of Formation.

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application to compounds of the other group-IIIB elements. Other reactions that involve high temperatures also may lead to unusual products<sup>5</sup>.

A great advantage of the electrochemical procedure<sup>6</sup> is its simplicity, requiring only a low-cost d.c. power supply and an appropriate vessel, often merely an open beaker. Increasing sophistication by incorporating different halogens, different electrolytes and either inert or reagent atmospheres expands the synthetic scope of the method.

Another procedure requiring a nonstandard laboratory setup is the initiation of reactions by laser irradiation. Thus,  $\text{BCl}_3$  irradiated with a  $\text{CO}_2$  laser reacts directly with  $\text{Me}_3\text{B}$ , yielding  $\text{MeBCl}_2$ . However,  $\text{BCl}_3$  may also be employed as a nonreacting sensitizer<sup>7</sup>. In a somewhat similar fashion, hexafluorobenzene may be made to react with  $\text{BCl}_3$  when a laser is employed to excite the  $1011\text{ cm}^{-1}$  rotation-vibration band of the former. Some decomposition of the  $\text{C}_6\text{F}_6$  occurs, but halogen exchange takes place initially yielding  $\text{BCl}_2\text{F}$ , which gives the disproportionation products  $\text{BCl}_3$  and  $\text{BF}_2\text{Cl}$  under the experimental conditions<sup>8</sup>. The method appears to have general scope for high-energy reactions but seems to be a little unpredictable at present and consequently it has not been employed widely.

Other general miscellaneous methods for preparing group-IIIB element-halogen bonds may be classified as use of electron-pair acceptor acid properties, oxidation or redox reactions, combination halogenations and thermolysis. These methods are discussed in turn.

One of the most common and straightforward methods of producing a group-IIIB element-halogen bond is to exploit the general electron-pair acceptor acid property of the compounds. Examples are legion and may be typified by<sup>9</sup>:



in which the  $\text{Cl}^-$  ion functions as an electron-pair donor. Virtually any compound having a labile halide is susceptible to this type of reaction<sup>10</sup>. Thus, in situ oxidation of the phosphorus center by  $\text{I}_2$  permits the formation from equimolar quantities of  $\text{PI}_3$ ,  $\text{I}_2$  and  $\text{AlI}_3$  of  $[\text{PI}_4][\text{AlI}_4]^{11}$ . The rate of reaction of various chlorides with  $\text{BCl}_3$  and the yield of the ensuing  $\text{M}[\text{BCl}_4]$  product ( $\text{M} = \text{K}, \text{Rb}, \text{Cs}, \text{R}_4\text{N}$ ) depend on the solvent employed<sup>12</sup>. Chloroform,  $\text{ONCl}$  or even  $\text{BCl}_3$  itself may be used. Reactions in  $\text{CHCl}_3$  or  $\text{BCl}_3$  remain incomplete even after 150 h in sealed ampules, while 100% conversion is achieved after 40 h using  $\text{ONCl}$  at low T.

Large groups attached to the group-IIIB center do not suppress the electron-pair acceptor acidity per se. Thus, addition of  $[\text{R}_4\text{N}]\text{X}$  to  $\text{In}[\text{Mn}(\text{CO})_5]_3$  in  $\text{MeOH}$  produces the  $[\text{R}_4\text{N}][\text{XInMn}_3(\text{CO})_{15}]$  salt<sup>13</sup>. Similarly, perfluoroalkylthallium(III) halides add  $\text{Br}^-$  from  $[\text{Et}_4\text{N}]\text{Br}$ , giving a reasonable yield of the salt<sup>14</sup>. Reactions may not, however, be as clean as would be desired. For example, perfluoroalkylthallium(III) halides tend to undergo reductive cleavage with  $\text{I}^-$  ion in  $\text{EtOH}$ ,  $\text{MeOH}$  or water, the precipitation of  $\text{TlI}$  being quantitative with long reaction times. In the presence of acid, however, little reduction occurs and  $\text{TlI}_4^-$  is produced<sup>15</sup>. Similarly, halide ions (except  $\text{F}^-$ ) react with  $\text{RTl}(\text{CO}_2\text{R}')_2$ , precipitating  $\text{TlX}$  and giving alkyl halides<sup>16</sup>. Sometimes scrambling processes complicate the acid-base reactions, yielding unexpected products, as in the formation of the mixed-halide ions  $[\text{AlX}_n\text{I}_{4-n}]^-$  from solutions of  $\text{AlI}_3$  and  $[\text{Pr}_4\text{N}]\text{I}$  in the methylene halides<sup>17</sup>. Also, halogen transfer may not be as complete as expected, as shown by the reaction in liq  $\text{HCl}$  of  $\text{AlCl}_3$  and acetyl chloride<sup>18</sup>. Here, some  $[\text{AlCl}_4]^-$  is formed, but with considerable quantities of  $[\text{Al}_2\text{Cl}_7]^-$  being present. That such processes may be solvent dependent is shown by the  $\text{AlBr}_3$ - $\text{R}_4\text{NBr}$  interaction. In  $\text{CH}_3\text{CN}$ ,



$[R_4N][AlBr_4]$  is obtained, while in EtBr, the product<sup>19</sup> is  $[R_4N][Al_2Br_7]$ . Even this may not be the end of complications, because Ga(III) may replace Al(III) in the  $[M_2Cl_7]$  species in melts and it is probable that Fe(III) does likewise<sup>20</sup>.

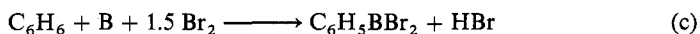
Oxidation with halogens is a useful method for preparing trivalent group-IIIB halides from lower oxidation states. While the method obviously is successful for all the group-IIIB elements<sup>21,22</sup>, it is a most valuable procedure for thallium because the stable Tl(I) halide may be suspended in a solvent and heated gently with the halogen to produce directly a solution of the desired Tl(III) halide. Thallic chloride solutions commonly are prepared this way in  $CH_3CN$  or in aqueous media and may be employed immediately in reactions after any xs halogen has been swept out with a gas stream. Addition of a different halogen to that in the TlX compound produces a mixed thallic halide<sup>23,24</sup>. In a variation of this procedure, reaction of  $Br_2$  vapor with solid TlCl over an extended time (ca. 25 h) produces  $Tl[TlCl_2Br_2]$ , which contains both thallium oxidation states<sup>25</sup>. Obviously, slow reactions with solids may enable novel compounds to be isolated. In a similar manner,  $Tl_2S$  and  $Tl_2Se$  react with halogens giving the halochalcogenides,  $Tl_2SX_4$  or  $Tl_2SeX_4$  ( $X = Br, I$ ) in alcohol, although  $Tl_2SeI_4$  is best obtained by melting  $Tl_2Se$  and  $I_2$  in a sealed tube at ca. 410 K and extracting the product with benzene<sup>26</sup>.

In other cases, the processes may be better classified as redox reactions since a halogen already bonded to a group-IIIB element is replaced by another that is more electronegative. Thus, the azido compounds  $N_3MI_2$  (where  $M = Ga, In$ ) are converted to the bromides by reaction with liq  $Br_2$  over 12 h<sup>27</sup>. Oxyhalides of gallium also may be prepared from GaOI by the action of  $F_2$ ,  $Cl_2$  or  $Br_2$  (each at successively higher temperature). Similarly, InOBr and InOCl may be obtained from the iodide, as has been reported for AlOCl also<sup>28</sup>. Certainly,  $F_2$  easily displaces other halogens from most inorganic halides and it is possible that  $AlF_3$  can be obtained easily by the displacement of  $I_2$  from  $AlI_3$ . Generally however, reagents such as  $ClF_3$  or  $BrF_3$  are preferred and high-valency metal fluorides are also effective<sup>29</sup>. The weak B—I bond lends itself to replacement in similar redox reactions, such procedures being very valuable in transformations involving boron ring systems<sup>30</sup>, although ring splitting is observed in the reaction of  $(IB)_2Se_3$  with bromine<sup>31</sup>.

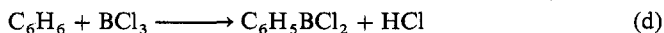
A number of syntheses exist in which a halogenation step is combined with some other process. In the synthesis of  $CsCuAlF_6$ , the fluorination of  $Cs[CuCl_3]$ , performed at 830 K over 3 d, is combined with the electron-pair acceptor acid character of the admixed  $AlF_3$  to yield the product<sup>32</sup>. Nitrosyl tetrafluoroborate is obtained commercially from ONCl in a reaction that employs HF as both a fluorinating agent and an electron-pair donor base. In liq  $SO_2$  at 243–258 K, or in  $CH_3NO_2$  below 273 K, the reaction proceeds in 90–100% yield:



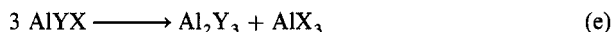
Simply pumping on the solid obtained for 10–20 min removes all the impurities because they are volatile<sup>33</sup>. In a reaction somewhat analogous to the preparation of organoaluminum halides, benzene, elemental boron and bromine combine to give  $PhBBr_2$  in the presence of a nickel catalyst<sup>34</sup>:



The reaction might well be electron-pair acceptor acid in character, however, since the organoboron dihalides are easily prepared by such procedures ( $AlCl_3$  catalyst):



Finally, a reaction of possible utility would be thermolysis in which a rearrangement of groups about the group-IIIB center causes the formation of new element-halogen bonds. For example:



(for Y = Se, Te) occur at progressively decreasing T (X = Cl > Br > I)<sup>35</sup>. The decomposition occurs directly in these cases, whereas other intermediate phases can be observed in the thermolysis of AlOBr or AlOI. Thermodynamics favors the dissociation, especially when the trihalide is volatile. Thermolysis may also be of value when a weakly bound ligand has to be removed. Thus,  $\text{TiCl}_3$ , easily prepared in  $\text{CH}_3\text{CN}$  solution, can be converted to the unsolvated form by pumping under vacuum (equivalent to thermolysis at RT). Care must always be exercised with Tl(III), however, because of its propensity for reduction, and although  $\text{TiCl}_3 \cdot 4 \text{H}_2\text{O}$  may be dehydrated over  $\text{P}_4\text{O}_{10}$ , attempts at thermal dehydration lead to the formation of  $\text{TiCl}$ <sup>23</sup>.

(B.D. JAMES)

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## **2.7. The Formation of the Halogen–Group-IA (Li, Na, K, Rb, Cs, Fr) and Group-IIA (Be, Mg, Ca, Sr, Ba, Ra) Metal Bond**

### **2.7.1. Introduction.**

The methods available for preparing the halides of the metals in groups IA and IIA are compared in Table 1<sup>1–8</sup>. The most common of these halides, NaCl and KCl, are found in huge natural deposits and are mined and purified by crystallization techniques. Most of the other chlorides and fluorides are manufactured by reacting metal oxides, carbonates or hydroxides with the appropriate hydrogen halides. Although some of the metal bromides and iodides occur naturally, they are produced primarily by conversion of Br<sub>2</sub> (from brines or sea water) and I<sub>2</sub> (largely from naturally occurring iodates) with metal oxides, carbonates or hydroxides.

The direct combination of metal and halogen can be a valuable method of preparing anhydrous halides. This is not a popular method for preparing fluorides because of problems associated with handling F<sub>2</sub>. Nickel reactors can be used for reactions involving F<sub>2</sub><sup>9</sup>.

Metal fluorides are most conveniently prepared by reacting aq HF with metal hydroxides or carbonates, although several other routes are available. Only BeF<sub>2</sub> is significantly sensitive to hydrolysis, and methods employing gaseous HF are best used to prepare this salt.

Several methods are available for preparing chlorides, bromides and iodides, although some routes to the heavier halides can present problems. Reaction of Br<sub>2</sub> with a metal hydroxide in aqueous solution, for example, normally gives a mixture of bromide and bromate. As this is in other ways a very desirable route to bromides, methods have been developed to reduce the bromate in situ.

The easily hydrolyzed halides of Be<sup>10</sup> and, to a lesser extent, those of Li and Mg are best prepared under nonaqueous conditions. Several routes employing the halogen, the hydrogen halide or a nonmetal halide are available.

**CAUTION:** many of the methods for preparing halides are potentially hazardous and especially those involving F<sub>2</sub> or HF. Fluorine reacts violently with many materials and extreme care must be exercised in its handling. All of the hydrogen halides are corrosive and should be handled with due care and attention. Both anhyd and aq HF (and nonmetal fluorides that easily produce HF) are dangerous substances that can be extremely damaging to skin, eyes, mucous membrane and lungs. In work with F<sub>2</sub>, HF, nonmetal fluorides and the highly toxic Cl<sub>2</sub>, the proper use of protective clothing, gloves, goggles, face shields and respiratory devices is important.

Some other nonmetal halides and notably the heavier boron halides can react explosively with water and must be handled with extreme care.

Many metal halides are severe poisons. Beryllium salts present a serious health hazard and contact can lead to pneumonitis (by inhalation of dust), dermatitis and conjunctivitis at

TABLE 1. PREPARATION OF THE HALIDES OF THE METALS OF GROUPS IA AND IIA

Method of preparation	Comments
A Direct combination of the elements (§2.7.2)	Useful for preparing pure, anhydrous halides and especially iodides. Reaction can be inhibited by the formation of unreactive halide films on the surface of the metal. Highly pure materials may not react and very high temperatures are required for combinations involving the lighter metals and the heavier halogens. The method is not usually recommended for fluoride preparations due to the special equipment required for generating and handling $F_2$ . Hydrogen halides halogenate metals in the gas phase or as aqueous solutions. Gas-phase reactions are useful for preparing those halides that are susceptible to hydrolysis. Aqueous acid reactions can be violent and difficult to control. Other halogenating agents can be used in place of hydrogen halides. Organomagnesium reagents are formed by the reaction of Mg with carbon-halogen compounds.
B Halogenation of metals by halides (§2.7.3)	Metal oxides, hydroxides and carbonates are all popular sources of the metals in these reactions. Reactions involving $Br_2$ and $I_2$ are of industrial importance but such reactions often produce products contaminated with metal halates unless reducing agents are present.
C Reaction of halogens with compounds of the metals (§2.7.4 and 2.7.6)	Metal oxides, hydroxides and carbonates are all popular sources of the metals in these reactions. Aqueous hydrogen halides are normally used but gaseous hydrogen halide reactions can be used where the products are susceptible to hydrolysis. Reactions with $HF$ often lead to the formation of bifluorides, which can be thermally decomposed to the fluorides.
D Reaction of hydrogen halides with compounds of the metals (§2.7.5)	Many nonmetal halides can be used but the most popular ones are $CCl_4$ , $SOCl_2$ , $S_2Br_2$ and $NH_4F$ . Metal iodides are not usually prepared by this method.
E Reaction of nonmetal halides with metal oxides (§2.7.6)	Useful for preparing beryllium halides.
F Reaction of metal carbides with halogens and hydrogen halides (§2.7.8)	Useful when one of the products can be removed from the reaction by precipitation or volatilization. Ion-exchange resin methods are useful for the preparation of dilute aqueous solutions of many halides.
G Metathetical reactions (§2.7.9)	

very low levels. Workers should wear gloves and protective clothing and should be especially aware of the danger of inhalation of beryllium-containing dusts.

(J.H. CLARK)

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## 2.7.2. from the Elements.

The direct combination of the halogens with the metals of groups IA and IIA represents a valuable method for preparing pure, anhydrous metal halides<sup>1–6</sup>. The method is particularly useful for preparing iodides, which can be most difficult to prepare by other methods.

One of the major problems associated with the direct combination method is the formation of a layer of halide on the surface of the metal; this can prevent complete reaction unless precautions are taken. With F<sub>2</sub>, complete reaction occurs at RT with all of the metals of groups IA and IIA except Be and Mg:



where M = Li, Na, K, Rb, Cs, Fr;



where M = Ca, Sr, Ba, Ra.

A protective layer of fluoride is formed on the surfaces of Be and Mg, although in the latter case warming the metal is sufficient to drive the reaction to completion.

Increasing the surface area of metals increases their rate of reaction with the halogens so that F<sub>2</sub>, Cl<sub>2</sub> and Br<sub>2</sub> all react efficiently at RT even with the less reactive metals of group IIA. Finely powdered metals such as Ca ignite in a stream of F<sub>2</sub>, Cl<sub>2</sub> or Br<sub>2</sub> when the gases are not completely anhydrous. Remarkably, even the group-IA metals fail to react with completely anhydrous halogens at RT. The role of water is presumably to help keep the surface of the metal clear or to assist reaction by the exothermic formation of metal hydroxides. **Violently exothermic reactions can also occur when the vapors of metals of groups IA or IIA are brought into contact with gaseous halogens.**

## 2.7. Formation of the Halogen-Group-IA and Group-IIA Metal Bond

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## 2.7.2. from the Elements.

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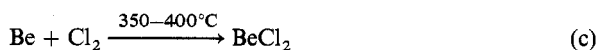
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When impure reagents are used, reactions can again be violent and difficult to control. Under these circumstances, the reaction can be moderated by carrying it out in a solvent. Typically, the halogen is dissolved in an inert solvent and the resulting solution is stirred, with heating if necessary, with the finely divided metal<sup>7</sup>. Metal amalgams can be used in place of the metal<sup>8</sup>.

The heavier halides of Be and Mg are commonly prepared by direct combination. The equipment and handling problems associated with the use of F<sub>2</sub> make the process unattractive as a route to BeF<sub>2</sub> or MgF<sub>2</sub>, although such reactions are very fast and quite efficient if carefully controlled.

Beryllium chloride can be prepared in a yield of up to 95% by heating Be turnings in a porcelain boat inside a borosilicate glass reactor to 350–400°C in a stream of dry Cl<sub>2</sub><sup>9</sup> or a Cl<sub>2</sub>-N<sub>2</sub> mix<sup>10</sup>:



The product can be swept through the reactor into a collection flask, where it forms a fluffy deposit. Alternatively, the product can be removed from the cooled reaction system by dissolution in dry diethyl ether.

Beryllium bromide can be prepared in the same way, using a Br<sub>2</sub>-rich vapor<sup>9–11</sup> generated by bubbling Ar through Br<sub>2</sub> warmed to ca. 50°C:



Temperatures as high as 500°C may be needed to give complete reaction. The product can be recovered in yields of better than 90% by extraction into cooled diethyl ether<sup>12</sup>.

The preparation of BeBr<sub>2</sub> by direct combination of the elements in a solvent such as diethyl ether is a convenient laboratory-scale preparation but it is not without its problems<sup>10–12</sup>. Bromine is added slowly to Be turnings covered with the solvent and the solution refluxed for several hours. At the end of the reaction, the solution is black, possibly due to the formation of brominated ethers and partial decomposition of BeBr<sub>2</sub>, which is sensitive to both water and oxygen. Repeated recrystallization of the BeBr<sub>2</sub> is not completely effective in removing the contaminants. Side products can be kept to a minimum by initiating the reaction at dry-ice temperatures. The Br<sub>2</sub> is slowly added to the cooled Be-diethyl ether system and once unreacted Br<sub>2</sub> is evident, the mixture is first warmed to 0°C and then slowly to reflux. The final solution is colorless but darkens with time.

Beryllium metal only reacts with I<sub>2</sub> at very high T:



The reaction is carried out<sup>13,14</sup> by heating beryllium chips in a stream of H<sub>2</sub> and I<sub>2</sub>. Below 500°C, reaction requires several days. The products are collected in evacuated glass bulbs. The major impurity is SiI<sub>4</sub>, formed by attack of BeI<sub>2</sub> on the glass, and this is best removed by heating the product mixture to ca. 85°C at which T the SiI<sub>4</sub> sublimates from the system. By this method, good yields of BeI<sub>2</sub> of purity better than 98% can be obtained but special care is required to protect the product from the atmosphere.

Anhydrous MgX<sub>2</sub> can be prepared in good yields by burning Mg in halogen-rich atmospheres<sup>15</sup> or by flowing the halogen or a halogen-N<sub>2</sub> mixture over the fine ground metal<sup>14</sup>. The reaction between Mg and F<sub>2</sub> can be violent and difficult to control, whereas



the Mg-I<sub>2</sub> combination demands high T. In a typical experiment Mg turnings are heated to 600°C in a porcelain boat set in a borosilicate glass reactor. Iodine vapor is then repeatedly passed through the reactor. Final heating of the reaction mixture results in loss of xs I<sub>2</sub> and the deposition of MgI<sub>2</sub> near the boat:



Unreacted Mg is left in the boat.

Magnesium halides other than MgF<sub>2</sub> can be prepared by slow addition of the halogen to finely ground Mg covered with a solvent such as diethyl ether. The resulting complexes MgX<sub>2</sub>·2 O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (X = Cl, Br or I) can be converted to the anhydrous halides<sup>16,17</sup> by heating under high vacuum at 230°C. The major problem with this method is the formation of impurities such as halogenated ethers and it can be difficult to obtain pure products<sup>12</sup>. The purity of the products can be improved at the cost of a lower yield by running the reaction at 0°C and by multiple recrystallizations of the halide from diethyl ether before final high-T drying.

Anhydrous halides of the heavier metals of group IIA can be prepared in the same way<sup>14</sup> as described for the halides of Be and Mg. Reactions are usually carried out by passing the halogen vapor diluted in an inert gas such as He or Ar over the heated, finely divided metal. The fluorides may be prepared in this way but reactions can be difficult to control.

The halides of the metals of group IA may be prepared by direct combination but many of these reactions (notably where combinations of heavier metals and lighter halogens are involved) are extremely violent and uncontrollable. Anhydrous halides, however, can be obtained in this way and the method is worth consideration for the preparation of the lithium salts LiCl, LiBr and LiI and other iodides of the metals of group IA<sup>15</sup>. The direct combination routes to these compounds are more easily controlled (especially if a solution of the halogen in an inert solvent is employed) and other routes to the compounds may be more troublesome.

**CAUTION:** Many direct combination reactions can be violently exothermic and all such reactions should be regarded as being extremely hazardous. Reactions involving F<sub>2</sub> or metal vapors are particularly dangerous. See §2.7.1.

(J.H. CLARK)

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13. R. E. Johnson, E. Staritzky, R. M. Douglass, *J. Am. Chem. Soc.*, **79**, 2037 (1957).
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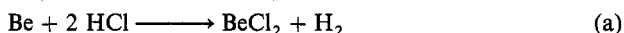
15. P. Pascal, ed., *Nouveau Traite de Chimie Minerale*, Masson, Paris, 1958-1963.
16. W. Blitz, G. F. Hüttig, *Z. Anorg. Allg. Chem.*, 119, 115 (1921).
17. W. Klemm, K. Beyersdorfer, J. Oryschkewitsch, *Z. Anorg. Allg. Chem.*, 256, 25 (1948).

## 2.7.3. by Halogenation

### 2.7.3.1. with Hydrogen Halides.

The reaction of a metal with a gaseous HX represents a route to pure, anhydrous metal halides<sup>1-4</sup>. Although HF is somewhat easier to handle than F<sub>2</sub>, reactions with HF demand special equipment and can be difficult to control. Reactions of the heavier metals of group IA and group IIA with HX may also be violent and difficult to control. The most useful applications of this method are in preparing the water-sensitive halides of the lighter metals.

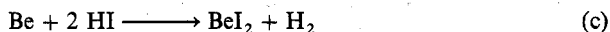
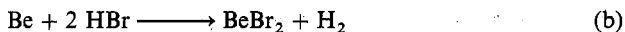
Beryllium chloride can be prepared by the action of dry HCl on Be heated to ca. 400°C:



In practice<sup>5,6</sup>, HCl is passed via a dessicant over the finely divided metal. Product yields are good although it is necessary to purify the product either by sublimation at 400-425°C in 1 atm of H<sub>2</sub> or Cl<sub>2</sub> or by repeated recrystallization from anhydrous diethyl ether.

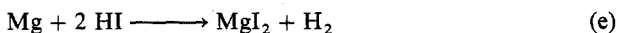
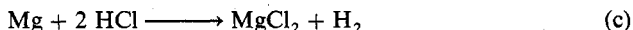
Beryllium metal reacts with aq HCl to produce hydrated BeCl<sub>2</sub><sup>7</sup>. Attempted dehydration of the product by refluxing in SOCl<sub>2</sub> produces a material containing appreciably less than the required amount of chlorine. It is likely that partial hydrolysis of the BeCl<sub>2</sub> occurs on dehydration.

The heavier beryllium halides may also be prepared by treating the heated metal with the appropriate HX gas<sup>2,7</sup>:



High T (>400°C) is required for quantitative conversion of the Be and the products require purification by methods similar to those described for BeCl<sub>2</sub>. Reaction of Be with aq HBr or aq HI is not a useful method for preparing BeBr<sub>2</sub> or BeI<sub>2</sub> due to extensive hydrolysis of the products.

Reaction of HCl, HBr or HI with Mg occurs readily at T > mp of the metal (>650°C)<sup>2,6</sup>:



Below 650°C only partial reaction occurs presumably as a result of the formation of unreactive halide films on the surface of the metal. Aqueous HX also converts Mg to its halides although subsequent dehydration of the products can be troublesome particularly with the heavier halides.

- 74      2.7. Formation of the Halogen-Group-IA and Group-IIA Metal Bond  
           2.7.3. by Halogenation  
           2.7.3.1. with Hydrogen Halides.

15. P. Pascal, ed., *Nouveau Traite de Chimie Minerale*, Masson, Paris, 1958-1963.

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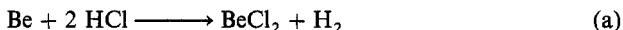
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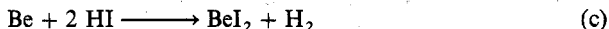
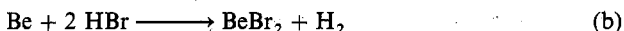
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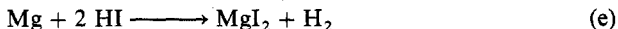
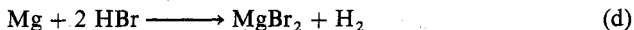
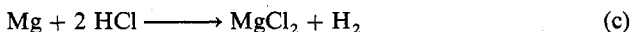
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Gaseous or aq HX reacts with the other metals of groups IA and IIA under conditions largely dependent on the reactivity of the metal and the HX. With the possible exception of lithium halides, there is no advantage in using HX gas as the products can be subsequently dehydrated with little or no loss in yield. Reactions are generally vigorous and efficient especially if the metal is used in a finely divided state (to overcome problems associated with the formation of halide films on the surface of the metal). Other methods for the preparation of these halides are however, usually preferred. One notable exception to this is when the metal is effectively extracted from a mixed ore as its halide by treatment with HX in aq soln. A useful example of this is the extraction of Cs as CsBr by reaction of the ore pollucite with hot aq HBr. The CsBr is concentrated by extraction with liq Br<sub>2</sub> taking advantage of the high solubility of CsBr<sup>8</sup>.

**CAUTION:** reactions involving the heavier metals (especially when used as vapors or in finely divided forms) and HF can be violently exothermic. See §2.7.1.

(J.H. CLARK)

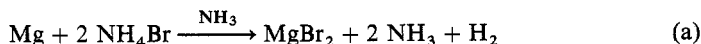
1. J. C. Bailar Jr., H. J. Emeleus, R. Nyholm, A. F. Trotman-Dickenson, eds., *Comprehensive Inorganic Chemistry*, Vols. 1 and 2, Pergamon, Oxford, 1973. Useful background reading.
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4. L. S. Topol, S. J. Yosim, *Syn. Inorg. Metal-Org. Chem.*, **47**, 3 (1973). Preparation of pure chlorides.
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## 2.7.3.2. with Miscellaneous Halides

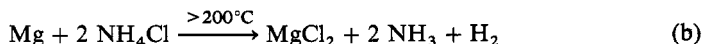
### 2.7.3.2.1. from Group-IA and Group-IIA Metals with Halides (Metal and Nonmetal).

The reactions of the metals of groups IA and IIA with halogenating agents can be considered alternatives to the direct reactions of the metals with halogens or HX<sup>1</sup>. The halogenating agents employed are usually tamed sources of X<sub>2</sub> or HX and may be preferred for reasons such as easier handling or more controlled reactivity. Like the most direct reactions with X<sub>2</sub> or HX the most useful preparations are where wet methods are inappropriate due to the sensitivity of the product to hydrolysis or where extremely pure materials are required.

Ammonium halides or ammonium hydrogen bihalides are useful sources of HX. They can usually be dried and handled with fewer precautions than are required for handling hydrogen halides. In NH<sub>3</sub> as the bulk solvent, ammonium halides react with the heavier group-IIA metals and the group-IA metals to give the respective metal halides<sup>2</sup>:



Very pure products can be obtained by this process. Reaction can also occur in the absence of a solvent (e.g., using a fused mixture), although higher T are required:



## 2.7.3. by Halogenation

75

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(J.H. CLARK)

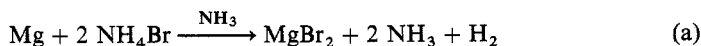
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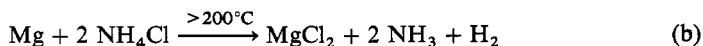
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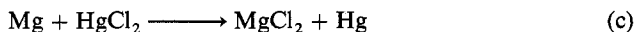
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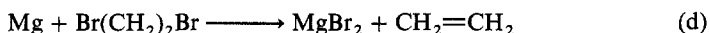


Various sources of halogen can be employed in the conversion of a group-IA or -IIA metal to its halide. The more active halogenating agents may themselves be difficult to handle and may not be easily purified. Mercuric halides are useful halogenating agents. They can be dried easily and the chloride, bromide and iodide are soluble in some organic solvents; e.g., mixing a solution of  $\text{HgCl}_2$  in THF with xs Mg and maintaining the system under reflux for several hours gives a good yield of very pure  $\text{MgCl}_2$ <sup>3</sup>:



The unreacted Mg and Hg can be removed from the product mixture as an amalgam by filtration. The filtrate is then evaporated in vacuo to give  $\text{MgCl}_2$  as a white solid. Both  $\text{MgBr}_2$  and  $\text{MgI}_2$  (using diethyl ether as the solvent) can be prepared in the same way. This is an especially good method for preparing pure  $\text{MgX}_2$ <sup>3</sup>.

Some organobromine and organochlorine compounds react with the more active metals of groups IA and IIA to give the respective metal halides (§2.7.3.2.2). The method is straightforward but impure products can be formed. Reaction of Mg with 1,2-dibromoethane, e.g., proceeds readily in refluxing diethyl ether with the evolution of ethylene gas<sup>3</sup>:



Once no further gas escapes, the product can be recovered simply by removing the solvent in vacuo. The product is appreciably less pure than that obtained by the analogous reaction with  $\text{HgBr}_2$ . Organochlorine compounds react only under more forcing conditions.

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(J.H. CLARK)

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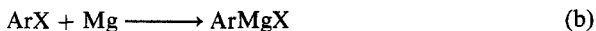
#### 2.7.3.2.2. from Alkaline-Earth Metals with Carbon-Halogen Compounds (Formation of Organomagnesium Reagents)

The insertion of a group IIA metal into a carbon-halogen bond is an important reaction as the resulting compounds may act as sources of the organic group in subsequent reactions. Organomagnesium halide reagents,  $\text{RMgX}$ , are by far the most important members of this class of compounds and are widely used in organic synthesis.

These reagents are usually prepared<sup>1,2</sup> by reaction of the corresponding alkyl or aryl halides with Mg in a complexing solvent such as an ether or an inert noncomplexing solvent such as benzene or toluene containing a complexing ether or amine:



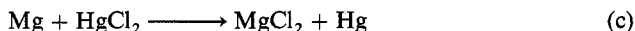
where R = alkyl or vinyl;



where Ar = aryl. Reactions are best carried out under a nitrogen atmosphere. The order of halide activity is  $\text{I} > \text{Br} > \text{Cl} > \text{F}$ . Primary, secondary or tertiary alkyl halides can be

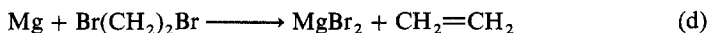
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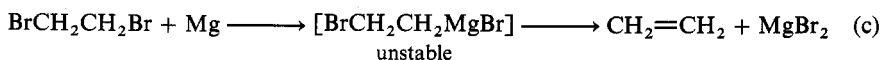


where R = alkyl or vinyl;



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used. A higher boiling solvent than diethyl ether (e.g., THF) is usually required for the less reactive vinyl and aryl halides. 1,2-Dihalogenoalkanes react with Mg but only the magnesium halide is obtained at the end of the reaction (see §2.7.3.2.1):

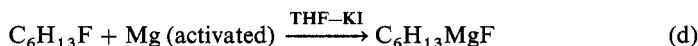


where X = Br.

The efficiency and scope of reactions (a) and (b) can be improved by

1. Use of higher reaction temperatures
2. Use of a more strongly coordinating solvent
3. Activation of the metal<sup>3</sup>

Several methods of activating the metal can be employed. Addition of I<sub>2</sub> or a reactive alkyl halide such as C<sub>2</sub>H<sub>5</sub>Br can greatly accelerate reactions. Transition-metal halides have been used as catalysts for these reactions<sup>4</sup>. A very active form of the metal can be produced by reducing magnesium salts in ethereal solvents with K or Na. The resulting Mg is in the form of a black powder and exhibits unusual reactivity toward alkyl and aryl halides especially when reactions are carried out in the presence of KI<sup>3</sup>. Thus organofluorine compounds such as 1-fluorohexane that do not react with the commercial metal, react with this active form of the metal:



After refluxing in THF containing KI for 1 h a yield of 69% of the fluoro reagent is obtained. Other less common reagents that can be obtained by this method include the derivative of dihalogenobenzenes:



Complete conversion of the aryl halide occurs within 0.25 h at 25°C with a Mg:halide mole ratio of 4:1 and a Mg:KI mole ratio of 2:1.

The formation of an organomagnesium halide is thought to occur via a radical reaction. The actual mechanism of reaction is probably very complex<sup>2,5</sup> but it is likely that the key steps are the one-electron transfer from Mg to the halide to form a radical anion and the dissociation of this species to furnish the alkyl or aryl radical.

The organomagnesium halide exists in equilibrium in solution with their parent metal halide and metal alkyl:

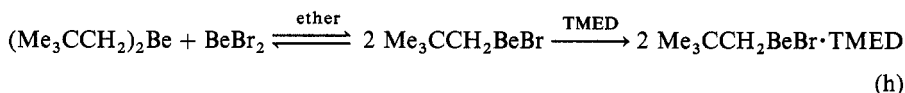


This is probably true for all organometallic compounds of group IIA. Thus organoberyllium halides RBeX (R = CH<sub>3</sub> and X = Cl) can be prepared in solution by mixing together equimolar amounts of the halide, BeX<sub>2</sub> and the alkyl, BeR<sub>2</sub> in an ethereal solvent<sup>6,7</sup>. The equilibrium lies in favor of RBeX and addition of dioxane to the ethereal solution results in slow precipitation of this compound:





Organoberyllium halides can be precipitated from solution by other complexing agents although the resulting product always contains at least 1 mol equiv of that agent<sup>8</sup>:



Organoberyllium halides have some value in organic synthesis<sup>2</sup>.

**CAUTION:** spontaneously violent reactions between Mg and carbon-halogen compounds can occur without warning—cooling may be necessary. See §2.7.1.

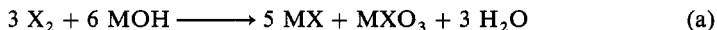
(J.H. CLARK)

1. J. M. Swan, D. St. C. Black, *Organometallics in Organic Synthesis*, Chapman and Hall, London, 1974. Useful background reading.
2. B. Y. Aylett, ed., *Organometallic Derivatives of the Main Group Elements*, Butterworths, London, 1975. Good general text.
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6. E. C. Ashby, R. Sanders, J. Carter, *J. Chem. Soc., Chem. Commun.*, 997 (1967).
7. J. R. Sanders, E. C. Ashby, J. H. Carter, II, *J. Am. Chem. Soc.*, **90**, 6385 (1968).
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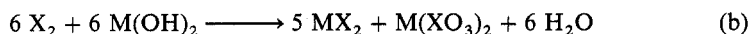
## 2.7.4. from Reaction of Halogens with Hydroxides, Carbonates, etc., of Group-IA and Group-IIA Metals (Formation of Halides by Disproportionation of the Halogen)

The reactions of free  $\text{Br}_2$  and  $\text{I}_2$  with the hydroxides of the metals of groups IA and IIA represent one of the most popular routes to the corresponding bromides and iodides<sup>1</sup>.

Although some alkali-metal bromides and iodides are found in natural salt deposits, they are produced primarily by conversion of bromine (produced from brines or sea water) or iodine (mostly extracted from naturally occurring calcium iodate) in such reactions. This method however, gives mixtures of bromide and bromate, or of iodide and iodate:



where  $\text{X} = \text{Br}$  or  $\text{I}$ ;

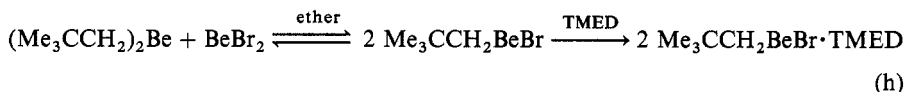


where  $\text{X} = \text{Br}$  or  $\text{I}$ .

The product mixture ( $\text{X} = \text{Br}$  or  $\text{I}$ ) is usually filtered to remove most of the less soluble halate then evaporated and the residual halate reduced by heating with carbon, or by a stream of  $\text{H}_2\text{S}$ , or with bisulfite. Thus  $\text{NaOH}$  in aq soln can be converted to its iodide by treatment with  $\text{I}_2$  followed by addition of  $\text{Na}_2\text{SO}_3$ <sup>2</sup>. Strontium bromide, e.g., can be prepared by treating  $\text{Sr}(\text{OH})_2$  in aq soln with less than equimolar  $\text{Br}_2$ <sup>3</sup>. The

78      2.7. Formation of the Halogen-Group-IA and Group-IIA Metal Bond  
 2.7.4. from Reaction of Halogens with Hydroxides, Carbonates, etc.

Organoberyllium halides can be precipitated from solution by other complexing agents although the resulting product always contains at least 1 mol equiv of that agent<sup>8</sup>:



Organoberyllium halides have some value in organic synthesis<sup>2</sup>.

**CAUTION: spontaneously violent reactions between Mg and carbon-halogen compounds can occur without warning—cooling may be necessary. See §2.7.1.**

(J.H. CLARK)

1. J. M. Swan, D. St. C. Black, *Organometallics in Organic Synthesis*, Chapman and Hall, London, 1974. Useful background reading.
2. B. Y. Aylett, ed., *Organometallic Derivatives of the Main Group Elements*, Butterworths, London, 1975. Good general text.
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8. G. E. Coates, B. R. Francis, *J. Chem. Soc., A*, 1305 (1971).

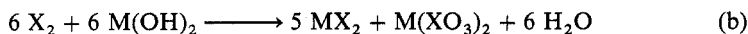
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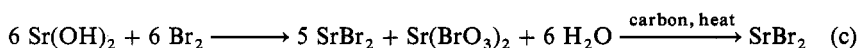
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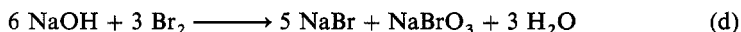
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resulting mixture of  $\text{SrBr}_2$  and  $\text{Sr}(\text{BrO}_3)_2$  is separated by heating with alcohol at  $90^\circ\text{C}$  (to precipitate the products) followed by calcination with carbon:



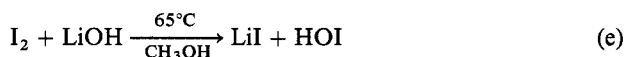
The final product is extracted into water. High T (typically  $> 500^\circ\text{C}$ ) may be required for the calcination stage of these reactions and chemical reductions are usually preferred in the laboratory, while calcination remains the method of choice in industry. Sodium bromide, e.g., is prepared in industry by the reaction of  $\text{Br}_2$  with  $\text{NaOH}$  <sup>4</sup>:



followed by high-T calcination of the evaporated product to give  $\text{NaBr}$ .

Pure  $\text{KI}$  can be prepared by heating a mixture of  $\text{I}_2$ ,  $\text{KOH}$  and  $\text{HCO}_2\text{H}$  in water to  $95\text{--}100^\circ\text{C}$  at pH 4.5 <sup>5</sup>. The product is crystallized from the cooled solution. Formic acid is a generally useful reagent for maintaining a low pH in halogen-metal hydroxide routes to metal halides <sup>6</sup>.

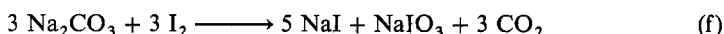
High-purity alkali-metal bromides and iodides can be prepared by direct reaction of  $\text{MeOH}$  soln of  $\text{Br}_2$  or  $\text{I}_2$  with the appropriate metal hydroxide <sup>7</sup>. Thus, slow addition of  $\text{LiOH}\cdot\text{H}_2\text{O}$  to a solution of  $\text{I}_2$  in  $\text{CH}_3\text{OH}$  gives  $\text{LiI}$  in a yield of better than 80%:



A number of alkali-metal halides can be prepared in high yield in this way. The products are generally very pure, containing only traces of halates or carbonates. Heavier alcohols or ketones can be used in place of  $\text{CH}_3\text{OH}$ .

Hydrazine hydrate has been used to improve the yield and purity of group-IA metal iodides obtained by reaction of the hydroxides with  $\text{I}_2$  <sup>8</sup>. Thus the hydroxide is treated with  $\text{I}_2$  and  $\text{HI}$  and the resulting mixture treated with  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ .

The reactions of carbonates of the metals of groups IA and IIA with the heavier halogens represent commercially important routes to the respective metal halides although product contamination is again a problem that must be overcome. The reactions of these carbonates with  $\text{I}_2$  leads to a mixture of the iodide and the iodate:

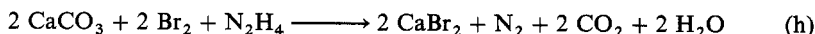


With the heavier metal carbonates such as  $\text{Cs}_2\text{CO}_3$ , a third solid product, the triiodide, is also formed. The use of  $\text{N}_2\text{H}_4$  as a reducing agent overcomes this problem <sup>9,10</sup>; e.g., when  $\text{Cs}_2\text{CO}_3$  reacts with  $\text{I}_2$  in the presence of  $\text{N}_2\text{H}_4$  at  $60^\circ\text{C}$ ,  $\text{CsI}$  is produced in a yield of 98–99%:

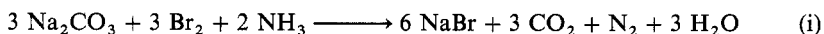


Somewhat more than equimolar  $\text{N}_2\text{H}_4$  is required for quantitative production of  $\text{CsI}$ . The final product should be calcined at  $450^\circ\text{C}$  for about an hour if highly pure materials are required.

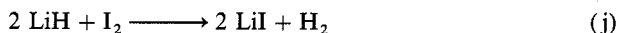
Bromides can also be prepared by this method or by similar methods employing other reducing agents. Thus, the carbonates of the heavier metals of group IIA can be converted to their bromides by treatment with  $\text{Br}_2$  and  $\text{N}_2\text{H}_4$  <sup>3</sup>:



Another commonly employed reducing agent is  $\text{NH}_3$ . Sodium carbonate, e.g., is quantitatively converted to  $\text{NaBr}$  by treatment with  $\text{Br}_2$  and  $\text{NH}_3$ <sup>3</sup>:

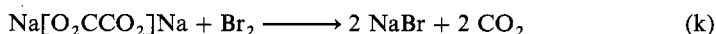


Hydrides of the metals of groups IA and IIA react with  $\text{X}_2$  to give the respective halides. The reactions of the heavier hydrides and the lighter halogens can be violently exothermic or explosive, but moderated reactions of  $\text{I}_2$  or  $\text{Br}_2$  with the hydrides of Li and the lighter members of group IIA can be useful routes to pure iodides or bromides, e.g.,  $\text{LiH}$  reacts with  $\text{I}_2$  in diethyl ether to give an excellent yield of  $\text{LiI}$ :



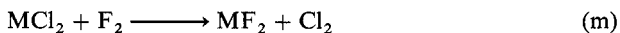
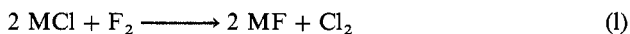
In practice, the  $\text{I}_2$  and xs  $\text{LiH}$  are combined and the ether, slowly added to the mixture<sup>11</sup>. Initially the reaction is vigorous but the final mixture should be refluxed for about 1 h to ensure complete conversion of the  $\text{I}_2$ . Filtration of the mixture followed by evaporation of the solvent and final vacuum drying gives a yield of 98 % of  $\text{LiI}$ . The purity of the product at this stage should be ca. 99 % and better purities can be achieved by passing on aqueous solution of the salt through a cation-exchange resin in its acid form<sup>11</sup>. More vigorous combinations of hydride and halogen such as  $\text{LiH}-\text{Br}_2$  may require cooling the reaction mixture.

Perhaps the most important advantage of the metal hydride-halogen route to metal halides is that the reaction only produces one solid product. This can be contrasted to the less expensive metal carbonate-halogen route which can produce two or more solid products unless a third reactant is introduced. Another good example of a reaction in the former class is the metal oxalate-halogen reaction. Thus sodium oxalate reacts with  $\text{Br}_2$  to give  $\text{NaBr}$  and gaseous  $\text{CO}_2$  only<sup>12</sup>:

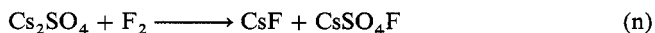


In practice, xs  $\text{Br}_2$  can be bubbled into an aqueous solution of the oxalate until no further  $\text{CO}_2$  escapes from the system. Workup is straightforward, involving evaporation and vacuum drying. This reaction is less hazardous than the metal hydride-halogen reaction but the latter is preferred for the preparation of water-sensitive halides.

Anhydrous fluorides can be prepared by the action of  $\text{F}_2$  on many metal salts. Reactions require special apparatus for handling the aggressive  $\text{F}_2$  and glass, for example, cannot ordinarily be used<sup>13</sup>. Metal chlorides undergo displacement reactions with  $\text{F}_2$  to give pure anhydrous fluorides:



Reactions can be difficult to control and may lead to unexpected products. Thus bubbling  $\text{F}_2$  through  $\text{Cs}_2\text{SO}_4$  in aq soln gives a precipitate of the unstable fluoroxysulfate,<sup>14,15</sup>:



In general, the metal salt- $\text{F}_2$  route to metal fluorides is best avoided unless highly pure, anhydrous products are required.

**CAUTION: Fluorine reacts violently with most materials and special care is required in handling the element. See §2.7.1.**

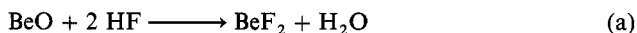
(J.H. CLARK)

1. J. C. Bailor Jr., H. J. Emeleus, R. Nyholm, A. F. Trotman-Dickenson, eds., *Comprehensive Inorganic Chemistry*, Vols. 1 and 2, Pergamon, Oxford, 1973. Valuable reference text.
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## 2.7.5. from Reaction of Hydrogen Halides with Oxides, Hydroxides, Carbonates, etc., of the Group-IA and Group-IIA Metals

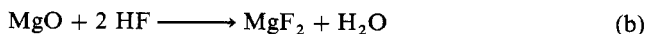
Hydrogen halides react with various compounds of the metals of groups IA and IIA to produce the corresponding metal halides<sup>1-6</sup>. Many of these reactions are rapid and efficient and because of this and the availability of HX and reactive metal compounds, this general route is a popular one. In most cases HX in aq soln can be used but in the special cases of easily hydrolyzed halides such as those of Be, HX gases are usually preferred if contamination of the product with basic halides is to be avoided. It can be difficult to avoid the production of bifluorides  $M[HF_2]$  or  $M[HF_2]_2$ , in reactions with HF but should these occur they may be thermally decomposed to the fluorides.

The oxides of the lighter metals are inert materials that only react under extremely harsh conditions. Beryllium oxide, e.g., is inert toward most materials, except HF. Reaction of BeO with anhyd HF at elevated T can give excellent yields of  $BeF_2$ <sup>1,7</sup>:



It is advisable to calcinate the oxide before hydrofluorination<sup>7</sup>. The calcination T affects the surface area of the final product so that by starting with a BeO sample calcinated at 500°C,  $BeF_2$  with a surface area of  $>20 \text{ m}^2 \text{ g}^{-1}$  can be obtained. Higher calcination T result in  $BeF_2$  samples of lower fluorine content and lower surface areas. The optimum T for reaction is 220°C. Reaction of BeO with aq HF can produce products contaminated with basic fluorides such as  $2 BeO \cdot 5 BeF_2$ , although the use of 40% aq HF results in  $BeF_2$  samples with high fluorine content after evaporation of the solutions to dryness<sup>1,7</sup>. It is generally advisable, however, to exclude water in all preparations of  $BeX_2$  where pure products are required owing to their hygroscopicity and ease of hydrolysis.

Magnesium fluoride is manufactured by the reaction of MgO with aq HF<sup>1,3</sup>:



## 2.7. Formation of the Halogen-Group-IA and Group-IIA Metal Bond

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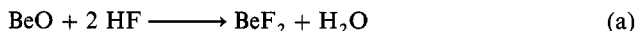
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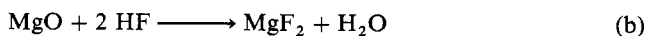
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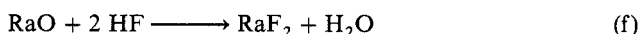
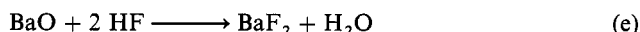
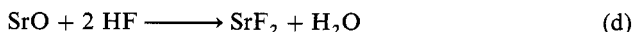
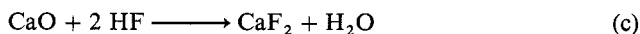
It is advisable to calcinate the oxide before hydrofluorination<sup>7</sup>. The calcination T affects the surface area of the final product so that by starting with a BeO sample calcinated at 500°C,  $BeF_2$  with a surface area of  $>20 \text{ m}^2 \text{ g}^{-1}$  can be obtained. Higher calcination T result in  $BeF_2$  samples of lower fluorine content and lower surface areas. The optimum T for reaction is 220°C. Reaction of BeO with aq HF can produce products contaminated with basic fluorides such as  $2 BeO \cdot 5 BeF_2$ , although the use of 40% aq HF results in  $BeF_2$  samples with high fluorine content after evaporation of the solutions to dryness<sup>1,7</sup>. It is generally advisable, however, to exclude water in all preparations of  $BeX_2$  where pure products are required owing to their hygroscopicity and ease of hydrolysis.

Magnesium fluoride is manufactured by the reaction of MgO with aq HF<sup>1,3</sup>:



Addition of HF to MgO can produce a gelatinous precipitate. This can be avoided by adding the oxide to the hot acid solution and allowing the hot solution to stand for several hours before filtration.

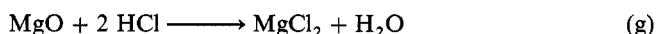
The fluorides of the heavier metals of group IIA can also be prepared by treating the metal oxides with HF<sup>1,3,8</sup>:



Concentrated aq HF soln can be employed and heating may be necessary to ensure good conversions of the oxides. Quantitative yields of pure, anhydrous fluorides are best obtained by flowing anhyd HF over the heated oxide in a suitable reactor.

The heavier halides of the metals of group IIA can also be prepared by reacting the oxide with HX. If the HX is contaminated with its parent halogen, it may be difficult to avoid contamination of the resulting metal halide with the corresponding metal halate. If this does prove to be a problem then the product mixture can be heated with carbon to reduce the halate to halide. If the reaction is carried out in water, concentration of the solution after reaction results in precipitation of a large part of the less soluble metal halate.

Magnesium oxide reacts with HCl to produce MgCl<sub>2</sub> in good yields:



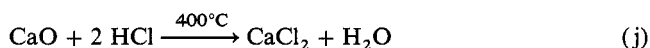
The reaction requires heating, although it is exothermic once initiated<sup>9</sup>. Reaction occurs at T as low as 50°C, although the optimum reaction temperature is about 200°C<sup>9</sup>. At higher T, hydrolysis of the MgCl<sub>2</sub> becomes a significant competing reaction:



At T > 500°C, the hydrolysis is almost complete:



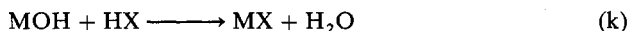
The corresponding reactions of the heavier oxides of the group IIA metals with anhyd HCl start at T between 90 and 160°C<sup>9,10</sup>. Calcium oxide, e.g., gives good yields of CaCl<sub>2</sub> on treatment with anhyd HCl at 400°C:



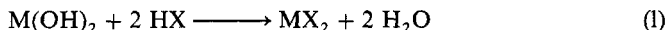
The oxides of the metals of group IA generally react with aq or anhyd HX. Many of these reactions and especially those involving the heavier oxides and the lighter hydrogen halides can be extremely exothermic and difficult to control. Competing hydrolysis reactions can be a problem in reactions involving the lighter members of the group and aqueous solutions of HBr or HI. The group-IA metal oxide–hydrogen halide route is of little practical value owing to the greater availability of other salts of these metals.

The neutralization of the hydroxides of the metals of groups IA and IIA with aq HX

soln is a well-known and convenient route to the corresponding halides with only a few exceptions<sup>1,3,4,10,11</sup>:

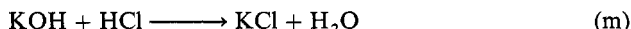


where M = Li, Na, K, Rb, Cr, Fr; X = F, Cl, Br, I;



where M = Mg, Ca, Sr, Ba, Ra; X = F, Cl, Br, I.

In a typical procedure, aq HCl is neutralized with KOH:



The resulting solution is evaporated to dryness and the solid residue calcined (except for salts that are susceptible to hydrolysis).

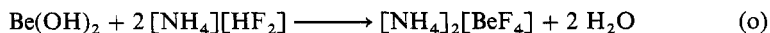
In the preparation of fluorides, it is advisable to add the aq HF to the aq hydroxide if the amount of  $\text{K}_2[\text{SiF}_6]$  (from attack of HF on glass) produced is to be kept to a minimum. Any fluorosilicate produced should be filtered from the solution before evaporation. Alternatively, polyethylene equipment can be used<sup>11</sup>.

The preparation of some of the halides of Li, Be and Mg present special problems due to the sensitivity of the products toward hydrolysis. In the case of Li, the wet method described can be used for the preparation of its halides but care is required in the final drying stages for the preparations of LiCl, LiBr and LiI. High-T drying of LiCl with traces of water present results in the formation of hydroxide or oxide impurities in the chloride. A simple method of overcoming this problem is to dry the LiCl under a stream of HCl gas<sup>12</sup>. Greater care is required in drying the more easily hydrolyzed LiBr and LiI. Hydrates of these salts such as  $\text{LiI} \cdot 3 \text{H}_2\text{O}$  usually result from evaporation of aqueous product mixtures. Then hydrates should be dried under vacuum and with slow heating<sup>13</sup>. Exposure of LiI (either in its anhydrous or hydrated forms) to the atmosphere can lead to oxidation of the salt to iodine.

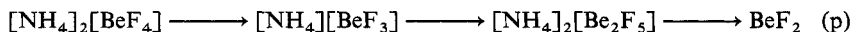
None of the beryllium halides can be easily prepared by wet methods such as the neutralization of an aqueous solution of the corresponding hydrogen halide with  $\text{Be}(\text{OH})_2$ . The reaction of  $\text{Be}(\text{OH})_2$  with aq HF gives a hydrate<sup>14</sup>:



A less direct but more successful method involves the initial preparation of  $[\text{NH}_4]_2[\text{BeF}_4]$  by dissolving  $\text{Be}(\text{OH})_2$  in aq  $[\text{NH}_4][\text{HF}_2]$  and evaporating the solution:



The fluoroberyllate is then thermally decomposed<sup>14</sup>, preferably at T as high as 240°C when the decomposition is thought to occur via two intermediate ammonium compounds<sup>15</sup>:



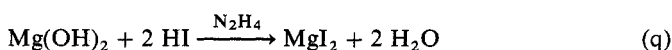
At lower T, the yield of  $\text{BeF}_2$  is poor.

The ease of hydrolysis of the beryllium halides increases from the fluoride to the iodide so that wet methods such as the hydroxide-aqueous acid route are best avoided in preparing the anhydrous salts  $\text{BeCl}_2$ ,  $\text{BeBr}_2$  and  $\text{BeI}_2$ . Attempted preparation of  $\text{BeCl}_2$  or  $\text{BeBr}_2$  by such a method gives the tetrahydrate which is very easily decomposed on

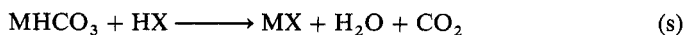
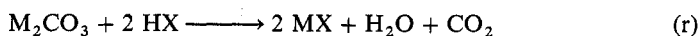


attempted dehydration. The iodide is so easily hydrolyzed by water that the tetrahydrate,  $\text{BeI}_2 \cdot 4 \text{H}_2\text{O}$ , cannot be prepared<sup>14</sup>. Direct reactions employing the anhydrous hydrogen halides can be used but it can be very difficult to ensure the dryness of the acid required to prevent hydrolysis.

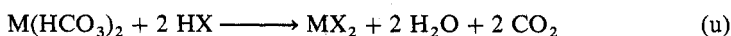
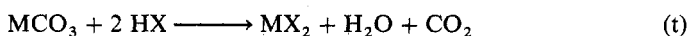
The heavier halides of magnesium are also susceptible to hydrolysis but to a lesser extent than those of Be. The anhydrous halides can be made via treatment of aqueous acids with  $\text{Mg}(\text{OH})_2$  but great care is required in the final product drying stage if pure products are to be obtained. Low-T drying under vacuum or drying under a stream of the corresponding HX gas are useful methods for minimizing product contamination. The low yields that often result from iodide oxidation in the preparation of  $\text{MgI}_2$  can be improved by running the neutralization in the presence of a reducing agent such as hydrazine<sup>16</sup>:



The reactions of the carbonates or bicarbonates of the metals of groups IA and IIA (with the exception of Be) with HX represent especially facile and usually efficient laboratory routes to the corresponding metal halides<sup>1,3,10,11</sup>:

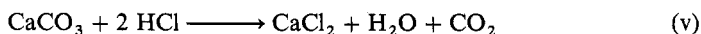


where  $\text{M} = \text{Li, Na, K, Rb, Cs, Fr}$ ;  $\text{X} = \text{F, Cl, Br, I}$ ;



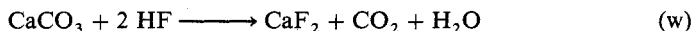
where  $\text{M} = \text{Mg, Ca, Sr, Ba, Ra}$ ;  $\text{X} = \text{F, Cl, Br, I}$ .

The reaction of  $\text{CaCO}_3$  with HCl is a reaction of industrial importance<sup>17,18</sup>:



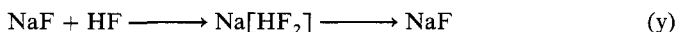
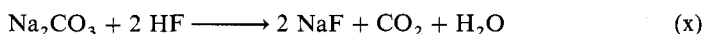
Anhydrous  $\text{CaCl}_2$  can be prepared by reaction with HCl gas. The initiation T for the dry-state reaction depends upon the nature of the  $\text{CaCO}_3$ . The reaction starts at 285°C with chalk, 300°C with limestone and 510°C with the pure carbonate. At 450°C, 90–97% yields of anhyd  $\text{CaCl}_2$  can be obtained after only 15 min reaction with chalk, whereas at the same T less than 55%  $\text{CaCl}_2$  is obtained after 2 h reaction with limestone.

Calcium fluoride can also be prepared in this way:

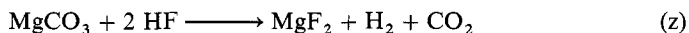


Reaction occurs at <100°C with 40% aq HF and solid  $\text{CaCO}_3$ <sup>11</sup>. Formation of  $\text{Ca}[\text{HF}_2]_2$  is best avoided by adding the HF until evolution of  $\text{CO}_2$  gas almost ceases. The filtered solid is then treated with dilute ethanoic acid until all effervescence stops. It is then thoroughly washed with hot water and finally dried at >200°C. The other fluorides of the metals of group IA and IIA (except beryllium) can be prepared similarly although for NaF, KF, RbF, CsF and  $\text{BaF}_2$ , all of which have significant water solubilities, it is best to treat the carbonate with xs HF followed by high-T drying (>300°C) of the product to decompose any bifluorides<sup>10</sup>. The formation of bifluorides can be used to

advantage; e.g., pure NaF can be obtained by converting impure NaF to crystalline Na[HF<sub>2</sub>] followed by thermal decomposition:

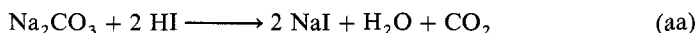


Magnesium fluoride is manufactured by the reaction of MgCO<sub>3</sub> with aq HF<sup>3</sup>:



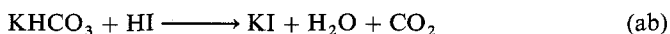
The production of a gelatinous precipitate of MgF<sub>2</sub> that can be difficult to filter can be avoided by addition of the carbonate to the acid solution. Particle size can be enhanced by keeping the solution hot for several hours.

The heavier halides of the metals of groups IA and IIA (except beryllium) can also be prepared by reacting the metal carbonate with HBr or HI. Thus NaI is formed in good yields on treatment of an aq Na<sub>2</sub>CO<sub>3</sub> soln with aq I<sub>2</sub>-free HI<sup>10</sup>.

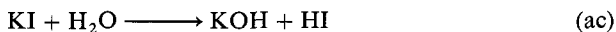


Evaporation of the resulting solution should be carried out in the absence of air so as to minimize production of NaIO<sub>3</sub>. Recrystallization of the residue can give the hydrate, which should be carefully dehydrated under vacuum.

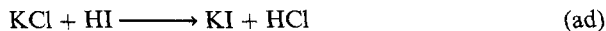
The reaction of KHCO<sub>3</sub> with pure aq HI is an excellent method for preparing pure KI<sup>19</sup>:



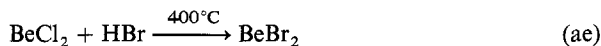
The HI should ideally be a fresh sample prepared from direct combination of the elements over a [Pt]asbestos catalyst. A conc aq HI soln is reacted with purified KHCO<sub>3</sub> and the resulting mixture evaporated in an atmosphere of dry H<sub>2</sub> until a considerable quantity of KI precipitates<sup>13</sup>. This effectively inhibits the hydrolysis reaction:



For any member of groups IA or IIA, the chloride is generally the most readily available and least expensive of the halides, so they are useful starting materials for the preparation of the other halides. Thus the chlorides of the metals of groups IA and IIA react with aq HBr and HI soln to produce the bromides and iodides, respectively<sup>20,21</sup>. Potassium chloride, for example, reacts on heating with excess 17% aq HI soln to produce KI in high yield:



Beryllium chloride is a notable exception. Competing hydrolysis occurs on heating a solution of BeCl<sub>2</sub> in aq HBr or HI. Use of anhyd HBr or HI<sup>10</sup> removes the possibility of hydrolysis but the halogen exchange reaction is very inefficient even at elevated T. Thus heating solid BeCl<sub>2</sub> to 400°C in a stream of anhyd HBr gives only 16% conversion to BeBr<sub>2</sub>:



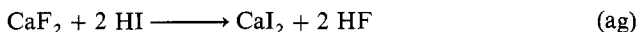
Fluorides can also be prepared from the corresponding chlorides by the action of anhyd or aq HF although the reactions of the acid with the appropriate carbonate,

hydroxide or oxide are more widely used<sup>10,22</sup>. Lithium fluoride for example, can be prepared by adding HF to an aq LiCl soln (30% by weight) containing a little HCl (ca. 1% by weight)<sup>23</sup>:



Evaporation of the resulting solution at T high enough to decompose any Li[HF<sub>2</sub>] (ca. 250°C) gives pure LiF.

Among the other halides of the metals of groups IA and IIA, only the naturally occurring materials such as CaF<sub>2</sub> are economically useful starting materials for the preparation of other halides by reaction with HX. Despite the high lattice energy of CaF<sub>2</sub>, the salt reacts on stirring in aq HI<sup>10</sup>:



**CAUTION: Reactions of hydrogen halides with some of the more reactive compounds (e.g., hydroxides and carbonates) can be vigorous and highly exothermic and may require cooling. See §2.7.1.**

(J.H. CLARK)

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## 2.7. Formation of the Halogen-Group-IA and Group-IIA Metal Bond

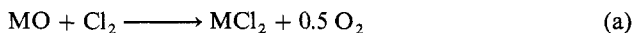
87

## 2.7.6. from Reaction of Oxides with Halogens.

**2.7.6. from Reaction of Oxides with Halogens.**

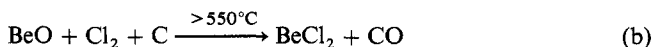
Because of the availability of most metal oxides, methods of converting oxides to halides by treatment with halogens are well established<sup>1,2</sup>. The oxides of the group-IIA metals are readily obtained by calcination of the carbonates and are therefore convenient and inexpensive precursors for their respective halides. The oxides of the group IA metals, however, are not easily obtained from the carbonates or other readily available salts and the conversion of group-IA metal oxides to their halides is a much less useful preparative method. In general, the method is most usefully exploited in the preparation of chlorides and bromides of group-IIA metals.

Reducing conditions are usually considered necessary to enable the reaction of Br<sub>2</sub> with a group-IIA metal oxide to proceed easily. The corresponding reactions with Cl<sub>2</sub> are generally more facile especially with the oxides of the heavier metals. These reactions may be accomplished in the absence of a reducing agent. Thus the chlorides of Ca, Sr, Ba and Ra can be prepared by the action of Cl<sub>2</sub> on the respective oxide<sup>3,4</sup>:



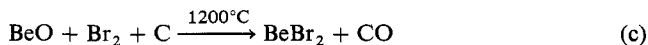
The only special precaution required for such reactions is the exclusion of O<sub>2</sub> from the systems.

The bromides of the group-IIA metals and the chlorides of Be and Mg are best prepared by first intimately mixing the oxide with a carbonaceous material and then pyrolyzing the mixture in the absence of air. Only then should the Cl<sub>2</sub> or Br<sub>2</sub> be introduced into the system. The preliminary step ensures good contact between the oxide and carbon. In a typical preparation, well-ground BeO and excess sucrose (typically up to 10 times the quantity by weight) are first heated together in air and then burned so as to leave an intimate BeO-carbon mixture<sup>5</sup>. The finely ground mixture is then heated to > 550°C in a dry N<sub>2</sub> atmosphere followed by exposure to a ca. 50:50 (by vol) mixture of Cl<sub>2</sub> and N<sub>2</sub>. Reaction proceeds smoothly under these conditions and the BeCl<sub>2</sub> product leaves the system as a smoke and collects in the cooler parts of the reactor as a white crystalline material. A yield of up to 70% BeCl<sub>2</sub> based on the BeO used can be readily obtained. Further conversion of unreacted BeO can be achieved by recharging with additional carbon as described above. In this way, almost quantitative conversion of the BeO can be achieved:



The product is best purified by sublimation under N<sub>2</sub> at a T of 380°C. Several sublimations are required to obtain a highly pure product but these can be carried out conveniently within the same apparatus<sup>6</sup>.

Reaction T as high as 1200°C are required for the corresponding reaction with Br<sub>2</sub><sup>7</sup>:

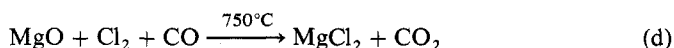


The T can probably be lowered somewhat without significant loss in reaction efficiency if the BeO-carbon mixture is preheated as described for the BeCl<sub>2</sub> preparation. The product should be sublimed under high vacuum at 310°C<sup>6</sup>.

Similar methods can be employed successfully for preparing all of the chlorides and bromides of the group-IIA metals. Heating is required in all cases but reaction T can be

much lower than those described above especially for reactions involving  $\text{Cl}_2$  or the heavier group-IIA metal oxides and where efficient premixing of the oxide and carbon is carried out. Product yields are usually very good and anhydrous materials are obtained, so the method is very useful for those halides that are especially sensitive to hydrolysis.

Reducing agents other than carbon itself can be employed in the oxide-halogen process. Carbon monoxide can be used typically by flowing CO over the treated oxide before exposure to the halogen<sup>8</sup>. Thus MgO can be chlorinated quantitatively only in the presence of a reducing agent such as CO<sup>6</sup>. The CO should be  $\text{H}_2$  free to avoid the formation of  $\text{H}_2\text{O}$  in situ. Initial treatment of MgO at  $750^\circ\text{C}$  is followed by treatment with a 50:50 (by vol)  $\text{Cl}_2$ -CO mixture. If the reaction is carried out by flowing the gases upward through the MgO, the product,  $\text{MgCl}_2$ , drips down from the reaction chamber and can be collected as a white granular material<sup>9</sup>:



In an improvement on this method, the oxide is first mixed with small quantities of sand to assist reduction.

Reactions of metal oxides with  $\text{F}_2$  can be troublesome. Thus reaction of BeO with  $\text{F}_2$  in a Ni reaction furnace at  $210^\circ\text{C}$  for 3 h gives a product that only contains ca. 10% of the expected fluorine for pure  $\text{BeF}_2$ <sup>10</sup>. The reaction of BeO with HF is a much more efficient process (see §2.7.5).

**CAUTION:** See §2.7.1.

(J.H. CLARK)

1. J. C. Bailor Jr., H. J. Emeleus, R. Nyholm, A. F. Trotman-Dickenson, eds., *Comprehensive Inorganic Chemistry*, Vols. 1 and 2, Pergamon, Oxford, 1973. Valuable reference text.
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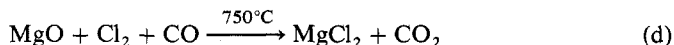
## 2.7.7. from Reactions of Oxides of the Group-IIA Metals with Nonmetal Halides (Excluding Hydrogen Halides).

Because of the availability of the oxides of the group-IIA metals, methods of converting oxides to halides are potentially very useful. Various nonmetal compound sources of halogen, apart from the HX and the halogens themselves, have been employed for this purpose. These include  $\text{CCl}_4$ ,  $\text{ClF}_3$ ,  $\text{COCl}_2$ ,  $\text{SOCl}_2$ ,  $\text{S}_2\text{Cl}_2$ ,  $\text{PCl}_5$ ,  $\text{NH}_4\text{F}$ ,  $[\text{NH}_4][\text{HF}_2]$ ,  $\text{CH}_3\text{COCl}$ ,  $\text{CBr}_4$ ,  $\text{S}_2\text{Br}_2$  and  $\text{SOBr}_2$ <sup>1-4</sup>. In most nonmetal halide-metal oxide reactions, water must be carefully excluded from the systems to avoid competing hydrolysis of the nonmetal halide.

88      2.7. Formation of the Halogen-Group-IA and Group-IIA Metal Bond  
 2.7.7. from Reactions of Oxides of Metals with Nonmetal Halides.

much lower than those described above especially for reactions involving  $\text{Cl}_2$  or the heavier group-IIA metal oxides and where efficient premixing of the oxide and carbon is carried out. Product yields are usually very good and anhydrous materials are obtained, so the method is very useful for those halides that are especially sensitive to hydrolysis.

Reducing agents other than carbon itself can be employed in the oxide-halogen process. Carbon monoxide can be used typically by flowing CO over the treated oxide before exposure to the halogen<sup>8</sup>. Thus MgO can be chlorinated quantitatively only in the presence of a reducing agent such as CO<sup>6</sup>. The CO should be  $\text{H}_2$  free to avoid the formation of  $\text{H}_2\text{O}$  in situ. Initial treatment of MgO at  $750^\circ\text{C}$  is followed by treatment with a 50:50 (by vol)  $\text{Cl}_2$ -CO mixture. If the reaction is carried out by flowing the gases upward through the MgO, the product,  $\text{MgCl}_2$ , drips down from the reaction chamber and can be collected as a white granular material<sup>9</sup>:



In an improvement on this method, the oxide is first mixed with small quantities of sand to assist reduction.

Reactions of metal oxides with  $\text{F}_2$  can be troublesome. Thus reaction of BeO with  $\text{F}_2$  in a Ni reaction furnace at  $210^\circ\text{C}$  for 3 h gives a product that only contains ca. 10% of the expected fluorine for pure  $\text{BeF}_2$ <sup>10</sup>. The reaction of BeO with HF is a much more efficient process (see §2.7.5).

**CAUTION:** See §2.7.1.

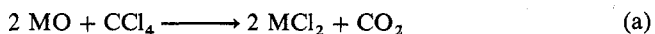
(J.H. CLARK)

1. J. C. Bailor Jr., H. J. Emeleus, R. Nyholm, A. F. Trotman-Dickenson, eds., *Comprehensive Inorganic Chemistry*, Vols. 1 and 2, Pergamon, Oxford, 1973. Valuable reference text.
2. Z. E. Jolles, ed., *Bromine and Its Compounds*, Benn, London, 1966. Good background reading.
3. K. D. Dobryshin, I. I. Bloshtein, *Tr. Leningrad. Tekhnol. Inst. Tsellyul.-Burn. Prom.*, 91 (1970); *Chem. Abstr.*, 74, 89,205 (1971).
4. P. Pascal, ed., *Nouveau Traite de Chimie Minerale*, Masson, Paris, 1958-1963.
5. G. B. Feild, *J. Am. Chem. Soc.*, 61, 1817 (1939).
6. G. Brauer, ed., *Handbook of Preparative Inorganic Chemistry*, Academic Press, New York, 1963. Detailed technical aspects of the experimental equipment.
7. N. Ya. Turova, A. V. Novoselova, K. H. Semenenko, *Zh. Neorg. Khim.*, 5, 117 (1960); *Chem. Abstr.*, 54, 17,135 (1960).
8. C. B. Wendell, M. J. Greene, *Fr. Pat.* 1,525,825 (1968); *Chem. Abstr.*, 71, 23,338 (1969).
9. W. D. Treadwell, A. Cohen, T. Zürner, *Helv. Chim. Acta*, 22, 449 (1939).
10. K. R. Hyde, D. J. O'Connor, E. Wait, *J. Inorg. Nucl. Chem.*, 6, 14 (1958).

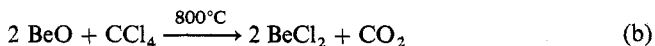
## 2.7.7. from Reactions of Oxides of the Group-IIA Metals with Nonmetal Halides (Excluding Hydrogen Halides).

Because of the availability of the oxides of the group-IIA metals, methods of converting oxides to halides are potentially very useful. Various nonmetal compound sources of halogen, apart from the HX and the halogens themselves, have been employed for this purpose. These include  $\text{CCl}_4$ ,  $\text{ClF}_3$ ,  $\text{COCl}_2$ ,  $\text{SOCl}_2$ ,  $\text{S}_2\text{Cl}_2$ ,  $\text{PCl}_5$ ,  $\text{NH}_4\text{F}$ ,  $[\text{NH}_4][\text{HF}_2]$ ,  $\text{CH}_3\text{COCl}$ ,  $\text{CBr}_4$ ,  $\text{S}_2\text{Br}_2$  and  $\text{SOBr}_2$ <sup>1-4</sup>. In most nonmetal halide-metal oxide reactions, water must be carefully excluded from the systems to avoid competing hydrolysis of the nonmetal halide.

Carbon tetrachloride reacts with the oxides of the heavier group-IIA metals at 250–330°C<sup>5</sup>:

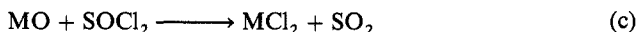


where M = Mg, Ca, Se, Ba, Ra. The analogous reaction of BeO with CCl<sub>4</sub> requires a T of 800°C for efficient halogenation<sup>6</sup>:



In practice, the CCl<sub>4</sub> is passed over a well-ground sample of the metal oxide heated to the required T.

Various salts of the group-IIA metals, including the oxides, react with SOCl<sub>2</sub> at elevated T. Appreciably higher T are required to react the oxides than for the analogous reactions of some other salts such as acetates and formates<sup>7</sup>. The general reaction:

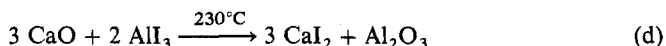


where M = Be, Mg, Ca, Sr, Ba, Ra, is a very useful one as the reaction T are less than those required for the MO-CCl<sub>4</sub> reaction. Furthermore, since SOCl<sub>2</sub> reacts selectively with any water present, the products are generally anhydrous.

Other reactive nonmetal chlorides such as COCl<sub>2</sub>, S<sub>2</sub>Cl<sub>2</sub>, PCl<sub>5</sub> and CH<sub>3</sub>COCl can also be used to convert oxides of the group-IIA metals into their respective anhydrous chlorides<sup>2</sup>. Reactions are usually accomplished by passing the nonmetal chloride vapor over the heated oxide in a dry N<sub>2</sub> atmosphere. Those reactions involving the formation of highly volatile side products are usually preferred so as to simplify the subsequent work-up and product purification.

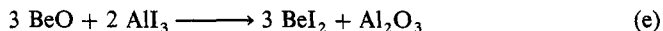
Similar reactions can be employed to prepare anhydrous bromides, although high reaction T may be required: e.g., S<sub>2</sub>Br<sub>2</sub> reacts with MgO only at 600°C to give MgBr<sub>2</sub><sup>8</sup>.

The nonmetal halide-metal oxide method is not generally used to prepare metal iodides largely due to the instability or unavailability of suitable nonmetal iodides. The pseudo-nonmetal halide, AlI<sub>3</sub>, however, is a useful source of iodine in such reactions<sup>9</sup>; e.g., CaO, is converted to its iodide by heating with AlI<sub>3</sub> at 230°C for 24 h:



The product CaI<sub>2</sub>, can be extracted by washing with H<sub>2</sub>O and subsequent dehydration under vacuum.

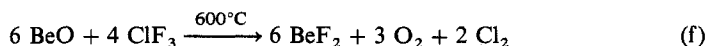
Beryllium iodide can be prepared by the reaction of BeO with the calculated amount of AlI<sub>3</sub> in a sealed tube<sup>10</sup>:



Anhydrous conditions are extremely important due to the sensitivity of BeI<sub>2</sub> and AlI<sub>3</sub> to hydrolysis.

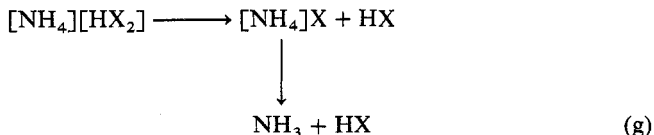
It is advisable to use freshly prepared AlI<sub>3</sub> (from the reaction of metallic Al with I<sub>2</sub> vapor) for such reactions.

Nonmetal fluorides capable of acting as fluorinating agents include ClF<sub>3</sub>, NH<sub>4</sub>F and XeF<sub>2</sub>. Reaction of BeO with ClF<sub>3</sub> requires high T<sup>12</sup>:

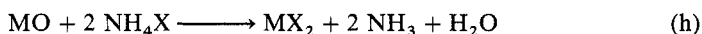


but even at 600°C, analysis of the product suggests less than 60% conversion to BeF<sub>2</sub> after 3 h. At 200°C the conversion is less than 20% after the same time. This reaction is more efficient than that of BeO with F<sub>2</sub> but less efficient than that of BeO with HF (see §2.7.5).

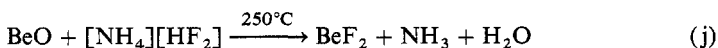
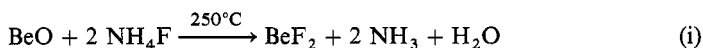
Reactions of the nonmetal halides described probably involve nucleophilic attack of oxide anion on the highly electrophilic S, P and C centers. In contrast to this, reactions of NH<sub>4</sub>X and [NH<sub>4</sub>][HX<sub>2</sub>] with the oxides of the metals of group IIA probably involve initial decomposition of the ammonium salts:



These ammonium salts can be regarded as convenient sources of HX. The general reaction:



is particularly useful for converting oxides to fluorides as NH<sub>4</sub>F or [NH<sub>4</sub>][HF<sub>2</sub>] are much easier to handle than alternative reagents such as ClF<sub>3</sub>, XeF<sub>2</sub>, F<sub>2</sub> or HF. Reactions are usually accomplished by heating an intimate solid mixture of the oxide and the [NH<sub>4</sub>]<sup>+</sup> salt. Thus BeO is efficiently converted to BeF<sub>2</sub> by reaction with NH<sub>4</sub>F or [NH<sub>4</sub>][HF<sub>2</sub>]<sup>12</sup>:



The reaction proceeds via formation of the BeF<sub>2</sub>·2 NH<sub>3</sub> complex, which is formed at 100°C and then decomposed to BeF<sub>2</sub> at 250°C. Similar reactions have been accomplished with the use of ultrasonic excitation as well as thermal energy. Thus MgF<sub>2</sub> is formed on heating MgO with NH<sub>4</sub>F or [NH<sub>4</sub>][HF<sub>2</sub>] in an ultrasonic field at 10–400 kHz<sup>13</sup>.

**CAUTION:** many nonmetal halides are hazardous substances that may react violently with water, releasing corrosive hydrogen halides. The more reactive nonmetal fluorides such as XeF<sub>2</sub> should be treated with the same care and attention as F<sub>2</sub> (see §2.7.1).

(J.H. CLARK)

1. J. C. Bailor Jr., H. J. Emeleus, R. Nyholm, A. F. Trotman-Dickenson, eds. *Comprehensive Inorganic Chemistry*, Vols. 1 and 2, Pergamon, Oxford, 1973. Valuable reference text.
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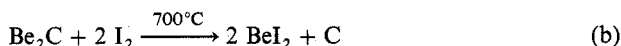
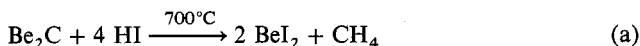


9. M. Chaigneau, *Bull. Chim. Soc. Fr.*, 886 (1957).
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13. V. I. Rodin, *USSR Pat.* 424,808 (1974); *Chem. Abstr.*, 81, 138,189 (1974).

## 2.7.8. from Reaction of Carbides of the Elements with Halogen and Hydrogen Halides

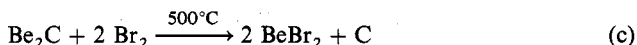
The reaction of a halogen or HX with a metal carbide is a useful route to anhydrous metal halides<sup>1</sup>. The method is especially useful where alternative wet methods cannot be used, that is for the preparation of metal halides that are susceptible to hydrolysis. The major disadvantage of the method is the high T required for reaction.

The reaction of Be<sub>2</sub>C with I<sub>2</sub> or HI is one of the best methods for preparing pure BeI<sub>2</sub><sup>2-5</sup>. The carbide is allowed to react with purified and dried HI or with a mixture of H<sub>2</sub> and I<sub>2</sub> in a quartz tube at 700°C:

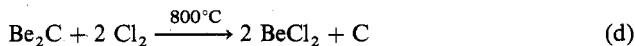


Higher reaction T do not result in significant improvements in the quality or quantity of the product. The major impurity present in the BeI<sub>2</sub> prepared in this way is SiI<sub>4</sub> which results from attack of BeI<sub>2</sub> on the glass. The SiI<sub>4</sub> can be removed by heating the product mixture to 85°C at which temperature it sublimes off. At higher T the BeI<sub>2</sub> sublimes off and this can be utilized in final product purification.

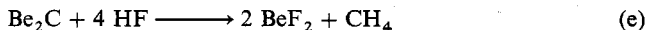
Similar methods can be employed for the preparation of other BeX<sub>2</sub>. The bromide is formed in good yield by the action of Br<sub>2</sub> on Be<sub>2</sub>C at 500°C<sup>3,6</sup>:



Formation of the chloride requires higher T<sup>3</sup>:



Fluorine is not usually used for the conversion of Be<sub>2</sub>C to BeF<sub>2</sub> due to its extreme reactivity and hazardous nature. Gaseous HF reacts with Be<sub>2</sub>C at elevated T<sup>6,7</sup>:



In all cases good yields of anhydrous products are obtained if the reactants are carefully dried and purified before use.

The carbides of the heavier metals of groups IIA and those of group IA will react with the halogens and HX. The reactions, however, do not represent useful routes to the metal halides. These carbides (with the exception of intercalation compounds) are strictly derivatives of acetylene (e.g., CaC<sub>2</sub>) and are generally more difficult to prepare in pure

## 2.7. Formation of the Halogen-Group-IA and Group-IIA Metal Bond 91

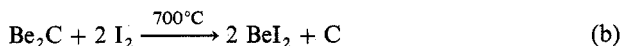
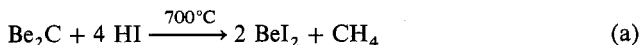
### 2.7.8. Reaction of Carbides of Elements with Halogen and Hydrogen Halides

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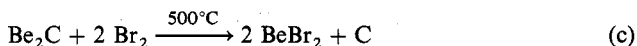
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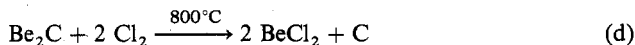


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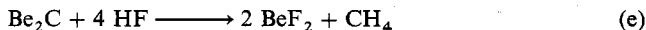
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The carbides of the heavier metals of groups IIA and those of group IA will react with the halogens and HX. The reactions, however, do not represent useful routes to the metal halides. These carbides (with the exception of intercalation compounds) are strictly derivatives of acetylene (e.g., CaC<sub>2</sub>) and are generally more difficult to prepare in pure

form, are often hygroscopic and can, on reaction with HX for example, give a mixture of products.

**CAUTION:** see §2.7.1.

(J.H. CLARK)

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6. P. Pascal, ed., *Nouveau Traite de Chimie Minerale*, Masson, Paris, 1958-1963.
7. J. H. Simons, ed., *Fluorine Chemistry*, Vol. 1, Academic Press, New York, 1950.

## 2.7.9. from Metathetical Reactions (Anion-Halide Exchange).

Among the different reactions that can be considered for preparing the halides of the metals of groups IA and IIA is the double transformation (metathetical) reaction:



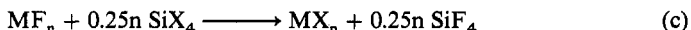
where MA is the source of the metal and M'X the source of the halogen. The reaction proceeds if one of the products can be removed from the reaction system by precipitation or volatilization. Ion-exchange resins (where A or M' is an insoluble polymeric matrix) can also be employed. Some halogen exchange reactions (i.e. A = halide) are industrially important<sup>1</sup>.

One useful solution to the problem of producing a mixture of products is the use of a volatile halogenating agent such as a boron, Si or carbon halide or a thermally unstable halogenating agent such as an ammonium halide. An experimentally simple route to anhyd metal bromides is based on the reaction of metal chlorides with BBr<sub>3</sub><sup>2,3</sup>:



where n = 1 or 2. The BBr<sub>3</sub> reacts exothermically with the metal chloride on mixing at or near RT, giving an almost quantitative yield of metal bromide since the BCl<sub>3</sub> side product is highly volatile under the conditions of the experiment. Water must be excluded from the reaction system to avoid hydrolysis of BBr<sub>3</sub>. The mechanism of the reaction probably involves reversible halide-ion abstraction by BX<sub>3</sub>, with halogenoborate anion intermediates.

The reaction of a metal fluoride with SiX<sub>4</sub> (X = Cl, Br or I) is an excellent method preparing anhydrous metal halides<sup>1</sup>:



where X = Cl, Br or I; n = 1 or 2. The reaction relies on the great difference between the free energies of formation of SiF<sub>4</sub> (1510 kJ mol<sup>-1</sup>) on one hand and of SiCl<sub>4</sub>, SiBr<sub>4</sub> or SiI<sub>4</sub> (560, 381, 136 kJ mol<sup>-1</sup>, respectively) on the other. The reactions require heating. Thus the transformation of LiF into LiCl using SiCl<sub>4</sub> is 250°C, whereas with NaF it is 400°C, and with KF it is 500°C. Silicon tetrahalides are more efficient halogenating agents than

92      2.7. Formation of the Halogen-Group-IA and Group-IIA Metal Bond  
 2.7.9. from Metathetical Reactions (Anion-Halide Exchange).

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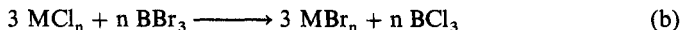
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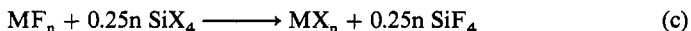
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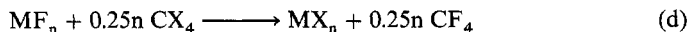
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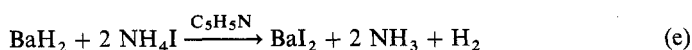
the hydrogen halides<sup>1</sup>. Water must be excluded from the reaction systems to avoid hydrolysis of the silicon tetrahalides.

Carbon tetrahalides can also be used to convert metal fluorides into their corresponding halides<sup>1</sup>:



where X = Cl, Br, I; n = 1 or 2. The free energy of formation of CF<sub>4</sub> is some 500 kJ mol<sup>-1</sup> more favorable than those of the heavier CX<sub>4</sub>. Reaction T are again high and the reactions are generally less efficient than those employing the silicon tetrahalides. Carbon tetrahalides, however, are much easier and safer to handle than SiX<sub>4</sub> or BX<sub>3</sub>.

The production of an unstable side product (M'A, where A = anion) in a metathetical reaction (Eq. a) can help to push the overall reaction to completion if the resulting decomposition products are gaseous under the conditions of the experiment. A good illustration of this is provided by the reaction of BaH<sub>2</sub> with NH<sub>4</sub>I in pyridine<sup>4</sup>. The products of the exchange reaction is expected to be BaI<sub>2</sub> and [NH<sub>4</sub>]H but the instability of the latter product results in the formation of gaseous NH<sub>3</sub> and H<sub>2</sub> which helps to drive the reaction to completion:



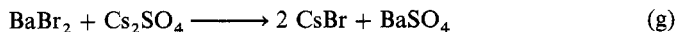
This reaction occurs spontaneously at RT on addition of NH<sub>4</sub>I-PA to a suspension of BaH<sub>2</sub>-PA. The hydride is used in excess and is filtered away from the PA solution of BaI<sub>2</sub> at the end of the reaction. Removal of the PA followed by drying of the solid product at 100°C under vacuum gives the adduct BaI<sub>2</sub>·C<sub>5</sub>H<sub>5</sub>N, which can be decomposed at 150-160°C in vacuo to give pure BaI<sub>2</sub> in a 97% yield. This is a particularly useful method for preparing BaI<sub>2</sub>, although it should also be suitable for many other metal halides of groups IA and IIA.

Metathetical reactions involving the production of an insoluble product or side product can also provide efficient routes to metal halides of groups IA and IIA. Thus the reaction of AlBr<sub>3</sub> (usually prepared fresh in solution by the reaction of bromine water with metallic Al) with metal hydroxides gives a solution of the metal bromide and a ppt of insoluble Al(OH)<sub>3</sub><sup>5</sup>:

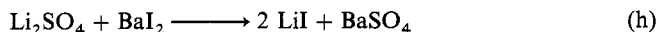


where n = 1 or 2.

Cesium bromide can be made by the reaction of a soluble bromide such as BaBr<sub>2</sub> with Cs<sub>2</sub>SO<sub>4</sub><sup>6</sup>:

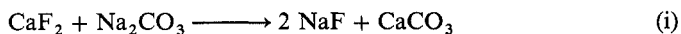


Similar reactions can be employed for the preparation of KBr, RbBr and FrBr<sup>7</sup>. The reactions are driven to near completion by the formation of insoluble BaSO<sub>4</sub>. Alkali-metal iodides can be prepared in good yields by similar reactions; e.g., LiSO<sub>4</sub> reacts with BaI<sub>2</sub> to give LiI in near quantitative yield:

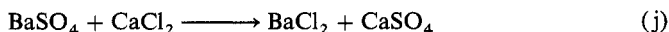


The xs Ba<sup>2+</sup> ions can be removed from the product mixture by precipitation with [NH<sub>4</sub>]<sub>2</sub>CO<sub>3</sub>. Pure LiI can be obtained by sublimating the evaporated filtrate at high T<sup>7</sup>.

High-T fusion reactions can be employed to prepare metal halides from insoluble starting materials. Thus fusion of a finely ground, well-mixed mixture of  $\text{CaF}_2$  and  $\text{Na}_2\text{CO}_3$  gives<sup>7</sup>  $\text{NaF}$ :



The reaction is quantitative and the  $\text{NaF}$  can be removed from the cooled mixture by thorough washing with water. Similarly,  $\text{BaCl}_2$  can be prepared in good yields by the fusion of a mixture of  $\text{BaSO}_4$  and  $\text{CaCl}_2$  at  $900\text{--}1000^\circ\text{C}$ <sup>7</sup>:



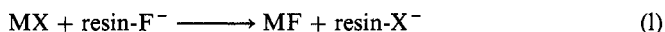
Excess  $\text{CaCl}_2$  should be used to maximize product formation. Once again the product is easily removed by washing the mixture in  $\text{H}_2\text{O}$  followed by evaporation and final drying.

Metathetical reactions can also be employed as routes to metal halides where more direct methods may fail to produce pure products. Thus the  $\text{Br}_2$ -potassium salt route to  $\text{KBr}$  (see §2.7.4) is troubled by competing  $\text{KBrO}_3$  production and this can be overcome by treating the potassium salt with a high oxidation state transition-metal bromide such as  $\text{Fe}_3\text{Br}_8$ <sup>8</sup>:



Methods based on the use of ion-exchange resins provide simple and direct routes to many halides of the metals of groups IA and IIA<sup>9</sup>. The major disadvantages of the technique is that reactions should be carried out using quite dilute solutions of reagents so as to avoid leakage of the undesired ion.

Anion- and cation-exchange resins can be employed, although the desired product must usually be soluble in water and multiple passes may be necessary to achieve good conversion. In a typical reaction an aqueous solution of a metal chloride, bromide or iodide is passed through an excess of anion-exchange resin in its  $\text{F}^-$  form until the eluent fails to give a precipitate with aq  $\text{AgNO}_3$ :



where  $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ . Exchange reactions that are not easily monitored by simple qualitative tests can be troublesome and often result in the formation of mixtures of product and reactant.

For cation-exchange reactions<sup>10</sup>, the conversion of a potassium salt to the corresponding sodium salt is quite easily accomplished since an exchanger such as the strongly acidic sulfonic acid resin exhibits a higher affinity for  $\text{K}$  than for  $\text{Na}$ . The opposite conversion is less easy to accomplish and even at very slow flow rates we would only be able to utilize a slight portion of the normal column capacity of the resin.

Several ion-exchange resins suitable for nonaqueous work are now commercially available and can be used for exchange reactions involving water-insoluble or water-sensitive materials. Care should be taken to avoid decomposition of the resin under nonaqueous conditions which can easily be promoted by the more basic anions such as fluoride<sup>11</sup>.

Astatine has been coprecipitated with  $\text{CsI}_3$  from an aq  $\text{I}_2\text{--I}^-$  soln, presumably as  $\text{CsAtI}_2$ <sup>12</sup>.

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**CAUTION:** some of the heavier nonmetal halides (e.g.,  $\text{BBr}_3$ ) are dangerous substances and can react explosively with water. See §2.7.1.

(J.H. CLARK)

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## 2.8. The Formation of the Halogen–Group-IB (Cu, Ag, Au) or Group-IIIB (Zn, Cd, Hg) Metal Bond

### 2.8.1. Introduction

This section reviews the formation of halogen-group-IB or group-IIIB metal bonds and is divided such that §2.8.2–§2.8.13 cover group-IB metal compounds and §2.8.14–§2.8.23 deal with group-IIIB metal compounds. Group-IB metal species in which the metal is in the 3+, 2+ or 1+ oxidation states are fully covered. However, the formation of fluoro compounds in which the metal oxidation state exceeds 3+, e.g.,  $\text{AuF}_5$ ,  $[\text{AuF}_6]^-$ ,  $[\text{CuF}_6]^{2-}$ , is only briefly mentioned because this area is fully reviewed in §2.11. In addition to binary halides and halogenoanions, the synthesis of organometal halides are also considered, as appropriate, in §2.8.5, 2.8.6 and 2.8.23.

(D. A. EDWARDS)

### 2.8.2. from the Elements.

Table 1 shows the oxidation states displayed by the group-IB metals in combination with the halogens; and Table 2 lists those halides obtained by direct reactions of the constituent elements.

The higher oxidation states are, as expected, displayed in combination with  $\text{F}_2$ . However, direct fluorination of the metals does not induce formation of the highest oxidation states e.g., fluorination of copper, which requires a temperature of 500°C to achieve a reasonable reaction rate<sup>1</sup> (see §2.8.7.1), affords only  $\text{CuF}_2$ , whereas both  $[\text{CuF}_6]^{2-}$  and  $[\text{CuF}_6]^{3-}$  are known. The 4+ oxidation state is known in  $\text{Cs}_2[\text{CuF}_6]$ , prepared by high-pressure fluorination of 1:1  $\text{Cs}[\text{CuCl}_3]$ – $\text{CsCl}$  mixtures<sup>2</sup> or by reacting  $\text{CsF}$  with  $\text{CuF}_2$  under a high fluorine pressure<sup>3</sup>. Single crystals of  $\text{Cs}_2[\text{CuF}_6]$  are obtained<sup>4</sup> by exposing  $\text{Cs}[\text{CuCl}_3]$  to a stream of  $\text{F}_2$  ( $350 \times 10^5 \text{ N m}^{-2}$ ) at 400°C for 5 wk, followed by 250°C for 1 wk. Copper(III), established in  $\text{K}_3[\text{CuF}_6]$ <sup>5</sup> and  $\text{K}_2\text{Na}[\text{CuF}_6]$ <sup>6</sup>, is obtained by fluorination of alkali-metal chloride– $\text{CuCl}_2$  mixtures.

TABLE 1. OXIDATION STATES OF  
GROUP-IB METALS IN BINARY  
HALIDES OR HALOANIONS

Cu		IV	III	II	I
Ag	V <sup>a</sup>	IV <sup>a</sup>	III	II	I
Au	V	IV <sup>a</sup>	III		I

<sup>a</sup> Not totally confirmed.



TABLE 2. GROUP-IB METAL HALIDES SYNTHESIZED BY METAL-HALOGEN REACTIONS

Oxidation state				
+3	AuF <sub>3</sub>	Au <sub>2</sub> Cl <sub>6</sub>	Au <sub>2</sub> Br <sub>6</sub>	
+2	CuF <sub>2</sub>	CuCl <sub>2</sub>	CuBr <sub>2</sub>	
	AgF <sub>2</sub>			
+1		CuCl	CuBr	CuI
	AgF	AgCl	AgBr	AgI
		AuCl	AuBr	AuI

Similarly, although fluorination of Ag at 250°C results only in the formation of AgF<sub>2</sub><sup>7</sup>, the highest oxidation state fluoride is AgF<sub>3</sub>. However, AgF<sub>3</sub> is isolated from reactions of Ag, AgF or preferably AgF<sub>2</sub> with KrF<sub>2</sub> in liq HF for 2 d at RT using polyperfluoroethylene apparatus<sup>8</sup>. This fluoride may be of the type Ag<sup>II</sup>[Ag<sup>IV</sup>F<sub>6</sub>], analogous to PdF<sub>3</sub>. Many salts containing the [AgF<sub>4</sub>]<sup>-</sup> anion (see §2.8.4.1) are known and high-pressure fluorination of a 2:1 CsF-AgF<sub>2</sub> mixture at 400°C produces Cs<sub>2</sub>[AgF<sub>6</sub>], held to be the mixed Ag(III), Ag(V) compound, Cs<sub>2</sub>[Ag<sup>III</sup><sub>0.5</sub>Ag<sup>V</sup><sub>0.5</sub>F<sub>6</sub>]<sup>9,10</sup>. Fluorination of Ag<sup>11</sup> over the temperature range 25–300°C and F<sub>2</sub> pressures of 50–600 torr (7–80 kN m<sup>-2</sup>) forms Ag<sub>2</sub>F, AgF and AgF<sub>2</sub>. No AgF<sub>2</sub> was produced at a F<sub>2</sub> pressure of 50 torr (7 kN m<sup>-2</sup>) regardless of temperature, while at 200 torr (27 kN m<sup>-2</sup>) the amount of AgF<sub>2</sub> increases as the temperature increases.

The situation with Au is even more intriguing. The only fluoride prepared from the elements (350°C and elevated pressure) is polymeric AuF<sub>3</sub><sup>12</sup>, in which the metal is in its most stable oxidation state. However, AuF<sub>3</sub> is isolable, although not by fluorination of the metal. It must be produced<sup>13</sup> by pyrolysis of [O<sub>2</sub>][AuF<sub>6</sub>] or [KrF][AuF<sub>6</sub>]. These salts arise from reactions of Au with F<sub>2</sub> and O<sub>2</sub> at elevated pressure and 350°C or with KrF<sub>2</sub> in HF, respectively. Other representative hexafluorodurate(V) species are Cs[AuF<sub>6</sub>] from fluorination of Cs[AuCl<sub>4</sub>] at 300°C<sup>14</sup>, [Xe<sub>2</sub>F<sup>11</sup>][AuF<sub>6</sub>] from XeF<sub>6</sub> at 400°C<sup>15</sup> and M[AuF<sub>6</sub>]<sub>2</sub> (M = Ca, Sr) from high-pressure fluorination of M[AuF<sub>4</sub>]<sub>2</sub><sup>16</sup>. Gold(IV) is not well characterized but is said to be present in [NO]<sub>2</sub>[AuF<sub>6</sub>]<sup>17</sup>. The existence of this only known example of a Au(IV) compound requires confirmation.

Although AgF is well-known, neither CuF nor AuF have been isolated. The reports of CuF in the early literature are now refuted, e.g., passage of F<sub>2</sub> mixed with Cl<sub>2</sub> over Cu<sup>18</sup> supposedly gave a red layer of CuF, but this was almost certainly Cu<sub>2</sub>O. A melt of CuF<sub>2</sub> at 950–1200°C loses F<sub>2</sub> and contains ~70% CuF. However, on solidification disproportionation to the metal and CuF<sub>2</sub> occurs<sup>19</sup>. Reactions of F<sub>2</sub> or HF with CuI fail to produce CuF, as does attempted reduction of a solution of CuF<sub>2</sub> in aq HF with Cu<sup>15</sup>. Mass spectral studies of CuF<sub>2</sub> detect CuF<sup>+</sup>, but its appearance potential indicates that it merely arises from fragmentation of gaseous CuF<sub>2</sub><sup>21</sup>. The monofluoride, is however, stabilized in the complex [CuF(PPh<sub>3</sub>)<sub>3</sub>]<sup>22</sup>.

The preparation of AuF was claimed<sup>23</sup>, but the work could not be repeated and estimated thermodynamic data imply its instability with respect to disproportionation to the metal and the trifluoride.

Although reactions of the group-IB metals with F<sub>2</sub> do not bring about formation of the highest oxidation states, the metal-chlorine systems provide a contrasting situation. Here direct reactions of the metals with Cl<sub>2</sub> yield CuCl<sub>2</sub>, AgCl and Au<sub>2</sub>Cl<sub>6</sub> (Table 2).

Anions containing the metals in these oxidation states are well known, e.g.,  $[\text{CuCl}_4]^{2-}$ ,  $[\text{AgCl}_2]^-$  and  $[\text{AuCl}_4]^-$ , but the stabilization of higher oxidation states has not been achieved, so species such as  $[\text{CuCl}_6]^{3-}$  or  $[\text{AgCl}_4]^{2-}$  are unknown.

The reaction of Cu with  $\text{Cl}_2$  at  $450^\circ\text{C}$  yields  $\text{CuCl}_2$ <sup>24</sup> (§2.8.7.1), but at significantly higher T  $\text{Cl}_2$  loss leads to  $\text{CuCl}$  (§2.8.11.1). The only stable Ag chloride is  $\text{AgCl}$ , which can be synthesized from the elements but is conveniently precipitated from aqueous chloride solutions by the addition of a soluble Ag salt. Two chlorides of gold can be prepared from the elements<sup>25,26</sup>. It is possible to prepare  $\text{AuCl}$  within the  $254\text{--}282^\circ\text{C}$  range, but  $<254^\circ\text{C}$   $\text{Au}_2\text{Cl}_6$  is the only product and  $>282^\circ\text{C}$  decomposition to the metal occurs (§2.8.3.1.1). The group-IB metal-bromine systems follow the pattern established for the chlorides. Thus  $\text{CuBr}_2$  and  $\text{CuBr}$  can be prepared from the elements and the dibromide by reaction in a sealed tube at  $300^\circ\text{C}$ <sup>27</sup>, but at higher T  $\text{CuBr}_2$  is unstable with respect to  $\text{CuBr}$  and  $\text{Br}_2$ <sup>28</sup>. The only bromide of Ag is  $\text{AgBr}$  and the bromides of Au,  $\text{Au}_2\text{Br}_6$  and  $\text{AuBr}$ , parallel the chlorides in their behavior, although  $\text{Au}_2\text{Br}_6$  is conveniently prepared by reacting the metal powder with bromine at RT<sup>29</sup> and  $\text{AuBr}$  by thermal decomposition of this tribromide.

The iodides present a different picture. Only the three monoiodides are stable, so there is no possibility of obtaining iodides in more than a single oxidation state on reacting the metals with excess iodine. The Cu(I) iodide results from combination of the elements at  $\sim 450^\circ\text{C}$ <sup>28</sup>, but is more usually prepared by the addition of  $\text{Cu}^{2+}$  to an aqueous iodide solution. Although the  $E^\circ$  for the  $\frac{1}{2}\text{I}_2/\text{I}^-$  system is more positive than that for  $\text{Cu}^{2+}/\text{Cu}^+$ ,  $\text{CuI}$  is produced because of its low solubility. The diiodide  $\text{CuI}_2$  has only a transitory existence in the  $\text{Cu}_{(\text{aq})}^{2+}/\text{I}_{(\text{aq})}^-$  system, but it can be stabilized in complexes such as  $[\text{CuI}_2(\text{imidazole})_4]$ . The Ag(I) iodide can be prepared from the elements but is invariably synthesized by precipitation from aqueous media. The Au(I) iodide results from the slow reaction of the metal with iodine in a sealed tube at  $120^\circ\text{C}$ <sup>30</sup>. Although  $\text{AuI}_3$  has been claimed, e.g., by reaction of  $\text{Au}_2\text{Cl}_6$  with cold aq  $\text{KI}$ , reduction occurs to yield  $\text{AuI}$  with perhaps  $[\text{AuI}_2]^-$ ,  $\text{I}_3^-$  and other anions.

There is no evidence that the other halides, mentioned in the early literature such as  $\text{AuCl}_2$ ,  $\text{AuBr}_2$ ,  $\text{Au}_2\text{I}_4$ ,  $\text{Ag}_2\text{Cl}$ ,  $\text{Ag}_2\text{Br}$  and  $\text{Ag}_3\text{Cl}_2$  have even a marginally stable existence; a tetramer of  $\text{AuCl}_2$ ,  $\text{Au}_4\text{Cl}_8$ , is known but contains two Au(I) and two Au(III) centers. It cannot be prepared from the elements (see §2.8.8.1).

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## 2.8.3.1. from the Metals

## 2.8.3.1.1. by Halogenation.

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## 2.8.3. Synthesis of the Group-IB Trihalides

### 2.8.3.1. from the Metals

#### 2.8.3.1.1. by Halogenation.

Gold(III) fluoride, chloride and bromide may be prepared by halogenation of the metal.

The polymeric golden-yellow fluoride cannot be prepared by heating Au wire in F<sub>2</sub> at a dull red heat, but when freshly precipitated Au powder is treated with F<sub>2</sub> at 350°C and elevated pressure in a Monel reaction vessel whose top is cooled to 20°C, needles of AuF<sub>3</sub> slowly collect on the cooled surface and may be purified by vacuum sublimation at 300°C<sup>1</sup>.

From the thermodynamics of the Au-Cl<sub>2</sub> system<sup>2-4</sup> at a Cl<sub>2</sub> pressure of 101.3 kN m<sup>-2</sup> (760 torr), Au<sub>2</sub>Cl<sub>6</sub> exists as the only species in both the solid and gas phases <254°C, while between 254 and 282°C gaseous Au<sub>2</sub>Cl<sub>6</sub> and solid AuCl are present and >282°C solid metal, gaseous Au<sub>2</sub>Cl<sub>6</sub> and gaseous Au<sub>2</sub>Cl<sub>2</sub> coexist. Therefore, Au<sub>2</sub>Cl<sub>6</sub> is best prepared by reaction of the metal with halogen <254°C. Typically<sup>5</sup>, Cl<sub>2</sub> is rapidly passed over Au at 240°C, when red Au<sub>2</sub>Cl<sub>6</sub> is formed and sublimes to the cooler parts of the apparatus. The reaction rate <200°C is slow, being limited by the rate of diffusion of Cl<sub>2</sub> through the surface layer of product. Only >200°C is a high reaction rate achieved as the chloride sublimes, thereby continually leaving a clean metal surface for further attack<sup>6</sup>. Chlorination of the metal using an electrically heated salt bath containing 53% KNO<sub>3</sub>, 40% NaNO<sub>2</sub> and 7% NaNO<sub>3</sub> to maintain a T of precisely 250°C is also useful<sup>7</sup>.

Bromine is the most reactive halogen toward Au as it reacts with the metal powder at RT<sup>8</sup> to afford dark brown Au<sub>2</sub>Br<sub>6</sub>. Alternatively, the bulk metal reacts with gaseous bromine at 150°C to give the tribromide, higher T causing decomposition to the monobromide.

**2.8.3. Synthesis of the Group-IB Trihalides**

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**2.8.3.1. from the Metals****2.8.3.1.1. by Halogenation.**

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18. F. Ebert, H. Woitinek, *Z. Anorg. Allg. Chem.*, **210**, 269 (1933).
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**2.8.3. Synthesis of the Group-IB Trihalides****2.8.3.1. from the Metals****2.8.3.1.1. by Halogenation.**

Gold(III) fluoride, chloride and bromide may be prepared by halogenation of the metal.

The polymeric golden-yellow fluoride cannot be prepared by heating Au wire in F<sub>2</sub> at a dull red heat, but when freshly precipitated Au powder is treated with F<sub>2</sub> at 350°C and elevated pressure in a Monel reaction vessel whose top is cooled to 20°C, needles of AuF<sub>3</sub> slowly collect on the cooled surface and may be purified by vacuum sublimation at 300°C<sup>1</sup>.

From the thermodynamics of the Au-Cl<sub>2</sub> system<sup>2-4</sup> at a Cl<sub>2</sub> pressure of 101.3 kN m<sup>-2</sup> (760 torr), Au<sub>2</sub>Cl<sub>6</sub> exists as the only species in both the solid and gas phases <254°C, while between 254 and 282°C gaseous Au<sub>2</sub>Cl<sub>6</sub> and solid AuCl are present and >282°C solid metal, gaseous Au<sub>2</sub>Cl<sub>6</sub> and gaseous Au<sub>2</sub>Cl<sub>2</sub> coexist. Therefore, Au<sub>2</sub>Cl<sub>6</sub> is best prepared by reaction of the metal with halogen <254°C. Typically<sup>5</sup>, Cl<sub>2</sub> is rapidly passed over Au at 240°C, when red Au<sub>2</sub>Cl<sub>6</sub> is formed and sublimes to the cooler parts of the apparatus. The reaction rate <200°C is slow, being limited by the rate of diffusion of Cl<sub>2</sub> through the surface layer of product. Only >200°C is a high reaction rate achieved as the chloride sublimes, thereby continually leaving a clean metal surface for further attack<sup>6</sup>. Chlorination of the metal using an electrically heated salt bath containing 53% KNO<sub>3</sub>, 40% NaNO<sub>2</sub> and 7% NaNO<sub>3</sub> to maintain a T of precisely 250°C is also useful<sup>7</sup>.

Bromine is the most reactive halogen toward Au as it reacts with the metal powder at RT<sup>8</sup> to afford dark brown Au<sub>2</sub>Br<sub>6</sub>. Alternatively, the bulk metal reacts with gaseous bromine at 150°C to give the tribromide, higher T causing decomposition to the monobromide.

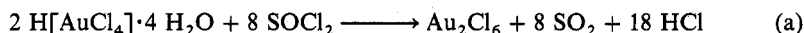
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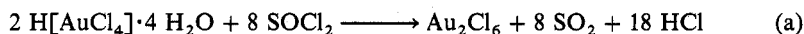
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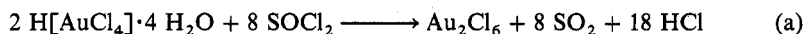
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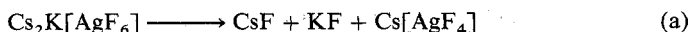
## 2.8.4. Synthesis of Complex Halide Derivatives

### 2.8.4.1. Tetrahalo Derivatives

Apart from the octahedral fluoro anions<sup>1</sup> [CuF<sub>6</sub>]<sup>3-</sup> and [AgF<sub>6</sub>]<sup>3-</sup>, discussed in §2.11, the simplest anionic species of the group-IB metals in their 3+ oxidation states are the square-planar tetrahaloanions [MX<sub>4</sub>]<sup>-</sup>. Such anions are known for Cu and Ag only where X = F, but for Au when X = F, Cl, Br and I, although [AuI<sub>4</sub>]<sup>-</sup> is unstable.

The first diamagnetic fluoride of Cu(II), orange Cs[CuF<sub>4</sub>] containing a planar anion, is obtained by high-pressure fluorination ( $350 \times 10^5$  N m<sup>-2</sup>, 400°C 7 h) of Cs[CuCl<sub>3</sub>] in an autoclave<sup>1</sup>.

The salts M[AgF<sub>4</sub>] (M = Na, K or Cs) are prepared<sup>2</sup> by fluorination of equimolar mixtures of alkali-metal chloride, nitrate or carbonate and silver nitrate or sulfate at 200–400°C. The products are yellow, diamagnetic solids that fume in air and react vigorously with water, liberating HF. The cesium salt also arises from the decomposition<sup>4</sup> of Cs<sub>2</sub>K[AgF<sub>6</sub>]:





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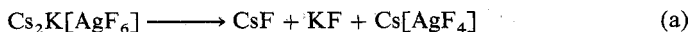
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**2.8.3.1.5. by Halogen Exchange.**

Au(III) fluoride is prepared from Au<sub>2</sub>Cl<sub>6</sub> by two halogen-exchange reactions. Direct fluorination at 200°C<sup>1</sup> and reaction with BrF<sub>3</sub><sup>2</sup> giving [BrF<sub>2</sub>][AuF<sub>4</sub>], which is then thermally decomposed, both produce AuF<sub>3</sub>. Although Au<sub>2</sub>Cl<sub>6</sub> is reported to react with cold aq KI to give Au<sub>2</sub>I<sub>6</sub>, this observation is unlikely to be correct (see §2.8.4.1).

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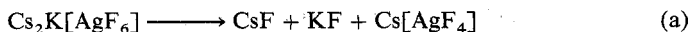
## 2.8.4. Synthesis of Complex Halide Derivatives

### 2.8.4.1. Tetrahalo Derivatives

Apart from the octahedral fluoro anions<sup>1</sup> [CuF<sub>6</sub>]<sup>3-</sup> and [AgF<sub>6</sub>]<sup>3-</sup>, discussed in §2.11, the simplest anionic species of the group-IB metals in their 3+ oxidation states are the square-planar tetrahaloanions [MX<sub>4</sub>]<sup>-</sup>. Such anions are known for Cu and Ag only where X = F, but for Au when X = F, Cl, Br and I, although [AuI<sub>4</sub>]<sup>-</sup> is unstable.

The first diamagnetic fluoride of Cu(II), orange Cs[CuF<sub>4</sub>] containing a planar anion, is obtained by high-pressure fluorination (350 × 10<sup>5</sup> N m<sup>-2</sup>, 400°C 7 h) of Cs[CuCl<sub>3</sub>] in an autoclave<sup>1</sup>.

The salts M[AgF<sub>4</sub>] (M = Na, K or Cs) are prepared<sup>2</sup> by fluorination of equimolar mixtures of alkali-metal chloride, nitrate or carbonate and silver nitrate or sulfate at 200–400°C. The products are yellow, diamagnetic solids that fume in air and react vigorously with water, liberating HF. The cesium salt also arises from the decomposition<sup>4</sup> of Cs<sub>2</sub>K[AgF<sub>6</sub>]:



2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond 101  
 2.8.4. Synthesis of Complex Halide Derivatives  
 2.8.4.1. Tetrahalo Derivatives

However, the reactions of AuCl, AuI and AuCN with  $F_2$ <sup>1</sup> all afford AuF<sub>3</sub>, but use of the iodide or cyanide leads to impure products and **the reactions are violent**.

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**2.8.3.1.4. from Metal Oxides.**

Gold(III) oxide<sup>1</sup> undergoes a solvolytic reaction with molten arsenic(III) bromide yielding Au<sub>2</sub>Br<sub>6</sub> and As<sub>2</sub>O<sub>3</sub>. Another relevant reaction of Au<sub>2</sub>O<sub>3</sub> is that with concentrated HClO<sub>4</sub> in a sealed tube at 160°C for ≥ 1 wk<sup>2</sup>. The red crystalline product, obtained in 40–70% yield, is the polymeric<sup>3</sup> chloride oxide AuOCl.

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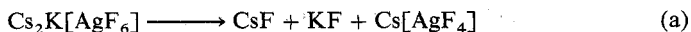
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**2.8.4.1. Tetrahalo Derivatives**

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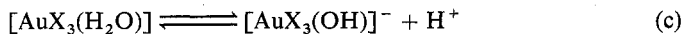
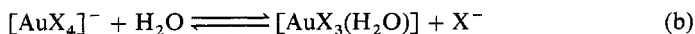
The salts M[AgF<sub>4</sub>] (M = Na, K or Cs) are prepared<sup>2</sup> by fluorination of equimolar mixtures of alkali-metal chloride, nitrate or carbonate and silver nitrate or sulfate at 200–400°C. The products are yellow, diamagnetic solids that fume in air and react vigorously with water, liberating HF. The cesium salt also arises from the decomposition<sup>4</sup> of Cs<sub>2</sub>K[AgF<sub>6</sub>]:



Fluorination of the product obtained on slowly heating a mixture of freshly precipitated  $\text{Ag}_2\text{O}$  and  $\text{BaHPO}_4$  at  $300^\circ\text{C}$  under  $\text{N}_2$  gives<sup>3</sup> the related barium salt,  $\text{Ba}[\text{AgF}_5]$ , which slowly evolves fluorine  $>200^\circ\text{C}$  leaving the  $\text{Ag}(\text{II})$  complex,  $\text{Ba}[\text{AgF}_4]$ . However, the authenticity of  $\text{Ba}[\text{AgF}_5]$  has been questioned<sup>2</sup>. Other methods for the synthesis of  $\text{M}[\text{AgF}_4]$  ( $\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ) are the reactions of  $\text{MF}$  with  $\text{AgF}_x$  ( $x = 1.9\text{--}2.0$ ) and  $\text{XeF}_2$  at  $>220^\circ\text{C}$ <sup>5</sup> and the reactions of  $\text{MF}$  and  $\text{AgF}_x$  ( $x = 1.6\text{--}1.7$ ) with fluorine ( $1\text{--}2 \times 10^5 \text{ N m}^{-2}$ ,  $200\text{--}300^\circ\text{C}$ ,  $10\text{--}35 \text{ h}$ )<sup>6</sup>. Reactions of  $\text{Ag}$  compounds with  $\text{O}_2\text{F}_2$  in  $\text{ClF}_3$  over several hours afford<sup>7</sup> the dioxygenyl complex  $\text{O}_2[\text{AgF}_4]$ .

Although  $\text{Au}$  does not dissolve in conc  $\text{HCl}$  or  $\text{HNO}_3$  separately, it dissolves in the mixed acid, aqua regia. Subsequent evaporation of such solutions, while repeatedly adding further  $\text{HCl}$  to remove all  $\text{HNO}_3$  and oxides of nitrogen<sup>8</sup>, gives light yellow deliquescent needles of chloroauric acid,  $\text{H}[\text{AuCl}_4] \cdot 4 \text{H}_2\text{O}$ , which<sup>9</sup> contains the  $[\text{H}_5\text{O}_2]^+$  cation. This strong acid is converted into salts  $\text{M}[\text{AuCl}_4]$  ( $\text{M} = \text{e.g., alkali metal}$ ) and by halogen exchange into  $[\text{AuF}_4]^-$  or  $[\text{AuBr}_4]^-$ . However, this exchange does not proceed in a similar manner with iodide ion, the mixed oxidation state compounds  $\text{M}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{I}_6$  being formed<sup>10,11</sup> rather than  $\text{M}[\text{AuI}_4]$ .

In an analogous manner  $\text{Au}$  dissolves in an aq  $\text{HNO}_3\text{--HBr}$  mixture to afford  $\text{H}[\text{AuBr}_4] \cdot 4 \text{H}_2\text{O}$ . An alternative route to these two acids is the reaction of  $\text{Au}_2\text{X}_6$  with aq  $\text{HX}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ). The two anions are hydrolyzed to some extent in aqueous solution<sup>12</sup>:



A claim<sup>13</sup> that  $[\text{AuBr}_4]^-$  reacts in nitromethane or nitrobenzene with further bromide ion to give such ions as  $[\text{AuBr}_5]^{2-}$ ,  $[\text{AuBr}_6]^{3-}$  or even  $[\text{Au}_2\text{Br}_{10}]^{4-}$  has been refuted<sup>12</sup>, reduction to  $\text{Au}(\text{I})$  actually occurring.

The  $[\text{AuF}_4]^-$  salts may be prepared by halogen exchange from  $[\text{AuCl}_4]^-$  species, using, e.g., alkali or barium salts with  $\text{F}_2$  at  $200\text{--}300^\circ\text{C}$ <sup>14,15</sup> or  $\text{BrF}_3$  at RT<sup>16</sup>. Bromine trifluoride is a versatile reagent for the preparation of others; e.g.,  $\text{Au}$  reacts with  $\text{BrF}_3$  in the presence of alkali-metal chlorides<sup>16</sup>,  $\text{N}_2\text{O}_4$ <sup>17</sup>,  $\text{ONCl}$ <sup>18</sup> or  $\text{Ag}$ <sup>19</sup> to give  $\text{M}[\text{AuF}_4]$  where  $\text{M} = \text{alkali metal}, \text{NO}_2^+, \text{NO}^+$  or  $\text{Ag}^+$ , respectively.

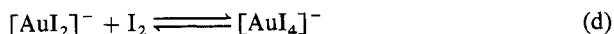
A variety of yellow  $[\text{AuCl}_4]^-$  salts are known. Hydrated salts, e.g.,  $\text{K}[\text{AuCl}_4] \cdot 2 \text{H}_2\text{O}$ ,  $\text{Na}[\text{AuCl}_4] \cdot 2 \text{H}_2\text{O}$  and  $\text{NH}_4[\text{AuCl}_4] \cdot \frac{3}{2} \text{H}_2\text{O}$ , may be isolated<sup>8,20</sup> by treating an aqueous solution of  $\text{Au}_2\text{Cl}_6$  or  $\text{H}[\text{AuCl}_4] \cdot 4 \text{H}_2\text{O}$ , strongly acidified with  $\text{HCl}$ , with an equimolar quantity of a concentrated aqueous solution of the appropriate chloride. Anhydrous salts can then be produced by recrystallization from absolute ethanol<sup>21</sup>. Anhydrous  $\text{Cs}[\text{AuCl}_4]$  is precipitated directly<sup>22</sup> by mixing aqueous solutions of  $\text{Na}[\text{AuCl}_4]$  and  $\text{CsCl}$ , and  $[\text{Ph}_4\text{As}][\text{AuCl}_4]$  is similarly prepared from  $\text{K}[\text{AuCl}_4]$  and  $\text{Ph}_4\text{AsCl}$  in water<sup>23</sup>. Quaternary ammonium salts  $[\text{R}_4\text{N}][\text{AuCl}_4]$  ( $\text{R} = \text{Me}, \text{Et}, \text{n-Pr}, \text{n-Bu}$  or  $\text{n-C}_3\text{H}_{11}$ ) have been obtained, either from  $\text{Na}[\text{AuCl}_4]$  and  $[\text{R}_4\text{N}]\text{Cl}$  in water<sup>22</sup>, or from  $\text{H}[\text{AuCl}_4] \cdot 4 \text{H}_2\text{O}$  and  $\text{R}_4\text{NCl}$  in ethanol<sup>24</sup>. The pyridinium salt  $[\text{pyH}][\text{AuCl}_4]$  results<sup>25</sup> from reacting  $\text{H}[\text{AuCl}_4] \cdot 4 \text{H}_2\text{O}$  with  $\text{py}$  in  $\text{H}_2\text{O}$ . Examples further illustrate the variety of known complexes are: (i)  $[\{\text{Me}_2\text{NC}(\text{Me})\text{O}\}_2\text{H}][\text{AuCl}_4]$ , (from the reaction of  $\text{N,N}$ -dimethylacetamide with  $\text{H}[\text{AuCl}_4] \cdot 4 \text{H}_2\text{O}$ ), the cation having two  $\text{N,N}$ -di-methylacetamide molecules symmetrically bonded to the unique hydrogen<sup>26</sup> and (ii)  $[\text{PCl}_4][\text{AuCl}_4]$ , present in both solid and molten  $\text{Au}_2\text{Cl}_6\text{--PCl}_5$  mixtures<sup>27</sup>. Reactions of  $\text{AuCl}_6$  with (i)  $x\text{S Cl}_2$  in a current of chlorine at  $60^\circ\text{C}$ , (ii)  $\text{SeCl}_4$  in refluxing  $\text{AsCl--POCl}_3$

mixed solvent or (iii)  $\text{TeCl}_4$  in refluxing  $\text{AsCl}_3$  i.e.  $[\text{ECl}_3][\text{AuCl}_4]$  ( $\text{E} = \text{S}, \text{Se}, \text{Te}$ , respectively)<sup>28</sup>.

The red-brown alkali-metal, tetraalkylammonium or tetraphenylarsonium tetrabromaurates(III) may be similarly prepared<sup>22,24,29</sup>. The complex  $\text{K}[\text{AuBr}_4]$  is used as a starting material for such syntheses and is itself conveniently prepared in quantitative yield<sup>30</sup> by reacting Au powder with bromine in the presence of aq  $\text{KBr}$  at  $55^\circ\text{C}$ , followed by recrystallization from  $\text{MeOH}$ . The anhydrous salt absorbs atmospheric moisture to produce a dihydrate. Electrochemical oxidation of a Au anode in a cell having a Pt wire cathode and  $[\text{Et}_4\text{N}]\text{Br}$  and  $\text{Br}_2$  in a 4:1  $\text{C}_6\text{H}_6$ - $\text{MeOH}$  mixed solvent with a high applied potential of ca. 50 V is<sup>31</sup> a quick and simple route to  $[\text{Et}_4\text{N}][\text{AuBr}_4]$ .

Red needles of  $\text{Cs}_3[\text{AuBr}_4]_2\text{Br}_3$  are obtained by adding stoichiometric  $\text{CsBr}$  to  $\text{H}[\text{AuBr}_4]$  and  $\text{Br}_3^-$  in aq  $\text{HBr}$ . Slow decomposition of this product at RT gives a compound derived from  $\text{Cs}_2[\text{AuBr}_4][\text{AuBr}_2]$  in which some of the  $[\text{AuBr}_2]^-$  anions are partly substituted by  $\text{Br}_3^-$ <sup>32,33</sup>.

Early syntheses of  $\text{AuI}_3$  and  $[\text{AuI}_4]^-$  employed aqueous iodide solutions, which are now known to effect reduction to  $\text{Au(I)}$  with the concomitant liberation of  $\text{I}_2$ . The products probably contain<sup>34</sup> such diverse species as  $\text{AuI}$ ,  $[\text{AuI}_2]^-$ ,  $\text{I}_3^-$  and even the mixed halo anions,  $[\text{AuCl}_2\text{I}_2]^-$ . An equilibrium constant of  $200 \text{ L mol}^{-1}$  has been quoted<sup>35</sup> for the process:

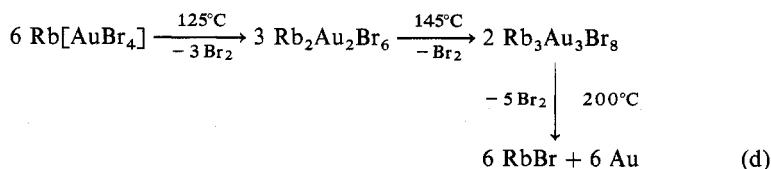


The only salt to be satisfactorily characterized is  $[\text{Et}_4\text{N}][\text{AuI}_4]$ , prepared<sup>34</sup> by condensing excess solid  $\text{HI}$  onto  $[\text{Et}_4\text{N}][\text{AuCl}_4]$  at  $-78^\circ\text{C}$ , then allowing the  $\text{HI}$  to melt under a stream of  $\text{N}_2$  or  $\text{He}$  which is subsequently used to sweep away the xs  $\text{HI}$ . The crystalline black product is moderately stable in air but dissolves with decomposition in water, acetone, acetonitrile or nitromethane.

Reactions of  $\text{H}[\text{AuCl}_4] \cdot 4 \text{H}_2\text{O}$  with a large excess of either aq  $\text{KI}$  or  $\text{NH}_4\text{I}$  leads to  $\text{K}_2[\text{Au}_2\text{I}_6]$  and  $[\text{NH}_4]_2[\text{Au}_2\text{I}_6]$ , respectively<sup>11</sup>. Cesium and rubidium analogs are prepared<sup>10</sup> by reacting a mixture of  $\text{H}[\text{AuCl}_4] \cdot 4 \text{H}_2\text{O}$  and conc aq  $\text{CsCl}$  soln or  $\text{RbCl}$  with  $\text{NaI}$  soln. These complexes involve linked  $-\text{Au}-\text{I}-\text{Au}-$  chains built up from equal numbers of linear  $[\text{AuI}_2]^-$  and square planar  $[\text{AuI}_4]^-$  ions. The coordination sphere of each  $\text{Au(I)}$  and  $\text{Au(III)}$  in  $\text{K}_2\text{Au}_2\text{I}_6$  is completed by long-range iodides producing compressed and elongated octahedra, respectively<sup>36</sup>.

Heated  $\text{M}_2\text{Au}_2\text{I}_6$  ( $\text{M} = \text{NH}_4, \text{K}$  or  $\text{Rb}$ ) loses  $\text{I}_2$  and forms a further type of mixed oxidation state complex,  $\text{M}_3\text{Au}_3\text{I}_8$ , whose structure is based on 3  $\text{M}^+$ , 2  $[\text{AuI}_2]^-$  and  $[\text{AuI}_4]^-$  units<sup>11</sup>. The related compound,  $\text{Rb}_2\text{Ag}[\text{Au}_3\text{I}_8]$ , which is close structurally to  $\text{Rb}_3\text{Au}_3\text{I}_8$ , with one-third of the  $\text{Rb}^+$  ions being replaced by  $\text{Ag}^+$  ions, is prepared in the presence of diethyl ether by reaction of  $\text{RbI}$ ,  $\text{AgNO}_3$  and Au with xs  $\text{I}_2$  and conc aq  $\text{HI}$ <sup>37</sup>.

Thermal decomposition of  $\text{M}[\text{AuX}_4]$  ( $\text{M} = \text{K}, \text{NH}_4$  or  $\text{Rb}$ ;  $\text{X} = \text{Cl}$  or  $\text{Br}$ )<sup>11</sup> with the exceptions of  $\text{NH}_4[\text{AuCl}_4]$  and  $\text{K}[\text{AuCl}_4]$  also cause halogen loss with successive formation of  $\text{M}_2[\text{Au}_2\text{X}_6]$  and  $\text{M}_3[\text{Au}_3\text{X}_8]$  of identical structures to their iodo-analogs just discussed, e.g:



The complex  $[\text{NH}_4][\text{AuCl}_4]$ , however, decomposes at  $140^\circ\text{C}$  directly into  $\text{AuCl}_3(\text{NH}_3)$  and  $\text{HCl}$  and  $\text{K}[\text{AuCl}_4]$  merely yields  $\text{Au}$ ,  $\text{KCl}$  and  $\text{Cl}_2$  at  $170^\circ\text{C}$ <sup>11</sup>.

The black, mixed-oxidation-state compound  $\text{Cs}_2[\text{Au}_2\text{Cl}_6]$ , known<sup>38</sup> for > 60 years, is prepared<sup>39</sup> by partial oxidation of  $\text{AuCl}$  in acid solution in the presence of  $\text{CsCl}$ . The effect of pressure on the structure of this compound is to move the  $\text{Cl}$  atoms toward a symmetrical position between the  $\text{Au(I)}$  and  $\text{Au(III)}$  atoms, so that at ca.  $52 \times 10^8 \text{ N m}^{-2}$  ( $5 \times 10^4 \text{ atm.}$ ) the  $\text{Au}$  atoms become indistinguishable, and only  $\text{Au(II)}$  is present<sup>40</sup>.

A further feature is that  $\text{Au(I)}$  can be replaced by  $\text{Ag(I)}$  without destroying the basic structural design; e.g.,  $\text{Cs}_2\text{AgAuCl}_6$ <sup>41</sup> contains linear  $[\text{Ag}^{\text{I}}\text{Cl}_2]^-$  and square-planar  $[\text{Au}^{\text{III}}\text{Cl}_4]^-$  moieties; whereas  $[\text{NH}_4]_6\text{Ag}_2\text{Au}_3\text{Cl}_{17}$  is built up of  $[\text{Ag}_2\text{Cl}_5]^{3-}$  and 3  $[\text{AuCl}_4]^-$  units<sup>42</sup>. These and other mixed-metal species such as  $\text{Cs}_4[\text{PdBr}_4][\text{AuBr}_4]_2$  are electrically conducting<sup>43</sup>.

Astatine in the 1- oxidation state coprecipitates with  $\text{AgI}$  from aqueous solution, presumably as  $\text{AgAt}$ <sup>44</sup>. Astatine in the so-called "zero oxidation state" absorbs strongly on metallic  $\text{Ag}$ . Presumably  $\text{AgAt}$  forms on the surface of the metal<sup>44</sup>. When "zero-state"  $\text{At}$  solutions are made alkaline, the  $\text{At}$  can be completely coprecipitated with  $\text{AgI}$ . It has been generally assumed that disproportionation takes place and that both  $\text{AgAt}$  and  $\text{AgAtO}_3$  precipitate. "Zero-state"  $\text{At}$  also absorbs strongly on metallic  $\text{Au}$ , which may indicate surface compound formation<sup>44</sup>.

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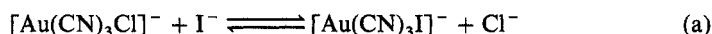
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42. J. C. Bowles, D. Hall, *Acta Crystallogr.*, **B31**, 2149 (1975).
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### 2.8.4.2. Cyanohalo Derivatives

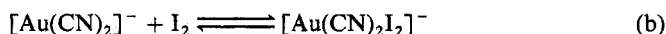
Two types of square-planar Au(III) cyanohalo anions are known:  $[\text{Au}(\text{CN})_3\text{X}]^-$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ) and  $\text{trans-}[\text{Au}(\text{CN})_2\text{X}_2]^-$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ )<sup>1</sup>.

The complex  $\text{K}[\text{Au}(\text{CN})_3\text{Cl}]$  is obtained, contaminated with  $\text{KCl}$ , by passing  $\text{Cl}_2$  through equimol  $\text{K}[\text{Au}(\text{CN})_4]$  and  $\text{KBr}$  in  $\text{MeOH}$ <sup>2</sup>. The  $\text{KBr}$  is apparently essential for substitution of a cyano group by chloride. Subsequent addition of  $\text{K}[\text{Au}(\text{CN})_3\text{Cl}]$  to a saturated aq  $\text{KBr}$  solution affords  $\text{K}[\text{Au}(\text{CN})_3\text{Br}]$  on crystallization. No solid compound containing the  $[\text{Au}(\text{CN})_3\text{I}]^-$  anion has been prepared, but the equilibrium constant for the reaction:



is <sup>3</sup>  $4.7 \times 10^4 \text{ mol L}^{-1}$ . Crystallization of a solution containing a 1:3 molar ratio of  $\text{K}[\text{AuCl}_4]$  and  $\text{K}[\text{Au}(\text{CN})_4]$  is an alternative route to  $\text{K}[\text{Au}(\text{CN})_3\text{Cl}]$ .

The  $\text{trans-}[\text{Au}(\text{CN})_2\text{X}_2]^-$  ( $\text{X} = \text{Cl}, \text{Br}$ , or  $\text{I}$ ) ions are best prepared by oxidative addition of halogen to  $[\text{Au}(\text{CN})_2]^-$ . Thus the pale yellow dichloro, bright yellow dibromo, and red brown diiodo anions may be isolated as potassium salts by passing  $\text{Cl}_2$  gas or adding a methanolic solution of bromine or iodine to an aqueous methanolic solution of  $\text{K}[\text{Au}(\text{CN})_2]$ , followed by evaporation<sup>2,4,5</sup>. The equilibrium constant for the reaction:



is  $\text{K} = 1.3 \times 10^4 \text{ mol L}^{-1}$ , and the kinetics lead to the conclusion that a concerted, one-step trans oxidative addition occurs. Oxidation using the triiodide ion is  $\sim 10^2$  times faster than by  $\text{I}_2$ <sup>6</sup>. The trans square-planar geometries of the  $[\text{Au}(\text{CN})_2\text{X}_2]^-$  anions are confirmed by vibrational spectroscopy<sup>7</sup>, and by the crystal structure of  $\text{K}[\text{Au}(\text{CN})_2\text{Cl}_2] \cdot \text{H}_2\text{O}$ <sup>8</sup>. A stopped-flow study of the replacement of bromide by chloride in  $\text{K}[\text{Au}(\text{CN})_2\text{Br}_2]$  shows that  $\text{K}[\text{Au}(\text{CN})_2\text{Cl}_2]$  is formed in a stepwise process via  $\text{trans-}[\text{Au}(\text{CN})_2\text{ClBr}]^-$ . Indeed, by dissolving equimol  $[\text{Me}_4\text{N}][\text{Au}(\text{CN})_2\text{Br}_2]$  and  $[\text{Me}_4\text{N}][\text{Au}(\text{CN})_2\text{Cl}_2]$  in the minimum volume of water at  $80\text{--}90^\circ\text{C}$  followed by cooling,  $[\text{Me}_4\text{N}][\text{Au}(\text{CN})_2\text{ClBr}]$  is obtained in 85% yield<sup>9</sup>.

Au(III) iodide complexes are susceptible to reduction; e.g., when a solution of  $\text{I}_2$  in ethanol is added to aq  $\text{K}[\text{Au}(\text{CN})_2]$  followed by evaporation, a mixed oxidation

## 2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond 105

## 2.8.4. Synthesis of Complex Halide Derivatives

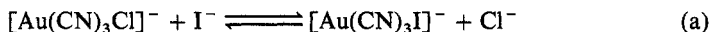
## 2.8.4.2. Cyanohalo Derivatives

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31. J. J. Habeeb, L. Neilson, D. G. Tuck, *Synth. React. Inorg. Metal-Org. Chem.*, **6**, 105 (1976).
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## 2.8.4.2. Cyanohalo Derivatives

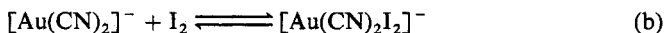
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The complex  $\text{K}[\text{Au}(\text{CN})_3\text{Cl}]$  is obtained, contaminated with KCl, by passing  $\text{Cl}_2$  through equimol  $\text{K}[\text{Au}(\text{CN})_4]$  and KBr in MeOH<sup>2</sup>. The KBr is apparently essential for substitution of a cyano group by chloride. Subsequent addition of  $\text{K}[\text{Au}(\text{CN})_3\text{Cl}]$  to a saturated aq KBr solution affords  $\text{K}[\text{Au}(\text{CN})_3\text{Br}]$  on crystallization. No solid compound containing the  $[\text{Au}(\text{CN})_3\text{I}]^-$  anion has been prepared, but the equilibrium constant for the reaction:



is  $3.47 \times 10^4 \text{ mol L}^{-1}$ . Crystallization of a solution containing a 1:3 molar ratio of  $\text{K}[\text{AuCl}_4]$  and  $\text{K}[\text{Au}(\text{CN})_4]$  is an alternative route to  $\text{K}[\text{Au}(\text{CN})_3\text{Cl}]$ .

The  $\text{trans-}[\text{Au}(\text{CN})_2\text{X}_2]^-$  (X = Cl, Br, or I) ions are best prepared by oxidative addition of halogen to  $[\text{Au}(\text{CN})_2]^-$ . Thus the pale yellow dichloro, bright yellow dibromo, and red brown diiodo anions may be isolated as potassium salts by passing  $\text{Cl}_2$  gas or adding a methanolic solution of bromine or iodine to an aqueous methanolic solution of  $\text{K}[\text{Au}(\text{CN})_2]$ , followed by evaporation<sup>2,4,5</sup>. The equilibrium constant for the reaction:



is  $K = 1.3 \times 10^4 \text{ mol L}^{-1}$ , and the kinetics lead to the conclusion that a concerted, one-step trans oxidative addition occurs. Oxidation using the triiodide ion is  $\sim 10^2$  times faster than by  $\text{I}_2$ <sup>6</sup>. The trans square-planar geometries of the  $[\text{Au}(\text{CN})_2\text{X}_2]^-$  anions are confirmed by vibrational spectroscopy<sup>7</sup>, and by the crystal structure of  $\text{K}[\text{Au}(\text{CN})_2\text{Cl}_2] \cdot \text{H}_2\text{O}$ <sup>8</sup>. A stopped-flow study of the replacement of bromide by chloride in  $\text{K}[\text{Au}(\text{CN})_2\text{Br}_2]$  shows that  $\text{K}[\text{Au}(\text{CN})_2\text{Cl}_2]$  is formed in a stepwise process via  $\text{trans-}[\text{Au}(\text{CN})_2\text{ClBr}]^-$ . Indeed, by dissolving equimol  $[\text{Me}_4\text{N}][\text{Au}(\text{CN})_2\text{Br}_2]$  and  $[\text{Me}_4\text{N}][\text{Au}(\text{CN})_2\text{Cl}_2]$  in the minimum volume of water at 80–90°C followed by cooling,  $[\text{Me}_4\text{N}][\text{Au}(\text{CN})_2\text{ClBr}]$  is obtained in 85% yield<sup>9</sup>.

Au(III) iodide complexes are susceptible to reduction; e.g., when a solution of  $\text{I}_2$  in ethanol is added to aq  $\text{K}[\text{Au}(\text{CN})_2]$  followed by evaporation, a mixed oxidation



state compound rather than  $K[Au(CN)_2I_2]$  is isolated. The black, pleochroic, crystalline product is  $K_5[Au_5(CN)_{10}I_2] \cdot 2 H_2O$  and possesses the structure  $4 K[Au(CN)_2] \cdot K[Au(CN)_2I_2] \cdot 2 H_2O$ <sup>10</sup>.

The related fulminato complexes  $[Ph_4As][Au(CNO)_2X_2]$  (X = Br or I) are prepared by oxidative addition of halogen in chloroform to  $[Ph_4As][Au(CNO)_2]$ <sup>11</sup>.

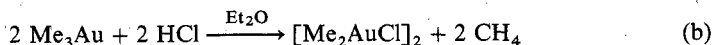
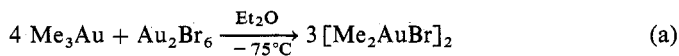
(D.A. EDWARDS)

1. A. G. Sharpe, *The Chemistry of Cyano Complexes of the Transition Metals*, Academic Press, London, 1976. Comprehensive monograph.
2. J. M. Smith, L. H. Jones, I. K. Kressin, R. A. Penneman, *Inorg. Chem.*, **4**, 369 (1965).
3. V. I. Dubinskii, G. V. Demidova, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **16**, 134 (1971).
4. M. O. Falten, D. A. Shirley, *J. Chem. Phys.*, **53**, 4249 (1970).
5. V. P. Dyadchenko, *Uspekhi Khim.*, **51**, 467 (1982); *Russ. Chem. Rev.*, **51**, 265 (1982).
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## 2.8.5. Synthesis of Organo Group-IB Halides

Only Au of the group-IB metals in their 3+ oxidation states forms organometal halides. The neutral compounds are of two types, the stable colorless monohalides,  $[R_2AuX]_2$ , and the less stable, colored dihalides,  $[RAuX_2]_2$ . No fluoride is known, attempts to prepare  $[Me_2AuF]_2$  being unsuccessful. Both types are dimeric, possessing square-planar geometry with  $[R_2Au(\mu-X)_2AuR_2]$  and unsymmetrical  $[R_2Au(\mu-X)_2AuX_2]$  structures, respectively, as shown by x-ray studies on  $[Et_2AuBr]_2$ <sup>1</sup> and  $[MeAuBr_2]_2$ <sup>2</sup>.

The  $[R_2AuX]_2$  compounds are prepared by alkylmagnesium halide alkylation of Au(III) in ether (see Table 1). In reactions employing  $RMgI$  (R = Me or Et),  $[R_2AuI]_2$  is formed by halogen exchange. Alkylmagnesium halide reagents are favored over organolithium reagents, as the latter react further to give  $R_3Au$  or  $[AuR_4]^-$  species. However, reactions of these compounds can provide less convenient routes to  $[R_2AuX]_2$  products<sup>9,11</sup>:



Although the formula  $AuMe_3$  is used, the product from treating  $Au_2Br_6$  with  $LiMe$  at  $-65^\circ C$  in ether may be  $Li[Me_3AuBr]$ , which is difficult to characterize, decomposing to Au, methane and ethane at  $-40^\circ C$ .

Two other routes have been devised to achieve halogen exchange in  $[R_2AuX]_2$  species;  $[R_2AuBr]_2$  (R = Me or Et) react with thallium(I) acetylacetonate to give the chelated complexes  $[R_2Au(acac)]$ , which on treatment with NaI in ethanol yield  $[R_2AuI]_2$ <sup>7,12</sup>. In the opposite direction, treatment of  $[Me_2AuI]_2$  in hexane with 0.2 mol  $L^{-1}$   $AgNO_3$  in 0.5 mol  $L^{-1}$   $HNO_3$  gives an aqueous layer containing the

106 2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond  
2.8.5. Synthesis of Organo Group-IB Halides

state compound rather than  $\text{K}[\text{Au}(\text{CN})_2\text{I}_2]$  is isolated. The black, pleochroic, crystalline product is  $\text{K}_5[\text{Au}_5(\text{CN})_{10}\text{I}_2] \cdot 2 \text{H}_2\text{O}$  and possesses the structure  $4 \text{K}[\text{Au}(\text{CN})_2] \cdot \text{K}[\text{Au}(\text{CN})_2\text{I}_2] \cdot 2 \text{H}_2\text{O}$ <sup>10</sup>.

The related fulminato complexes  $[\text{Ph}_4\text{As}][\text{Au}(\text{CNO})_2\text{X}_2]$  (X = Br or I) are prepared by oxidative addition of halogen in chloroform to  $[\text{Ph}_4\text{As}][\text{Au}(\text{CNO})_2]$ <sup>11</sup>.

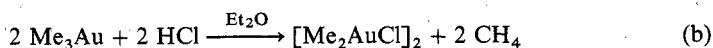
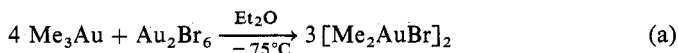
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## 2.8.5. Synthesis of Organo Group-IB Halides

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The  $[\text{R}_2\text{AuX}]_2$  compounds are prepared by alkylmagnesium halide alkylation of Au(III) in ether (see Table 1). In reactions employing  $\text{RMgI}$  (R = Me or Et),  $[\text{R}_2\text{AuI}]_2$  is formed by halogen exchange. Alkylmagnesium halide reagents are favored over organolithium reagents, as the latter react further to give  $\text{R}_3\text{Au}$  or  $[\text{AuR}_4]^-$  species. However, reactions of these compounds can provide less convenient routes to  $[\text{R}_2\text{AuX}]_2$  products<sup>9,11</sup>:



Although the formula  $\text{AuMe}_3$  is used, the product from treating  $\text{Au}_2\text{Br}_6$  with  $\text{LiMe}$  at  $-65^\circ\text{C}$  in ether may be  $\text{Li}[\text{Me}_3\text{AuBr}]$ , which is difficult to characterize, decomposing to Au, methane and ethane at  $-40^\circ\text{C}$ .

Two other routes have been devised to achieve halogen exchange in  $[\text{R}_2\text{AuX}]_2$  species;  $[\text{R}_2\text{AuBr}]_2$  (R = Me or Et) react with thallium(I) acetylacetonate to give the chelated complexes  $[\text{R}_2\text{Au}(\text{acac})]$ , which on treatment with NaI in ethanol yield  $[\text{R}_2\text{AuI}]_2$ <sup>7,12</sup>. In the opposite direction, treatment of  $[\text{Me}_2\text{AuI}]_2$  in hexane with  $0.2 \text{ mol L}^{-1}$   $\text{AgNO}_3$  in  $0.5 \text{ mol L}^{-1}$   $\text{HNO}_3$  gives an aqueous layer containing the

TABLE 1. REACTIONS OF GOLD(III) COMPOUNDS WITH GRIGNARD REAGENTS

Gold compound	Alkylmagnesium halide reagent	Product	Ref.
Au <sub>2</sub> X <sub>6</sub> <sup>a</sup>	EtMgBr	[Et <sub>2</sub> AuX] <sub>2</sub>	3
AuCl <sub>3</sub> (py)	n-PrMgBr	[n-Pr <sub>2</sub> AuBr] <sub>2</sub>	4
H[AuBr <sub>4</sub> ]·4 H <sub>2</sub> O <sup>b</sup>	EtMgBr	[Et <sub>2</sub> AuBr] <sub>2</sub>	3, 5
AuCl <sub>3</sub> (py)	BrMg(CH <sub>2</sub> ) <sub>5</sub> MgBr	[(CH <sub>2</sub> ) <sub>5</sub> AuBr] <sub>2</sub> <sup>c</sup>	6
AuCl <sub>3</sub> (py)	MeMgI	[Me <sub>2</sub> AuI] <sub>2</sub>	7, 8
Au <sub>2</sub> Br <sub>6</sub>	Me <sub>3</sub> CCH <sub>2</sub> MgCl	[(Me <sub>3</sub> CCH <sub>2</sub> ) <sub>2</sub> AuBr] <sub>2</sub>	9
AuX <sub>3</sub>	RMgX	[R <sub>2</sub> AuX] <sub>2</sub> <sup>d</sup>	10

<sup>a</sup> X = Cl or Br.

<sup>b</sup> H[AuBr<sub>4</sub>]·4 H<sub>2</sub>O is a poor starting material as the water present destroys some of the alkylmagnesium halide reagent.

<sup>c</sup> Low yield of this pentamethylene compound isolated after workup by treating [(CH<sub>2</sub>)<sub>5</sub>Au(en)]Br with xs HBr.

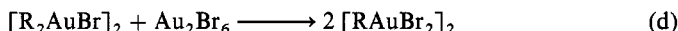
<sup>d</sup> X = Cl, R = Et, n-Pr, i-Pr, PhCH<sub>2</sub>, cyclo-C<sub>6</sub>H<sub>11</sub>; X = Br, R = as above and n-Bu, i-Bu, i-C<sub>3</sub>H<sub>11</sub>, PhCH<sub>2</sub>CH<sub>2</sub>.

cis-[Me<sub>2</sub>Au(OH)<sub>2</sub>]<sup>+</sup> cation. Addition of NaX (X = Cl or Br) soln precipitates<sup>13</sup> [Me<sub>2</sub>AuX]<sub>2</sub>.

The unstable monoalkyl dihalide dimers [RAuX<sub>2</sub>]<sub>2</sub> are prepared<sup>2,6,7</sup> as bromides by halogenation of the dialkyl monobromide dimers:



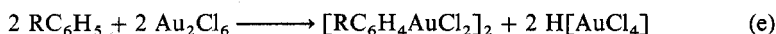
An alternative route is:



The [RAuBr<sub>2</sub>]<sub>2</sub> compounds prepared by these two methods include those with R = Me, Et, n-Pr, n-C<sub>5</sub>H<sub>11</sub>, PhCH<sub>2</sub> and PhCH<sub>2</sub>CH<sub>2</sub>. Reaction of [Me<sub>2</sub>Au(acac)] with Br<sub>2</sub> in CHCl<sub>3</sub> also leads<sup>7</sup> to [MeAuBr<sub>2</sub>]<sub>2</sub>.

Another reaction also<sup>14</sup> leads to a σ-bonded organogold(III) halide. The π complex [Au<sub>2</sub>Cl<sub>6</sub>(MeC≡CMe)], prepared from Au<sub>2</sub>Cl<sub>6</sub> with a deficiency of but-2-yne at low temperatures, spontaneously rearranges to [Cl<sub>2</sub>Au(μ-Cl)<sub>2</sub>AuCl(MeC≡CClMe)] containing the 2-chloro-1-methylpropenyl (chlorovinyl) group.

Neutral arylgold(III) halides are obtained when arenes react with anhyd Au<sub>2</sub>Cl<sub>6</sub> to give, e.g., dimeric arylgold(III) dichlorides, [RC<sub>6</sub>H<sub>4</sub>AuCl<sub>2</sub>]<sub>2</sub> with R = H, Me, Et, i-Pr, t-Bu or Ph<sup>15-17</sup>. A 4- to 10-fold excess of arene is added to a suspension of Au<sub>2</sub>Cl<sub>6</sub> in CCl<sub>4</sub> at RT<sup>17</sup>. After ~1 min, diethyl ether is added to stop the reaction, a yellow solution of [RC<sub>6</sub>H<sub>4</sub>AuCl<sub>2</sub>(OEt<sub>2</sub>)] and a brown precipitate of [HAuCl<sub>4</sub>(OEt<sub>2</sub>)<sub>x</sub>] being present at this stage. Evaporation of the solution leaves yellow, crystalline [RC<sub>6</sub>H<sub>4</sub>AuCl<sub>2</sub>]<sub>2</sub>.



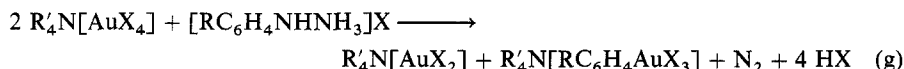
Contrary to previous observations<sup>15,16</sup> little HCl is evolved, but if diethyl ether is not added and the reaction continues further, polychlorinated arenes, e.g., 1,2,4,5-C<sub>6</sub>H<sub>2</sub>Cl<sub>4</sub> from C<sub>6</sub>H<sub>6</sub>, are formed as a result of the thermal instability of the [RC<sub>6</sub>H<sub>4</sub>AuCl<sub>2</sub>]<sub>2</sub> products.

These are electrophilic substitutions at the aromatic ring and so are metallation (auration) reactions, and reactions employing alkylbenzenes give 4-alkylphenyl-Au(III) dichlorides by para substitution. The possible auration reactions are limited by two factors. First, a vacant coordination site on Au is required. Thus,  $\text{Au}_2\text{Cl}_6$  may be employed, but species such as  $\text{H}[\text{AuCl}_4]$  or  $[\text{AuCl}_3(\text{ligand})]$  cannot<sup>15,16</sup>. Second, simple complex formation rather than auration occurs if the arene has suitable substituents present, e.g.:



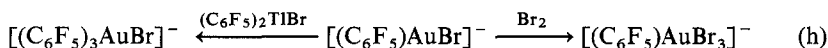
with  $\text{R} = \text{Ph}$ ,  $p\text{-MeC}_6\text{H}_4$ , or  $\text{PhCH}_2$ <sup>18</sup>.

For organogold(III) halide anions the simplest synthesis is the addition of chloride ion to  $[\text{PhAuCl}_2]_2$  yielding the  $[\text{PhAuCl}_3]^-$  anion<sup>19</sup>. However, the air- and moisture-stable pale yellow monoaryl anions are best prepared<sup>20</sup> by reacting an arylhydrazine hydrohalide,  $[\text{RC}_6\text{H}_4\text{NHNH}_3]\text{X}$  ( $\text{R} = \text{H}$ ,  $p\text{-Cl}$ ,  $p\text{-Br}$  or  $p\text{-NO}_2$ ), with  $\text{R}'_4\text{N}[\text{AuX}_4]$  ( $\text{R}' = \text{Et}$  or  $n\text{-Bu}$ ;  $\text{X} = \text{Cl}$  or  $\text{Br}$ ):



The iodide  $n\text{-Bu}_4\text{N}[\text{PhAuI}_3]$  is prepared by metathesis using  $n\text{-Bu}_4\text{NI}$ . As one-half of the Au(III) is reduced to Au(I) in the form of  $[\text{AuX}_2]^-$  anions, this reaction is discussed further in §2.8.12.

The perfluorophenylgold(III) anions,  $[(\text{C}_6\text{F}_5)_3\text{AuBr}_3]^-$  and  $[(\text{C}_6\text{F}_5)_3\text{AuBr}]^-$ , isolated as their  $n\text{-Bu}_4\text{N}^+$  salts, are prepared<sup>21</sup> by oxidative addition:



The  $[(\text{C}_6\text{Cl}_5)_2\text{AuI}_2]^-$  anion is similarly prepared by iodination of  $[(\text{C}_6\text{Cl}_5)_2\text{Au}]^-$  in dichloromethane<sup>22</sup>. The compounds  $\text{cis-}[\text{Me}_4\text{N}][\text{R}_2\text{AuCl}_2]$  are prepared by reacting  $[\text{Me}_4\text{N}][\text{AuCl}_4]$  with  $\text{R}_2\text{Hg}$  in refluxing acetone ( $\text{R} = o\text{-O}_2\text{NC}_6\text{H}_4$ ,  $2\text{-Me-6-O}_2\text{NC}_6\text{H}_3$ )<sup>23</sup>. The chloride ligands can be replaced by cyanide groups. The salts  $[\text{Bu}_4\text{N}][(\text{C}_6\text{F}_5)_2\text{AuX}_2]$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ) are also used to prepare such species as  $[(\text{C}_6\text{F}_5)_2\text{AuX}']_2$  ( $\text{X}' = \text{Cl}$ ,  $\text{Br}$ ,  $\text{N}_3$ ,  $\text{SCN}$ ,  $\text{CF}_3\text{CO}_2$ ),  $[(\text{C}_6\text{F}_5)_2\text{Au}(\text{acac})]$ ,  $[(\text{C}_6\text{F}_5)_2\text{AuCl}(\text{py})]$ ,  $[(\text{C}_6\text{F}_5)_2\text{Au}(\text{R})\text{Cl}]^-$  ( $\text{R} = \text{C}_6\text{F}_5$ ,  $2,4,6\text{-C}_6\text{F}_3\text{H}_2$ ) and  $[(\text{C}_6\text{F}_5)_2\text{L}][(\text{C}_6\text{F}_5)_2\text{AuCl}_2]$ , where  $\text{L} = 2,2'\text{-bipy}$  or  $1,10\text{-phen}$ <sup>24</sup>.

The only alkyl Au(III) halo anions<sup>25</sup> are the  $\text{cis-}[\text{Me}_2\text{AuX}_2]^-$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$  or  $\text{I}$ ) species. The colorless salts  $[\text{Ph}_4\text{As}][\text{Me}_2\text{AuX}_2]$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) arise from reactions of  $[\text{Me}_2\text{AuX}]_2$  with  $\text{Ph}_4\text{AsX}$  in benzene-acetone. An alternative starting material is the tetrameric hydroxide  $[\text{Me}_2\text{Au}(\text{OH})]_4$ , whose dissolution in methanol containing  $0.2 \text{ mol L}^{-1}$   $\text{HCl}$  at  $0^\circ\text{C}$  followed by neutralization with  $\text{Cs}_2\text{CO}_3$  and evaporation yields  $\text{Cs}[\text{Me}_2\text{AuCl}_2]$ , whereas reaction of the hydroxide dissolved in the minimum of ethanol containing  $0.2 \text{ mol L}^{-1}$   $\text{HI}$  with  $\text{Ph}_4\text{AsCl}$  gives light yellow  $[\text{Ph}_4\text{As}][\text{Me}_2\text{AuI}_2]$ . The  $\text{cis-}[\text{Me}_2\text{AuCl}_2]^-$  anion can also be stabilized in the complex salts  $\text{cis-}[\text{Me}_2\text{Au}(\text{bipy})][\text{Me}_2\text{AuCl}_2]$  and  $\text{cis-}[\text{Me}_2\text{Au}(\text{phen})][\text{Me}_2\text{AuCl}_2]$  prepared by reacting  $[\text{Me}_2\text{AuCl}]_2$  with the appropriate chelating ligand<sup>26</sup>.

(D.A. EDWARDS)

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## 2.8.6. Synthesis of Complexes

## 2.8.6.1. Complexes with Group-VB Donors.

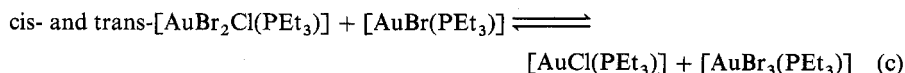
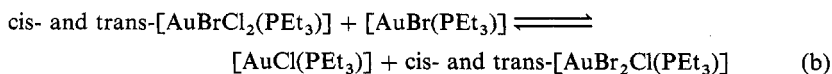
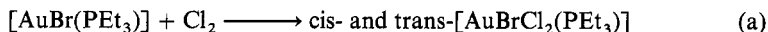
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## 2.8.6. Synthesis of Complexes of Au Trihalides by the Halogenation of Au(I) Complexes

### 2.8.6.1. Complexes with Group-VB Donors.

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Early work<sup>1</sup> on the halogenation of  $[\text{AuX}(\text{PEt}_3)]$  (X = Cl, Br or I) in  $\text{CHCl}_3$  or  $\text{CCl}_4$  gave  $[\text{AuX}_3(\text{PEt}_3)]$ , where  $\text{X}_3 = \text{Cl}_3, \text{Br}_3$  or  $\text{I}_3$  and also apparently  $\text{Cl}_2\text{Br}, \text{ClBr}_2, \text{Cl}_2\text{I}, \text{ClI}_2, \text{Br}_2\text{I}, \text{BrI}_2$  or  $\text{ClBrI}$ . It was said that, e.g.,  $[\text{AuClI}_2(\text{PEt}_3)]$  could be prepared either from  $[\text{AuCl}(\text{PEt}_3)]$  and  $\text{I}_2$  or from  $[\text{AuI}(\text{PEt}_3)]$  and  $\text{ICl}$ . While the trichloro, tribromo, and triiodo complexes are correctly formulated, the mixed halide complexes are really mixtures of all possible isomers of all possible  $[\text{AuX}_n\text{Y}_{3-n}(\text{PEt}_3)]$  species<sup>2</sup>, formed by rapid redox reactions between Au(I) and Au(III) species, e.g.:



A similar picture emerges<sup>3</sup> from the products formed by  $[\text{AuCl}(\text{PMe}_2\text{Ph})]$  with  $\text{Br}_2$  and  $[\text{AuBr}(\text{PMe}_2\text{Ph})]$  with  $\text{Cl}_2$ .

**2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond 109****2.8.6. Synthesis of Complexes****2.8.6.1. Complexes with Group-VB Donors.**

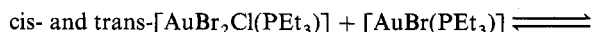
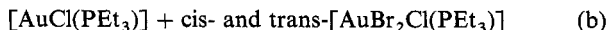
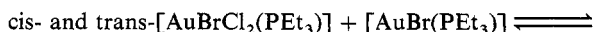
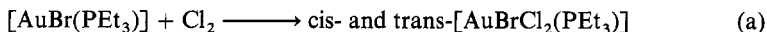
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A similar picture emerges<sup>3</sup> from the products formed by  $[\text{AuCl}(\text{PMe}_2\text{Ph})]$  with  $\text{Br}_2$  and  $[\text{AuBr}(\text{PMe}_2\text{Ph})]$  with  $\text{Cl}_2$ .

The halogenation of the binuclear bis-phosphine-bridged complexes  $[\text{ClAu}(\mu\text{-Ph}_2\text{PNHPPH}_2)\text{AuCl}]^4$  and  $[\text{ClAu}(\mu\text{-Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)\text{AuCl}]^5$  are particularly significant. Stable metal-metal bonded Au(II) intermediates of the type  $[\text{XClAu}(\mu\text{-Ph}_2\text{PYPPh}_2)\text{AuClX}]$  ( $\text{Y} = \text{NH}$ ,  $\text{X} = \text{Cl}$ ;  $\text{Y} = (\text{CH}_2)_3$ ,  $\text{X} = \text{Cl}$  or  $\text{Br}$ ) are isolated, although the final products are the anticipated



and



However, oxidation of  $[\text{ClAu}(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)\text{AuCl}]^5$  giving  $[\text{X}_2\text{ClAu}(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)\text{AuClX}_2]$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) proceeds through the mixed oxidation state intermediates  $[\text{X}_2\text{ClAu}^{\text{III}}(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)\text{Au}^{\text{I}}\text{Cl}]$  (see Table 1).

Dihalogold(III) complexes are synthesized by the oxidative addition of bromine to  $[\text{AuX}(\text{PPh}_3)]$  and  $[\text{AuX}(\text{AsPh}_3)]$  ( $\text{X} = \text{NCO}$ ,  $\text{SCN}$  or  $\text{SeCN}$ ), which produces  $[\text{Au}(\text{NCO})\text{Br}_2(\text{PPh}_3)]$  and  $[\text{Au}(\text{NCO})\text{Br}_2(\text{AsPh}_3)]$ , but displacement of the  $\text{SCN}$  and  $\text{SeCN}$  groups merely leaves  $[\text{AuBr}_3(\text{PPh}_3)]$  or  $[\text{AuBr}_3(\text{AsPh}_3)]$ <sup>12</sup>.

The halogenation of binuclear pentahalophenylgold(I) complexes, e.g.:



gives  $[\text{X}_2(\text{C}_6\text{F}_5)\text{Au}(\mu\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)\text{Au}(\text{C}_6\text{F}_5)\text{X}_2]$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ;  $n = 1, 2$  or  $4$ )<sup>13,14</sup>.

The dark red chelate complex  $\text{trans-}[\text{AuI}_2(\text{diars})_2]\text{I}$ , formed by reaction of iodine with  $[\text{Au}(\text{diars})_2]\text{I}$ , contains tetragonally distorted octahedral Au(III) rather than square planar<sup>15</sup>. Bromination of the AuBr complexes with  $\text{Ph}_2\text{PC}_6\text{H}_4\text{CH}=\text{CH}_2$  or  $\text{Ph}_2\text{PC}_6\text{H}_4\text{CH}_2\text{CH}=\text{CH}_2$  proceeds in an unexpected manner.

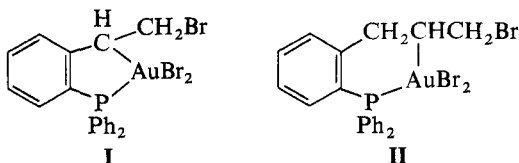


TABLE 1. GOLD TRIHALIDE COMPLEXES FORMED BY HALOGENATION

Reactants	Products	Ref.
$[\text{AuBr}(\text{PMe}_3)] + \text{Br}_2$	$[\text{AuBr}_3(\text{PMe}_3)]$	6
$[\text{AuCl}(\text{PPh}_3)] + \text{Cl}_2$	$[\text{AuCl}_3(\text{PPh}_3)]$	7
$[\text{Au}(\text{C}_6\text{F}_5)(\text{AsPh}_3)] + \text{Br}_2$	$[\text{AuBr}_3(\text{AsPh}_3)] + [\text{AuBr}_2(\text{C}_6\text{F}_5)(\text{AsPh}_3)]$	8
$[\text{Au}(\text{C}_6\text{F}_5)(\text{AsPh}_3)] + \text{I}_2$	$[\text{AuI}_3(\text{AsPh}_3)] + [\text{AuI}(\text{AsPh}_3)]$	8
$[\text{AuBr}(\text{PPh}_2\text{Fc})] + \text{Br}_2^a$	$[\text{AuBr}_3(\text{PPh}_2\text{Fc})]$	9
$[\text{AuPh}(\text{PPh}_3)] + \text{Br}_2$	$[\text{AuBr}_3(\text{PPh}_3)]^b$	10
$[\text{AuXL}] + \text{X}_2^c$	$[\text{AuX}_3\text{L}]$	11
$[\text{AuCl}(\text{PPh}_3)] + \text{Br}_2$	$[\text{AuClBr}_2(\text{PPh}_3)]$	11
$[\text{AuBr}(\text{PPh}_3)] + \text{Cl}_2$	$[\text{AuBrCl}_2(\text{PPh}_3)]$	11

<sup>a</sup> in  $\text{CHCl}_3$  at  $-5^\circ\text{C}$ ; 74% yield.

<sup>b</sup> via  $[\text{AuBr}(\text{PPh}_3)] + \text{PhBr}$

<sup>c</sup>  $\text{X} = \text{Cl}$  or  $\text{Br}$ ;  $\text{L} = \text{PPh}_3$ ,  $\text{PMePh}_2$ ,  $\text{PEtPh}_2$ ,  $\text{PhEt}_2\text{Ph}$ ,  $\text{P}(\text{C}_6\text{H}_4\text{Me-}p)_3$  or  $\text{AsPh}_3$ ; in  $\text{CHCl}_3$ .

TABLE 2. HALOGEN OXIDATION OF SOME PENTAHALOARYLGOLD(I) COMPLEXES

Reactants	Products	Ref.
$[\text{Au}(\text{C}_6\text{F}_5)(\text{PPh}_3)] + \text{Br}_2$	$[\text{AuBr}_2(\text{C}_6\text{F}_5)(\text{PPh}_3)]$	17
$[\text{AuR}(\text{PET}_3)] + \text{X}_2 \text{ or } \text{TiCl}_3^a$	$[\text{AuX}_2\text{R}(\text{PET}_3)]$	18
$[\text{Au}(\text{C}_6\text{Cl}_5)(\text{AsPh}_3)] + \text{TiCl}_3$	$\text{cis}-[\text{AuCl}_2(\text{C}_6\text{Cl}_5)(\text{AsPh}_3)]$	8
$[\text{Au}(\text{C}_6\text{Cl}_5)(\text{AsPh}_3)] + \text{Cl}_2$	$\text{trans}-[\text{AuCl}_2(\text{C}_6\text{Cl}_5)(\text{AsPh}_3)]^b$	8

<sup>a</sup> R = C<sub>6</sub>F<sub>5</sub> or C<sub>6</sub>Cl<sub>5</sub>; X = Cl, Br or I.<sup>b</sup> The trans isomer slowly rearranges to the cis form, whereas oxidation by TiCl<sub>3</sub> gives the cis isomer directly.

Although both products I and II have the stoichiometry [AuBr<sub>3</sub>(ligand)], they are not AuBr<sub>3</sub> derivatives, auration as well as bromination of the terminal methylene groups having occurred<sup>16</sup>.

Examples of the halogenation of mononuclear pentahaloarylgold(I) complexes are given in Table 2. Whereas organogold(I) complexes usually react with halogens by Au—C σ-bond cleavage, pentahaloarylgold(I) complexes can often be oxidized, leaving the Au—C bond intact.

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### 2.8.6.2. Complexes with Group-VIB Donors.

Au(III) halide-group-VIB donor ligand complexes are prepared by halogenation of Au(I) compounds, but none contains an oxygen-bonded ligand.



## 2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond 111

## 2.8.6. Synthesis of Complexes

## 2.8.6.2. Complexes with Group-VIB Donors.

TABLE 2. HALOGEN OXIDATION OF SOME PENTAHALOARYLGOLD(I) COMPLEXES

Reactants	Products	Ref.
$[\text{Au}(\text{C}_6\text{F}_5)(\text{PPh}_3)] + \text{Br}_2$	$[\text{AuBr}_2(\text{C}_6\text{F}_5)(\text{PPh}_3)]$	17
$[\text{AuR}(\text{PEt}_3)] + \text{X}_2$ or $\text{TiCl}_3$ <sup>a</sup>	$[\text{AuX}_2\text{R}(\text{PEt}_3)]$	18
$[\text{Au}(\text{C}_6\text{Cl}_5)(\text{AsPh}_3)] + \text{TiCl}_3$	cis- $[\text{AuCl}_2(\text{C}_6\text{Cl}_5)(\text{AsPh}_3)]$	8
$[\text{Au}(\text{C}_6\text{Cl}_5)(\text{AsPh}_3)] + \text{Cl}_2$	trans- $[\text{AuCl}_2(\text{C}_6\text{Cl}_5)(\text{AsPh}_3)]$ <sup>b</sup>	8

<sup>a</sup> R =  $\text{C}_6\text{F}_5$  or  $\text{C}_6\text{Cl}_5$ ; X = Cl, Br or I.<sup>b</sup> The trans isomer slowly rearranges to the cis form, whereas oxidation by  $\text{TiCl}_3$  gives the cis isomer directly.

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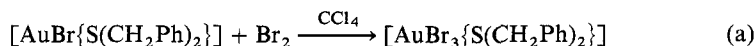
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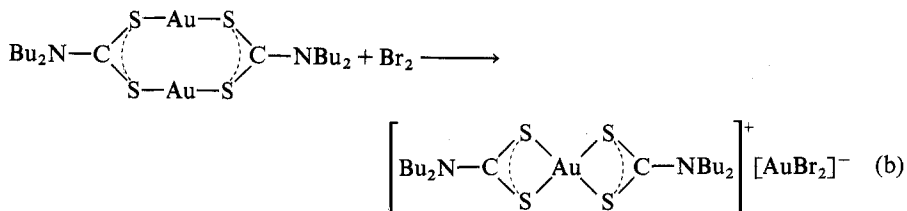
Halogen oxidations of Au(I) halide-dialkyl sulfide complexes  $[\text{AuX}(\text{SR}_2)]$  to give  $[\text{AuX}_3(\text{SR}_2)]$  products provide examples<sup>1</sup> of this type of reaction:



The binuclear complexes  $[\text{X}\text{Au}\{\mu\text{-RS}(\text{CH}_2)_n\text{SR}\}\text{AuX}]$  react with halogens<sup>2</sup>, but in the ionic Au(III) products  $[\text{AuX}_2\{\text{RS}(\text{CH}_2)_n\text{SR}\}]^+\text{Y}^-$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ;  $\text{R} = \text{Me}$  or  $\text{Et}$ ;  $n = 2$  or  $3$ ;  $\text{Y} = \text{AuCl}_4, \text{Br}$  or  $\text{I}$ ) the sulfur donor ligands have changed to a chelating mode of coordination.

The complex  $[\text{Au}(\text{C}_6\text{F}_5)(\text{THT})]$  ( $\text{THT} = \text{tetrahydrothiophene}$ ) undergoes halogenation in  $\text{CH}_2\text{Cl}_2$  to yield  $\text{trans-}[\text{Au}(\text{C}_6\text{F}_5)\text{X}_2(\text{THT})]$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ), which slowly rearrange on standing to the *cis* isomers<sup>3</sup>.

Dithiocarbamate complexes of Au(III) may be prepared from the dimers  $[\text{Au}(\text{S}_2\text{CNR}_2)]_2$ , ( $\text{R} = \text{Me}, \text{Et}, n\text{-Pr}, n\text{-Bu}$ , or  $n\text{-C}_9\text{H}_{19}$ ). The first step in the reaction involves a change from a bridging to a chelating mode of coordination for the sulfur-donor ligand<sup>4</sup>:



This Au(I), Au(III) complex can be further oxidized with exchange of dithiocarbamate ligands between metal centers:



The kinetics of this reaction show that a 1:1 charge-transfer complex formed initially decomposes in a rate-determining step to give the Au(I), Au(III) complex<sup>5</sup>.

The dark green metal-metal-bonded Au(II) dimers  $[\text{Au}(\mu\text{-S}_2\text{CNEt})\text{X}]_2$  ( $\text{X} = \text{Br}, \text{I}, \text{SCN}, \text{SeCN}$ ) are the products of reacting  $[\text{Au}(\text{SCNEt}_2)]_2$  with  $\text{Br}_2, \text{I}_2, (\text{SCN})_2$  or  $(\text{SeCN})_2$  in  $\text{CS}_2$  at  $-78^\circ\text{C}$ . On warming to RT, rearrangement to the Au(I), Au(III) complexes  $[\text{Au}(\text{S}_2\text{CNEt}_2)_2][\text{AuX}_2]$  occurs. The latter salts are the initial products when the reactions are carried out at RT in  $\text{CHCl}_3$  using 1:1 molar ratio of reactants. Use of 1:2 ratios gives  $[\text{Au}(\text{S}_2\text{CNEt}_2)_2]\text{X}_2$  products ( $\text{X} = \text{Br}, \text{SCN}, \text{SeCN}$ )<sup>6</sup>.

The metal itself can be oxidized in the  $\text{Me}_2\text{SO-HBr}$  system to give<sup>7</sup> some  $[\text{AuBr}_3(\text{SMe}_3)]$ .

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- 2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond 113  
2.8.7. Synthesis of the Group-IB Dihalides from the Metals  
2.8.7.1. by Halogenation Reactions.
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## 2.8.7. Synthesis of the Group-IB Dihalides from the Metals

Whereas Cu forms  $\text{CuF}_2$ ,  $\text{CuCl}_2$  and  $\text{CuBr}_2$ , only  $\text{AgF}_2$  is known for Ag and there is no dihalide of Au. The halide  $\text{Au}_4\text{Cl}_8$  contains Au(I) and Au(III) (see §2.8.8).

### 2.8.7.1. by Halogenation Reactions.

The direct fluorination of Cu at  $500^\circ\text{C}$  produces<sup>1</sup>  $\text{CuF}_2$  as a colorless, hygroscopic solid that readily forms a blue dihydrate. As a result of the formation of a protective  $\text{F}_2$  film, Cu is only slowly corroded by  $\text{F}_2$  at lower T and is, therefore, extensively used for the construction of equipment in which  $\text{F}_2$  can be prepared, handled and stored. Investigation of the Cu- $\text{F}_2$  system under high-vacuum conditions at  $20\text{--}250^\circ\text{C}$  and fluoride pressures between  $0.8$  and  $8.0\text{ kN m}^{-2}$  ( $6\text{--}60$  torr)<sup>2</sup> shows that in these corrosion processes the first layer of product forms a barrier between the two reactants, one of which must migrate across this barrier. If the growth rate of the product layer is controlled simply by the rate of movement of reactant through the barrier, i.e., a strictly diffusion-controlled process, a parabolic law is obeyed. However, the data obtained on the Cu- $\text{F}_2$  system rule out a simple diffusive process and the product layer suffers random cracking and consequent mechanical breakdown. Kinetics at  $\text{F}_2$  pressures  $1.33\text{--}17.33\text{ kN m}^{-2}$  ( $10\text{--}130$  torr) at  $450^\circ\text{C}$  also lack agreement with a parabolic rate law<sup>3</sup>. The reaction rate is pressure-dependent, suggesting that  $\text{F}_2$  rather than copper diffuses through the barrier layer of  $\text{CuF}_2$ , the reaction thereby taking place at the Cu- $\text{CuF}_2$  interface.

Anhydrous  $\text{CuCl}_2$  can be prepared<sup>4</sup> by reacting  $\text{P}_4\text{O}_{10}$ -dried  $\text{Cl}_2$  gas with electrolytic Cu at  $450^\circ\text{C}$  in a flow system. The yellow-brown  $\text{CuCl}_2$  is very hygroscopic, rapidly forming a green dihydrate. At higher T  $\text{CuCl}_2$  loses  $\text{Cl}_2$  to give the monochloride (see §2.8.11). The corrosion of Cu by  $\text{Cl}_2$ <sup>5</sup> at  $15\text{--}320^\circ\text{C}$  where the metal ignites gives approximate corrosion rates which show that  $\text{Cl}_2$  can be handled in Cu equipment  $\leq 200^\circ\text{C}$ .

The reaction of  $\text{P}_4\text{O}_{10}$ -dried  $\text{Br}_2$  with Cu in a sealed tube at  $300^\circ\text{C}$  gives anhyd  $\text{CuBr}_2$ <sup>6</sup>. A flow method using bromine vapor carried in a nitrogen stream is less effective since  $>150^\circ\text{C}$   $\text{CuBr}_2$  loses bromine, producing  $\text{CuBr}$ . The corrosion of Cu foil by bromine vapor<sup>7</sup> at  $50\text{--}500^\circ\text{C}$  with a bromine pressure of  $8.8\text{ kN m}^{-2}$  ( $66$  torr) follows a parabolic rate law between  $100\text{--}300^\circ\text{C}$ , but  $>300^\circ\text{C}$  the diffusion process is not rate determining. The product layer consists of a mixture of  $\text{CuBr}_2$  and  $\gamma\text{-CuBr}$ , the proportion of monobromide increasing with temperature.

An alternative route to  $\text{CuBr}_2$  is the electrochemical oxidation of a Cu anode in a cell with a platinum cathode and an electrolyte of bromine in a  $\text{MeOH-C}_6\text{H}_6$  mixed solvent. Crystals of  $\text{CuBr}$  are formed, but addition of ether to the filtrate also yields black microcrystals of  $\text{CuBr}_2$ . The  $\text{CuBr}:\text{CuBr}_2$  product ratio is typically  $\sim 0.3:0.7$ <sup>8</sup>.

$\text{Ag(II)}$  fluoride, being more reactive than  $\text{CuF}_2$ , finds use in various oxidative fluorination reactions. **CAUTION:  $\text{AgF}_2$  may react explosively with organic compounds, often after an induction period.** It is prepared as a black solid by reaction of  $\text{F}_2$  on Ag gauze or powder in a flow system<sup>9,10</sup>. External cooling may be necessary to control the initial reaction rate, but then the temperature may slowly be increased to  $250^\circ\text{C}$ . The product reacts instantly with water, liberating  $\text{O}_3$  as one of the products. As purification is difficult, complete reaction needs to be achieved to produce a pure sample. This is best

accomplished using Ag powder. A reported yellow modification of  $\text{AgF}_2$  is likely to be  $\text{AgF}_2$  contaminated with  $\text{AgF}$ . However, another modification is stable at  $60 \times 10^5 \text{ kN m}^{-2}$  (60 kbar) but metastable at ordinary pressures<sup>11</sup>. Reaction of the metal with  $\text{ClF}_3$  at  $120^\circ\text{C}$  in an autoclave is an alternative route to  $\text{AgF}_2$ <sup>12</sup>, as is reaction of the metal with  $\text{ClF}_3$  and  $\text{F}_2$  in  $\text{HF}$  soln at RT<sup>13</sup>.

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### 2.8.7.2. by Hydrohalogenation Reactions.

Copper and Ag resist attack by anhyd  $\text{HF}$  gas owing to the formation of protective fluoride films. High-T corrosion tests show<sup>1</sup>, e.g., that in a system held at  $500^\circ\text{C}$   $\text{HF}$  is capable of penetrating bulk Cu only to a depth of approximately  $0.004 \text{ mm d}^{-1}$ . However, the reaction between Cu powder and gaseous  $\text{HF}$  at  $500^\circ\text{C}$  is used<sup>2</sup> to prepare  $\text{CuF}_2$ . Copper cannot be effectively fluorinated using liq  $\text{HF}$  because such reactions can obviously only be attempted below the critical temperature of ca.  $225^\circ\text{C}$ .

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### 2.8.7.3. by Hydrohalic Acids.

Gold is the most noble metal, not reacting with hydrohalic acids. It does, however, react with aq  $\text{HCl}$  or  $\text{HBr}$  in the presence of strong oxidizing agents such as  $\text{HNO}_3$ ,  $\text{OCl}^-$  or  $\text{Fe}^{3+}$ , to form  $[\text{AuCl}_4]^-$  or  $[\text{AuBr}_4]^-$  (see §2.8.4.1). Gold, however, shows no tendency to form stable species in the  $2+$  oxidation state in aqueous media<sup>1</sup> so need not be considered here. The formation of stable  $\text{Ag(II)}$  halides by reacting Ag with aqueous hydrohalic acids is also ruled out. Even allowing for the limited applicability of standard

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 2.8.7. Synthesis of the Group-IB Dihalides from the Metals  
 2.8.7.3. by Hydrohalic Acids.

accomplished using Ag powder. A reported yellow modification of  $\text{AgF}_2$  is likely to be  $\text{AgF}_2$  contaminated with  $\text{AgF}$ . However, another modification is stable at  $60 \times 10^5 \text{ kN m}^{-2}$  (60 kbar) but metastable at ordinary pressures<sup>11</sup>. Reaction of the metal with  $\text{ClF}_3$  at  $120^\circ\text{C}$  in an autoclave is an alternative route to  $\text{AgF}_2$ <sup>12</sup>, as is reaction of the metal with  $\text{ClF}_3$  and  $\text{F}_2$  in  $\text{HF}$  soln at RT<sup>13</sup>.

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### 2.8.7.2. by Hydrohalogenation Reactions.

Copper and Ag resist attack by anhyd  $\text{HF}$  gas owing to the formation of protective fluoride films. High-T corrosion tests show<sup>1</sup>, e.g., that in a system held at  $500^\circ\text{C}$   $\text{HF}$  is capable of penetrating bulk Cu only to a depth of approximately  $0.004 \text{ mm d}^{-1}$ . However, the reaction between Cu powder and gaseous  $\text{HF}$  at  $500^\circ\text{C}$  is used<sup>2</sup> to prepare  $\text{CuF}_2$ . Copper cannot be effectively fluorinated using liq  $\text{HF}$  because such reactions can obviously only be attempted below the critical temperature of ca.  $225^\circ\text{C}$ .

Both metals also resist attack by gaseous hydrogen chloride. Cu only reacts at a reasonable rate with hydrogen chloride in a flow system  $> 800^\circ\text{C}$ , and then the product is  $\text{CuCl}$  rather than  $\text{CuCl}_2$ <sup>3,4</sup>.

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### 2.8.7.3. by Hydrohalic Acids.

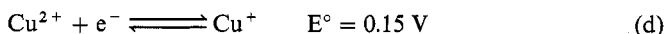
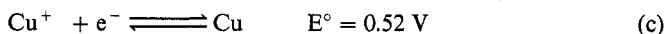
Gold is the most noble metal, not reacting with hydrohalic acids. It does, however, react with aq  $\text{HCl}$  or  $\text{HBr}$  in the presence of strong oxidizing agents such as  $\text{HNO}_3$ ,  $\text{OCl}^-$  or  $\text{Fe}^{3+}$ , to form  $[\text{AuCl}_4]^-$  or  $[\text{AuBr}_4]^-$  (see §2.8.4.1). Gold, however, shows no tendency to form stable species in the  $2+$  oxidation state in aqueous media<sup>1</sup> so need not be considered here. The formation of stable  $\text{Ag(II)}$  halides by reacting Ag with aqueous hydrohalic acids is also ruled out. Even allowing for the limited applicability of standard

potentials and their considerable variation when applied to real chemical situations, Ag(II) in aqueous systems should oxidize  $\text{H}_2\text{O}$ , being itself reduced<sup>2</sup>:



Silver(II) fluoride instantly reacts with water (see §2.8.7.1), liberating oxygen and even ozone<sup>3</sup>. Silver metal withstands chemical attack by 40% HF, even at the boiling point of the acid.

Copper is therefore the only metal of the group that needs further consideration. The standard potentials<sup>2</sup>:



indicate that Cu is also noble, standing above hydrogen in  $E^\circ$  value. However, this does not mean that Cu is incapable of liberating hydrogen gas and forming dihalides (apart from the iodide where the equilibrium  $2 \text{Cu}^+ \rightleftharpoons \text{Cu} + \text{Cu}^{2+}$  lies far to the left) on treatment with aqueous hydrohalic acid. Copper would be strictly noble if no attack occurred by an acid of normal activity containing noncoordinating anions, free from oxygen but saturated with hydrogen at  $101.3 \text{ kNm}^{-2}$  (1 atm) pressure and containing Cu ions at normal activity<sup>4</sup>. Thus if Cu is placed in pure dil HCl, free of  $\text{O}_2$  and  $\text{H}_2$ , it should displace a little  $\text{H}_2$  at first. However, as soon as the  $\text{H}_2$  and the  $\text{Cu}^+$  concentrations are such that the potential established for  $\text{H}_2 \rightleftharpoons 2 \text{H}^+ + 2 \text{e}^-$  equals that established for  $2 \text{Cu}^+ + 2 \text{e}^- \rightleftharpoons 2 \text{Cu}$ , the emf disappears and attack ceases. This occurs before the solution is saturated with hydrogen, so  $\text{H}_2$  is unlikely to be evolved. It is, therefore, only slightly imprecise to suggest that Cu is not attacked by dil HCl as long as air is excluded. However, if air or oxygen is allowed free access to the system the metal is rapidly attacked, giving a blue-green solution from which crystals of  $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$  may be isolated. Presumably the minute amounts of  $\text{Cu}^+$  present are constantly being oxidized, and so the two potentials mentioned above never reach a position of balance. Copper is similarly attacked by aqueous hydrofluoric acid as long as there is access of air or oxygen. The hydrate  $\text{CuF}_2 \cdot 2 \text{H}_2\text{O}$  can be crystallized from the solution.

Hydrogen is also liberated when Cu is treated with hot concentrated hydrochloric acid, or with aqueous hydrobromic or hydriodic acids, even in the absence of oxygen or air. In these systems attack occurs because of the formation of complex anions such as  $[\text{CuX}_2]^-$ ,  $[\text{CuX}_3]^{2-}$  or  $[\text{Cu}_2\text{X}_3]^-$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ). Once again  $\text{Cu}^+$  is removed as quickly as it is formed, thus the concentration of  $\text{Cu}^+$  is kept so low that the concentration of hydrogen becomes high enough for it to be evolved. These anions contain Cu in the 1+ oxidation state, and since this state is somewhat favored for  $\text{X} = \text{Br}$  and completely so for  $\text{X} = \text{I}$ ,  $\text{CuBr}$  or  $\text{CuI}$  can be obtained on dilution of solutions. However, in the presence of air or oxygen, the chlorocuprate(I) anions are readily oxidized and from such solutions  $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$  can be obtained.

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## 2.8.8. Synthesis of Group-IB Dihalides by Other Procedures

### 2.8.8.1. by Halogenation of Lower Valent Halides.

Silver(II) fluoride is prepared by fluorination of either AgF or AgCl in the range 150–250°C. External cooling may be necessary to control the reaction rate at first<sup>1,2</sup>. A useful alternative approach involves dissolving AgF in anhyd HF and passing in F<sub>2</sub> diluted with nitrogen<sup>3</sup>. Chlorine trifluoride has also been used to fluorinate AgF and AgCl e.g.; good yields of AgF<sub>2</sub> can be obtained by reacting AgF with ClF<sub>3</sub> at 100°C for > 1 d<sup>4</sup> or treating AgCl with ClF<sub>3</sub> at 250°C in a Monel metal apparatus<sup>5</sup>. Fluorination of AgCl or AgNO<sub>3</sub> using XeF<sub>2</sub>, F<sub>2</sub>, ClF<sub>5</sub> or ClF<sub>3</sub> is reported to give AgF<sub>x</sub> ( $\chi = 1.9\text{--}2.0$ )<sup>6,7</sup>.

Anhydrous CuF<sub>2</sub> has similarly been prepared by fluorination of Cu(I) halides, e.g., CuI at 100°C<sup>8</sup>, or CuCl in the range 100–550°C<sup>9</sup>. The reaction between CuCl and BrF<sub>3</sub> also affords CuF<sub>2</sub>, but impure<sup>10</sup>.

Cu(II) chloride and bromide can also be prepared by halogenation of the appropriate Cu(I) halide; e.g., a sealed-tube reaction between CuBr and P<sub>2</sub>O<sub>5</sub>-dried bromine using a temperature gradient between RT and 330°C affords black crystals of CuBr<sub>2</sub><sup>11</sup>. The mixed halides CuClBr and CuClI, which on x-ray evidence are not mixtures of CuCl<sub>2</sub> and CuX<sub>2</sub> (X = Br or I), have been prepared by reacting the halogen with CuCl<sup>12</sup>.

Anhydrous Cu(II) halides can also be prepared by halogen-exchange reactions. Thus reactions of anhyd CuCl<sub>2</sub> or CuBr<sub>2</sub> with F<sub>2</sub> or ClF<sub>3</sub> at < 500°C have been used to give CuF<sub>2</sub><sup>9,13,14</sup>; Cu(II) bromide has been prepared by the RT reaction:



The BCl<sub>3</sub> is easily eliminated (bp 12°C/760 mm), leaving CuBr<sub>2</sub><sup>15</sup>.

Finally, the black, air-sensitive halide Au<sub>4</sub>Cl<sub>8</sub> results from the reaction of the carbonyl halide Au(CO)Cl with Au<sub>2</sub>Cl<sub>6</sub> in a chlorinated solvent such as SOCl<sub>2</sub> under nitrogen. It is not a Au(II) halide, however, having equal numbers of square-planar Au(III) and linear Au(I) arrays linked alternatively into a cyclic chairlike Au<sub>4</sub>Cl<sub>8</sub> eight-atom ring<sup>16</sup>. This halide can also be prepared<sup>17</sup> from the RT reaction of Au<sub>2</sub>Cl<sub>6</sub> and CO (2:1 mol equiv) in SOCl<sub>2</sub> for 36 h.

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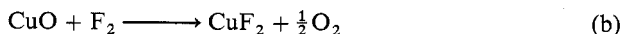
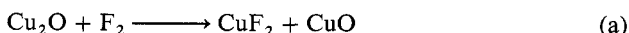
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### 2.8.8.2. by Halogenation of Metal Oxides.

The fluorination of Ag(I) oxide<sup>1</sup>, although not an important route, can be used to prepare AgF<sub>2</sub>. Fluorinations of the Ag(I) salts AgNO<sub>3</sub><sup>2,3</sup>, AgOCN<sup>4</sup> and AgCN<sup>5</sup> are also used.

**The latter takes place at RT with explosive violence, and the cyanide should be diluted with CaF<sub>2</sub> and the F<sub>2</sub> used under reduced pressure to moderate the reaction.** Many gaseous products are formed, such as CF<sub>3</sub>NF<sub>2</sub>, COF<sub>2</sub> and C<sub>2</sub>F<sub>6</sub>.

Both Cu<sub>2</sub>O and CuO react with F<sub>2</sub> to give CuF<sub>2</sub>, although these reactions are not of practical utility; e.g., Cu<sub>2</sub>O reacts at 325–500°C to give a mixture of CuO and CuF<sub>2</sub>, but only a 65% conversion of CuO to CuF<sub>2</sub> is achieved <500°C. The same report shows that fluorinations of Cu<sub>2</sub>S, CuS or even CuSO<sub>4</sub> are more effective methods<sup>6</sup>. The rate of the fluorination of spherical CuO powder at 82–151°C using fluorine pressures between 40 and 800 torr (5.0–107 kN m<sup>-2</sup>) is controlled by the diffusion of the reacting species through a spherical shell of CuF<sub>2</sub><sup>7</sup>. The kinetic data do not, however, allow identification of the diffusing species. In similar fashion, it is found<sup>8</sup> that the reaction of F<sub>2</sub> with Cu<sub>2</sub>O powders at 152–207°C using F<sub>2</sub> pressures between 50 and 800 torr (7–107 kN m<sup>-2</sup>) occurs by a two-step mechanism, the first of which obeys a linear kinetic law:



CuF<sub>2</sub> is also prepared by reacting CuO with ClF<sub>3</sub><sup>9</sup> and BrF<sub>3</sub><sup>10</sup>.

Other methods employed include the high-T reaction of CuO with S<sub>2</sub>Cl<sub>2</sub><sup>11</sup> and the bromination of Cu<sub>2</sub>O<sup>12</sup>.

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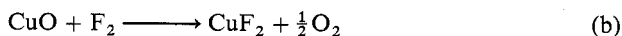
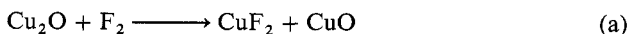
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Both Cu<sub>2</sub>O and CuO react with F<sub>2</sub> to give CuF<sub>2</sub>, although these reactions are not of practical utility; e.g., Cu<sub>2</sub>O reacts at 325–500°C to give a mixture of CuO and CuF<sub>2</sub>, but only a 65% conversion of CuO to CuF<sub>2</sub> is achieved <500°C. The same report shows that fluorinations of Cu<sub>2</sub>S, CuS or even CuSO<sub>4</sub> are more effective methods<sup>6</sup>. The rate of the fluorination of spherical CuO powder at 82–151°C using fluorine pressures between 40 and 800 torr (5.0–107 kN m<sup>-2</sup>) is controlled by the diffusion of the reacting species through a spherical shell of CuF<sub>2</sub><sup>7</sup>. The kinetic data do not, however, allow identification of the diffusing species. In similar fashion, it is found<sup>8</sup> that the reaction of F<sub>2</sub> with Cu<sub>2</sub>O powders at 152–207°C using F<sub>2</sub> pressures between 50 and 800 torr (7–107 kN m<sup>-2</sup>) occurs by a two-step mechanism, the first of which obeys a linear kinetic law:



CuF<sub>2</sub> is also prepared by reacting CuO with ClF<sub>3</sub><sup>9</sup> and BrF<sub>3</sub><sup>10</sup>.

Other methods employed include the high-T reaction of CuO with S<sub>2</sub>Cl<sub>2</sub><sup>11</sup> and the bromination of Cu<sub>2</sub>O<sup>12</sup>.

(D.A. EDWARDS)

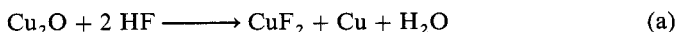
1. E. Gruner, W. Klemm, *Naturwissenschaften*, **25**, 59 (1937).
2. O. Ruff, M. Giese, *Z. Anorg. Allg. Chem.*, **219**, 143 (1934).
3. O. Glemser, H. Richert, *Z. Anorg. Allg. Chem.*, **307**, 313 (1961).
4. A. Ya. Yakubovich, M. A. Englin, S. P. Makarov, *Zh. Obshch. Khim.*, **30**, 2374 (1960); *Chem. Abstr.*, **55**, 17,336c (1961).
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6. H. M. Haendler, L. H. Towle, E. F. Bennett, W. L. Patterson, *J. Am. Chem. Soc.*, **76**, 2178 (1954).
7. R. L. Ritter, H. A. Smith, *J. Phys. Chem.*, **70**, 805 (1966).
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9. J. M. Crabtree, C. S. Lees, K. Little, *J. Inorg. Nucl. Chem.*, **1**, 213 (1955).
10. H. J. Emeléus, A. A. Woolf, *J. Chem. Soc.*, 164 (1950).

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### 2.8.8.3. by Reactions of Metal Oxides with Hydrohalic Acids.

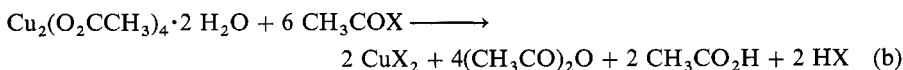
Silver(II) will be reduced in aqueous media so reactions of Ag oxides with hydrohalic acids lead to Ag(I) halides (see §2.8.7.3). Only Cu, therefore, is considered here.

Blue crystals of  $\text{CuF}_2 \cdot 2 \text{H}_2\text{O}$  may be prepared by dissolving CuO in the minimum quantity of 40 % aq HF and evaporating the solution to low bulk at  $\sim 70^\circ\text{C}$ . The product can be recrystallized from dil HF <sup>1</sup>. Copper(I) oxide reacts with aq HF by disproportionation:



As expected, CuO also reacts with aq HCl or HBr to give the hydrates, green  $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$  and olive-green  $\text{CuBr}_2 \cdot 4 \text{H}_2\text{O}$  <sup>2</sup>. The three hydrates can be prepared by action of aq HX (X = F, Cl or Br) on  $\text{Cu}[\text{OH}]_2$ ,  $\text{CuCO}_3$  or basic carbonates such as malachite  $\text{Cu}_2[\text{OH}]_2\text{CO}_3$  or azurite  $\text{Cu}_3[\text{OH}]_2[\text{CO}_3]_2$  <sup>2</sup>.

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where X = Cl, Br.

Use of acetyl iodide, however, leads to Cu(I) iodide.

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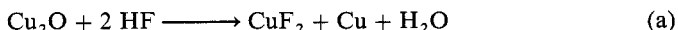
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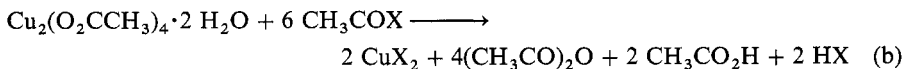
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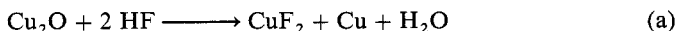
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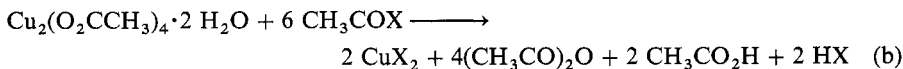
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Thermal decomposition of the hydrates as a method of preparing the anhydrous halides is considered first:  $\text{CuF}_2$  cannot be prepared in this manner for at  $\sim 130^\circ\text{C}$   $\text{CuF}_2 \cdot 2 \text{H}_2\text{O}$  is converted into the basic salt  $\text{Cu}(\text{OH})\text{F} \cdot \text{CuF}_2$ , which decomposes at  $\sim 400^\circ\text{C}$  leaving a mixture of  $\text{CuO}$  and  $\text{CuF}_2$ <sup>3-5</sup>. The dihydrate of  $\text{Cu}(\text{II})$  chloride can be dehydrated to the yellow-brown anhydrous salt by heating in air at  $\sim 200^\circ\text{C}$ . However, at higher T decomposition to  $\text{CuCl}$  may occur and both chlorides oxidize to leave  $\text{CuO}$ <sup>5</sup>. The high-vacuum dehydration of  $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$  at  $100^\circ\text{C}$  is a superior method<sup>6</sup>. The hydrates of  $\text{Cu}(\text{II})$  bromide lose water on heating but this is not a recommended method for preparing  $\text{CuBr}_2$  because at moderate T the anhydrous bromide loses bromine, leaving  $\text{CuBr}$ .

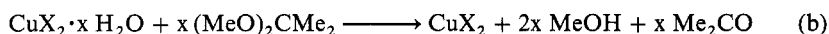
A method applicable to all the hydrated  $\text{Cu}(\text{II})$  dihalides is dehydration in a stream of dry hydrogen halide gas at elevated T. The passage of  $\text{HF}$  gas at  $400^\circ\text{C}$  over  $\text{CuF}_2 \cdot 2 \text{H}_2\text{O}$  in  $\text{Cu}$  or  $\text{Ni}$  apparatus is recommended for the preparation of  $\text{CuF}_2$ <sup>7</sup>, and dehydration of  $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$  may be carried out<sup>6</sup> in  $\text{HCl}$  gas at  $150^\circ\text{C}$ .

Thionyl chloride is often used for dehydrating  $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$ <sup>8-10</sup>:

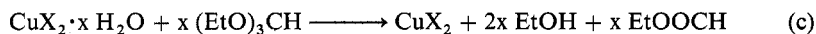


Although some workers recommend the use of freshly distilled, refluxing  $\text{SOCl}_2$ , the dehydration proceeds rapidly at RT. No precautions against the presence of moisture or air are necessary, the apparatus used is simple and the byproducts are gaseous. Thionyl chloride cannot be used for dehydrating halides other than chlorides because of the risk of halogen exchange.

Two organic reagents not limited to chloride systems, 2,2-dimethoxypropane<sup>11</sup> and triethylorthoformate<sup>12</sup>, are effective in giving anhyd  $\text{CuCl}_2$  and  $\text{CuBr}_2$  from their hydrates:



where  $\text{X} = \text{Cl}$  or  $\text{Br}$ ;



where  $\text{X} = \text{Cl}$  or  $\text{Br}$ . The  $\text{Cu}(\text{II})$  halides are initially obtained as alcoholates from these reactions, but such complexes easily lose these weakly bonded ligands on gentle warming, especially in vacuum.

(D.A. EDWARDS)

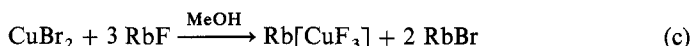
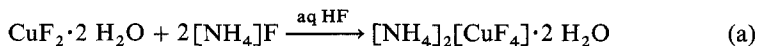
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- 120 2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond  
 2.8.10. Synthesis of Complex Halides from the Dihalides of Group-IB

### 2.8.10. Synthesis of Complex Halides Derived from the Dihalides of Group-IB

Halocuprates(II), particularly chlorides, possessing a wide variety of stoichiometries and structures have been characterized<sup>1</sup>. It is not appropriate to discuss the structural types here, but compounds whose solid state structures<sup>2</sup> are well established have been selected to illustrate the synthetic methods available. Fluoroargentates(II) are also discussed.

Fluorocuprates(II)<sup>2</sup> are usually prepared by reactions in solution, e.g.:



As a result of variable and random  $\text{OH}^-/\text{F}^-$  isomorphous substitution the distorted perovskite,  $\text{K}[\text{CuF}_3]$  is difficult to obtain pure<sup>3</sup>. Preparations in MeOH are best carried out in the absence of water, otherwise  $\text{Cu}[\text{OH}]\text{F}$  forms<sup>4</sup>. Pure  $\text{K}[\text{CuF}_3]$  results<sup>5</sup> from the reaction of  $\text{Cu}(\text{OH})_2$  with  $\text{KHF}_2$  (1:2) and a small amount of 40% aq HF at  $\text{pH} \leq 4$ . Solid-state reactions have also been employed; e.g., heating MF or  $\text{MHF}_2$  [M = alkali metal or Tl(I)] with  $\text{CuF}_2$  in vacuo or under  $\text{N}_2$  gives either  $\text{M}[\text{CuF}_3]$  or  $\text{M}_2[\text{CuF}_4]$  complexes. The latter are rare examples of tetragonally compressed octahedral species<sup>6</sup>. The complexes  $[\text{NH}_4][\text{CuF}_3]$  and  $[\text{NH}_4]_2[\text{CuF}_4]$  have been prepared by subjecting intimate mixtures of  $[\text{NH}_4]\text{F}$  and  $\text{CuF}_2$  to high pressures<sup>7</sup>. High-T reactions produce fluoro complexes of other stoichiometries; e.g., (i) a  $\text{BaF}_2\text{-CuF}_2$  melt at  $1100^\circ\text{C}$  gives<sup>8</sup>  $\text{Ba}_2[\text{CuF}_6]$  containing tetragonally distorted  $[\text{CuF}_6]^{4-}$  octahedra; (ii)  $\text{KF}$  and  $\text{CuF}$  (3:2 molar) at  $800\text{--}850^\circ\text{C}$  in an evacuated Pt ampule give<sup>9</sup>  $\text{K}_3[\text{Cu}_2\text{F}_7]$ ; (iii) annealing  $\text{C}_3\text{F}$  and  $\text{CuF}_2$  under Ar in a Au tube for 190 d at  $630^\circ\text{C}$  gives<sup>10</sup>  $\text{Cs}_4[\text{Cu}_3\text{F}_{10}]$ , whereas an analogous net action at  $760^\circ\text{C}$  gives<sup>11</sup>  $\text{Cs}_7[\text{Cu}_6\text{F}_{19}]$ .

The methods available for the synthesis of chlorocuprates(II) are summarized in Table 1. The range of stoichiometries is remarkable, and types other than those listed are known. A brief description of the structure of each anion is given in the table in order to highlight the impossibility of relating structure to stoichiometry without adequate physical evidence. The preparations are straightforward, usually involving crystallization from aqueous or alcoholic solutions. Fusion of reactants in the absence of solvent can be employed, e.g., in the preparation of  $\text{Cs}[\text{CuCl}_3]$ ,  $\text{Cs}_2[\text{CuCl}_4]$ ,  $\text{Ag}[\text{CuCl}_3]$ <sup>12</sup>,  $\text{NH}_4[\text{CuCl}_3]$  and  $\text{NH}_4[\text{CuCl}_4]$ <sup>13</sup>.

A smaller variety of bromocuprate(II) stoichiometries and structures are known. They can be prepared by similar routes to their chloroanalogs:



where M = e.g.,  $\text{MeNH}_3$ ,  $\text{EtNH}_3$ ,  $\text{Et}_4\text{N}$ , piperidinium;

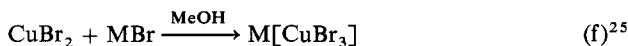




TABLE 1. SYNTHESIS OF CHLOROCUPRATES(II) FROM SOLUTION

Reactants	Solvent	Product	Structure of anion	Ref.
$\text{CuCl}_2, 2 \text{H}_2\text{O} + \text{KCl} \quad (2:1)$	Aq HCl	$\text{KCuCl}_3$	$[\text{Cu}_2\text{Cl}_6]^{2-}$ stacked to form distorted octahedral chains	14
$\text{CuCl}_2 + \text{CsCl} \quad (1:2)$	$\text{H}_2\text{O}$	$\text{Cs}_2\text{CuCl}_4$	Flattened tetrahedral	15
$\text{CuCl}_2 + \text{CsCl} \quad (2:1)$	$\text{H}_2\text{O}$	$\text{CsCuCl}_3$	Infinite distorted octahedral chains; face sharing	16
$\text{CuCl}_2 + \text{RbCl} \quad (2:3)$	MeOH	$\text{Rb}_3\text{Cu}_2\text{Cl}_7$	Corner-shared elongated octahedra	17
$\text{CuCl}_2 + \text{M}(\text{NH}_3)_6\text{Cl}_3 \quad (1:1)$	Aq HCl	$[\text{M}(\text{NH}_3)_6][\text{CuCl}_5]^\text{a}$	Trigonal bipyramidal	18
$\text{CuCl}_2 + \text{Co}(\text{en})_3\text{Cl}_3 \quad (1:1)$	Aq HCl	$[\text{Co}(\text{en})_3]_2[\text{Cu}_2\text{Cl}_8]\text{Cl}_2$	Two trigonal bipyramids fused along an equatorial axial edge	19
$\text{CuCl}_2 + \text{amine HCl} \quad (1:2)$	$\text{H}_2\text{O}, \text{MeOH}$ or EtOH	$[\text{amine H}]_2\text{CuCl}_4^\text{b}$		20-22
$\text{CuCl}_2 + \text{Me}_3\text{NHCl} \quad (5:1)$	n-PrOH	$[\text{Me}_3\text{NH}]_2\text{Cu}_4\text{Cl}_{10}$	Bibridged tetramer	23
$\text{CuCl}_2, 2 \text{H}_2\text{O} + [\text{AEPH}_3]\text{Cl}_3 \quad (1:1)$	MeOH	$[\text{AEPH}_3]\text{CuCl}_5, 2 \text{H}_2\text{O}^\text{d}$	Square pyramidal	24
$\text{CuCl}_2 + \text{Ph}_4\text{PCl} \quad (1:1)$	$\text{H}_2\text{O}$ or EtOH	$[\text{Ph}_4\text{P}]\text{CuCl}_3$	$[\text{Cu}_2\text{Cl}_6]^{2-}$ units	25, 26
$\text{CuCl}_2 + \text{Et}_4\text{NCl} \quad (1:1)$	n-Pr-OH, 12 mol $\text{L}^{-1}$ HCl	$[\text{Et}_4\text{N}]_4[\text{Cu}_4\text{Cl}_{12}]$	Chain of two inner distorted trigonal bipyramids and two outer distorted tetrahedra	27
$\text{CuCl}_2 \cdot 2 \text{H}_2\text{O} + [\text{pipzH}_2]\text{Cl}_2^\text{e} \quad (4:1)$	Conc HCl	$[\text{pipzH}_2][\text{Cu}_2\text{Cl}_6]^\text{e}$	Infinite chain of $[\text{Cu}_2\text{Cl}_6]^{2-}$ dimers	28

<sup>a</sup>  $\text{M} = \text{Co}^{3+}, \text{Cr}^{3+}, \text{Rb}^{3+}, \text{Ru}^{3+}$ .

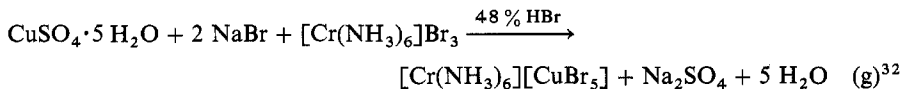
<sup>b</sup> amine = e.g.,  $\text{RNH}_2$  ( $\text{R} = \text{Me}, \text{Et}, \text{n-Pr}, \text{i-Pr}, \text{Ph}$ ),  $\text{Me}_2\text{NH}$ ,  $\text{Me}_3\text{N}$ .

<sup>c</sup> Various types, e.g.,  $[\text{PhCH}_2\text{CH}_2\text{NH}(\text{Me})\text{H}]_2\text{CuCl}_4$  is square planar at  $25^\circ\text{C}$  but distorted tetrahedral at  $90^\circ\text{C}$ .

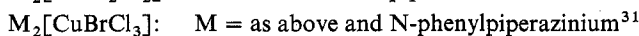
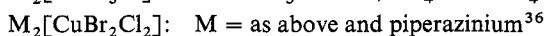
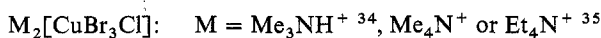
<sup>d</sup>  $\text{AEPH}_3 = \text{N-(2-aminomethyl)piperazinium}$ .

<sup>e</sup>  $\text{pipzH}_2 = \text{piperazinium}$ .

where  $M = \text{Ph}_4\text{P}, \text{Ph}_4\text{Sb}, \text{PrPh}_3\text{P};$

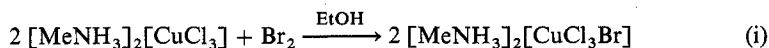


Examples involving mixed haloanions are prepared by reacting the correct molar proportions of either  $\text{CuCl}_2$  with an amine hydrobromide or  $\text{CuBr}_2$  with an amine hydrochloride in MeOH or EtOH:



The trigonal-bipyramidal  $[\text{CuBr}_3\text{Cl}_2]^{3-}$  has been isolated as the  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  salt by reacting  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  with  $[\text{Cr}(\text{NH}_3)_6]\text{Br}_3$  in an aq HCl-HBr mixture<sup>32</sup>.

Halocuprates(II) are synthesized by oxidative methods. In anhyd MeOH, CuBr reacts with  $\text{NH}_4\text{F}$  in the presence of dry  $\text{O}_2$  gas, producing a precipitate of  $\text{NH}_4[\text{CuF}_3]$  and liberating  $\text{NH}_3$ <sup>38</sup>. Electrochemical oxidation of a Cu anode in a cell containing a platinum cathode and an electrolyte of  $[\text{Et}_4\text{N}]\text{Br}$  and  $\text{Br}_2$  in  $\text{C}_6\text{H}_6$ -MeOH is a route to  $[\text{Et}_4\text{N}]_2\text{CuBr}_4$ <sup>39</sup>. Mixed halide complexes are prepared by halogen oxidation of halocuprate(I) anions<sup>40</sup> e.g.:



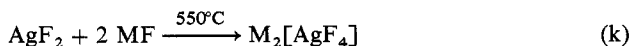
Fluoroargentates(II) must be synthesized by dry methods because of their powerful oxidizing or fluorinating ability toward a range of solvents. Three types are known:

1. Those containing square-planar  $[\text{AgF}_4]^{2-}$
2. Those containing polymeric  $[\text{AgF}_3]_n^{n-}$  in a perovskite structure
3.  $\text{Ba}_2[\text{AgF}_6]$

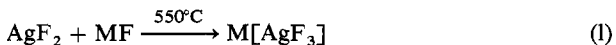
Two preparative methods have been employed, either fluorination of silver sulfate-group-II metal carbonate mixtures<sup>41</sup>, or heating  $\text{AgF}_2$ -alkali-metal fluoride mixtures<sup>42,43</sup>. The compounds isolated are:



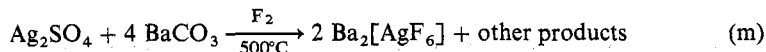
where  $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Cd}, \text{Hg};$



where  $\text{M} = \text{K}, \text{Rb}, \text{Cs};$



where M = K, Rb, Cs;



A novel route to  $\text{NO}[\text{AgF}_3]$  is the RT reaction of  $\text{AgF}_3$  with liq NOF in metal apparatus<sup>44</sup>.

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- 124 2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond  
 2.8.11. Synthesis of Group-IB Monohalides  
 2.8.11.1. by Halogenation of the Metals.

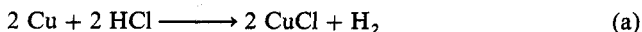
## 2.8.11. Synthesis of Group-IB Monohalides

The monohalides form the largest group for a single oxidation state of the group-IB metals. The known compounds are CuX (X = Cl, Br and I), AgX (X = F, Cl, Br and I) and AuX (X = Cl, Br and I).

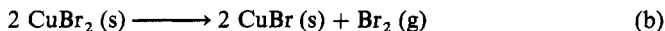
### 2.8.11.1. by Halogenation of the Metals.

Each of the monohalides listed in §2.8.11 may, given the correct experimental conditions, be synthesized by direct reaction of the metal with a halogen. However, this is rarely the method of choice.

Copper(I) halides are normally prepared by reducing aq Cu<sup>2+</sup> soln (see §2.8.11.2). Should CuCl or CuBr be prepared by halogenation of the metal, care is required to ensure that the reaction T is high enough to prevent dihalide formation (see §2.8.7.1). Although, in principle, CuCl can be prepared by reacting Cu with Cl<sub>2</sub> at ~1000°C, at which T CuCl<sub>2</sub> is unstable with respect to CuCl and Cl<sub>2</sub>, the usual high-T method is the reaction of the metal with HCl gas at 800–1000°C in a quartz flow system<sup>1,2</sup>:



Burning Cu foil in Br<sub>2</sub> vapor is used to prepare CuBr, any CuBr<sub>2</sub> being decomposed by subsequently heating the product at 300°C in vacuo<sup>3</sup>. Alternatively, the reaction may be carried out in a sealed tube using a T gradient between 20 and 450°C. Under these conditions the bromine partial pressure exceeds the equilibrium pressure over CuBr and CuBr<sub>2</sub>, so the latter is not produced<sup>2</sup>. In the decomposition:



the equilibrium pressure reaches 1 atm (101.3 kN m<sup>-2</sup>) at ~250°C<sup>4</sup>.

Copper(I) iodide may be prepared by heating Cu with I<sub>2</sub> in an evacuated tube at ~450°C<sup>2,3</sup>. The Cu(I) halides may be purified by sublimation over freshly reduced Cu gauze in an evacuated tube. Alternately, CuCl and CuBr can be distilled or sublimed at high T under dynamic vacuum; CuI can also be distilled, but cocondensation of iodine can be a problem. A final purification step is zone refining<sup>5</sup>.

Reaction of Cu with molten IBr<sup>6</sup> or electrochemical oxidation of a Cu anode in the presence of Br<sub>2</sub> in MeOH–C<sub>6</sub>H<sub>6</sub><sup>7</sup> (see §2.8.7.1) is also used to prepare CuBr. When heated with NH<sub>4</sub>Cl to 100°C and above, Cu affords<sup>8</sup> CuCl. A common method for producing Cu(I) halides involves reacting Cu with boiling aqueous hydrohalic acid. With HCl or HBr, soluble Cu(I) complex anions (see §2.8.12) form; they decompose on addition of H<sub>2</sub>O, precipitating CuCl or CuBr. With HI, CuI precipitates directly.

Although the Ag(I) halides can be prepared by halogenation of the metal using halogen or HX at high T<sup>9</sup>, much of the interest in such systems is concerned with corrosion processes. Fluorination of Ag produces AgF<sub>2</sub> (see §2.8.7.1), although if the F<sub>2</sub> is subsequently replaced by flowing CH<sub>4</sub> or C<sub>2</sub>H<sub>6</sub> at ~200°C the final product is AgF<sup>10</sup>. Direct fluorination of finely divided Ag at RT using a 1:10 mixture of F<sub>2</sub> with N<sub>2</sub> produces<sup>11</sup> AgF.

The classical analytical methods for the estimation of Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> involve precipitation of insoluble Ag halides from aqueous solution (solubilities in water at 25°C

in  $\text{mg L}^{-1}$ : AgCl, 30; AgBr, 5.5; AgI; 0.05) Ag(I) fluoride is soluble in water ( $18 \times 10^5 \text{ mg L}^{-1}$  at  $25^\circ\text{C}$ ) and so cannot be prepared by precipitation. The salts AgCl, AgBr and AgI are therefore usually prepared by metathesis, between, for example,  $\text{AgNO}_3$  and a sodium or potassium halide solution. The well-known light sensitivity of the Ag(I) halides and their consequent importance in photography has generated a vast literature on their precipitation and properties. The HT cubic form of AgI also displays high ionic conductivity as a result of the mobility of  $\text{Ag}^+$  ions. Much work has therefore been published on its use as a solid electrolyte.

Au(I) disproportionates in aqueous solution:



unless the compound has low solubility or is strongly complexed, so there is no possibility of precipitating Au(I) halides in the manner in which Ag(I) halides are formed.

The thermodynamics of the Au-Cl<sub>2</sub> system (see §2.8.3.1.1) show that with a Cl<sub>2</sub> pressure of 760 torr ( $101 \text{ kN m}^{-2}$ ) solid AuCl is formed between 254 and  $282^\circ\text{C}$ , together with gaseous Au<sub>2</sub>Cl<sub>6</sub>. In principle, therefore, it should be possible to prepare AuCl by chlorination of Au. It is not a useful method, however, for  $<254^\circ\text{C}$  Au<sub>2</sub>Cl<sub>6</sub> is the sole product, yet above  $300^\circ\text{C}$  rapid decomposition to the metal occurs. A similar situation exists for the Au-Br<sub>2</sub> system, so both AuCl and AuBr are better synthesized by thermal decomposition of the trihalides (see §2.8.11.2). Since AuI<sub>3</sub> is unknown, AuI can be prepared by iodination of the metal at  $120^\circ\text{C}$  in a sealed tube to give light yellow crystals<sup>12</sup>.

Ag(I) fluoride is usually prepared by reacting Ag<sub>2</sub>O or Ag<sub>2</sub>CO<sub>3</sub> with 20–40% HF<sup>13</sup>. Evaporation and drying in the absence of light leaves  $\text{AgF} \cdot 4 \text{ H}_2\text{O}$ ; which  $>18.7^\circ\text{C}$  loses water to give  $\text{AgF} \cdot 2 \text{ H}_2\text{O}$ . The anhydrous fluoride can be obtained by heating either hydrate in a stream of HF gas.

Silver(I) oxide is much more reactive toward halogens and halides than is the metal, reacting with F<sub>2</sub>, Br<sub>2</sub>, or aqueous hydrohalic acids at RT to give Ag(I) halides.

when a conc soln of AgF, obtained by dissolving Ag<sub>2</sub>O in conc aq HF, is saturated with AgI at 323 K, crystals of the moisture- and light-sensitive mixed halides Ag<sub>2</sub>IF $\cdot$ H<sub>2</sub>O and Ag<sub>7</sub>I<sub>2</sub>F<sub>5</sub> $\cdot$ 2½ H<sub>2</sub>O are deposited. They decompose in air, leaving AgF and AgI<sup>14,15</sup>.

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- 126 2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond  
 2.8.11. Synthesis of Group-IB Monohalides  
 2.8.11.2. by Reduction of Higher Valent Halides.

### 2.8.11.2. by Reduction of Higher Valent Halides.

The reductions fall into two categories: (i) the formation of Cu(I) and Au(I) chlorides and bromides by thermal decomposition of higher halides and (ii) the synthesis of Cu(I) halides by reduction of aq Cu(II) solutions.

(i) Thermal decompositions. When heated  $> 300^{\circ}\text{C}$   $\text{CuCl}_2$  loses  $\text{Cl}_2$  to give  $\text{CuCl}$ , which in the presence of air is oxidized to  $\text{CuO}$ <sup>1,2</sup>. Loss of  $\text{Br}_2$  from  $\text{CuBr}_2$   $> 150^{\circ}\text{C}$  similarly yields  $\gamma\text{-CuBr}$  which  $> 425^{\circ}\text{C}$  in air gives  $\text{CuO}$ <sup>1-4</sup>.

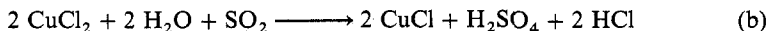
Pyrolysis of  $\text{Au}_2\text{Cl}_6$  gives  $\text{AuCl}$ , which decomposes into the metal and  $\text{Cl}_2$   $> 200^{\circ}\text{C}$ . The conditions producing the best yields of  $\text{AuCl}$  are debatable, heating at  $160$  or  $185^{\circ}\text{C}$  in air<sup>5,6</sup>,  $175^{\circ}\text{C}$ <sup>5</sup> or  $235^{\circ}\text{C}$ <sup>7</sup> in a stream of  $\text{HCl}$  gas or  $95^{\circ}\text{C}$  in  $\text{N}_2$ <sup>8</sup> having been proposed. Crystalline  $\text{AuCl}$  has been prepared by vapor transport of  $\text{Au}_2\text{Cl}_6$  under an atmosphere of  $\text{Cl}_2$ . The  $\text{Au}_2\text{Cl}_6$  at one end of a quartz tube is heated to  $247^{\circ}\text{C}$  and  $\text{AuCl}$  is deposited at the other end of the tube held at  $272^{\circ}\text{C}$ <sup>9</sup>. Thermal decomposition of  $\text{Au}_2\text{Br}_6$  in a stream of argon at  $100^{\circ}\text{C}$ <sup>7</sup> or in air at  $200^{\circ}\text{C}$ <sup>8</sup> yields  $\text{AuBr}$ .

(ii) Aqueous Methods. Although  $\text{AuCl}$  and  $\text{AuBr}$  disproportionate in aqueous media,  $\text{AuI}$  can be obtained by reduction of  $\text{H}[\text{AuCl}_4] \cdot 4 \text{H}_2\text{O}$  using aqueous iodide, presumably because of its low solubility<sup>8</sup>.

Only low concentrations of  $\text{Cu}^+$  ( $< 10^{-2} \text{ mol L}^{-1}$ ) can exist in aq  $\text{Cu}$  soln. Although the equilibrium:

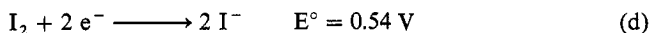
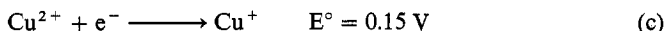


lies to the right for Cu(I) salts such as the sulfate, which, therefore, disproportionates in water, it can be displaced in favor of Cu(I) for insoluble salts. Copper(I) halides provide such examples, their solubilities at  $25^{\circ}\text{C}$  being  $\text{CuCl}$ ,  $110 \text{ mg L}^{-1}$ ;  $\text{CuBr}$ , 29;  $\text{CuI}$ , 0.42. So the addition of a suitable reducing agent to aq  $\text{CuCl}_2$  or  $\text{CuBr}_2$ , or more commonly  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  in the presence of  $\text{Cl}^-$  or  $\text{Br}^-$ , effects precipitation of the Cu(I) halide<sup>10,11</sup>. Favored reducing agents are Cu metal,  $\text{SO}_2$  or  $[\text{SO}_3]^{2-}$ :

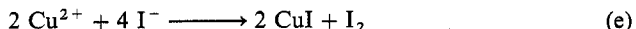


The use of  $\text{SO}_2$  as reducing agent can produce S contamination, causing point defects that change the intrinsic colors of  $\text{CuCl}$  and  $\text{CuBr}$  even at very low concentrations<sup>12</sup>. Other reducing agents used include  $\text{SnCl}_2$ ,  $\text{N}_2\text{H}_4$ ,  $\text{NH}_2\text{OH}$ ,  $\text{Zn}$ ,  $\text{Al}$ ,  $[\text{S}_2\text{O}_4]^{2-}$  and ascorbic acid.

Copper(I) iodide may similarly be prepared by the addition of  $\text{I}^-$  to an aq  $\text{Cu}^{2+}$  solution, but no additional reducing agent is required. Despite the relative standard potentials:



iodide ion is oxidized by  $\text{Cu}^{2+}$ , because of the insolubility of  $\text{CuI}$ <sup>10,13,14</sup>:



The reaction of  $\text{CuO}$  with hydriodic acid follows the same path. Although  $\text{CuI}_2$  may initially be formed in these reactions, it immediately suffers an internal redox reaction.

The reactions of  $\text{Cu}_2(\text{O}_2\text{CMe})_4$  with either  $\text{CH}_3\text{COI}$ <sup>2</sup> or  $\text{I}_2$  in acetone<sup>15</sup> also afford  $\text{CuI}$ . Both reactions are carried out in anhydrous acetic acid. The addition of  $\text{CH}_3\text{COCl}$

or  $\text{CH}_3\text{COBr}$  to a boiling solution of  $\text{Cu}_2(\text{O}_2\text{CMe})_4$  in an acetic acid-acetic anhydride mixture similarly leads to  $\text{CuCl}$  or  $\text{CuBr}$ , respectively<sup>2</sup>.

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## 2.8.12. Synthesis of Complex Halides Derived from Monohalides of Group-IB

Although no fluorometallate(I) anions are known for these metals and the haloaurates(I) are invariably linear  $[\text{AuX}_2]^-$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ), the structures and stoichiometries of the halocuprates(I) and haloargentates(I) range from simple mononuclear species, e.g.,  $[\text{MX}_2]^-$  ( $\text{M} = \text{Cu}, \text{Ag}; \text{X} = \text{Cl}, \text{Br}, \text{I}$ ), to highly complex ones, e.g.,  $[\text{Cu}_{36}\text{I}_{56}]^{20-}$ . The stoichiometries of a majority of the halocuprates(I) and haloargentates(II) fall into two major types,  $[\text{M}_n\text{X}_{n+1}]^-$  and  $[\text{M}_n\text{X}_{n+2}]^{2-}$ , examples containing five or fewer metal atoms being listed in Table 1. The stoichiometries, however, do not indicate the structural nature of the anions; many of the isolated solid compounds contain polynuclear anions

TABLE 1. STOICHIOMETRIES OF SOME HALOMETALLATE(I) ANIONS<sup>a</sup>

$[\text{M}_n\text{X}_{n+1}]^-$ type:	
$[\text{MX}_2]^-$	$\text{M} = \text{Cu}, \text{Ag}, \text{Au}; \text{X} = \text{Cl}, \text{Br}, \text{I}$
$[\text{M}_2\text{X}_3]^-$	$\text{M} = \text{Cu}, \text{Ag}; \text{X} = \text{Cl}, \text{Br}, \text{I}$
$[\text{M}_3\text{X}_4]^-$	$\text{M} = \text{Cu}, \text{X} = \text{Cl}, \text{I}; \text{M} = \text{Ag}, \text{X} = \text{I}$
$[\text{M}_4\text{X}_5]^-$	$[\text{Cu}_4\text{Cl}_3\text{I}_2]^-$ , $[\text{Ag}_4\text{I}_5]^-$
$[\text{M}_5\text{X}_6]^-$	$[\text{Ag}_5\text{I}_6]^-$
$[\text{M}_n\text{X}_{n+2}]^{2-}$ type:	
$[\text{MX}_3]^{2-}$	$\text{M} = \text{Cu}, \text{X} = \text{Cl}, \text{Br}, \text{I}; \text{M} = \text{Ag}, \text{X} = \text{I}$
$[\text{M}_2\text{X}_4]^{2-}$	$\text{M} = \text{Cu}, \text{X} = \text{Br}, \text{I}; \text{M} = \text{Ag}, \text{X} = \text{Cl}, \text{Br}$
$[\text{M}_3\text{X}_5]^{2-}$	$[\text{Cu}_3\text{Cl}_5]^{2-}$ , $[\text{Ag}_3\text{Br}_5]^{2-}$
$[\text{M}_4\text{X}_6]^{2-}$	$\text{M} = \text{Cu}, \text{X} = \text{Br}, \text{I}$
$[\text{M}_5\text{X}_7]^{2-}$	$\text{M} = \text{Cu}, \text{X} = \text{Br}, \text{I}$

<sup>a</sup> Up to five metal atoms only.

## 2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond 127

## 2.8.12. Synthesis of Complex Halides from Monohalides of Group-IB

or  $\text{CH}_3\text{COBr}$  to a boiling solution of  $\text{Cu}_2(\text{O}_2\text{CMe})_4$  in an acetic acid-acetic anhydride mixture similarly leads to  $\text{CuCl}$  or  $\text{CuBr}$ , respectively<sup>2</sup>.

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$[\text{M}_n\text{X}_{n+1}]^-$ type:	
$[\text{MX}_2]^-$	$\text{M} = \text{Cu}, \text{Ag}, \text{Au}; \text{X} = \text{Cl}, \text{Br}, \text{I}$
$[\text{M}_2\text{X}_3]^-$	$\text{M} = \text{Cu}, \text{Ag}; \text{X} = \text{Cl}, \text{Br}, \text{I}$
$[\text{M}_3\text{X}_4]^-$	$\text{M} = \text{Cu}, \text{X} = \text{Cl}, \text{I}; \text{M} = \text{Ag}, \text{X} = \text{I}$
$[\text{M}_4\text{X}_5]^-$	$[\text{Cu}_4\text{Cl}_3\text{I}_2]^-$ , $[\text{Ag}_4\text{I}_5]^-$
$[\text{M}_5\text{X}_6]^-$	$[\text{Ag}_5\text{I}_6]^-$
$[\text{M}_n\text{X}_{n+2}]^{2-}$ type:	
$[\text{MX}_3]^{2-}$	$\text{M} = \text{Cu}, \text{X} = \text{Cl}, \text{Br}, \text{I}; \text{M} = \text{Ag}, \text{X} = \text{I}$
$[\text{M}_2\text{X}_4]^{2-}$	$\text{M} = \text{Cu}, \text{X} = \text{Br}, \text{I}; \text{M} = \text{Ag}, \text{X} = \text{Cl}, \text{Br}$
$[\text{M}_3\text{X}_5]^{2-}$	$[\text{Cu}_3\text{Cl}_5]^{2-}$ , $[\text{Ag}_3\text{Br}_5]^{2-}$
$[\text{M}_4\text{X}_6]^{2-}$	$\text{M} = \text{Cu}, \text{X} = \text{Br}, \text{I}$
$[\text{M}_5\text{X}_7]^{2-}$	$\text{M} = \text{Cu}, \text{X} = \text{Br}, \text{I}$

<sup>a</sup> Up to five metal atoms only.



constructed by sharing of  $\text{MX}_4$  tetrahedra in various ways. In general, the coordination of Cu(I) or Ag(I) increases with decreasing size of the cation, the geometry of the anion in the crystalline state being determined by the degree of dilution imposed on the halide ligands by the cations<sup>1,2</sup>. For example, in  $[\text{Cu}(\text{NH}_3)_4][\text{CuCl}_2]_2$ <sup>3</sup>,  $[\text{Ni}(\text{en})_2][\text{AgBr}_2]_2$ <sup>4</sup>,  $[\text{Me}_4\text{N}][\text{AgX}_2]$  ( $\text{X} = \text{Cl}$ <sup>5</sup>,  $\text{I}$ <sup>6</sup>) and  $[\text{Sr}(\text{H}_2\text{O})_8][\text{AgI}_2]_2$ <sup>7</sup> the anions form infinite chains by edge sharing of tetrahedra. In  $\text{K}_2[\text{CuCl}_3]$ <sup>8</sup> and  $\text{K}_2[\text{AgI}_3]$ <sup>9</sup> the tetrahedra share corners to form infinite chains and in  $\text{M}[\text{Cu}_2\text{Cl}_3]$  ( $\text{M} = \text{Cs}$ <sup>10</sup>,  $\text{Me}_4\text{N}$ <sup>11</sup>,  $\text{Me}_4\text{P}$ <sup>12</sup>),  $[\text{PhN}_2][\text{Cu}_2\text{Br}_3]$ <sup>13</sup>,  $\text{M}[\text{Cu}_2\text{I}_3]$  ( $\text{M} = \text{Cs}$ <sup>14</sup>,  $\text{Me}_3\text{S}$ <sup>15</sup>),  $[\text{Et}_4\text{N}][\text{Ag}_2\text{X}_3]$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ )<sup>16</sup> or  $\text{Cs}[\text{Ag}_2\text{I}_3]$ <sup>10</sup> the anions form infinite double chains of tetrahedra sharing corners. Less frequently, 2 or 3-coordinate mononuclear anions may be present in the solid state. Examples containing linear  $[\text{MX}_2]^-$  anions, like their  $[\text{AuX}_2]^-$  analog, are  $\text{M}[\text{CuX}_2]$  ( $\text{M} = \text{Bu}_4\text{N}$ ,  $\text{X} = \text{Cl}$ ,  $\text{Br}$ <sup>17</sup>;  $\text{M} = \text{Pr}_4\text{N}$ ,  $\text{X} = \text{Cl}$ <sup>1</sup>;  $\text{M} = \text{Ph}_4\text{P}$ ,  $\text{X} = \text{Cl}$ ,  $\text{Br}$ <sup>18</sup>;  $\text{M} = \text{K}(18\text{-crown-6})$ ,  $\text{X} = \text{I}$ <sup>19</sup>). Mononuclear trigonal planar anions are present in, e.g.,  $[\text{MePh}_3\text{P}]_2[\text{MX}_3]$  ( $\text{M} = \text{Cu}$ ,  $\text{X} = \text{Br}$ ,  $\text{I}$ ;  $\text{M} = \text{Ag}$ ,  $\text{X} = \text{I}$ )<sup>20</sup> and  $[\text{Me}_4\text{P}]_2[\text{CuBr}_3]^-$ <sup>2</sup>. A few compounds contain discrete dinuclear  $[\text{M}_2(\mu\text{-X})_2\text{X}_2]^{2-}$  anions, e.g.,  $[\text{Et}_4\text{N}]_2[\text{Cu}_2\text{Br}_4]$ <sup>21</sup>,  $\text{M}_2[\text{Cu}_2\text{I}_4]$  ( $\text{M} = \text{Pr}_4\text{N}$ <sup>22</sup>,  $\text{Bu}_4\text{N}$ <sup>23</sup>) and  $[\text{Ph}_4\text{P}][\text{Ag}_2\text{X}_4]$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ )<sup>24</sup>. A very uncommon type is illustrated by  $[\text{Me}_4\text{N}]_3[\text{Cu}_2(\mu\text{-Br})\text{Br}_4]$ <sup>25</sup>, which contains two trigonal-planar units sharing a common bromide ligand.

Exceptions to the classification in Table 1 are by no means rare, examples being provided by  $[\text{CuI}_4]^{3-}$ <sup>26</sup>,  $[\text{Cu}_2\text{Cl}_5]^{3-}$ <sup>27</sup>,  $[\text{Ag}_2\text{Cl}_5]^{3-}$ <sup>20</sup>,  $[\text{Cu}_2\text{I}_5]^{3-}$ <sup>28</sup>,  $[\text{Cu}_2\text{I}_6]^{4-}$ <sup>29,30</sup>,  $[\text{Cu}_4\text{I}_8]^{4-}$ <sup>29</sup>,  $[\text{Cu}_5\text{Cl}_{16}]^{11-}$ <sup>31</sup>,  $[\text{Cu}_6\text{Br}_9]^{3-}$ <sup>32</sup>,  $[\text{Cu}_6\text{I}_{11}]^{5-}$ <sup>33</sup>,  $[\text{Cu}_7\text{Cl}_{10}]^{3-}$ <sup>34</sup> and  $[\text{Cu}_8\text{I}_{13}]^{5-}$ <sup>29</sup>. There are also many iodoargentates(I) containing more than five metal atoms. These and related species such as  $[\text{Ag}_4\text{I}_5]^-$ ,  $[\text{Cu}_5\text{Br}_7]^{2-}$  and  $[\text{Cu}_4\text{Cl}_3\text{I}_2]^-$  have been extensively studied because of their high solid-state electrical conductivities. The largest discrete example is  $[\text{PYH}]_{24}[\text{Cu}_{36}\text{I}_{56}]\text{I}_4$ , which contains 36  $\text{CuI}_4$  tetrahedra joined by two or three common edges<sup>29</sup>.

The Cu and Ag halo anions are most often prepared by adding halide ion to  $\text{CuX}$  or  $\text{AgX}$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ , or  $\text{I}$ ) in such solvents as water, alcohols, acetone dichloromethane, *N,N*-dimethylformamide, acetonitrile or nitromethane, followed by crystallization. Selected compounds prepared in this manner are given in Tables 2 and 3.

Electrochemical oxidation of a Cu anode is a useful route to halocuprates(I)<sup>26</sup>. The cell has a Pt cathode and an electrolyte of tetraethylammonium halide in MeCN and an alkyl or aryl halide. Compounds isolated include the  $[\text{Et}_4\text{N}]^+$  salts of  $[\text{Cu}_2\text{Cl}_5]^{3-}$ ,  $[\text{Cu}_2\text{Cl}_3]^-$ ,  $[\text{CuBr}_3]^{2-}$ ,  $[\text{CuI}_2]^-$  and  $[\text{CuI}_4]^{3-}$ , the latter being a rare mononuclear tetrahedral example. An alternative route to iodicuprates (I), which starts with the metal, is the reaction of *xs* Cu powder with organic triiodides, e.g.,  $\text{RI}_3$  ( $\text{R} = \text{Me}_4\text{N}$ ,  $\text{Pr}_4\text{N}$ ), or organic iodide-iodine mixtures in refluxing organic solvents, e.g., chloroform or acetone<sup>30,33,50-52</sup>. Both known and new iodicuprates(I) have been prepared, the compounds isolated by precipitation depending on size, type and charge distribution of the  $\text{R}^+$  cation. Examples prepared include (a)  $[\text{Me}_4\text{N}][\text{Cu}_2\text{I}_3]$ , possessing a novel chain structure in which  $\text{CuI}_4$  tetrahedra are linked alternately via common edges and faces<sup>50</sup>; (b)  $[\text{Pr}_4\text{N}]_2[\text{Cu}_5\text{I}_7]$ , containing five cyclic, condensed  $\text{CuI}_4$  tetrahedra<sup>50</sup>; (c)  $[\text{R}_4\text{N}]_2[\text{Cu}_2\text{I}_4]$  ( $\text{R} = \text{Et}$ <sup>33</sup>, *n*-Pr<sup>50</sup>), containing  $[\text{ICu}(\mu\text{-I})_2\text{CuI}]^{2-}$  anions; (d)  $[\text{Mepy}][\text{CuI}_2]$  (*Mepy* = *N*-methylpyridinium), containing chains of edge-sharing  $\text{CuI}_4$  tetrahedra<sup>51</sup>; (e)  $[\text{Pr}_4\text{N}][\text{Cu}_3\text{I}_4]$ , containing isolated chains of face-sharing  $\text{CuI}_4$  tetrahedra<sup>52</sup>; (f)  $[\text{py}_2\text{CH}_2]_2[\text{Cu}_2\text{I}_6]$  ( $\text{py}_2\text{CH}_2$  = dipyridiniomethane) containing edge-sharing  $\text{CuI}_4$  tetrahedra<sup>30</sup> and (g)  $[\text{Et}_4\text{N}]_6[\text{Cu}_6\text{I}_{11}]\text{I}$ , the anion of which has the six Cu atoms arranged as a trigonal prism, five faces and six corners of which contain the 11 I atoms<sup>33</sup>.

TABLE 2. SYNTHESIS OF HALOGENOCUPRATES(I)

Example	Method	Ref.
$[\text{Cu}(\text{NH}_3)_4][\text{CuCl}_2]_2$	Mix solutions of $[\text{Cu}(\text{NH}_3)_4]\text{Cl}_2$ and CuCl in conc aq KCl	3
$[\text{Et}_3\text{NH}][\text{CuCl}_2]$	Mix CuCl and $[\text{Et}_3\text{NH}]\text{Cl}$ dry powders, product isolated as an oil	35
$[\text{Bu}_4\text{N}][\text{CuCl}_2]$	React $[\text{Bu}_4\text{N}][\text{HSO}_4]$ with NaCl and CuCl in $\text{H}_2\text{O}$	36
$[\text{Me}_2\text{NH}_2][\text{Cu}_2\text{Cl}_3]$	CuCl + $[\text{Me}_2\text{NH}_2]\text{Cl}$ (1:1) in EtOH-HCl	37
$[\text{Me}_4\text{P}][\text{Cu}_2\text{Cl}_3]$	CuCl + $[\text{Me}_4\text{P}]\text{Cl}$ (1:1) in EtOH- $\text{CH}_2\text{Cl}_2$ under $\text{N}_2$	12
$\text{Cs}[\text{Cu}_2\text{X}_3]$	Synproportionation of solid $\text{CsX}-\text{CuX}$ mixtures (1:2) in closed Cu vessel (X = Cl, Br)	38
$\text{Rb}[\text{Cu}_3\text{Cl}_4]$	Fuse CuCl + RbCl	39
$\text{K}_2[\text{CuCl}_3]$	Add CuCl to sat soln KCl in aq HCl in absence of $\text{O}_2$	8
$[\text{Ph}_3\text{RP}][\text{CuBr}_2]$	CuBr + $[\text{Ph}_3\text{RP}]\text{Br}$ (1:1) in EtOH (R = Et, n-Pr, n-Bu)	40
$[\text{Cu}(\text{en})_2][\text{CuBr}_3]^a$	$\text{Cu}(\text{en})_2\text{Br}_2$ + CuBr in aq $[\text{NH}_4]\text{Br}$	41
$[\text{Ph}_3\text{MeP}]_2[\text{CuBr}_3]$	CuBr + $[\text{Ph}_3\text{MeP}]\text{Br}$ (1:3) in EtOH under $\text{N}_2$	20
$[\text{pyH}]_2[\text{Cu}_5\text{Br}_7]$	Melt of CuBr and xs $[\text{pyH}]\text{Br}$	42
$[\text{Et}_3\text{MeN}]_3[\text{Cu}_6\text{Br}_9]$	CuBr + $[\text{Et}_3\text{MeN}]\text{Br}$ (1:1) in EtOH- $\text{CH}_2\text{Cl}_2$ under $\text{N}_2$	43
$[\text{K}(18\text{-crown-6})][\text{CuI}_2]$	CuI + 18-crown-6 in presence of KI	19
$[\text{MePh}_3\text{P}][\text{Cu}_2\text{I}_3]$	CuI + large xs $[\text{MePh}_3\text{P}]\text{I}$ in $\text{MeNO}_2$	44
$[\text{MePh}_3\text{As}][\text{Cu}_3\text{I}_4]$	CuI + $[\text{MePh}_3\text{As}]\text{I}$ (1:2) in $\text{MeNO}_2$	20
$[\text{K}(\text{crown})]_2[\text{Cu}_4\text{I}_6]$	CuI + crown in presence of KI (crown = 12-crown-4, 15-crown-5, or dibenzo-24-crown-8)	19
$[\text{MePh}_3\text{P}]_2[\text{CuI}_3]$	CuI + $[\text{MePh}_3\text{P}]\text{I}$ (1:2) in acetone under $\text{N}_2$	20
$\text{Cs}_3[\text{Cu}_2\text{I}_5]$	CuI + CsI in MeCN or acetone or solid-state reaction	28
$[\text{pyH}]_{24}[\text{Cu}_{36}\text{I}_{56}]\text{I}_4$	CuI + $[\text{pyH}]\text{I}$ (2:3) in refluxing acetone	29
$[\text{pyH}][\text{CuBrI}]^b$	CuI dissolved in boiling acetone solution of $[\text{pyH}]\text{Br}$	41
$\text{Cs}[\text{Cu}_4\text{Cl}_3\text{I}_2]$	CuCl + CuI + CsCl intimate mixture melted at $320^\circ\text{C}$ in sealed tube under $\text{N}_2$	45

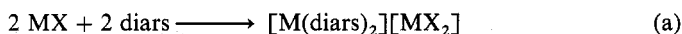
<sup>a</sup> en = 1,2-diaminoethane.

<sup>b</sup> py = pyridine

TABLE 3. SYNTHESIS OF HALOGENOARGENTATES(I)

Example	Method	Ref.
[Me <sub>4</sub> N][AgX <sub>2</sub> ]	AgX + [Me <sub>4</sub> N]X in N,N-dimethyl formamide (X = Cl, I)	5, 6
Cs[AgCl <sub>2</sub> ]	AgCl + CsCl (1:1), melt at $\approx 310^\circ\text{C}$	46
[Et <sub>4</sub> N][Ag <sub>2</sub> Cl <sub>3</sub> ]	AgCl + [Et <sub>4</sub> N]Cl (1:1) in MeCN	16
[Ph <sub>4</sub> As] <sub>3</sub> [Ag <sub>2</sub> Cl <sub>5</sub> ]	AgCl + [Ph <sub>4</sub> As]Cl·H <sub>2</sub> O (1:2) in MeCN	20
[Ph <sub>4</sub> P] <sub>2</sub> [Ag <sub>2</sub> X <sub>4</sub> ]	AgX + [Ph <sub>4</sub> P]X (1:1) in MeCN (X = Cl, Br)	24
[Ph <sub>4</sub> P][AgBr <sub>2</sub> ]	AgBr + [Ph <sub>4</sub> P]Br (1:2) in MeCN	20
[Et <sub>4</sub> N][Ag <sub>2</sub> Br <sub>3</sub> ]	AgBr + [Et <sub>4</sub> N]Br (1:1) in N,N-dimethyl-formamide	16
[Ph <sub>3</sub> MeP] <sub>3</sub> [AgBr <sub>4</sub> ]	AgBr + [Ph <sub>3</sub> MeP]Br (1:2) in MeCN	20
[Sr(H <sub>2</sub> O) <sub>8</sub> ][AgI <sub>2</sub> ] <sub>2</sub>	Saturated aq SrI <sub>2</sub> + AgI soln	7
[MeNH=CMe <sub>2</sub> ][Ag <sub>2</sub> I <sub>3</sub> ]	Shake AgI + [MeNH <sub>3</sub> ]I in acetone	47
Cs <sub>2</sub> [AgI <sub>3</sub> ]	CsI + AgI in N,N-dimethylformamide	48
K <sub>2</sub> [AgI <sub>3</sub> ]	Saturate a warm conc KI soln with AgI	49

The reactions of monohalides with ligands may also be useful, e.g.<sup>53,54</sup>:



where M = Cu, Ag; X = Cl, Br, I. Copper(I) acetate has also been employed as a starting material. Reaction with MeCOCl in MeCN–MeCO<sub>2</sub>H gives chlorocuprate(I) solutions, from which Rb<sub>2</sub>[CuCl<sub>3</sub>], Cs<sub>3</sub>[Cu<sub>2</sub>Cl<sub>5</sub>] and [Me<sub>4</sub>N][Cu<sub>2</sub>Cl<sub>3</sub>] are obtained by adding metal acetate or [Me<sub>4</sub>N]Cl under nitrogen<sup>27</sup>.

Halocuprate(I) anions can also be generated by reducing appropriate Cu(II) compounds; e.g., passage of SO<sub>2</sub> into an CuCl<sub>2</sub> soln containing xs KCl gives K[CuCl<sub>2</sub>]. Boiling aq CuBr<sub>2</sub> soln and xs KBr produces K[CuBr<sub>2</sub>] and the reaction between aq Cu<sup>2+</sup> and xs KI gives K[CuI<sub>2</sub>]. An excess of the potassium halide is necessary to prevent precipitation of Cu(I) halide. Examples of other reductions of CuCl<sub>2</sub> that have been used to prepare chlorocuprate(I) anions involve the addition of Et<sub>3</sub>P, the cyclophosphazene N<sub>6</sub>P<sub>6</sub>(NMe<sub>2</sub>)<sub>12</sub> and Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>Net<sub>2</sub>. The products are [Et<sub>3</sub>PCl][Cu<sub>2</sub>Cl<sub>3</sub>]<sup>55</sup>, [N<sub>6</sub>P<sub>6</sub>(NMe<sub>2</sub>)<sub>12</sub>CuCl][CuCl<sub>2</sub>]<sup>56</sup> and [Ph<sub>2</sub>P(O)(CH<sub>2</sub>)<sub>2</sub>NHEt<sub>2</sub>][CuCl<sub>2</sub>]<sup>57</sup>, respectively, the oxidation and protonation of the aminophosphine in the last example resulting from the presence of adventitious water in the EtOH or THF used as solvent.

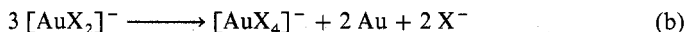
A novel route to [Ag<sub>2</sub>I<sub>3</sub>]<sup>–</sup> species<sup>47</sup> involves the alkylation of N,N-dimethylformamide by alkyl iodides in the presence of Ag<sub>2</sub>O. Thus, reaction of MeI with Ag<sub>2</sub>O in this solvent affords [Me<sub>4</sub>N][Ag<sub>2</sub>I<sub>3</sub>]. Silver(I) acetate can also be a useful starting material. It reacts with [Bu<sub>4</sub>N]I in aqueous acetone to give [Bu<sub>4</sub>N][Ag<sub>3</sub>I<sub>4</sub>]<sup>58</sup>.

The high molecular weight iodoargentates(I) and a number of halocuprate(I) analogs, e.g., [pyH]<sub>2</sub>[Cu<sub>5</sub>Br<sub>7</sub>]<sup>42</sup> and M[Cu<sub>4</sub>Cl<sub>3</sub>I<sub>2</sub>] (M = Rb, Cs)<sup>45</sup>, display high conductivities in the solid state as a result of fast metal-ion transport<sup>59</sup> through the complex structures. For example, Rb[Ag<sub>4</sub>I<sub>5</sub>] has four molecules in the unit cell, the 20 iodide ions forming 56 tetrahedra by face sharing. The 16 Ag<sup>+</sup> cations are distributed over the 56 sites in a nonuniform manner, the tetrahedra forming a network for fast Ag<sup>+</sup> ion

transport. Many others, e.g.,  $[\text{Ag}_{13}\text{I}_{15}]^{2-}$ ,  $[\text{Ag}_{18}\text{I}_{23}]^{5-}$  and  $[\text{Ag}_{31}\text{I}_{39}]^{8-}$ , also involve face-shared tetrahedra with random  $\text{Ag}^+$  distribution<sup>60-62</sup>, but  $[\text{pyH}][\text{Ag}_5\text{I}_6]$  has face-shared octahedra as well as tetrahedra<sup>59</sup>.

The addition of 4 mol equiv  $\text{AgI}$  to saturated aq MI soln at 40–70°C is a route to  $\text{M}[\text{Ag}_4\text{I}_5]$  ( $\text{M} = \text{K}, \text{Rb}, \text{Cs}$  or  $\text{NH}_4$ )<sup>63</sup>, which decompose to  $\text{AgI}$  and  $\text{M}_2\text{AgI}_3$  in the presence of moisture, and  $\text{Rb}[\text{Ag}_4\text{I}_5]$  is metastable < 27°C<sup>59</sup>. Quarternary ammonium salts are prepared by intimately mixing  $\text{AgI}$  and  $[\text{R}_4\text{N}]\text{I}$  and annealing in closed vessels under argon at 125–165°C. Alternatively, the reactants can be made into a paste with water, then vacuum dried before grinding, pelletizing and annealing<sup>60,64,65</sup>. The products are  $[\text{R}_4\text{N}][\text{Ag}_n\text{I}_{n+1}]$  ( $n = 2, 4, 6, 7$  and  $8$ ) and  $[\text{R}_4\text{N}]_2[\text{Ag}_{13}\text{I}_{15}]$ . The solid-state reaction between 9:1 molar proportions of  $\text{AgI}$  and  $[\text{Me}_3\text{N}(\text{CH}_2)_2\text{NMe}_3]\text{I}_2$  affords  $[\text{Me}_3\text{N}(\text{CH}_2)_2\text{NMe}_3]_4[\text{Ag}_{31}\text{I}_{39}]$ <sup>62</sup>.

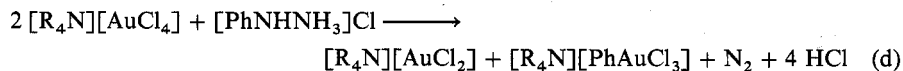
Finally, the haloaurate(I) anions  $[\text{AuCl}_2]^-$  and  $[\text{AuBr}_2]^-$  disproportionate in water:



so early reports that  $[\text{AuX}_4]^-$  is reduced to  $[\text{AuX}_2]^-$  in water are unlikely to be correct. The stability of  $[\text{AuX}_2]^-$  in water increases with increasing size of halogen,  $[\text{AuI}_2]^-$  resulting from the addition of aqueous iodide to  $\text{AuI}$ <sup>66</sup>. Reduction of  $[\text{AuX}_4]^-$  ( $\text{X} = \text{Cl}, \text{Br}$ ) by  $\text{I}^-$  in aq soln has been studied by stopped-flow spectrophotometry. Use of xs  $\text{I}^-$  leads<sup>67</sup> to  $[\text{AuI}_2]^-$ . The ions  $[\text{AuCl}_2]^-$  and  $[\text{AuBr}_2]^-$  are stable in acetonitrile<sup>68</sup>:



where  $\text{X} = \text{Cl}$  or  $\text{Br}$ . The key to the preparations of tetraalkylammonium salts<sup>69</sup> is selecting a reducing agent that does not reduce  $[\text{R}_4\text{N}][\text{AuX}_4]$  ( $\text{R} = \text{Et}$  or  $n\text{-Bu}$ ) to the metal. The reducing agent for  $\text{X} = \text{Cl}$  is  $[\text{PhNHNH}_3]\text{Cl}$  in ethanol:



The reaction proceeds with part of the  $\text{Au(III)}$  being reduced and the remainder converted into a phenylgold anion (see §2.8.5). The reducing agent employed with  $[\text{AuBr}_4]^-$  is acetone in ethanol:



The iodides  $[\text{R}_4\text{N}][\text{AuI}_2]$  are obtained by metathesis of  $[\text{R}_4\text{N}][\text{AuBr}_2]$  and  $[\text{R}_4\text{N}]\text{I}$  in ethanol. The iodide  $[\text{Au}(\text{diars})_2][\text{AuI}_2]$  results from the reaction of  $\text{AuI}$  with  $[\text{Au}(\text{diars})_2]\text{I}$ <sup>70</sup>. Similarly, compounds of empirical formulas  $[\text{AuX}(\text{C}_5\text{H}_5\text{N})]$  ( $\text{X} = \text{Cl}, \text{I}$ ) are actually  $[\text{Au}(\text{C}_5\text{H}_5\text{N})_2][\text{AuX}_2]$ , the cations and anions being weakly linked by long metal-metal interactions<sup>71</sup>.

The compounds  $\text{M}_2\text{Au}_2\text{X}_6$  and  $\text{M}_2\text{Au}_3\text{X}_8$  ( $\text{M} = \text{alkali metal}; \text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ) which contain both  $[\text{AuX}_4]^-$  and  $[\text{AuX}_2]^-$  ions are discussed in §2.8.4.1.

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### 2.8.13. Synthesis of Ag Subfluoride.

The unique Ag subfluoride  $\text{Ag}_2\text{F}$  is prepared by two methods. The first involves treatment of AgF solutions with additional finely divided silver prepared by the addition of metaformaldehyde<sup>1</sup> or ammonium formate<sup>2</sup> to ammoniacal  $\text{AgNO}_3$  soln. The AgF soln is prepared by adding 40% HF soln to  $\text{Ag}_2\text{CO}_3$ . The precipitated Ag is then added to xs AgF soln and crystals of  $\text{Ag}_2\text{F}$  are formed on evaporation at 50–90°C<sup>1</sup>.

The second route to  $\text{Ag}_2\text{F}$  is the cathodic reduction of AgF soln using low current densities. A saturated AgF soln, prepared as above at 50°C in a Pt dish, is electrolyzed. The dish serves as the cathode and a Ag rod is used as the anode. The maximum current density of the cathode is  $0.002 \text{ A cm}^{-2}$ , the voltage drop across the electrodes 1.4 V and the current 0.07–0.1 A. Using these conditions  $\sim 20 \text{ g}$  can be produced in  $\sim 48 \text{ h}^{3-5}$ . The  $\text{Ag}_2\text{F}$  should be stored in vacuo as it is hydrolyzed by water (and thermally decomposed at  $\sim 100^\circ\text{C}$ ) to regenerate Ag and AgF.

The electrolysis of AgF–HF solutions using platinum electrodes under similar experimental conditions is claimed to produce higher Ag oxides with a defect structure stable only in the presence of foreign anions, but certainly containing Ag in an oxidation state  $> 2^{6,7}$ ; however, the product is now known<sup>8,9</sup> to be the unusual compound  $[\text{Ag}_7\text{O}_8][\text{HF}_2]$ . This salt contains  $[\text{Ag}_6\text{O}_8]^+$  polyhedra that act as clathrates to enclose the remaining  $\text{Ag}^+$  and  $[\text{HF}_2]^-$  ions. The cation can be regarded as  $[\text{Ag}_2^{\text{I}}\text{Ag}_5^{\text{II}}\text{O}_8]^+$ , but since all six Ag atoms of the  $[\text{Ag}_6\text{O}_8]^+$  polyhedron are structurally equivalent, it is preferable to refer to an average metal oxidation state of  $2\frac{2}{3}$ .

In view of the similar preparative conditions employed for  $[\text{Ag}_7\text{O}_8][\text{HF}_2]$  and  $\text{Ag}_2\text{F}$ , the conductivity of both solids, and the fact that the former has been characterized by x-ray crystallography<sup>9</sup>, it is perhaps surprising that the authenticity of  $\text{Ag}_2\text{F}$  appears not to have been questioned. However, whereas  $[\text{Ag}_7\text{O}_8][\text{HF}_2]$  is described as a black crystalline material, with %Ag of 81.89% and a face-centered cubic unit cell with  $a = 9.824^9$  (or  $9.834^6$ ,  $9.842^7$ ),  $\text{Ag}_2\text{F}$  is produced as yellow-green plates with a metallic appearance, with %Ag = 91.91% and a hexagonal (anti- $\text{CdI}_2$ ) unit cell with  $a = 2.989$ ,  $c = 5.710^{10}$  (or  $a = 2.996$ ,  $c = 5.691^{11}$ ). The evidence, therefore, suggests that  $\text{Ag}_2\text{F}$  is genuine, and the preparation and unit cell parameters of both compounds are established<sup>11,12</sup>.

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## 2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond 133

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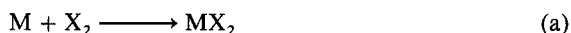
134 2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond  
 2.8.14. Synthesis of the Group-IIB Dihalides from the Metals  
 2.8.14.1. by Halogenation Reactions.

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6. W. S. Graff, H. H. Stadelmaier, *J. Electrochem. Soc.*, 105, 446 (1958).
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9. A. C. Gossard, D. K. Hindermann, M. B. Robin, N. A. Kuebler, T. H. Geballe, *J. Am. Chem. Soc.*, 89, 7121 (1967).
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## 2.8.14. Synthesis of the Group-IIB Dihalides from the Metals

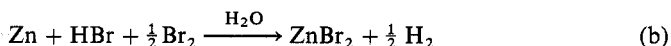
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A straightforward preparation of the group-IIB halides involves oxidation of the metal by the diatomic halogens:



The metals burn in  $F_2$ , but the reaction becomes less exothermic as the atomic weight of the halogen increases.

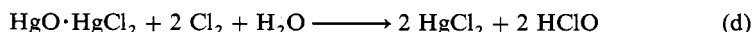
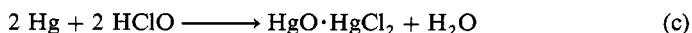
Powdered Zn burns in  $F_2$  to produce<sup>1</sup>  $ZnF_2$ ; in the reaction of Zn and  $Cl_2$  dry  $Cl_2$  does not react at RT, but damp  $Cl_2$  does<sup>2</sup>. However, a  $Cl_2$  and HCl gas mixture at 400°C produces<sup>3</sup> pure  $ZnCl_2$ . Zinc powder and  $Br_2$  react at 550°C<sup>4</sup> or in  $Et_2O$  soln<sup>5</sup> at RT. A mixture of HBr and  $Br_2$  when combined with Zn powder reacts by<sup>6</sup>:



The  $ZnBr_2$  is obtained by evaporating the solution and subliming the products in a stream of  $HBr-N_2$ . Zinc iodide is prepared from Zn powder and  $I_2$  in  $H_2O$ <sup>7</sup> or  $Et_2O$ <sup>8</sup>. When  $Et_2O$  is employed, the hemietherate,  $ZnI_2 \cdot \frac{1}{2} Et_2O$ , is obtained. In either reaction, however,  $ZnI_2$  can be obtained by first heating the product to remove the solvent and finally vacuum distilling or subliming the  $ZnI_2$  at 400°C.

Cadmium metal reacts with the halogens by Eq. (a). Powdered Cd and  $F_2$  held at 300°C for 1 h produces<sup>9</sup>  $CdF_2$ . Early attempts used damp  $Cl_2$  to produce<sup>2</sup>  $CdCl_2$ , but  $CdCl_2$  is prepared<sup>10</sup> in the absence of  $O_2$  and  $H_2O$ . Cadmium bromide forms in a boiling  $H_2O-Br_2$  soln<sup>11</sup> or when  $Br_2$  is heated to 450°C with Cd metal<sup>12</sup>. However, HBr should be added to the  $Br_2-H_2O$  soln in order to prevent hydrolysis of the  $CdBr_2$  to  $CdOHBr$ . The  $CdBr_2$  can be purified by sublimation in an  $HBr-N_2$  gas stream. Cadmium iodide forms when Cd metal and  $I_2$  are mixed in  $H_2O$ .

When Hg is burned in  $F_2$  a useful fluorinating agent,  $HgF_2$ , is formed<sup>14</sup>. Mercury(II) chloride can be prepared analogously by heating Hg and  $Cl_2$  together to 250°C<sup>15</sup>. By bubbling  $Cl_2$  through an NaCl solution containing a dispersion of Hg metal<sup>16,17</sup>:





134 2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond  
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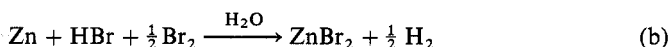
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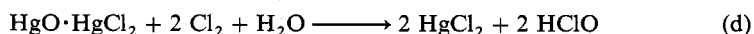
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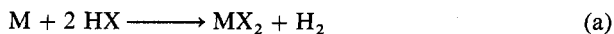
Atomic chlorine produced by the UV irradiation of Cl<sub>2</sub> reacts with moist Zn powder to produce<sup>23</sup> ZnCl<sub>2</sub>.

(T.B. BRILL)

1. H. Moissan, *Ann. Chim. Phys.*, **24**, 224 (1891).
2. R. Cowper, *J. Chem. Soc.*, **43**, 153 (1833).
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#### 2.8.14.2. by Hydrohalogenation Reactions.

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(T.B. BRILL)

2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond 135  
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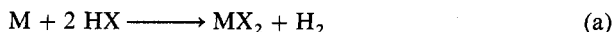
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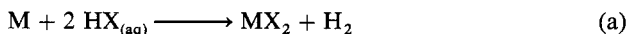
(T.B. BRILL)

136 2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond  
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**2.8.14.3. by Hydrohalic Acids.**

The reaction rate of Zn and Cd metals with aqueous hydrogen halides is determined by surface roughness, metal particle size and the purity of the metal. Impure Zn and Cd react more vigorously owing to the large overvoltage between the metals and the H<sub>2</sub> product. The rate is also proportional to the concentration of the acid:



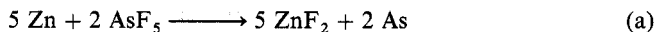
Zinc reacts with aq HCl, HBr and HI<sup>1</sup>; Cd reacts with HF<sup>2</sup> or HI<sup>3</sup>, yielding the halide after evaporation of the water. Addition of small amounts of HNO<sub>3</sub> and heat aids in the reactions of mercury<sup>4</sup> with conc aq HCl or HBr to yield HgCl<sub>2</sub> or HgBr<sub>2</sub><sup>5,6</sup>.

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4. W. Nernst, *Chem. Ber.*, **30**, 1560 (1897).
5. A. Harding, *Chem. Ber.*, **14**, 2085 (1881).
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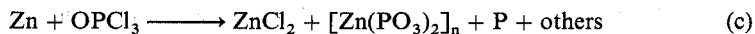
Halogenating agents react with Zn, Cd or Hg to produce dihalides. Zinc(II) fluoride is prepared by the action of NOF·3 HF<sup>1</sup> or AsF<sub>5</sub><sup>2</sup> on Zn metal:



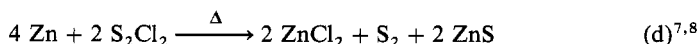
or by SF<sub>6</sub><sup>3</sup> on Zn:



Zinc(II) chloride forms from Zn powder with acetyl chloride in 95% EtOH for 30 min<sup>4</sup>, SiCl<sub>4</sub><sup>5</sup> or from OPCl<sub>3</sub><sup>6</sup>:



or from other acetyl chlorides<sup>7-9</sup>:

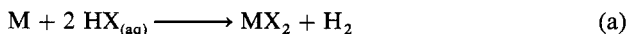


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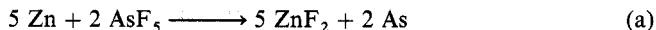
Zinc reacts with aq HCl, HBr and HI<sup>1</sup>; Cd reacts with HF<sup>2</sup> or HI<sup>3</sup>, yielding the halide after evaporation of the water. Addition of small amounts of HNO<sub>3</sub> and heat aids in the reactions of mercury<sup>4</sup> with conc aq HCl or HBr to yield HgCl<sub>2</sub> or HgBr<sub>2</sub><sup>5,6</sup>.

(T.B. BRILL)

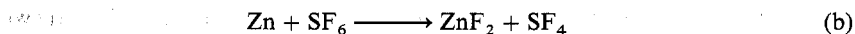
1. W. Spring, E. van Aubel, *Ann. Chim. Phys.*, **11**, 505 (1887).
2. J. J. Berzelius, *Pogg. Ann.*, **1**, 26 (1824).
3. G. G. Schlessinger, *Inorganic Laboratory Preparations*, Chemical Publishing Company, New York, 1962, p. 18-19.
4. W. Nernst, *Chem. Ber.*, **30**, 1560 (1897).
5. A. Harding, *Chem. Ber.*, **14**, 2085 (1881).
6. E. G. Moeys, U.S. Pat. 1,312,743 (1919); *Chem. Abstr.*, **13**, 2577 (1919).

**2.8.14.4. by Nonmetal Halides.**

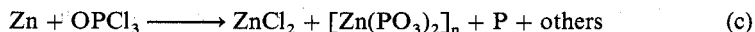
Halogenating agents react with Zn, Cd or Hg to produce dihalides. Zinc(II) fluoride is prepared by the action of NOF·3 HF<sup>1</sup> or AsF<sub>5</sub><sup>2</sup> on Zn metal:



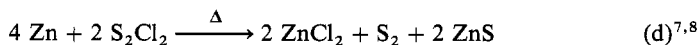
or by SF<sub>6</sub><sup>3</sup> on Zn:



Zinc(II) chloride forms from Zn powder with acetyl chloride in 95% EtOH for 30 min<sup>4</sup>, SiCl<sub>4</sub><sup>5</sup> or from OPCl<sub>3</sub><sup>6</sup>:



or from other acetyl chlorides<sup>7-9</sup>:

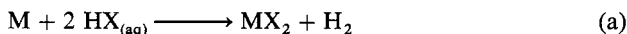


136 2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond  
 2.8.14. Synthesis of the Group-II B Dihalides from the Metals  
 2.8.14.4. by Nonmetal Halides.

1. C. Poulenc, *C. R. Hebd. Seances Acad. Sci.*, **116**, 581 (1893); see also N. N. Beketoff, *Z. Angew. Chem.*, **13**, 470 (1900).
2. E. L. Muetterties, J. E. Castle, *J. Inorg. Nucl. Chem.*, **18**, 148 (1961).
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**2.8.14.3. by Hydrohalic Acids.**

The reaction rate of Zn and Cd metals with aqueous hydrogen halides is determined by surface roughness, metal particle size and the purity of the metal. Impure Zn and Cd react more vigorously owing to the large overvoltage between the metals and the H<sub>2</sub> product. The rate is also proportional to the concentration of the acid:



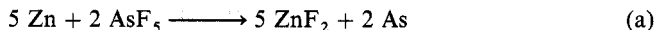
Zinc reacts with aq HCl, HBr and HI<sup>1</sup>; Cd reacts with HF<sup>2</sup> or HI<sup>3</sup>, yielding the halide after evaporation of the water. Addition of small amounts of HNO<sub>3</sub> and heat aids in the reactions of mercury<sup>4</sup> with conc aq HCl or HBr to yield HgCl<sub>2</sub> or HgBr<sub>2</sub><sup>5,6</sup>.

(T.B. BRILL)

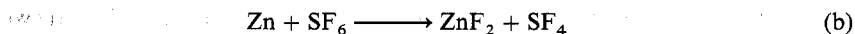
1. W. Spring, E. van Aubel, *Ann. Chim. Phys.*, **11**, 505 (1887).
2. J. J. Berzelius, *Pogg. Ann.*, **1**, 26 (1824).
3. G. G. Schlessinger, *Inorganic Laboratory Preparations*, Chemical Publishing Company, New York, 1962, p. 18-19.
4. W. Nernst, *Chem. Ber.*, **30**, 1560 (1897).
5. A. Harding, *Chem. Ber.*, **14**, 2085 (1881).
6. E. G. Moeys, U.S. Pat. 1,312,743 (1919); *Chem. Abstr.*, **13**, 2577 (1919).

**2.8.14.4. by Nonmetal Halides.**

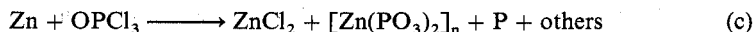
Halogenating agents react with Zn, Cd or Hg to produce dihalides. Zinc(II) fluoride is prepared by the action of NOF·3 HF<sup>1</sup> or AsF<sub>5</sub><sup>2</sup> on Zn metal:



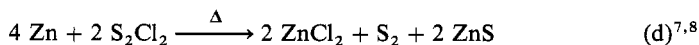
or by SF<sub>6</sub><sup>3</sup> on Zn:

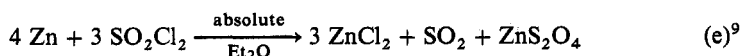


Zinc(II) chloride forms from Zn powder with acetyl chloride in 95% EtOH for 30 min<sup>4</sup>, SiCl<sub>4</sub><sup>5</sup> or from OPCl<sub>3</sub><sup>6</sup>:



or from other acetyl chlorides<sup>7-9</sup>:

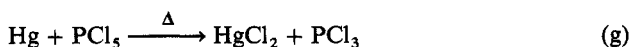




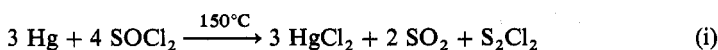
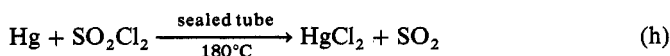
Cadmium(II) fluoride forms when Cd powder reacts with  $\text{NOF} \cdot 3 \text{ HF}$ <sup>1</sup>,  $\text{SF}_6$ <sup>3</sup> or  $\text{IF}_5$ <sup>10</sup>:



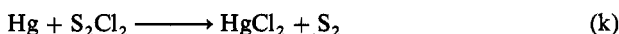
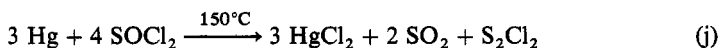
Heating Cd with  $\text{S}_2\text{Cl}_2$  yields  $\text{CdCl}_2$  similarly to eq (d)<sup>7,8</sup>. The preparation of Hg(II) halides by this method is more popular; e.g.,  $\text{NOF} \cdot 3 \text{ HF}$  reacts with Hg metal to produce a mixture of  $\text{HgF}_2$  and  $\text{Hg}_2\text{F}_2$ <sup>1</sup>. Chlorine trifluoride and Hg react at 120 °C for 3 h yielding<sup>11</sup>  $\text{HgF}_2$ . The action of  $\text{NOCl}$  on Hg at RT in a sealed tube produces<sup>12</sup>  $\text{HgCl}_2$ ;  $\text{PCl}_5$  and Hg require heating<sup>13</sup>:



With suluryl chloride<sup>14</sup>:



and  $\text{S}_2\text{Cl}_2$ <sup>15</sup>, each reacts with Hg to transfer chloride. With xs Hg:



Mercury(II) bromides form on heating Hg with  $\text{PBr}_3$ <sup>16</sup>,  $\text{IBr}$ <sup>17</sup> or  $\text{SOBr}_2$ <sup>18</sup>. Phosphorus(III) iodide reacts with Hg in  $\text{CS}_2$  to yield  $\text{HgI}_2$ <sup>18</sup>.

(T.B. BRILL)

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17. V. Gutmann, *Monatsh. Chem.*, **82**, 280 (1951).
18. J. A. Besson, *Bull. Chem. Soc. Fr.*, **15**, 909 (1896).

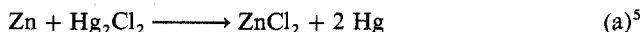
- 138 2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond  
 2.8.15. Synthesis of the Group-IIIB Dihalides from Metal Oxides  
 2.8.15.1. by Halogenation.

#### 2.8.14.5. by Metal Halides.

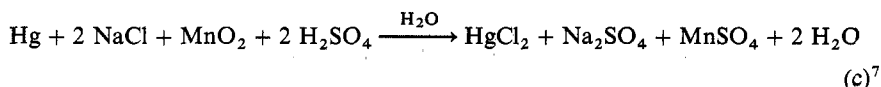
Zinc and cadmium react with xs  $\text{HgCl}_2$  to produce  $\text{ZnCl}_2$  and  $\text{CdCl}_2$ , and the reaction of group-IIIB metals with many other metal halides may be employed to produce the halides.

Zinc electrolyzes with  $\text{CuCl}$ ,  $\text{CuBr}$  or  $\text{CuI}$  in  $\text{CH}_3\text{CN}$  to give the  $\text{ZnX}_2 \cdot \text{CH}_3\text{CN}$  solvate complex<sup>1</sup>. Heating removes the  $\text{CH}_3\text{CN}$ , providing the anhyd  $\text{ZnX}_2$  salt. The reaction of  $\text{Zn}$  and  $\text{PbCl}_2$  produces  $\text{ZnCl}_2$ <sup>2</sup>, while trituration and heating of  $\text{Zn}$  and  $\text{HgI}_2$  yields  $\text{ZnI}_2$  and a zinc amalgam<sup>3</sup>. Cadmium reacts with  $\text{HgI}_2$  similarly. Electrolysis of  $\text{Cd}$  in  $\text{CH}_3\text{CN}$  with  $\text{CuBr}$  and  $\text{CuI}$  leads to  $\text{CdBr}_2$  and  $\text{CdI}_2$ <sup>1</sup>. Aluminum triiodide reacts with  $\text{Zn}$ ,  $\text{Cd}$  and  $\text{Hg}$  to produce the group-IIIB diiodide<sup>4</sup>.

Zinc and  $\text{Cd}$  react with  $\text{Hg}_2\text{Cl}_2$ :



Mercury is oxidized in the presence of  $\text{Cl}^-$  salts to form  $\text{HgCl}_2$ , e.g.:



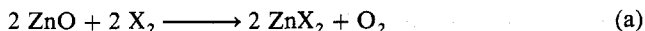
(T.B. BRILL)

1. H. Schmid, *Z. Anorg. Allg. Chem.*, 271, 305 (1953).
2. H. Grünauer, *Z. Anorg. Allg. Chem.*, 39, 389 (1904).
3. J. B. Berthemot, *J. Pharm. Sci. Accessoires*, 14, 610 (1828).
4. M. Chaigneau, *Bull. Soc. Chim. Fr.*, 886 (1957).
5. F. Feigl, L. I. Miranda, H. A. Suter, *J. Chem. Ed.*, 21, 18 (1944).
6. F. M. Seibert, G. A. Hulett, H. S. Taylor, *J. Am. Chem. Soc.*, 39, 38 (1917).
7. P. L. Geiger, *Jahrb. Pharm. Berlin*, 346 (1820).

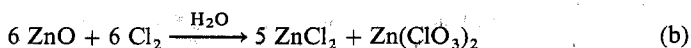
### 2.8.15. Synthesis of the Group-IIIB Dihalides from Metal Oxides

#### 2.8.15.1. by Halogenation.

Zinc(II) oxide, known as the mineral zincite, reacts directly with gaseous halogens:



Reaction with  $\text{F}_2$ <sup>1</sup> and  $\text{Cl}_2$ <sup>2</sup> does not occur in the cold but does take place at 500°C. Chlorine atoms from the photochemical dissociation of  $\text{Cl}_2$  react with moist  $\text{ZnO}$  to produce  $\text{ZnCl}_2$ <sup>3</sup>. A suspension of  $\text{ZnO}$  in  $\text{H}_2\text{O}$  also reacts with  $\text{Cl}_2$  gas<sup>4</sup>:



Cadmium(II) oxide reacts with  $\text{F}_2$ <sup>5</sup> and  $\text{Cl}_2$ <sup>2</sup> in the same way at 450°C as  $\text{ZnO}$  in Eq (a);  $\text{Cl}_2$ ,  $\text{O}_2$ <sup>2</sup> and  $\text{Cl}_2\text{O}$ <sup>6</sup> are also produced.

The reaction of  $\text{HgO}$  with  $\text{Cl}_2$  takes place at red heat to yield  $\text{HgCl}_2$  and  $\text{O}_2$ <sup>7</sup>, or  $\text{Cl}_2\text{O}$ <sup>6</sup>. In boiling  $\text{H}_2\text{O}$  the products are  $\text{HgCl}_2$  and  $\text{Hg}(\text{ClO}_3)_2$ <sup>7</sup>. Bromine and  $\text{I}_2$  in react with  $\text{HgO}$  in boiling  $\text{H}_2\text{O}$  to give  $\text{HgX}_2$  and  $\text{Hg}(\text{XO}_3)_2$ <sup>8</sup>.

(T.B. BRILL)



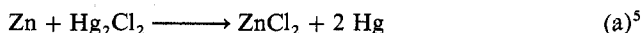
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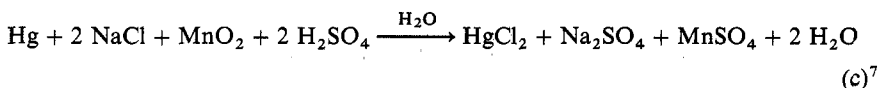
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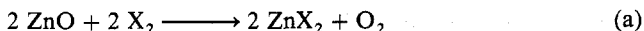
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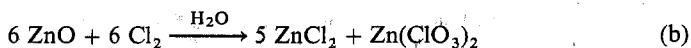
## 2.8.15. Synthesis of the Group-IIIB Dihalides from Metal Oxides

### 2.8.15.1. by Halogenation.

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Cadmium(II) oxide reacts with  $\text{F}_2$ <sup>5</sup> and  $\text{Cl}_2$ <sup>2</sup> in the same way at 450°C as  $\text{ZnO}$  in Eq (a);  $\text{Cl}_2$ ,  $\text{O}_2$ <sup>2</sup> and  $\text{Cl}_2\text{O}$ <sup>6</sup> are also produced.

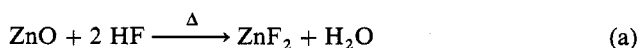
The reaction of  $\text{HgO}$  with  $\text{Cl}_2$  takes place at red heat to yield  $\text{HgCl}_2$  and  $\text{O}_2$ <sup>7</sup>, or  $\text{Cl}_2\text{O}$ <sup>6</sup>. In boiling  $\text{H}_2\text{O}$  the products are  $\text{HgCl}_2$  and  $\text{Hg}(\text{ClO}_3)_2$ <sup>7</sup>. Bromine and  $\text{I}_2$  in react with  $\text{HgO}$  in boiling  $\text{H}_2\text{O}$  to give  $\text{HgX}_2$  and  $\text{Hg}(\text{XO}_3)_2$ <sup>8</sup>.

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### 2.8.15.2. by Hydrogen Halides and Hydrohalic Acids.

Zinc oxide reacts with HF at red heat<sup>1</sup>:



The reaction with HCl occurs both with and without a solvent. Zinc oxide dissolves in dil HCl which, on evaporation, yields hydrated  $\text{ZnCl}_2$ . The reaction also occurs with gaseous HCl to give  $\text{ZnCl}_2$  and  $\text{H}_2\text{O}$ <sup>2</sup>. Gaseous HBr reacts with ZnO to produce  $\text{ZnBr}_2$  which may be purified by sublimation in an HBr- $\text{N}_2$  gas stream<sup>3</sup>, whereas aqueous HI yields  $\text{ZnI}_2$ , which can be isolated by cooling and evaporation<sup>3</sup>.

Cadmium oxide and HF combine at red heat to produce  $\text{CdF}_2$  and  $\text{H}_2\text{O}$ <sup>4</sup>, whereas CdO forms when HCl gas or a dil HCl soln is heated with CdO<sup>5</sup>. Aqueous HI and solid CdO yield  $\text{CdI}_2$ <sup>6</sup>.

Anhydrous  $\text{HgF}_2$  can be produced by the action of a 15:1 HF- $\text{O}_2$  gas mixture on HgO at 380–450°C<sup>7</sup>. The hydrate  $\text{HgF}_2 \cdot 2 \text{H}_2\text{O}$  is obtained when 50% aq HF and HgO react<sup>8</sup>. Mercury(II) oxide and HCl produce  $\text{HgCl}_2$  when heated<sup>5,9</sup>, and hot aq HBr yields<sup>10,11</sup>  $\text{HgBr}_2$ .

(T.B. BRILL)

1. C. Poulenc, *C. R. Hebd. Seances Acad. Sci.*, 116, 581 (1893).
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9. L. S. Lilich, Yu S. Varshavskii, *J. Gen. Chem. USSR*, 26, 337 (1956).
10. C. Lowig, *Mag. Pharm.*, 33, 7 (1828).
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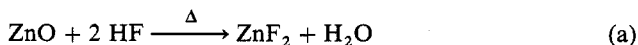
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2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond 139  
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3. G. M. Garde, Indian Pat. 122,119; October 30, 1971; *Chem. Abstr.*, 77; P37,202h (1972).
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Zinc oxide reacts with HF at red heat<sup>1</sup>:



The reaction with HCl occurs both with and without a solvent. Zinc oxide dissolves in dil HCl which, on evaporation, yields hydrated  $\text{ZnCl}_2$ . The reaction also occurs with gaseous HCl to give  $\text{ZnCl}_2$  and  $\text{H}_2\text{O}$ <sup>2</sup>. Gaseous HBr reacts with ZnO to produce  $\text{ZnBr}_2$  which may be purified by sublimation in an HBr- $\text{N}_2$  gas stream<sup>3</sup>, whereas aqueous HI yields  $\text{ZnI}_2$ , which can be isolated by cooling and evaporation<sup>3</sup>.

Cadmium oxide and HF combine at red heat to produce  $\text{CdF}_2$  and  $\text{H}_2\text{O}$ <sup>4</sup>, whereas CdO forms when HCl gas or a dil HCl soln is heated with CdO<sup>5</sup>. Aqueous HI and solid CdO yield  $\text{CdI}_2$ <sup>6</sup>.

Anhydrous  $\text{HgF}_2$  can be produced by the action of a 15:1 HF- $\text{O}_2$  gas mixture on HgO at 380–450°C<sup>7</sup>. The hydrate  $\text{HgF}_2 \cdot 2 \text{H}_2\text{O}$  is obtained when 50% aq HF and HgO react<sup>8</sup>. Mercury(II) oxide and HCl produce  $\text{HgCl}_2$  when heated<sup>5,9</sup>, and hot aq HBr yields<sup>10,11</sup>  $\text{HgBr}_2$ .

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6. C. D. Ragland, *Am. Chem. J.*, 22, 418 (1899). G. G. Schlessinger, *Inorganic Laboratory Preparations*, Chemical Publishing Company, New York, 1962, pp. 18–19.
7. E. L. Muetterties, U.S. Pat. 2,757,070 (1956); *Chem. Abstr.*, 50, 10,657 (1956).
8. R. Finkener, *Ann. Physik.*, 110, 147,628 (1860); see also A. L. Henne, T. Midgley, *J. Am. Chem. Soc.*, 58, 884 (1936).
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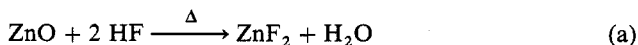
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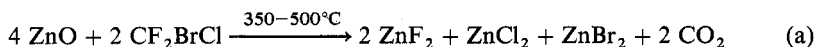
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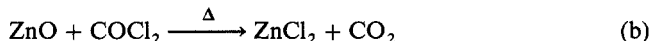
### 2.8.15.3. by Other Halogenating Agents.

Numerous halogenating agents drawn from the first-row transition metals and main-group elements convert the group-IIIB oxides to the dihalides.

Zinc fluoride is obtained when  $\text{PF}_3$  reacts with  $\text{ZnO}$  at  $500^\circ\text{C}$ , but  $\text{Zn}_3\text{P}_2$  and  $\text{Zn}_3(\text{PO}_3)_2$  are also isolated<sup>1</sup>. The reaction of  $\text{CF}_2\text{BrCl}$  with  $\text{ZnO}$  produces  $\text{ZnF}_2$  and other halides<sup>2</sup>:



Zinc chloride forms when  $\text{ZnO}$  reacts with organic chlorinating agents such as gaseous  $\text{COCl}_2$ <sup>3</sup>,  $\text{CH}_3\text{C}(\text{O})\text{Cl}$  in 95% EtOH for 30 min or gaseous  $\text{CCl}_4$ <sup>4</sup>, e.g.:



Boron trichloride and  $\text{ZnO}$  at  $500^\circ\text{C}$  produce anhyd  $\text{ZnCl}_2$ <sup>5</sup>. The decomposition of a melt formed when  $\text{ZnO}$  and  $\text{NH}_4\text{Cl}$  are heated together at  $340^\circ\text{C}$  forms the complex salt  $\text{NH}_4\text{ZnCl}_3$ , which at  $400^\circ\text{C}$  decomposes to  $\text{ZnCl}_2$ ,  $\text{NH}_3$  and  $\text{HCl}$ <sup>6</sup>. Zinc oxide and  $\text{S}_2\text{Cl}_2$  with<sup>7</sup> or without<sup>8</sup> the presence of  $\text{Cl}_2$  gas yield  $\text{ZnCl}_2$  at  $450^\circ\text{C}$ :



Cadmium chloride may be prepared from  $\text{CdO}$  by the action of  $\text{S}_2\text{Cl}_2$  at elevated temperatures<sup>8</sup>, or by heating  $\text{CdO}$  and  $\text{NH}_4\text{Cl}$  together at  $\geq 400^\circ\text{C}$ <sup>6</sup>. Cadmium halides also form when  $\text{CdO}$  reacts with  $\text{CF}_2\text{BrCl}$  at  $400-500^\circ\text{C}$ <sup>2</sup>.

Mercury(II) oxide reacts with  $\text{PhC}(\text{O})\text{Cl}$  to yield  $\text{HgCl}_2$ <sup>9</sup>:

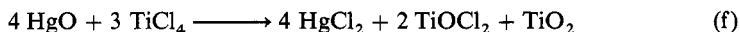


Alkali metal halides and an  $\text{HgO}$  suspension in  $\text{H}_2\text{O}$  react at  $40-50^\circ\text{C}$  to produce  $\text{HgCl}_2$ <sup>10,11</sup>:



Boron tribromide and  $\text{HgO}$  combine to form  $\text{HgBr}_2$ <sup>12</sup>.

Other halogenating agents drawn from first-row transition metals such as  $\text{TiCl}_4$ <sup>13</sup>, and main-group elements such as  $\text{PbCl}_2$ ,  $\text{AlCl}_3$ ,  $\text{AsCl}_3$  and  $\text{TeI}_4$ , react with  $\text{HgO}$ , e.g.:



(T.B. BRILL)

1. M. Chaigneau, M. Santarromana, *C. R. Hebd. Seances Acad. Sci., Ser. C*, 278, 1453 (1974).
2. M. Chaigneau, M. Chastagnier, *Bull. Soc. Chim. Fr.*, 11, 2357 (1974).
3. A. N. Ketov, V. V. Pechkovskii, L. P. Kostin, *Sb. Nauchn. Tr., Permsk. Politckhn. Inst.*, 3 (1963); *Chem. Abstr.*, 62, 3642e (1965).
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5. B. Attwood, R. A. J. Shelton, *J. Inorg. Nucl. Chem.*, 26, 1758 (1964).
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8. H. Funk, K. H. Berndt, G. Henze, *Wiss. Z. Martin-Luther Univ. Halle-Wittenburg*, 6, 815 (1957); *Chem. Abstr.*, 54, 12,860g (1960).
9. A. McGookin, H. Page, *J. Chem. Soc.*, 2769 (1951).
10. J. Fonberg, *Ann. Chim. Phys.*, 1, 300 (1864).
11. W. Bersch, *Z. Phys. Chem.*, 8, 383 (1891).

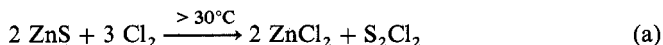
12. P. M. Druce, M. F. Lappert, *J. Chem. Soc., A*, 3595 (1971).  
 13. P. Ehrlich, W. Engel, *Z. Anorg. Allg. Chem.*, 322, 217 (1963).

## 2.8.16. Synthesis of the Group-IIB Dihalides from Metal Sulfides

### 2.8.16.1. by Halogenation.

The principal ore of Zn is sphalerite, or zinc blende, ZnS. Cadmium occurs in the mineral greenockite, CdS, but more commonly as an impurity in Zn ores. The most important commercial source of Hg is cinnabar, HgS. Thus the halogenation of the metal sulfides to produce the more chemically reactive halides is of major importance.

Zinc sulfide reacts with  $F_2$  and  $Cl_2$  to form  $ZnF_2$  and  $ZnCl_2$ . The formation of  $ZnCl_2$  by this route is an industrial method<sup>1</sup>:



The reaction may be run under conditions which produce S instead of  $S_2Cl_2$  as a product<sup>2</sup>. A sealed tube containing ZnS and  $I_2$  heated to  $200^\circ\text{C}$  yields  $ZnI_2$ <sup>3</sup>.

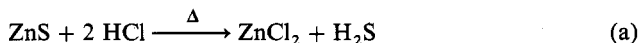
Cadmium sulfide and  $F_2$  form  $CdF_2$ <sup>4</sup>. The reaction of HgS and  $Cl_2$ ,  $Br_2$  or  $I_2$  produces the Hg(II) halide e.g., HgS burns in  $Cl_2$  forming  $HgCl_2$  and  $S_2Cl_2$ <sup>5</sup>. The reaction of HgS with  $Br_2$ <sup>6</sup> or  $Br_2$  in  $H_2O$ <sup>7</sup> yields  $HgBr_2$ , while trituration of HgS and  $I_2$  in EtOH liberates  $HgI_2$ <sup>3</sup>.

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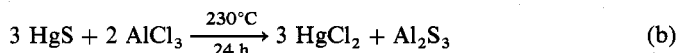
### 2.8.16.2. by Other Halogenating Agents.

Zinc sulfide can be chlorinated using anhyd  $HCl$ <sup>1</sup> or hot conc  $HCl$ <sup>2</sup>:



The sulfur chloride,  $S_2Cl_2$ , reacts with ZnS in anhydrous acetic acid to yield  $ZnCl_2$  which is obtained on evaporation<sup>3</sup>. Metal chlorides may also be used e.g.,  $CuCl_2$  in boiling  $H_2O$  converts ZnS to  $ZnCl_2$  with  $CuS$  as a product<sup>4</sup>, while  $FeCl_3$  reacts with wet ZnS to produce  $ZnCl_2$ <sup>5</sup>.

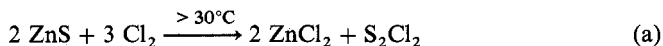
A commercial preparation of  $ZnCl_2$  involves roasting ZnS with  $NaCl$ <sup>6</sup>. A melt of ZnS, CdS or HgS and  $AlCl_3$  produces the respective group-IIB chloride<sup>7</sup>, e.g.:



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Zinc sulfide reacts with F<sub>2</sub> and Cl<sub>2</sub> to form ZnF<sub>2</sub> and ZnCl<sub>2</sub>. The formation of ZnCl<sub>2</sub> by this route is an industrial method<sup>1</sup>:



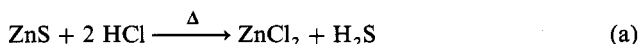
The reaction may be run under conditions which produce S instead of S<sub>2</sub>Cl<sub>2</sub> as a product<sup>2</sup>. A sealed tube containing ZnS and I<sub>2</sub> heated to 200°C yields ZnI<sub>2</sub><sup>3</sup>.

Cadmium sulfide and F<sub>2</sub> form CdF<sub>2</sub><sup>4</sup>. The reaction of HgS and Cl<sub>2</sub>, Br<sub>2</sub> or I<sub>2</sub> produces the Hg(II) halide e.g., HgS burns in Cl<sub>2</sub> forming HgCl<sub>2</sub> and S<sub>2</sub>Cl<sub>2</sub><sup>5</sup>. The reaction of HgS with Br<sub>2</sub><sup>6</sup> or Br<sub>2</sub> in H<sub>2</sub>O<sup>7</sup> yields HgBr<sub>2</sub>, while trituration of HgS and I<sub>2</sub> in EtOH liberates HgI<sub>2</sub><sup>3</sup>.

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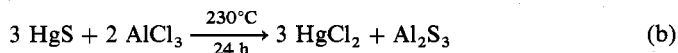
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The sulfur chloride, S<sub>2</sub>Cl<sub>2</sub>, reacts with ZnS in anhydrous acetic acid to yield ZnCl<sub>2</sub> which is obtained on evaporation<sup>3</sup>. Metal chlorides may also be used e.g., CuCl<sub>2</sub> in boiling H<sub>2</sub>O converts ZnS to ZnCl<sub>2</sub> with CuS as a product<sup>4</sup>, while FeCl<sub>3</sub> reacts with wet ZnS to produce ZnCl<sub>2</sub><sup>5</sup>.

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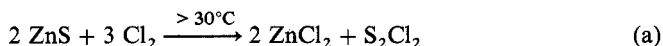
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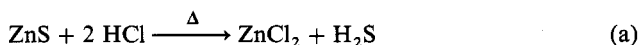
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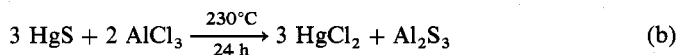
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A commercial preparation of ZnCl<sub>2</sub> involves roasting ZnS with NaCl<sup>6</sup>. A melt of ZnS, CdS or HgS and AlCl<sub>3</sub> produces the respective group-II B chloride<sup>7</sup>, e.g.:

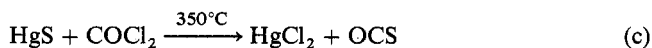




142    2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond  
2.8.17. Synthesis of Group-IIB Halides from Metal Oxy Salts  
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Nonmetal halogenating agents such as a boiling conc HBr soln<sup>8</sup>, S<sub>2</sub>Cl<sub>2</sub><sup>9</sup> and COCl<sub>2</sub> at 350°C<sup>10</sup> produce Hg(II) halides, e.g.:



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Soluble group-IIB salts and carbonates are useful starting points in the synthesis of group-IIB halides because conditions are not drastic. The reactions are run in H<sub>2</sub>O, so hydrates form when they are stable. These must be dehydrated if the anhydrous form is sought.

Smithsonite, ZnCO<sub>3</sub>, may be converted to hydrated ZnF<sub>2</sub> by heating in the presence of 40% HF<sup>1,2</sup>. Drying at 200°C removes some water<sup>1</sup>, but complete dehydration may require 800°C in vacuum<sup>2</sup>. Liquid HF and ZnCO<sub>3</sub> also lead to ZnF<sub>2</sub><sup>3</sup>. Zinc chloride results when ZnCO<sub>3</sub><sup>1</sup> or ZnSO<sub>4</sub> is subjected to HCl. Dry HCl at 220–250°C produces anhyd ZnCl<sub>2</sub><sup>4</sup>, but in H<sub>2</sub>O hydrated ZnCl<sub>2</sub> appears<sup>2</sup>.

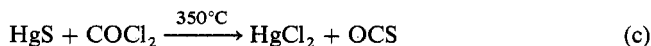
Cadmium carbonate reacts with 40% HF to give hydrated CdF<sub>2</sub><sup>5</sup>. Evaporation of the solution followed by heating at 150°C in vacuum removes the hydrated H<sub>2</sub>O. The reaction of CdCO<sub>3</sub> or Cd(NO<sub>3</sub>)<sub>2</sub> with conc HCl followed by evaporation produces CdCl<sub>2</sub> with some hydration<sup>6</sup>. The anhydrous salt is obtained by distilling the CdCl<sub>2</sub> in an HCl–N<sub>2</sub> gas stream. Cadmium bromide prepared from CdCO<sub>3</sub> and HBr solution can be dehydrated by heating to 200°C. Final purification is achieved by subliming the CdBr<sub>2</sub> in a stream of dry CO<sub>2</sub><sup>7</sup>. The preparation of CdI<sub>2</sub> from CdCO<sub>3</sub> and aq HI is straightforward<sup>8</sup>. Mercury(II) nitrate and sulfate react with gaseous or aq<sup>6</sup> HCl<sup>9</sup> to yield HgCl<sub>2</sub>.

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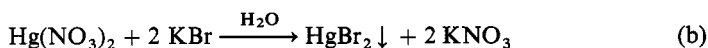
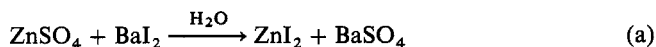
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The principle of combining a water-soluble  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  or  $\text{Hg}^{2+}$  salt with that of a soluble halide to produce a less soluble group-IIB halide or counter salt is readily applied:



Zinc chloride is prepared by combining soluble  $\text{Zn}^{2+}$  salts with soluble  $\text{Cl}^-$  salts in  $\text{H}_2\text{O}$ . If an immiscible organic solvent that is able to complex with  $\text{ZnCl}_2$  is also added, then the complex can be isolated and decomposed to give  $\text{ZnCl}_2$ <sup>1</sup>. This method also applies to the preparation of  $\text{CdCl}_2$ . Dry metathesis in which  $\text{ZnSO}_4$  and  $\text{CaCl}_2$  are combined and heated leads to  $\text{ZnCl}_2$ <sup>2</sup>, which can be sublimed.

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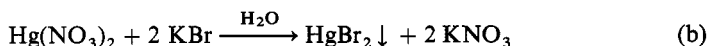
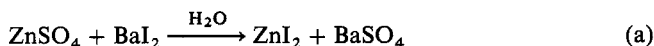
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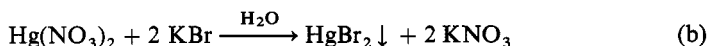
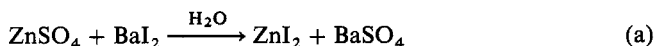
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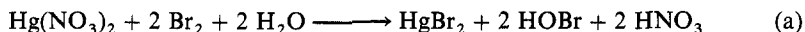
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Iodination of  $\text{Hg}(\text{OAc})_2$  to produce  $\text{HgI}_2$  occurs with  $\text{I}_2$  and  $\text{Me}_2\text{CO}$  in glacial  $\text{AcOH}$  <sup>3</sup> or when  $\text{MeI}$  in  $\text{H}_2\text{O}$  is shaken with  $\text{Hg}(\text{OAc})_2$  for 12 h <sup>5</sup>.

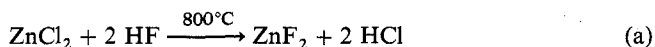
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1. G. W. Watt, P. S. Gentile, E. P. Helvenston, *J. Am. Chem. Soc.*, **77**, 2752 (1955).
2. V. R. Gonzalez, *Rev. Fac. Cien. Univ. Oviedo*, **7**, 83 (1966); *Chem. Abstr.*, **65**, 14,823b (1966).
3. H. D. Hardt, R. Bollig, *Angew. Chem., Int. Ed. Engl.*, **4**, 869 (1965).
4. W. Sievers, *Chem. Ber.*, **24**, 644 (1888).
5. F. Bodroux, *C. R. Hebd. Seances Acad. Sci.*, **130**, 1622 (1900).

## 2.8.18. Synthesis of the Group-IIIB Dihalides by Halide-Halide Exchange.

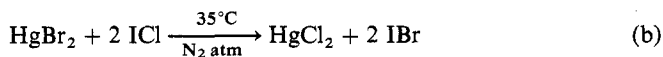
Anion metathesis among the group-IIIB dihalides follows the hard (class a) and soft (class b) acid-base principles. With  $\text{Hg}(\text{II})$ , which is soft, a softer halide replaces a harder one; hence  $\text{I} > \text{Br} > \text{Cl} > \text{F}$  in the tendency to bond to  $\text{Hg}$ . Zinc(II) and Cd(II) show the reverse behavior; i.e.,  $\text{F}^-$  replaces  $\text{Cl}^-$  in the dihalides, although the trend is not as pronounced with Cd.

Zinc fluoride can be prepared by reacting  $\text{ZnCl}_2$  or  $\text{ZnBr}_2$  with a fluoride salt or  $\text{HF}$ . Hydrogen fluoride reacts at  $800^\circ\text{C}$  <sup>1</sup>:



The same reaction is observed with  $\text{CdCl}_2$  and  $\text{HF}$  <sup>1</sup>. Anhydrous  $\text{ZnF}_2$  and  $\text{CdF}_2$  form when  $\text{ZnCl}_2$  <sup>2</sup> or  $\text{CdCl}_2$  <sup>3</sup> react with  $\text{NH}_4\text{F}$ , but the reaction of  $\text{CdCl}_2$  with  $\text{BBr}_3$  yields  $\text{CdBr}_2$  because of the greater affinity of B and Cl than B and Br.

Mercury(II) fluoride can be prepared from  $\text{HgCl}_2$  and  $\text{F}_2$  <sup>5-7</sup>. When  $\text{HgI}_2$  is combined with  $\text{F}_2$ , the mixture inflames in the cold producing  $\text{HgF}_2$  and  $\text{IF}_3$  <sup>8</sup>. Mercury(II) chloride and  $\text{ICl}_3$  are formed when  $\text{Cl}_2$  is passed through an aqueous suspension of  $\text{HgI}_2$  <sup>9</sup>. Metathesis occurs between  $\text{HgBr}_2$  and  $\text{ICl}$  <sup>10</sup>:



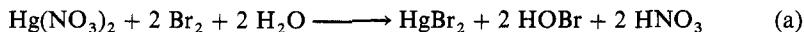
Mercury(II) bromide results when aq  $\text{HgCl}_2$  and  $\text{Br}_2$  <sup>11</sup> or an alkali-metal bromide salt <sup>12</sup> are heated on a water bath. In keeping with hard-soft acid-base ideas,  $\text{KCl}$  and  $\text{HgBr}_2$  do not react <sup>12</sup>. Mercury(II) iodide forms from  $\text{HgCl}_2$  and  $\text{I}_2$  in  $\text{Et}_2\text{O}$  <sup>11</sup>. The reaction also occurs when  $\text{HgCl}_2$  is heated with aq  $\text{HI}$  <sup>13</sup> or  $\text{KI}$  <sup>14,15</sup> to produce  $\text{HgI}_2$ . Methyl iodide and  $\text{HgCl}_2$  in  $\text{Et}_2\text{O}$  produce  $\text{HgI}_2$  when exposed to sunlight <sup>16</sup>.

(T.B. BRILL)

1. C. Poulenc, *C. R. Hebd. Seances Acad. Sci.*, **116**, 581 (1893).
2. W. Mills, *Br. Pat.* 20377 (1895).
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2.8.18. Synthesis of the Group-IIIB Dihalides by Halide-Halide Exchange.

Chlorination to  $\text{HgCl}_2$  occurs when  $\text{Hg}(\text{NO}_3)_2$  reacts with  $\text{AcCl}$ <sup>2</sup>. Aqueous  $\text{Hg}(\text{NO}_3)_2$  reacts with  $\text{Cl}_2$  and  $\text{Br}_2$  to yield  $\text{HgCl}_2$  and  $\text{HgBr}_2$ <sup>4</sup>:



Iodination of  $\text{Hg}(\text{OAc})_2$  to produce  $\text{HgI}_2$  occurs with  $\text{I}_2$  and  $\text{Me}_2\text{CO}$  in glacial  $\text{AcOH}$ <sup>3</sup> or when  $\text{MeI}$  in  $\text{H}_2\text{O}$  is shaken with  $\text{Hg}(\text{OAc})_2$  for 12 h<sup>5</sup>.

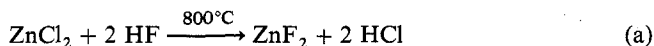
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5. F. Bodroux, *C. R. Hebd. Seances Acad. Sci.*, **130**, 1622 (1900).

## 2.8.18. Synthesis of the Group-IIIB Dihalides by Halide-Halide Exchange.

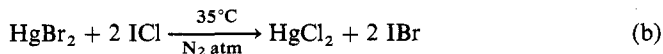
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6. G. Brauer, *Handbook of Preparative Inorganic Chemistry*, Vol. 1, 2nd ed., Academic Press, Inc., New York, 1963, p. 244.
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8. H. Moissan, *Le fluor et ses Composés*, Paris (1900) p. 227.
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12. T. Harth, *Z. Anorg. Allg. Chem.*, 18, 326 (1896).
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16. M. C. Schuyten, *Chem. Z.*, 19, 1683 (1895).

## 2.8.19. Synthesis from Dehydration of Hydrates of the Group-IIB Dihalides.

The group-IIB halides crystallize as hydrates from aqueous solution or when water is present from the reaction or the atmosphere. This tendency to hydrate is most pronounced when the ionic potential of the cations is large, i.e., for  $\text{Zn}^{2+} > \text{Cd}^{2+} > \text{Hg}^{2+}$ , and when the anion is small. In the latter instance,  $\text{ZnI}_2$  forms hydrates at  $< \text{RT}$ , but,  $\text{CdI}_2$ ,  $\text{HgI}_2$  or  $\text{Hg}_2\text{I}_2$  form no known hydrates. Hydrates of  $\text{ZnF}_2$ ,  $\text{CdF}_2$  and  $\text{HgF}_2$  are all known. Dehydration of these salts is accomplished by heating or chemical methods.

The Zn halides show the greatest tendency toward crystalline hydration and are highly deliquescent when prepared in the anhydrous form. Some dehydration of  $\text{ZnF}_2 \cdot 4 \text{H}_2\text{O}$  occurs at  $100^\circ\text{C}$ <sup>1</sup>, but  $800^\circ\text{C}$  in a dry atmosphere may be necessary<sup>2</sup>;  $\text{ZnF}_2 \cdot 4 \text{H}_2\text{O}$  can also be dehydrated in a current of  $\text{HF}$ <sup>3</sup>. The dihydrate loses water on heating but can form  $\text{ZnF}_2 \cdot \frac{1}{2} \text{H}_2\text{O}$  in addition to  $\text{ZnF}_2$ <sup>4</sup>;  $\text{ZnO}$  may also form<sup>4</sup>.

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TABLE 1. THE  $\text{ZnCl}_2 \cdot n \text{H}_2\text{O}$  COMPOSITION AND TEMPERATURE RANGE OF STABILITY FOR VARIOUS WEIGHTS PER CENT  $\text{ZnCl}_2$ - $\text{H}_2\text{O}$  SOLUTION<sup>5</sup>

Composition	Wt % $\text{ZnCl}_2$ in $\text{H}_2\text{O}$	Temperature range ( $^\circ\text{C}$ )
$\text{ZnCl}_2 \cdot 4 \text{H}_2\text{O}$	51	$< -30$
$\text{ZnCl}_2 \cdot 3 \text{H}_2\text{O}$	71.6	$-30$ – $6.5$
$\text{ZnCl}_2 \cdot 2\frac{1}{2} \text{H}_2\text{O}$	75.5	$6.5$ – $12.5$
$\text{ZnCl}_2 \cdot 1\frac{1}{2} \text{H}_2\text{O}$	77	$12.5$ – $25$
$\text{ZnCl}_2 \cdot \text{H}_2\text{O}$	80.9	$25$
$\text{ZnCl}_2$	81.2	$> 25$



## 2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond 145

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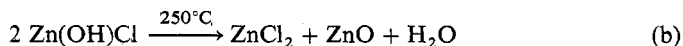
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$\text{ZnCl}_2 \cdot \text{H}_2\text{O}$	80.9	$25$
$\text{ZnCl}_2$	81.2	$> 25$

Zinc bromide occurs as  $\text{ZnBr}_2 \cdot 3 \text{H}_2\text{O}$  and  $\text{ZnBr}_2 \cdot 2 \text{H}_2\text{O}$ . The trihydrate exists when  $\text{ZnBr}_2$  in  $\text{H}_2\text{O}$  is 78% by weight at  $< 0^\circ\text{C}$ <sup>10</sup>. At 80–85 wt%  $\text{ZnBr}_2$  and at 0–35°C,  $\text{ZnBr}_2 \cdot 2 \text{H}_2\text{O}$  is present<sup>10</sup>. Above this temperature and composition  $\text{ZnBr}_2$  exists<sup>11</sup>. Dehydration of the  $\text{ZnBr}_2$  occurs on heating. The di- and tetrahydrates of  $\text{ZnI}_2$  are known. The tetrahydrate converts to the dihydrate at  $-7^\circ\text{C}$ . The dihydrate is stable in the  $-7$  to  $0^\circ\text{C}$  region when the  $\text{ZnI}_2$  wt% in  $\text{H}_2\text{O}$  is  $< 80$  wt%<sup>12</sup>. At  $> 0^\circ\text{C}$  and at  $> 80$  wt%  $\text{ZnI}_2$  in  $\text{H}_2\text{O}$ ,  $\text{ZnI}_2$  exists in the nonhydrated form<sup>13</sup>.

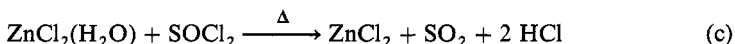
Cadmium fluoride may form as  $\text{CdF}_2 \cdot 2 \text{H}_2\text{O}$ , which slowly dehydrates at RT<sup>14</sup>. The anhydrous material can be obtained by heating  $\text{CdF}_2$  to  $150^\circ\text{C}$  in vacuum<sup>15</sup>. Cadmium chloride has several hydrates, e.g.,  $\text{CdCl}_2 \cdot 4 \text{H}_2\text{O}$ ,  $\text{CdCl}_2 \cdot 2\frac{1}{2} \text{H}_2\text{O}$  and  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ . The tetrahydrate is stable in contact with  $\text{H}_2\text{O}$  when the  $\text{CdCl}_2$  wt% is  $< 47$   $< -5^\circ\text{C}$ . In the range 47–57 wt%  $\text{CdCl}_2$  and at  $-5$  to  $34^\circ\text{C}$ ,  $\text{CdCl}_2 \cdot 2\frac{1}{2} \text{H}_2\text{O}$  occurs. At 57–60 wt%  $\text{CdCl}_2$  and at  $34$ – $102^\circ\text{C}$ ,  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$  exists<sup>10,13</sup>. The anhydrous salt can be obtained by distilling the  $\text{CdCl}_2$  in an  $\text{HCl-N}_2$  stream<sup>16</sup>. Cadmium bromide hydrates as  $\text{CdBr}_2 \cdot 4 \text{H}_2\text{O}$  and  $\text{CdBr}_2 \cdot \text{H}_2\text{O}$ . The tetrahydrate exists at  $< 36^\circ\text{C}$  for  $< 60$  wt%  $\text{CdBr}_2$  and  $\text{H}_2\text{O}$ . In the 60–71 wt% range, the mono-hydrate is present  $< 245^\circ\text{C}$ <sup>10,13</sup>. Dehydration of  $\text{CdBr}_2 \cdot 4 \text{H}_2\text{O}$  is accomplished by sublimation in a stream of an inert atmosphere, such as  $\text{CO}_2$ <sup>17</sup>, or heating at  $200^\circ\text{C}$ . Dehydration also occurs at RT over  $\text{H}_2\text{SO}_4$ <sup>18</sup>. Cadmium iodide does not form a hydrate.

The only important hydrate of the mercury halides is  $\text{HgF}_2 \cdot 2 \text{H}_2\text{O}$ , which cannot be dehydrated by heating<sup>19</sup>. Heat causes loss of  $\text{HF}$  in addition to  $\text{H}_2\text{O}$ . The Hg-containing products are a mixture of  $\text{HgO}$ ,  $\text{HgOHF}$  and  $\text{HgF}_2$ <sup>20</sup>.

Zinc chloride can be prepared from other Zn-containing compounds by heating. Although not formally a dehydration process, these reactions merit mention here<sup>21</sup>:



Finally, a nonthermal method for obtaining anhyd  $\text{ZnCl}_2$  and  $\text{CdCl}_2$  involves refluxing freshly distilled  $\text{SOCl}_2$  with the moist  $\text{ZnCl}_2$  or  $\text{CdCl}_2$ <sup>22</sup>:



The  $\text{CdCl}_2$  or  $\text{ZnCl}_2$  obtained by this method should be stored over  $\text{KOH}$  for 12 h to remove xs  $\text{SOCl}_2$ .

(T.B. BRILL)

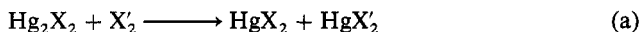
1. J. C. G. de Marignac, *Ann. Chim. Phys.*, **60**, 30 (1860).
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22. A. R. Pray, *Inorg. Synth.* 5, 154 (1957).

## 2.8.20. Synthesis of Mercury(II) Halides from Mercury(I) Halides

### 2.8.20.1. by Halogenation.

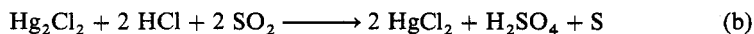
Elemental halogens and the hydrohalic acids react with Hg(I) halides to produce Hg(II) halides, either dry or in aqueous solution:



Chlorine reacts with  $\text{Hg}_2\text{F}_2$  producing  $\text{HgF}_2$  and  $\text{HgCl}_2$ . The  $\text{HgCl}_2$  product can be sublimed from the mixture by heating at  $>275^\circ\text{C}$ <sup>1</sup>. Elemental  $\text{Br}_2$  reacts with  $\text{Hg}_2\text{F}_2$  at  $400^\circ\text{C}$  to yield  $\text{HgF}_2$  and  $\text{HgBr}_2$ <sup>1</sup>.

Mercury(I) chloride reacts with  $\text{Cl}_2$ ,  $\text{Br}_2$  and  $\text{I}_2$  by Eq (a) to produce  $\text{HgCl}_2$  and  $\text{HgBr}_2$  or  $\text{HgI}_2$ . The reaction rate is  $\text{I}_2 > \text{Br}_2 > \text{Cl}_2$ <sup>2</sup>. Bromine water reacts with  $\text{Hg}_2\text{Cl}_2$  to yield  $\text{HgCl}_2$  and  $\text{HgBr}_2$ <sup>1</sup>, while solid or dissolved  $\text{I}_2$  reacts with  $\text{Hg}_2\text{Br}_2$  to give  $\text{HgI}_2$  and  $\text{Br}_2$  as products<sup>3</sup>.

Another class of halogenating agents is the hydrohalic acids. The reaction of aq HI and  $\text{Hg}_2\text{I}_2$  yields  $\text{HgI}_2$  and  $\text{Hg}$ <sup>4</sup>. Mercury(I) chloride reacts with  $\text{HCl}$  in  $\text{SO}_2$ <sup>5</sup> or  $\text{SeO}_2$ <sup>5</sup>:



Sulfur trioxide oxidizes  $\text{Hg}_2\text{Br}_2$  and  $\text{Hg}_2\text{I}_2$  to Hg(II) salts<sup>7</sup>:



The products may be heated to sublime away the  $\text{HgBr}_2$ . Light slowly disproportionates  $\text{Hg}_2\text{Cl}_2$  to  $\text{HgCl}_2$  and  $\text{Hg}$ , so  $\text{Hg}_2\text{Cl}_2$  is stored in amber-colored bottles.

Other Hg(I) salts participate in halogenation reactions, the most notable being  $\text{Hg}_2(\text{NO}_3)_2$ , which is solubilized with  $\text{HNO}_3$ . With  $\text{I}_2$   $\text{Hg}_2(\text{NO}_3)_2$  in boiling  $\text{H}_2\text{O}$  precipitates  $\text{HgI}_2$ . Boiling conc  $\text{HCl}$  reacts with  $\text{Hg}_2(\text{NO}_3)_2$ <sup>9</sup>:



Mercury(I) oxide and  $\text{BBr}_3$  form  $\text{HgBr}_2$ , while iodine and  $\text{Hg}_2\text{O}$  may be trituated together and the residue extracted with  $\text{EtOH}$  to dissolve and remove  $\text{HgI}_2$ <sup>11</sup>.

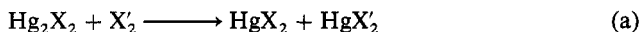
2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond 147  
 2.8.20. Synthesis of Mercury(II) Halides from Mercury(I) Halides  
 2.8.20.1. by Halogenation.

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## 2.8.20. Synthesis of Mercury(II) Halides from Mercury(I) Halides

### 2.8.20.1. by Halogenation.

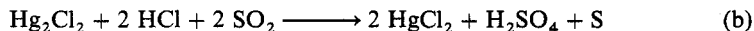
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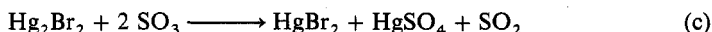
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## 148 2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond

### 2.8.21. Synthesis of Mercury(I) Halides

#### 2.8.21.1. by Metathesis Reactions of Other Mercury(I) Salts.

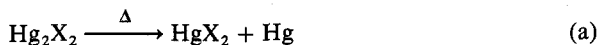
Mixed Hg(II) halides, HgBrI, HgBrCl, HgFBr, etc., form when Hg<sub>2</sub>F<sub>2</sub>, Hg<sub>2</sub>Cl<sub>2</sub>, Hg<sub>2</sub>Br<sub>2</sub> and Hg<sub>2</sub>I<sub>2</sub> are heated with Br<sub>2</sub> and I<sub>2</sub><sup>12,13</sup>.

(T.B. BRILL)

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#### 2.8.20.2. by Disproportionation Reactions.

Mercury(I) halides disproportionate to yield Hg(II) halides and elemental mercury:



Mercury(I) fluoride requires heating to 450°C<sup>1</sup>. Boiling Hg<sub>2</sub>Cl<sub>2</sub> in water or heating the solid yields HgCl<sub>2</sub> and Hg<sup>2</sup>. Mercury(I) bromide and iodide undergo decomposition when heated<sup>3</sup>, but the reaction is usually not complete.

(T.B. BRILL)

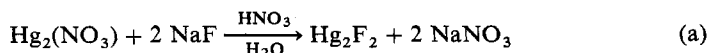
1. O. Ruff, G. Bahlau, *Chem. Ber.*, 51, 1752 (1918).
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### 2.8.21. Synthesis of Mercury(I) Halides

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Exchange of anions is a facile means of synthesizing Hg(I) halides. In most cases a soluble Hg(I) salt or Hg<sub>2</sub>CO<sub>3</sub> is used because the halide products are insoluble. Acidification is often necessary to prevent the formation of Hg<sub>2</sub>O.

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The pale yellow Hg<sub>2</sub>F<sub>2</sub> is sublimed from the dried reaction product by heating to >260°C. Some etching of glass containers is observed. Alternatively, freshly prepared

**148 2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond****2.8.21. Synthesis of Mercury(I) Halides****2.8.21.1. by Metathesis Reactions of Other Mercury(I) Salts.**

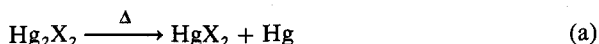
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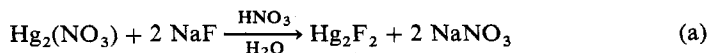
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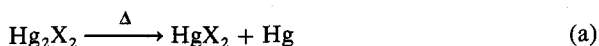
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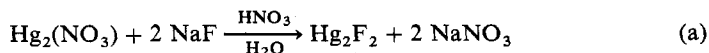
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Mercury(I) fluoride, a useful fluorinating agent, may be prepared by adding an alkali-metal fluoride to HNO<sub>3</sub>-acidified Hg<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub><sup>1</sup>:



The pale yellow Hg<sub>2</sub>F<sub>2</sub> is sublimed from the dried reaction product by heating to >260°C. Some etching of glass containers is observed. Alternatively, freshly prepared

$\text{Hg}_2\text{CO}_3$  reacts with 40 vol % HF by heating on a water bath to produce  $\text{Hg}_2\text{F}_2$  <sup>2-4</sup>. The reaction of AgF with  $\text{Hg}_2\text{Cl}_2$  in acidified  $\text{H}_2\text{O}$  precipitates AgCl, which is filtered and the solution evaporated to produce  $\text{Hg}_2\text{F}_2$  <sup>2</sup>.

Mercury(I) chloride, known as calomel, has historical importance as a medicinal. The addition of alkali-metal chlorides to dissolved Hg(I) salts precipitates  $\text{Hg}_2\text{Cl}_2$  <sup>5</sup>. The commercial preparation involves adding NaCl to aq  $\text{Hg}_2(\text{NO}_3)_2$  acidified with  $\text{HNO}_3$ . The  $\text{Hg}_2\text{Cl}_2$  produced is filtered, washed, dried and sublimed<sup>6</sup>. A dry method of preparing  $\text{Hg}_2\text{Cl}_2$  involves heating  $\text{Hg}_2\text{SO}_4$  and NaCl for 5–6 h. The  $\text{Hg}_2\text{Cl}_2$  sublimes as the reaction progresses<sup>7</sup>. Mercury(I) oxide reacts similarly with HCl to produce  $\text{Hg}_2\text{Cl}_2$  <sup>8</sup>.

Mercury(I) bromide is precipitated by metathesis of KBr and  $\text{Hg}_2(\text{NO}_3)_2$  in dil  $\text{HNO}_3$ , filtered, washed, dried and sublimed<sup>9</sup>. Alternatively, grinding  $\text{Hg}_2\text{Cl}_2$  and KBr together in  $\text{H}_2\text{O}$  produces  $\text{Hg}_2\text{Br}_2$  and KCl <sup>10</sup>.

Mercury(I) iodide, a light-sensitive, yellow compound, can be difficult to obtain pure. Mercury(I) iodide sublimes red, but turns yellow on cooling. The addition of KI to an  $\text{HNO}_3$ -acidified  $\text{Hg}_2(\text{NO}_3)_2$  soln produces  $\text{Hg}_2\text{I}_2$  which can be filtered, washed and dried in a vacuum<sup>11</sup>. The product must be filtered rapidly from the  $\text{HNO}_3$  solution to prevent oxidation to  $\text{HgI}_2$ . Metathesis of alkali-metal iodides with  $\text{Hg}_2\text{Cl}_2$  and  $\text{Hg}_2\text{Br}_2$  leads to  $\text{Hg}_2\text{I}_2$ . When  $\text{Hg}_2\text{Cl}_2$  and KI are mixed in  $\text{H}_2\text{O}$ , the impure  $\text{Hg}_2\text{I}_2$  produced is often green in color, owing to the presence of mercury metal<sup>12</sup>. The  $\text{Hg}_2\text{I}_2$  may also be prepared from  $\text{Hg}_2\text{Br}_2$  <sup>10</sup> or xs  $\text{Hg}_2\text{O}$ <sup>13</sup> and a dil KI solution. Organoiodine compounds also react with Hg(I) salts to produce  $\text{Hg}_2\text{I}_2$ ; e.g.,  $\text{Hg}_2(\text{NO}_3)_2$  and EtI react on a water bath to produce  $\text{Hg}_2\text{I}_2$  <sup>14</sup>.

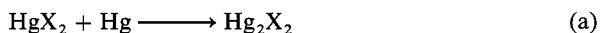
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### 2.8.21.2. by Reduction of Mercury(II) Halides.

It was known to the alchemists that  $\text{HgCl}_2$  and Hg would react to form  $\text{Hg}_2\text{Cl}_2$ . Since the earliest days of chemistry reducing agents have been found to convert Hg(II) to Hg(I).

Mercury(II) chloride,  $\text{HgBr}_2$  and  $\text{HgI}_2$  react with Hg:





**2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond 149****2.8.21. Synthesis of Mercury(I) Halides****2.8.21.2. by Reduction of Mercury(II) Halides.**

$\text{Hg}_2\text{CO}_3$  reacts with 40 vol % HF by heating on a water bath to produce  $\text{Hg}_2\text{F}_2$ <sup>2-4</sup>. The reaction of AgF with  $\text{Hg}_2\text{Cl}_2$  in acidified  $\text{H}_2\text{O}$  precipitates AgCl, which is filtered and the solution evaporated to produce  $\text{Hg}_2\text{F}_2$ <sup>2</sup>.

Mercury(I) chloride, known as calomel, has historical importance as a medicinal. The addition of alkali-metal chlorides to dissolved Hg(I) salts precipitates  $\text{Hg}_2\text{Cl}_2$ <sup>5</sup>. The commercial preparation involves adding NaCl to aq  $\text{Hg}_2(\text{NO}_3)_2$  acidified with  $\text{HNO}_3$ . The  $\text{Hg}_2\text{Cl}_2$  produced is filtered, washed, dried and sublimed<sup>6</sup>. A dry method of preparing  $\text{Hg}_2\text{Cl}_2$  involves heating  $\text{Hg}_2\text{SO}_4$  and NaCl for 5–6 h. The  $\text{Hg}_2\text{Cl}_2$  sublimes as the reaction progresses<sup>7</sup>. Mercury(I) oxide reacts similarly with HCl to produce  $\text{Hg}_2\text{Cl}_2$ <sup>8</sup>.

Mercury(I) bromide is precipitated by metathesis of KBr and  $\text{Hg}_2(\text{NO}_3)_2$  in dil  $\text{HNO}_3$ , filtered, washed, dried and sublimed<sup>9</sup>. Alternatively, grinding  $\text{Hg}_2\text{Cl}_2$  and KBr together in  $\text{H}_2\text{O}$  produces  $\text{Hg}_2\text{Br}_2$  and KCl<sup>10</sup>.

Mercury(I) iodide, a light-sensitive, yellow compound, can be difficult to obtain pure. Mercury(I) iodide sublimes red, but turns yellow on cooling. The addition of KI to an  $\text{HNO}_3$ -acidified  $\text{Hg}_2(\text{NO}_3)_2$  soln produces  $\text{Hg}_2\text{I}_2$  which can be filtered, washed and dried in a vacuum<sup>11</sup>. The product must be filtered rapidly from the  $\text{HNO}_3$  solution to prevent oxidation to  $\text{HgI}_2$ . Metathesis of alkali-metal iodides with  $\text{Hg}_2\text{Cl}_2$  and  $\text{Hg}_2\text{Br}_2$  leads to  $\text{Hg}_2\text{I}_2$ . When  $\text{Hg}_2\text{Cl}_2$  and KI are mixed in  $\text{H}_2\text{O}$ , the impure  $\text{Hg}_2\text{I}_2$  produced is often green in color, owing to the presence of mercury metal<sup>12</sup>. The  $\text{Hg}_2\text{I}_2$  may also be prepared from  $\text{Hg}_2\text{Br}_2$ <sup>10</sup> or xs  $\text{Hg}_2\text{O}$ <sup>13</sup> and a dil KI solution. Organoiodine compounds also react with Hg(I) salts to produce  $\text{Hg}_2\text{I}_2$ ; e.g.,  $\text{Hg}_2(\text{NO}_3)_2$  and EtI react on a water bath to produce  $\text{Hg}_2\text{I}_2$ <sup>14</sup>.

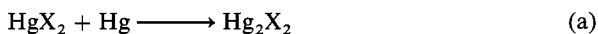
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**2.8.21.2. by Reduction of Mercury(II) Halides.**

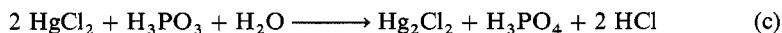
It was known to the alchemists that  $\text{HgCl}_2$  and Hg would react to form  $\text{Hg}_2\text{Cl}_2$ . Since the earliest days of chemistry reducing agents have been found to convert Hg(II) to Hg(I).

Mercury(II) chloride,  $\text{HgBr}_2$  and  $\text{HgI}_2$  react with Hg:

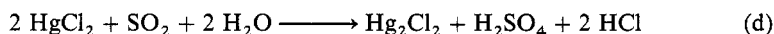


When  $X = \text{Cl}^1$  or  $\text{Br}^2$ , heat and trituration are required<sup>1</sup>. When  $X = \text{I}$ , an EtOH soln may be employed<sup>3</sup>. Other metals can be used in place of Hg, e.g., Cu<sup>4</sup>.

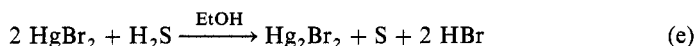
Reducing agents based on main-group oxides and oxy salts react with  $\text{HgCl}_2$  to yield  $\text{Hg}_2\text{Cl}_2$ . Phosphorous<sup>5</sup> and hypophosphorous<sup>6</sup> acids react with  $\text{HgCl}_2$ <sup>5</sup> without heating:



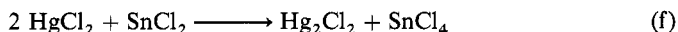
Various sulfur oxides reduce  $\text{Hg(II)}$ . Sulfur dioxide in the presence of  $\text{H}_2\text{O}$  reacts<sup>7</sup>:



$\text{Li}_2\text{SO}_3$  in  $\text{H}_2\text{O}$  also reacts<sup>8</sup>. An alcohol solution of  $\text{H}_2\text{S}$  added dropwise to  $\text{HgBr}_2$  in EtOH reacts<sup>9</sup>:

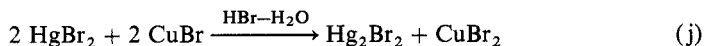
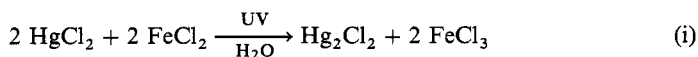
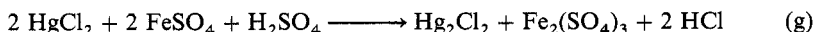


Tin(II) in  $\text{H}_2\text{O}$  or organic solvents reduces  $\text{HgCl}_2$ <sup>10</sup>:

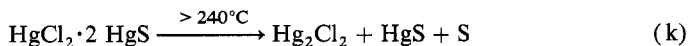


which may be run in a KI-EtOH- $\text{H}_2\text{O}$  soln to yield  $\text{Hg}_2\text{I}_2$ <sup>11</sup>.

Transition-metal-reducing agents can also be employed, e.g., iron(II)<sup>12,13</sup> and Cu(I)<sup>4</sup>:



Homogeneous reduction of aq  $\text{HgBr}_2$  by  $\text{H}_2$  to  $\text{Hg}_2\text{Br}_2$  occurs in a pressure bomb at  $120^\circ\text{C}$ <sup>14</sup>. Mixed salts of  $\text{Hg(II)}$  undergo oxidation-reduction<sup>15</sup>:



Photolysis reactions can play a role in the production of  $\text{Hg(I)}$  halides; e.g.,  $\text{Hg}_2\text{Cl}_2$  can be produced from  $\text{HgCl}_2$  by UV radiation<sup>16</sup>, or by irradiation of an aq  $\text{HgCl}_2$ ,  $\text{N}_2\text{H}_4 \cdot \text{HCl}$  and  $\text{HCl}$  by 180 kV X-rays<sup>17</sup>.

(T.B. BRILL)

1. O. Wolff, *Chem.-Z.*, **36**, 1039 (1912).
2. W. Matthies, *Ann. Physik.*, **17**, 675 (1905).
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## 2.8.21. Synthesis of Mercury(I) Halides

## 2.8.21.3. by Oxidation of the Mercury Metal.

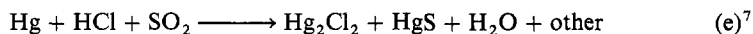
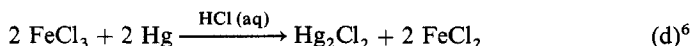
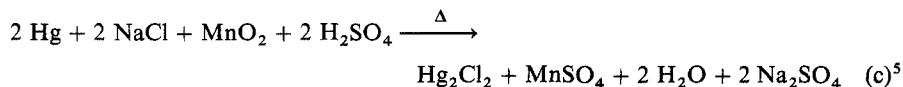
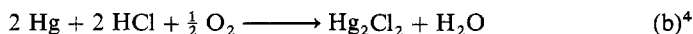
10. G. A. Linhart, E. Q. Adams, *J. Am. Chem. Soc.*, **39**, 948 (1917).
11. A. Agrestini, *Boll. Chim. Farm.*, **70**, 418 (1931); *Chem. Abstr.*, **25**, 4481 (1931).
12. C. W. Hempel, *Ann. Chem.*, **107**, 97 (1958).
13. C. Winther, *Z. Elektrochem.*, **18**, 138 (1912).
14. G. J. Korinek, J. Halpern, *Can. J. Chem.*, **34**, 1372 (1956).
15. J. Lamure, *C. R. Hebd. Seances Acad. Sci.*, **225**, 525 (1947).
16. F. Krause, K. Berge, *J. Prakt. Chem.*, **136**, 257 (1933).
17. R. Schrader, S. Schoenherr, M. Eerdmann, *Z. Chem.*, **4**, 108 (1964).

## 2.8.21.3. by Oxidation of the Mercury Metal.

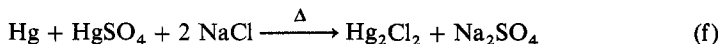
Mercury(0) reacts with elemental halogens to produce  $\text{Hg}_2\text{X}_2$  compounds. These reactions use xs Hg, and hence the product is often contaminated. Chlorine and xs Hg combine on heating with<sup>1</sup> or without<sup>2</sup> air present to give  $\text{Hg}_2\text{Cl}_2$ . The iodide analog has been prepared by triturating Hg with  $\text{I}_2$ , an  $\text{I}_2$ -EtOH soln or a  $\text{KI}_3$  soln<sup>3</sup>. The product contains some  $\text{HgI}_2$  in addition to  $\text{Hg}_2\text{I}_2$ , which may be removed by leaching with EtOH:



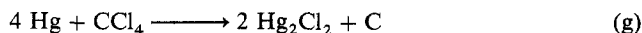
Oxidizing agents, such as  $\text{O}_2$ ,  $\text{MnO}_2$ , Fe(III) and  $\text{SO}_2$ -HCl gas mixtures in the presence of chloride oxidize Hg(0) to Hg(I):



The  $\text{Hg}_2\text{Cl}_2$  is sublimed from the product in each case. Autooxidation-reduction reactions of Hg(0) and Hg(II) produce  $\text{Hg}_2\text{Cl}_2$ , e.g.:



This reaction is a dry method requiring only heat<sup>8</sup>. The carbon tetrahalides  $\text{CCl}_4$ ,  $\text{CBr}_4$  and  $\text{CI}_4$  react with Hg at 600–700°C to produce  $\text{Hg}_2\text{X}_2$  and C<sup>9</sup>:



(T.B. BRILL)

1. M. Berthelot, *C. R. Hebd. Seances Acad. Sci.*, **91**, 871 (1880).
2. I. Bhadrui, *Z. Anorg. Allg. Chem.*, **13**, 407 (1847).
3. J. B. Berthemot, *J. Pharm. Sci. Accessoires*, **17**, 456 (1831).
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5. P. L. Geiger, *Berlin Jahrb. Pharm.*, **355** (1819).
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7. M. Chaigneau, M. Santarromana, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **263**, 678 (1966).
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9. G. Tammann, *Z. Anorg. Allg. Chem.*, **115**, 145 (1921).

## 2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond 151

## 2.8.21. Synthesis of Mercury(I) Halides

## 2.8.21.3. by Oxidation of the Mercury Metal.

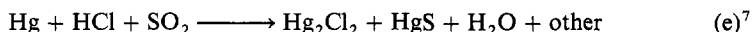
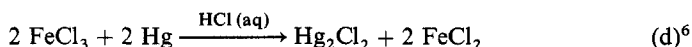
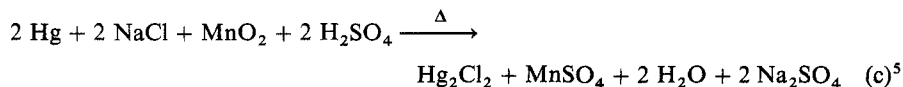
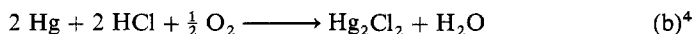
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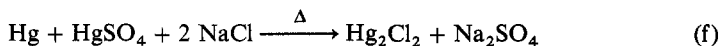
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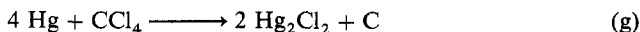
Oxidizing agents, such as  $\text{O}_2$ ,  $\text{MnO}_2$ ,  $\text{Fe(III)}$  and  $\text{SO}_2$ -HCl gas mixtures in the presence of chloride oxidize  $\text{Hg(0)}$  to  $\text{Hg(I)}$ :



The  $\text{Hg}_2\text{Cl}_2$  is sublimed from the product in each case. Autooxidation-reduction reactions of  $\text{Hg(0)}$  and  $\text{Hg(II)}$  produce  $\text{Hg}_2\text{Cl}_2$ , e.g.:



This reaction is a dry method requiring only heat<sup>8</sup>. The carbon tetrahalides  $\text{CCl}_4$ ,  $\text{CBr}_4$  and  $\text{CI}_4$  react with Hg at 600–700°C to produce  $\text{Hg}_2\text{X}_2$  and  $\text{C}^0$ :



(T.B. BRILL)

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2. I. Bhadrui, *Z. Anorg. Allg. Chem.*, **13**, 407 (1847).
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- 152 2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond  
2.8.22. Synthesis of Complex Halides of Group-IIB.

### 2.8.22. Synthesis of Complex Halides of Group-IIB.

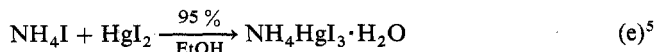
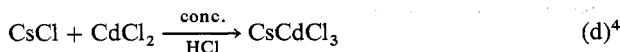
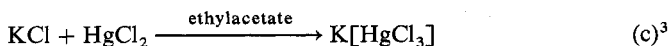
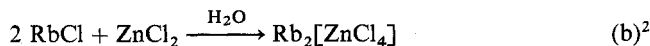
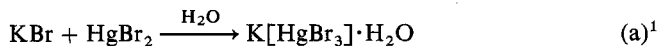
This area was major subtopic of inorganic chemistry during the 19th and early 20th centuries. Less work has been conducted since, and it is now directed toward new syntheses of the group-IIB halide complexes. The early emphasis stemmed from the ready availability of the starting materials and the easy formation of the complexes. The mercury salts were interesting for their pharmaceutical properties.

Numerous complexes are conceivable, particularly when account is taken of the counterions. Cations ranging in size from  $H^+$  to large organic cations, and in chemistry through monovalent and divalent cations of simple and complex inorganic and organo-metallic species, form salts with the group-IIB halide anions.

The strong affinity of the group-IIB ions for halides means that complexes form whenever excess halide is present. In fact the  $Hg^{2+}$  complexes of  $Cl^-$ ,  $Br^-$  and  $I^-$  are among the most stable halide complexes known. Two principal routes can be summarized.

**Method A:** The most common route to the group-IIB halide complexes involves dissolution of the constituent salts (usually in stoichiometric ratio) in a solvent (usually  $H_2O$ ) followed by evaporation or cooling. In some cases a nonaqueous solvent is used, such as acetonitrile, ethanol, methanol or acetone. Some complexes form over a wide range of mole ratios of the constituent salts, while others form only in a narrow range of concentrations. This concentration factor makes it difficult to predict the stoichiometry that will form. When moisture is present the salt may appear as a hydrate.

Reactions (a)–(e) illustrate the use of method A:



Variations to this solution method involve replacing the halide salts:

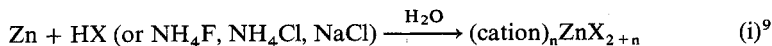
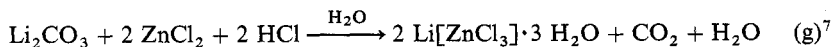
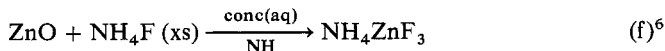


TABLE 1. TYPICAL HALIDE COMPLEXES OF  $Zn^{2+}$ ,  $Cd^{2+}$  AND  $Hg^{2+}$  a

Stoichiometry	$Zn^{2+}$	$Cd^{2+}$	$Hg^{2+}$
$[MX_3]^-$ (X = F, Cl, Br, I)	$NH_4ZnF_3 \cdot 6$ (A)	$NH_4CdF_3 \cdot 6,20$ (A)	$KHgF_3 \cdot 26a$ (A)
	$NaZnF_3 \cdot 6$ (A)	$KCdF_3 \cdot 20$ (A)	$NH_4HgCl_3 \cdot 27,28$ (A, B)
	$KZnF_3 \cdot 16$ (A)	$RbCdF_3 \cdot 20$ (A)	$NaHgCl_3 \cdot 2$ $H_2O$ $^{29}$ (A)
	$HZnCl_3 \cdot 2$ $H_2O$ $^{17}$ (A)	$TlCdF_3 \cdot 20$ (A)	$KHgCl_3$ $^{30}$ (A)
	$LiZnCl_3 \cdot 3$ $H_2O$ $^7$ (A)	$NH_4CdCl_3 \cdot 21,41$ (A, B)	$KHgCl_3 \cdot H_2O$ $^{30}$ (A)
	$KZnCl_3 \cdot 2$ $H_2O$ $^7$ (A)	$KCdCl_3 \cdot 23$ (A)	$KHgCl_3 \cdot 2$ $H_2O$ $^{30}$ (A)
	$NH_4ZnBr_3 \cdot 3$ $H_2O$ $^7$ (A)	$KCdCl_3 \cdot H_2O$ $^{22}$ (A)	$RbHgCl_3 \cdot 31$ (A)
	$NaZnBr_3 \cdot H_2O$ $^{18}$ (A)	$RbCdCl_3 \cdot 24$ (A)	(amine $H^+$ ) $HgCl_3$ $^{32}$ (A)
	$KZnBr_3 \cdot 2$ $H_2O$ $^{18}$ (A)	$CsCdCl_3 \cdot 4,51$ (A, B)	$NH_4HgBr_3 \cdot 33$ (A)
	$NaZnI_3 \cdot 3$ $H_2O$ $^{19}$ (A)	$NH_4CdBr_3 \cdot 25$ (A)	$NaHgBr_3 \cdot 10,30$ (A, B)
		$KCdBr_3 \cdot H_2O$ $^{22}$ (A)	$NaHgBr_3 \cdot 2$ $H_2O$ $^{30}$ (A)
		$RbCdBr_3 \cdot 24$ (A)	$KHgBr_3$ $^{30}$ (B)
		$CsCdBr_3 \cdot 4$ (A)	$KHgBr_3 \cdot H_2O$ $^{34}$ (A)
		$CuCdBr_3 \cdot 20$ (B)	$KHgBr_3 \cdot 2$ $H_2O$ $^{30}$ (A)
		$KCdI_3 \cdot 19$ (A)	$CsHgBr_3 \cdot 35$ (A)
		$CsCdI_3 \cdot 4$ (A)	(amine $H^+$ ) $HgBr_3$ $^{36}$ (A)
		$CsCdI_3 \cdot H_2O$ $^4$ (A)	$NH_4HgI_3 \cdot H_2O$ $^8$ (A)
			$NaHgI_3 \cdot 37$ (A)
			$KHgI_3 \cdot 38$ (A)
			$KHgI_3 \cdot H_2O$ $^5$ (A)
			$RbHgI_3 \cdot 39$ (A)
$[M_2X_5]^-$			$CsHgI_3 \cdot 35$ (A)
			(amine $H^+$ ) $HgI_3$ $^{40}$ (A)
	$HZn_2Cl_5 \cdot 2$ $H_2O$ $^{17}$ (A)	$NH_4Cd_2Cl_5 \cdot 41$ (B)	$KHg_2Br_5 \cdot 10$ (B)
$[M_2X_6]^{2-}$			$NH_4Hg_2I_5 \cdot 13$ (A)
			(amine $H^+$ ) $Hg_2I_5$ $^{42}$ (A)
			$CsHg_2I_5 \cdot 10,35$ (A,B)
			$MgHg_2Cl_6 \cdot 6$ $H_2O$ $^{44}$ (A)
		$CaCd_2Cl_6 \cdot 7$ $H_2O$ $^{43}$ (A)	$BaHg_2Cl_6 \cdot 6$ $H_2O$ $^{44}$ (A)
		$SrCd_2Cl_6 \cdot 7$ $H_2O$ $^{43}$ (A)	
		$BaCd_2Cl_6 \cdot 5$ $H_2O$ $^1$ (A)	

TABLE 1. (Continued)

Stoichiometry	Zn <sup>2+</sup>	Cd <sup>2+</sup>	Hg <sup>2+</sup>
[M <sub>2</sub> X <sub>7</sub> ] <sup>3-</sup>		Rb <sub>3</sub> Cd <sub>2</sub> F <sub>7</sub> <sup>20</sup> (B)	Rb <sub>3</sub> Hg <sub>2</sub> I <sub>7</sub> <sup>10</sup> (B)
[M <sub>3</sub> X <sub>8</sub> ] <sup>2-</sup>			SrHg <sub>3</sub> Cl <sub>8</sub> ·2 H <sub>2</sub> O <sup>45</sup> (A)
			BaHg <sub>3</sub> Cl <sub>8</sub> ·2 H <sub>2</sub> O <sup>45</sup> (A)
			Cs <sub>2</sub> Hg <sub>3</sub> I <sub>8</sub> <sup>35</sup> (A)
[MX <sub>4</sub> ] <sup>2-</sup>	(NH <sub>4</sub> ) <sub>2</sub> ZnF <sub>4</sub> ·2 H <sub>2</sub> O <sup>6</sup> (A)	K <sub>2</sub> CdF <sub>4</sub> <sup>20</sup> (B)	(C <sub>5</sub> H <sub>6</sub> N) <sub>2</sub> HgF <sub>4</sub> ·2 H <sub>2</sub> O <sup>55a</sup> (A)
	K <sub>2</sub> ZnF <sub>4</sub> <sup>46</sup> (A)	Rb <sub>2</sub> CdF <sub>4</sub> <sup>20</sup> (A, B)	(NH <sub>4</sub> ) <sub>2</sub> HgCl <sub>4</sub> <sup>10</sup> (B)
	(NH <sub>4</sub> ) <sub>2</sub> ZnCl <sub>4</sub> <sup>47</sup> (A)	Cs <sub>2</sub> CdF <sub>4</sub> <sup>20</sup> (B)	(NH <sub>4</sub> ) <sub>2</sub> HgCl <sub>4</sub> ·H <sub>2</sub> O <sup>10</sup> (A)
	Na <sub>2</sub> ZnCl <sub>4</sub> ·3 H <sub>2</sub> O <sup>7</sup> (A)	H <sub>2</sub> CdCl <sub>4</sub> ·7 H <sub>2</sub> O <sup>52</sup> (A)	(amine H <sup>+</sup> ) <sub>2</sub> HgCl <sub>4</sub> <sup>56</sup> (A)
	K <sub>2</sub> ZnCl <sub>4</sub> <sup>7</sup> (A)	Na <sub>2</sub> CdCl <sub>4</sub> <sup>23</sup> (B)	K <sub>2</sub> HgCl <sub>4</sub> <sup>30</sup> (A)
	Rb <sub>2</sub> ZnCl <sub>4</sub> <sup>2</sup> (A)	Cs <sub>2</sub> CdCl <sub>4</sub> <sup>51</sup> (A, B)	K <sub>2</sub> HgCl <sub>4</sub> ·H <sub>2</sub> O <sup>57</sup> (A)
	Cs <sub>2</sub> ZnCl <sub>4</sub> <sup>48</sup> (A)	BaCdCl <sub>4</sub> ·4 H <sub>2</sub> O <sup>1</sup> (A)	Rb <sub>2</sub> HgCl <sub>4</sub> <sup>31</sup> (A)
	MgZnCl <sub>4</sub> ·6 H <sub>2</sub> O <sup>49</sup> (A)	(NH <sub>4</sub> ) <sub>2</sub> CdBr <sub>4</sub> <sup>53</sup> (B)	Cs <sub>2</sub> HgCl <sub>4</sub> <sup>31</sup> (A)
	BaZnCl <sub>4</sub> <sup>43</sup> (B)	Na <sub>2</sub> CdBr <sub>4</sub> <sup>53</sup> (B)	(NH <sub>4</sub> ) <sub>2</sub> HgBr <sub>4</sub> <sup>33</sup> (A)
	BaZnCl <sub>4</sub> ·4 H <sub>2</sub> O <sup>49</sup> (A)	K <sub>2</sub> CdBr <sub>4</sub> <sup>33</sup> (B)	(amine H <sup>+</sup> ) <sub>2</sub> HgBr <sub>4</sub> <sup>58</sup> (A)
	BaZnCl <sub>4</sub> ·6 H <sub>2</sub> O <sup>49</sup> (A)	Cs <sub>2</sub> CdBr <sub>4</sub> <sup>4</sup> (A)	Na <sub>2</sub> HgBr <sub>4</sub> <sup>10,59</sup> (A, B)
	(NH <sub>4</sub> ) <sub>2</sub> ZnBr <sub>4</sub> <sup>19</sup> (A)	BaCdBr <sub>4</sub> ·H <sub>2</sub> O <sup>22</sup> (A)	K <sub>2</sub> HgBr <sub>4</sub> <sup>10,38</sup> (A, B)
	(NH <sub>4</sub> ) <sub>2</sub> ZnBr <sub>4</sub> ·H <sub>2</sub> O <sup>19</sup> (A)	(NH <sub>4</sub> ) <sub>2</sub> CdI <sub>4</sub> ·2 H <sub>2</sub> O <sup>21</sup> (A)	Cs <sub>2</sub> HgBr <sub>4</sub> <sup>35</sup> (A)
	K <sub>2</sub> ZnBr <sub>4</sub> ·2 H <sub>2</sub> O <sup>50</sup> (A)	Na <sub>2</sub> CdI <sub>4</sub> ·6 H <sub>2</sub> O <sup>21</sup> (A)	SrHgBr <sub>4</sub> <sup>60</sup> (A)
	Cs <sub>2</sub> ZnBr <sub>4</sub> <sup>48</sup> (A)	K <sub>2</sub> CdI <sub>4</sub> <sup>21,54</sup> (A, B)	BaHgBr <sub>4</sub> <sup>60</sup> (A)
	(NH <sub>4</sub> ) <sub>2</sub> ZnI <sub>4</sub> <sup>19</sup> (A)	Cs <sub>2</sub> CdI <sub>4</sub> <sup>4,51</sup> (A, B)	H <sub>2</sub> HgI <sub>4</sub> <sup>61</sup> (A)
	Cs <sub>2</sub> ZnI <sub>4</sub> <sup>48</sup> (A)	SrCdI <sub>4</sub> ·8 H <sub>2</sub> O <sup>55</sup> (A)	(NH <sub>4</sub> ) <sub>2</sub> HgI <sub>4</sub> <sup>13</sup> (A)
		BaCdI <sub>4</sub> ·5 H <sub>2</sub> O <sup>19</sup> (A)	(NH <sub>4</sub> ) <sub>2</sub> HgI <sub>4</sub> ·H <sub>2</sub> O <sup>65</sup> (A)
			Na <sub>2</sub> HgI <sub>4</sub> <sup>10,37</sup> (A, B)
			Na <sub>2</sub> HgI <sub>4</sub> ·4 H <sub>2</sub> O <sup>37</sup> (A)
			K <sub>2</sub> HgI <sub>4</sub> <sup>38</sup> (A)
			Rb <sub>2</sub> HgI <sub>4</sub> <sup>39</sup> (A)
			Cs <sub>2</sub> HgI <sub>4</sub> <sup>35</sup> (A)
			(amine H <sup>+</sup> ) <sub>2</sub> HgI <sub>4</sub> <sup>42</sup> (A)

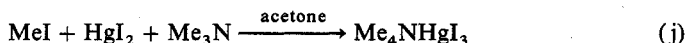
$[MX_3]^{3-}$	$(NH_4)_3ZnCl_5^{47}$ (A) $Cs_3ZnCl_5^{48}$ (A) $(NH_4)_3ZnBr_5 \cdot H_2O^7$ (A) $Cs_3ZnBr_5^{48}$ (A) $Cs_3ZnI_5^{48}$ (A)	$Ag_2HgI_4^{62,63}$ (A, B) $Cu_2HgI_4^{64}$ (A) $ZnHgI_4^{65}$ (A) $CdHgI_4^{66}$ (A) $Cs_3HgBr_5^{35}$ (A) $Cs_3HgI_5^{35}$ (A)
$[MX_6]^{4-}$	$Co(NH_3)_6[CdCl_5]^{67}$ (A) $Cs_3CdBr_5^4$ (A) $Cs_3CdI_5^4$ (A)	$(NH_4)_4HgCl_6^{10}$ (B) $(NH_4)_4HgBr_6^{10}$ (B) $Rb_4HgI_6^{10}$ (B)
$[MX_2Y]^-$	$(NH_4)_4CdCl_6^{22,41}$ (A, B) $K_4CdCl_6^{22,23}$ (A, B) $Rb_4CdCl_6^{24}$ (A) $Cs_4CdCl_6^{51}$ (B) $M_2CdCl_6 \cdot 12 H_2O^1$ (A) (M = Mg, Ca, Mn, Co, Ni) $Cu_2CdCl_6 \cdot 4 H_2O^1$ (A) $K_4CdBr_6^1$ (A) $Rb_4CdBr_6^{68}$ (A) $K_4CdI_6^{10}$ (B) $(Pr_4N)CdCl_2Br^{69}$ (A) $(Pr_4N)CdCl_2I^{69}$ (A) $(Pr_4N)CdBr_2Cl^{69}$ (A) $(Pr_4N)CdBr_2I^{69}$ (A) $(Pr_4N)CdI_2Cl^{69}$ (A) $(Pr_4N)CdI_2Br^{69}$ (A) $K_2CdCl_2I_2^{73}$ (A)	$NH_4HgCl_2Br^{70}$ (A) $HHgCl_2^{71}$ (A) $MeNH_3HgBr_2I^{70}$ (A) $HHgI_2Br^{71}$ (A) $MeNH_3HgBrI_2^{70}$ (A) $Na_2HgCl_2Br_2^{59}$ (A) $(NH_4)_2HgCl_2Br_2^{70}$ (A) $K_2HgCl_2Br_2^{72}$ (A) $(MeNH_3)_2HgCl_2I_2^{70}$ (A) $(MeNH_3)_2HgBr_2I_2^{70}$ (A) $Rb_2HgBr_2I_2^{39}$ (A) $Cs_3HgCl_3Br_2^{35}$ (A)
$[MX_2Y_2]^{2-}$		
$[MX_3Y_2]^{3-}$		

\* A refers to preparation from a solution phase and B refers to preparation from a melt.

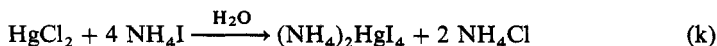


Method B: A less commonly used method to prepare group-IIB halide complexes employs a binary mixture of the components in a melt. In some cases equilibrium phase diagrams have been constructed<sup>10</sup>; e.g., mixing  $\text{CdCl}_2$  and  $\text{NH}_4\text{Cl}$  in 2:1, 1:1 and 1:4 molar ratios and melting forms<sup>11</sup> compounds having stoichiometry  $\text{NH}_4\text{Cd}_2\text{Cl}_5$ ,  $\text{NH}_4\text{CdCl}_3$  and  $(\text{NH}_4)_4\text{CdCl}_6$ .

In addition, many obscure reactions produce group-IIB halide complexes; e.g.,  $\text{HgI}_2$  can insert into  $\text{MeI}$ <sup>12</sup>:



Metathesis can occur with some salts if the equilibrium constant favors it<sup>5</sup>:



In some instances  $\text{NH}_2\text{HgCl}$  decomposes to yield complexes;  $\text{NH}_2\text{HgCl}$  reacts in a dil EtOH soln of  $\text{Br}_2$  to yield  $(\text{NH}_4)_4\text{HgCl}_2\text{Br}_4$ <sup>13</sup>. A 1:3 ratio of  $\text{NH}_2\text{HgCl}$  and  $\text{MeI}$  in a sealed tube at 100°C for 10–12 h produces  $\text{NH}_4\text{Hg}_2\text{I}_5$ <sup>13</sup>.

Complexes can be formed from one another; e.g., when  $\text{Rb}_3\text{Hg}_4\text{Cl}_{11} \cdot \text{H}_2\text{O}$  is heated to volatilize  $\text{HgCl}_2$  and  $\text{H}_2\text{O}$   $\text{RbHgCl}_3$  is produced<sup>14</sup>.

Several factors are important in the synthesis of these complexes. First, the soft or class b behavior of  $\text{Hg}^{2+}$  means that halide ligands form complexes whose strength follows the order:  $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$ , whereas  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  show only slight b character. Second, hydrates frequently form when  $\text{H}_2\text{O}$  is present. Third, the neutral  $\text{MX}_2$  molecules have some affinity for one another, leading to aggregation and polynuclear species. The tendency to aggregate is greatest for the mercury(II) halides, and species such as  $[\text{Hg}_2\text{Cl}_5]^-$ ,  $[\text{Hg}_3\text{Cl}_7]^-$ ,  $[\text{Hg}_6\text{Cl}_{13}]^-$ ,  $[\text{Hg}_2\text{Br}_5]^-$  and  $[\text{Hg}_3\text{I}_8]^{2-}$  can form. Fourth, the stoichiometry is not necessarily indicative of the structure; e.g.,  $(\text{NH}_4)_3\text{ZnCl}_5$  is best formulated as a double salt,  $(\text{NH}_4)_2\text{ZnCl}_4 \cdot \text{NH}_4\text{Cl}$ , according to the crystal structure<sup>15</sup>.

Table 1 lists the group-IIB halide salts. Not all of these compounds have been subjected to modern methods of analysis, nor is the table comprehensive. The synthesis method A (solution) and B (melt) is given in each case.

(T.B. BRILL)

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- 158 2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond  
 2.8.23. Synthesis of Organo Group-IIB Halides  
 2.8.23.1. by Oxidative Addition of Alkyl and Aryl Halides to the Metals.

## 2.8.23. Synthesis of Organo Group-IIB Halides

Organozinc halides are among the first organometallic compounds known<sup>1</sup>. However, it is the organomercury halides that dominate the area of organo group-IIB halides. The mercurials have utility in organic synthesis and are both stable and tractable. The Zn and Cd analogs, while having some importance in synthesis, are more tedious to work with than Hg and so are far less extensively studied. The organo Zn and Cd halides resemble one another in that they frequently require handling in an inert atmosphere and can be hard to isolate. Reviews of organometallic Zn<sup>2,3</sup>, Cd<sup>2,4-7</sup> and Hg<sup>8-11</sup> are available.

**CAUTION: Volatile alkyl mercurials are cumulative toxins and highly poisonous. They should be handled only in closed system. Organocadmium compounds are also very toxic. Alkyl zinc compounds can spontaneously inflame in air.**

(T.B. BRILL)

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### 2.8.23.1. by Oxidative Addition of Alkyl and Aryl Halides to the Metals.

Alkylzinc halides can be prepared in an inert atmosphere by oxidative addition of the alkyl halide to Zn dust using DMF solvent and a small amount of I<sup>-</sup> as an initiator<sup>1</sup>. A mixture of alkyl bromides and iodides reacts directly in an inert atmosphere with Zn containing a small amount of Cu<sup>2</sup>. These reactions resemble the original synthesis of alkyl zinc halides<sup>3</sup>:



Aryl and allyl bromides react with Zn dust in THF<sup>4</sup>, while perfluoroalkyl and aryl iodides react in dioxane and diglyme at 100°C to produce<sup>5</sup> RZnX.

Now that metals can be obtained in an extremely finely divided state and even as metal atoms for use in organic synthesis, these reactions have become even more facile. Activated Zn oxidatively adds to all alkyl iodides and aryl bromides<sup>6</sup>. Zinc and Cd atoms

- 158 2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond  
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 2.8.23.1. by Oxidative Addition of Alkyl and Aryl Halides to the Metals.

## 2.8.23. Synthesis of Organo Group-IIB Halides

Organozinc halides are among the first organometallic compounds known<sup>1</sup>. However, it is the organomercury halides that dominate the area of organo group-IIB halides. The mercurials have utility in organic synthesis and are both stable and tractable. The Zn and Cd analogs, while having some importance in synthesis, are more tedious to work with than Hg and so are far less extensively studied. The organo Zn and Cd halides resemble one another in that they frequently require handling in an inert atmosphere and can be hard to isolate. Reviews of organometallic Zn<sup>2,3</sup>, Cd<sup>2,4-7</sup> and Hg<sup>8-11</sup> are available.

**CAUTION: Volatile alkyl mercurials are cumulative toxins and highly poisonous. They should be handled only in closed system. Organocadmium compounds are also very toxic. Alkyl zinc compounds can spontaneously inflame in air.**

(T.B. BRILL)

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9. H. Straub, K. P. Zeller, H. Leditschke, in *Houben-Weyl, Methoden der Organischen Chemie*, Georg Thieme Verlag, Stuttgart, 1973, XIII 2b; see also L. G. Makarova, in *Organometallic Reactions*, Vols. 1, 2, E. I. Becker, M. Tsutsui, eds., Wiley-Interscience, New York, 1970.
10. B. J. Wakefield, *Adv. Inorg. Chem. Radiochem.*, **11**, 341 (1968).
11. A. J. Bloodworth, in *The Chemistry of Mercury*, C. A. McAuliffe, ed., MacMillan, Toronto, 1977.

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Now that metals can be obtained in an extremely finely divided state and even as metal atoms for use in organic synthesis, these reactions have become even more facile. Activated Zn oxidatively adds to all alkyl iodides and aryl bromides<sup>6</sup>. Zinc and Cd atoms

can be cocondensed in ether or hydrocarbons and react with RX (X = Br, I for Zn and I for Cd)<sup>7</sup>. Many of these organo Zn and Cd halides are solvated adducts. However, perfluoroalkyl iodides react with Zn atoms to give  $R_FZnI$  as unsolvated but unstable adducts<sup>8</sup>.

Electrolysis of solutions containing alkyl halides and neutral bidentate donors with Cd anodes produces complexed alkyl Cd halides<sup>9</sup>. Cadmium in DMSO, TMF and DMF oxidatively adds to  $IC_6F_5$  to yield  $ICdC_6F_5$ <sup>10</sup>.

The earliest preparation of the Hg—C bond involved insertion of Hg into the C—I bond in the presence of sunlight<sup>11</sup>:



The reaction can be extended to RCl and RBr compounds, but the reactivity trend is  $RCl < RBr < RI$ . The yields of mercurial are low. Allyl mercuric iodide is an exception in that it forms readily when allyl iodide and Hg are warmed.

The oxidative addition reactions are not a useful synthetic method for organomercury halides. However, one useful reaction leading to aryl mercury halides involves stirring an aryldiazonium chloride with finely divided Hg at 0–5°C<sup>12</sup>:

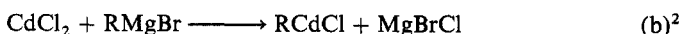
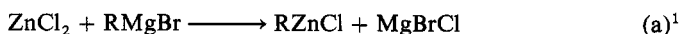


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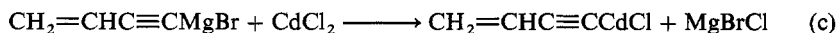
1. R. Bucort, R. Joly, *C. R. Hebd. Seances Acad. Sci.*, 254, 1655 (1962).
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11. E. Frankland, *Ann. Chem.*, 85, 365 (1853).
12. R. E. McClure, E. Lowry, *J. Am. Chem. Soc.*, 53, 319 (1931).

### 2.8.23.2. by Transmetallation Reactions Involving the Metal Halides.

The preparation of RMX compounds (R = aryl, alkyl; M = Zn, Cd, Hg; X = Cl, Br, I) by the use of an organomagnesium halide reagent is routine. The addition of anhydrous group-IIB halide in ether to an alkylmagnesium halide reagent in an equimolar ratio produces alkyl and aryl metal halides:



For Cd, vinyl alkylmagnesium halides do not react, but acetylenic reagents do<sup>3</sup>:



2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond 159  
 2.8.23. Synthesis of Organo Group-IIB Halides  
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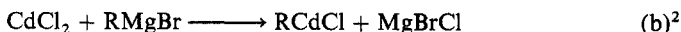
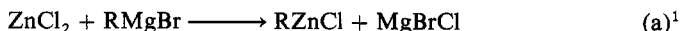


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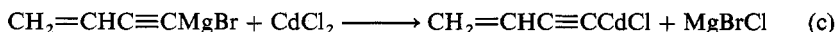
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9. J. J. Habeeb, A. Osman, D. G. Tuck, *J. Organomet. Chem.*, **146**, 213 (1978); see also V. Lucchini, P. R. Wells, *J. Organomet. Chem.*, **92**, 283 (1975).
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11. E. Frankland, *Ann. Chem.*, **85**, 365 (1853).
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2.8.23.2. by Transmetallation Reactions Involving the Metal Halides.

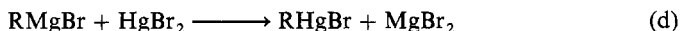
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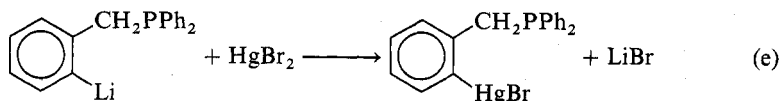


Aryl, alkenyl and primary, secondary and tertiary alkyl Hg halides can be prepared using an organomagnesium halide<sup>4,5</sup>:



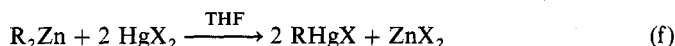
The reaction proceeds in  $\text{Et}_2\text{O}$ , THF and in some cases xylene and heptane. Free Mg must be removed from the alkylmagnesium halide reagent. The yield of mercurial for  $\text{R} = \text{C}_1$  to  $\text{C}_3$  is higher than for  $\text{C}_4$  to  $\text{C}_7$ . For alkyls the yield is primary > secondary > tertiary<sup>6</sup>.

Another route to organo group-IIB halides involves organolithium reagents<sup>7</sup>. Aryl and alkyl Li react with  $\text{CdX}_2$ <sup>8</sup>. Reactions of aryl and alkyl lithium with  $\text{HgX}_2$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ) readily form  $\text{RHgX}$  compounds<sup>7,9</sup>, e.g.<sup>10</sup>:



Alkyl and aryl exchange occurs between numerous other organo main group or organo transition-metal halide compounds and organo or halo group-IIB compounds to give  $\text{RMX}$ . Most of these reactions involve Hg<sup>4</sup>, but redistribution reactions for Zn and Cd are important. Exchange occurs between organomercury compounds and salts or other derivatives of Zn, Cd, Hg, B, In, Tl, fourth, fifth, sixth main-group elements, I, V, Zr, Ti, Cr, Mn, Fe, Co, An, Ag, Pt. Thus, the reactions below only survey the field.

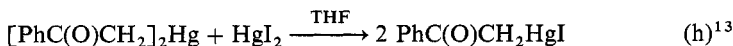
Alkene and alkyne transfer from  $\text{R}_2\text{Zn}$  to  $\text{HgX}_2$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ) takes place<sup>11</sup>:



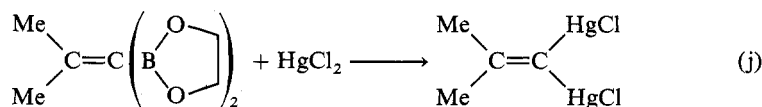
Alkyl mercurials also undergo redistribution with  $\text{HgX}_2$  in ether to give mixed products<sup>12</sup>:



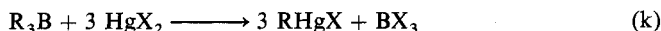
The rate of the reaction follows the order  $\text{Cl} > \text{Br} > \text{I}$ , e.g.:



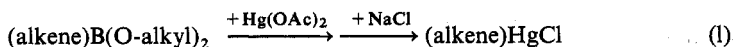
Organoboric acids and esters transfer aromatic and aliphatic groups to Hg<sup>14</sup>, but also can be used to prepare unusual alkyl derivatives of Hg<sup>15</sup>:



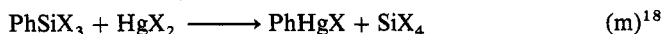
In related reactions organoboric esters and boranes produce alkylations and arylations in ether at RT or below<sup>16</sup>:



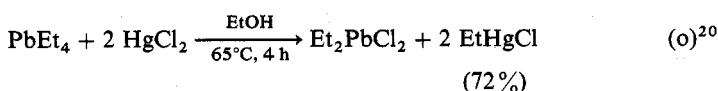
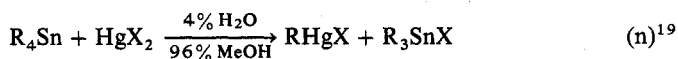
Or in a multistep variation on Eq. (j)<sup>17</sup>:



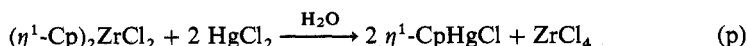
Derivatives of Si, Sn and Pb can be used as alkylating and arylating agents toward Hg:



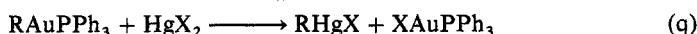
60–65°C, X = Cl, Br, I;



Transition-metal organometallics undergo exchange with  $\text{HgX}_2$ . Shaking  $(\eta^5\text{-Cp})_2\text{ZrCl}_2$  with  $\text{HgCl}_2$  in  $\text{H}_2\text{O}$  produces<sup>21</sup>  $\text{CpHgCl}$ :



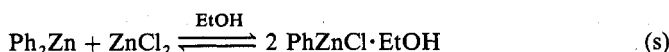
Organogold compounds alkylate Hg<sup>22</sup>:



and  $\text{CdR}_2$  and  $\text{CdX}_2$  undergo redistribution reactions in ether to produce organocadmium halides<sup>23</sup>:



Similarly,  $\text{ZnX}_2$  and  $\text{ZnR}_2$  compounds also experience redistribution when mixed<sup>25</sup>:



(T.B. BRILL)

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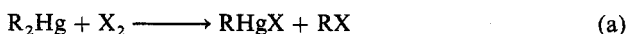


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### 2.8.23.3. by Halogenation of Alkyl Mercury Derivatives.

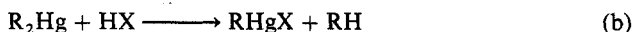
Organomercury halides are prepared by reacting certain diorganomercurials or organomercury salts with halogens or hydrogen halides. Metathesis reactions between organomercury salts and alkali-metal halides can be placed in this same category of reactions.

Halogens react with dialkyl and diaryl mercury<sup>1,2</sup>:

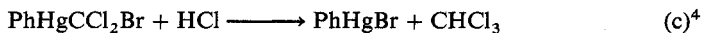


The reaction rate follows the trend aryl > alkyl and  $\text{Cl}_2 > \text{Br}_2 > \text{I}_2$ . Some dialkyls of Hg inflame in the presence of  $\text{Cl}_2$ .

Hydrohalic acids react with mercurials to form organomercury halides using moderate temperatures and moderate acid concentrations<sup>3</sup>:



The rate of the reaction follows the trend  $\text{HBr} > \text{HCl}$ . In DMSO and dioxane, the rate is alkene > aryl > alkyl. Hydrogen chloride also reacts with  $\text{PhHgCCl}_2\text{Br}$  to produce  $\text{PhHgBr}$  in toluene at 80°C:



Metathesis reactions yield organomercury halides, e.g., in the exchange of  $\text{OAc}^-$  for  $\text{Cl}^-$ . This is because  $\text{Hg}(\text{OAc})_2$  is a frequent starting material in the synthesis of  $\text{Hg}-\text{C}$  bonds. If the more readily purified halide compound is desired, then  $\text{OAc}^-$  is readily replaced by  $\text{Cl}^-$  using  $\text{KCl}$  or  $\text{NaCl}$ <sup>5</sup>:



If  $\text{Br}^-$  or  $\text{I}^-$  are used, symmetrization of the mercurial occurs unless the halides are in excess.

While they are little likely to find use in synthesis, several interesting reactions merit

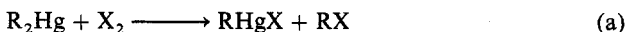
162 2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond  
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23. N. I. Sheverdina, I. E. Paleeva, E. D. Delinskaya, K. A. Kocheshkov, *Dokl. Akad. Nauk SSSR*, **125**, 348 (1959); **143**, 1123 (1962).
24. W. Bremser, M. Winokur, J. D. Roberts, *J. Am. Chem. Soc.*, **92**, 1080 (1970).
25. N. I. Sheverdina, L. V. Abramova, K. A. Kocheshko, *Dokl. Akad. Nauk SSSR*, **134**, 111 (1960).

**2.8.23.3. by Halogenation of Alkyl Mercury Derivatives.**

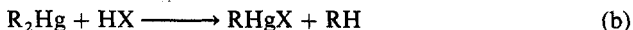
Organomercury halides are prepared by reacting certain diorganomercurials or organomercury salts with halogens or hydrogen halides. Metathesis reactions between organomercury salts and alkali-metal halides can be placed in this same category of reactions.

Halogens react with dialkyl and diaryl mercury<sup>1,2</sup>:

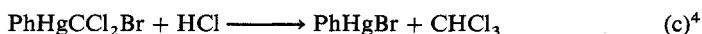


The reaction rate follows the trend aryl > alkyl and  $\text{Cl}_2 > \text{Br}_2 > \text{I}_2$ . Some dialkyls of Hg inflame in the presence of  $\text{Cl}_2$ .

Hydrohalic acids react with mercurials to form organomercury halides using moderate temperatures and moderate acid concentrations<sup>3</sup>:



The rate of the reaction follows the trend  $\text{HBr} > \text{HCl}$ . In DMSO and dioxane, the rate is alkene > aryl > alkyl. Hydrogen chloride also reacts with  $\text{PhHgCCl}_2\text{Br}$  to produce  $\text{PhHgBr}$  in toluene at 80°C:



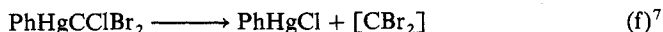
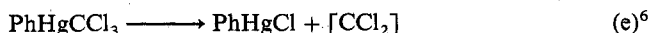
Metathesis reactions yield organomercury halides, e.g., in the exchange of  $\text{OAc}^-$  for  $\text{Cl}^-$ . This is because  $\text{Hg}(\text{OAc})_2$  is a frequent starting material in the synthesis of Hg—C bonds. If the more readily purified halide compound is desired, then  $\text{OAc}^-$  is readily replaced by  $\text{Cl}^-$  using KCl or NaCl<sup>5</sup>:



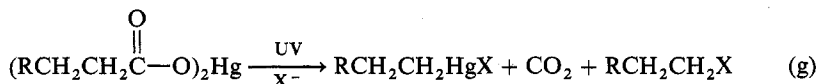
If  $\text{Br}^-$  or  $\text{I}^-$  are used, symmetrization of the mercurial occurs unless the halides are in excess.

While they are little likely to find use in synthesis, several interesting reactions merit

mention because organomercuric halides are products. Carbenes are produced in the decomposition of trihalomethylphenyl mercury:



Photolysis of mercuric(II) salts of carboxylic acids in the presence of halide ion produces decarboxylation. In the presence of halide ion, replacement of one of the remaining alkyl groups occurs<sup>8</sup>:



where R = alkyl and aryl.

(T.B. BRILL)

1. I. P. Beletskaya, L. V. Ermanson, O. A. Reutov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 231 (1965).
2. G. A. Razuvaev, A. V. Savitsky, *Dokl. Akad. Nauk SSSR*, 85, 575 (1952).
3. M. S. Kharasch, M. W. Grafflin, *J. Am. Chem. Soc.*, 47, 1948 (1925); see also M. S. Kharasch, S. Weinhouse, *J. Org. Chem.*, 1, 209 (1936); H. S. Zimmer, S. Makower, *Naturwissenschaften*, 41, 551 (1954); R. E. Dessy, J. Y. Kim, *J. Am. Chem. Soc.*, 82, 686 (1960); 83, 1167 (1961).
4. D. Seyferth, J. Y.-P. Mui, L. J. Todd, *J. Am. Chem. Soc.*, 86, 2961 (1964).
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7. E. E. Schweizer, G. J. O'Neill, *J. Org. Chem.*, 29, 851 (1963).
8. Yu. A. Ol'dekop, N. A. Maier, A. L. Isakhanyan, *Vestsi Akad. Navuk B., SSR. Ser. Khim. Navuk*, 116 (1973); *Chem. Absir.*, 78, 97,776 (1973).

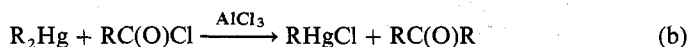
#### 2.8.23.4. by Reactions of Dialkyls with Acid Chlorides.

The reaction of organocadmium compounds with acyl chlorides is a synthetic route to ketones<sup>1-4</sup>. This reaction is carried out with  $\text{R}_2\text{Cd}$  and excess acyl chloride so that the final cadmium product is  $\text{CdCl}_2$ . However, if an equimolar quantity of reagents is used, the final cadmium product is  $\text{RCdCl}$ :



Refluxing benzene is used. Zinc reacts similarly, but more vigorously than Cd.

Mercurials react with acyl chlorides to produce ketones. The reaction is often run in the presence of  $\text{AlCl}_3$  in order to make use of milder conditions<sup>5,6</sup>:



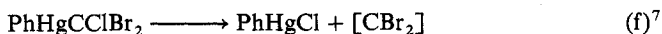
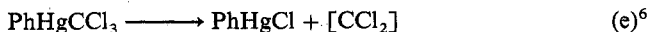
The reaction is not very selective when R = aryl, and the yields are often low<sup>7</sup>. For this reason Zn and Cd reagents are considered much better for the production of ketones.

(T.B. BRILL)

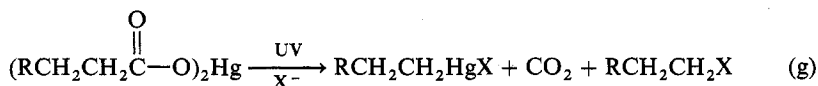
1. H. Gilman, J. F. Nelson, *Recl. Trav. Chim. Pays-Bas*, 55, 518 (1936).
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**2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond 163****2.8.23. Synthesis of Organo Group-IIIB Halides****2.8.23.4. by Reactions of Dialkyls with Acid Chloride.**

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Photolysis of mercuric(II) salts of carboxylic acids in the presence of halide ion produces decarboxylation. In the presence of halide ion, replacement of one of the remaining alkyl groups occurs<sup>8</sup>:



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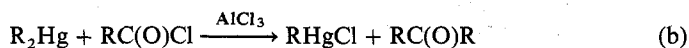
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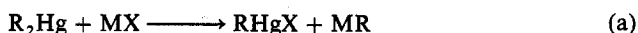
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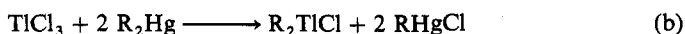
### 2.8.23.5. by Reactions of the Dialkyls and Metal and Nonmetal Halides.

Many exchange reactions are known in which a halide compound reacts with a diorganomercurial to produce an organomercuric halide.



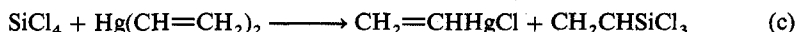
where MX is a halide of most of the group-IIIB, -IVB, -VB and -VIB elements as well as some transition elements. A few RMX compounds where M is Zn and Cd also form in this reaction. The subject has been reviewed<sup>1</sup>, so only a few reactions in this large area are noted.

Alkane, alkenes and aryl groups can be retained by Hg in the presence of  $TiCl_3$ <sup>2</sup>:



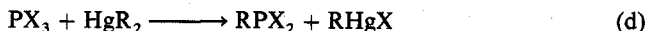
in  $Et_2O$  at RT for 1-12 h. The reaction can also be carried out in a sealed tube without solvent.

Silicon tetrachloride reacts with unsaturated diallyl mercurials<sup>3</sup>:



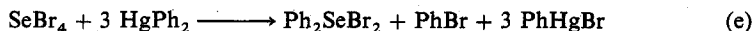
The reactivity follows the trend aryl < vinyl, aldehydes. Alkyls probably do not react. The aryl exchange is effected in a heated sealed tube. The vinyl and aldehyde reactions can be carried out in refluxing in an inert solvent. Germanium tetrachloride reacts similarly<sup>4</sup>.

Phosphorus(III) chloride and bromide react with dialkyl, dialkenyl and diaryl mercury:

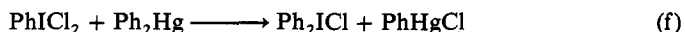


Aryl and alkyl mercurials generally require heating at 200-250°C without solvents in a sealed tube for several days<sup>5</sup>. Dialkenyl Hg reacts under milder conditions<sup>6</sup>, and  $AsCl_3$  reacts like  $PX_3$  under similar conditions<sup>7</sup>.

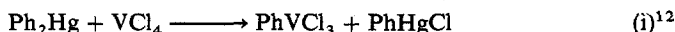
Selenium(IV) bromide reacts in  $CS_2$  with  $Ph_2Hg$  to give  $PhHgBr$ <sup>8</sup>:



An important synthetic reaction employs aryl iodine chloride in reaction with  $R_2Hg$  in  $H_2O$  or an organic solvent<sup>9</sup>:



Transition-metal halides convert  $Ph_2Hg$  to arylmercuric halides:



164 2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond  
 2.8.23. Synthesis of Organo Group-IIIB Halides  
 2.8.23.5. by Reactions of the Dialkyls and Metal and Nonmetal Halides.

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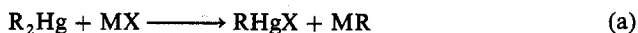
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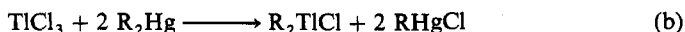
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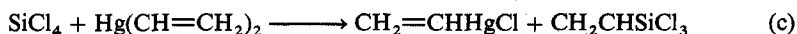
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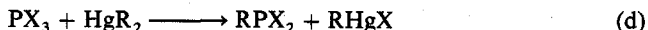
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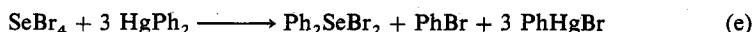
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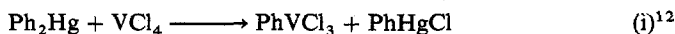
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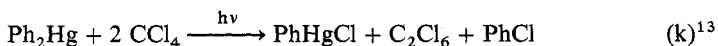
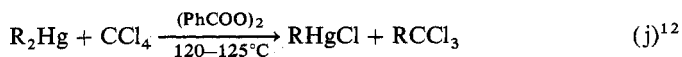
An important synthetic reaction employs aryl iodine chloride in reaction with  $\text{R}_2\text{Hg}$  in  $\text{H}_2\text{O}$  or an organic solvent<sup>9</sup>:



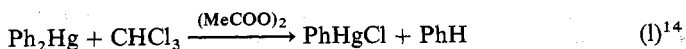
Transition-metal halides convert  $\text{Ph}_2\text{Hg}$  to arylmercuric halides:



Chlorocarbons exchange with  $R_2Hg$  in the presence of catalytic amounts of acetyl peroxide or benzoylperoxide by a radical process<sup>12</sup>. The reaction also occurs by photoactivation<sup>13</sup>:



Aryls are more reactive than alkyls:



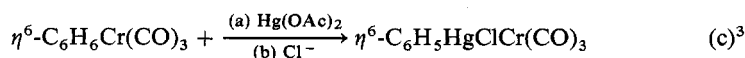
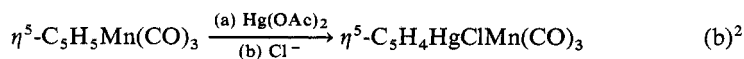
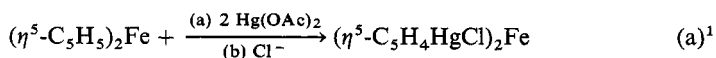
The symmetrization between  $R_2M$  and  $MX_2$  ( $M = Zn, Cd, Hg; X = Cl, Br, I$ ) (discussed in §2.8.23.2) are also relevant to the reactions in this section.

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5. A. Michaelis, *Ann. Chem.*, 181, 288 (1876); 293, 261 (1896); see also H. Hartman, C. Beerman, H. Czempik, *Z. Anorg. Allg. Chem.*, 287, 261 (1956).
6. F. Guichard, *Chem. Ber.*, 32, 1572 (1899).
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8. H. M. Leicester, *J. Am. Chem. Soc.*, 60, 619 (1938).
9. C. Willgerodt, *Chem. Ber.*, 30, 56 (1897); 31, 915 (1898).
10. G. A. Razuvaev, I. F. Bogdanov, *Zh. Obshch. Khim.*, 3, 367 (1933).
11. W. L. Carrick, W. T. Reichle, F. Pennella, J. J. Smith, *J. Am. Chem. Soc.*, 82, 3887 (1960).
12. A. N. Nesmeyanov, A. E. Borison, E. I. Golubera, A. I. Kovredov, *Tetrahedron*, 18, 683 (1962).
13. G. A. Razuvaev, Yu. A. Ol'dekop, *Dokl. Akad. Nauk SSSR*, 64, 77 (1949); *Chem. Abstr.*, 45, 3344 (1951).
14. A. E. Borisov, *Izv. Akad. Nauk, SSSR, Otd. Khim. Nauk*, 524 (1951).

#### 2.8.23.6. by Cleavage of the C—H Bond by Mercuric Halides.

Mercury salts are unusual in directly cleaving certain C—H bonds to form a  $CHgX$  linkage. This reaction is general for aromatics, but a few aliphatic compounds that are receptive to electrophilic attack at the carbon atom also participate:

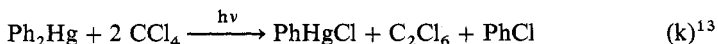
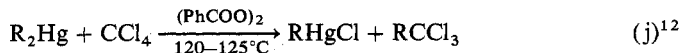


## 2.8. Formation of the Halogen (Cu, Ag, Au) or (Zn, Cd, Hg) Metal Bond 165

## 2.8.23. Synthesis of Organo Group-IB Halides

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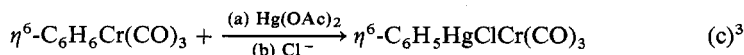
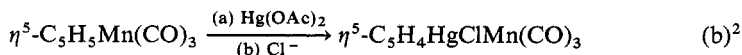
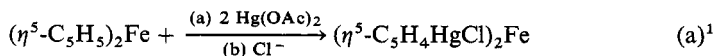
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8. H. M. Leicester, *J. Am. Chem. Soc.*, 60, 619 (1938).
9. C. Willgerodt, *Chem. Ber.*, 30, 56 (1897); 31, 915 (1898).
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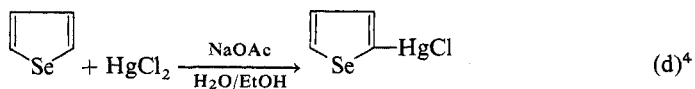
## 2.8.23.6. by Cleavage of the C—H Bond by Mercuric Halides.

Mercury salts are unusual in directly cleaving certain C—H bonds to form a  $CHgX$  linkage. This reaction is general for aromatics, but a few aliphatic compounds that are receptive to electrophilic attack at the carbon atom also participate:





The reaction is useful when the organic substrate is very reactive because  $\text{HgX}_2$  is not highly reactive<sup>4</sup>:



(T.B. BRILL)

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## 2.9. Formation of the Halogen–Transition and –Inner–Transition–Metal Bond

### 2.9.1. Introduction

This chapter covers the reactions used to give transition-metal and inner-transition-metal halides, which are prepared from the metal, from metal derivatives and from metal salts.

### 2.9.2. by Direct Reaction of the Metals with Halogens.

This is the most widely used method for preparing binary halides in their maximum oxidation state. Comprehensive reviews are available on the preparations and properties of transition metal halides<sup>1–5</sup>. The laboratory techniques and conditions used for such syntheses depend upon the desired halide. Fluorides and chlorides are often prepared in flow systems, whereas bromides can be prepared either in a flow line or in a sealed system. Iodides are generally prepared by heating the metal and halogen together. Because the halides prepared by this method are so numerous and the reaction conditions so diverse the section is subdivided to consider the reactions according to the halogen involved.

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#### 2.9.2.1. Synthesis of Metal Fluorides from the Elements.

Direct fluorination generally forms the maximum-valent metal fluoride. Binary fluorides of elements towards the left of the table are readily prepared by this method. Toward the right of the d block the highest oxidation state becomes more difficult to attain and, when formed, these fluorides are very reactive and unstable. In some cases the lower valent fluorides form along with the maximum-valent fluoride and can be obtained pure by this method if a suitable separation technique is available.

Direct fluorination reactions are mostly carried out in a flow-line system using Ni apparatus. Because its success depends on removing the metal fluoride as it forms this method is suitable only for preparing covalent, volatile fluorides, generally formed by those elements on the left of the d block. Once formed the fluorides should be handled in a vacuum system, preferably of Ni; some of the more reactive fluorides can extract moisture from glass, despite rigorous drying. The problems encountered in fluorination

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reactions, studied<sup>1</sup> with reference to compounds of general formula  $MF_6$ , are impurities in the fluorine gas, the high T required and the large exothermic heats of formation for fluorination reactions. Perhaps the greatest problem in handling many transition-metal fluorides, common also to the other halides, is the necessity to exclude air and moisture completely. Even slight traces of 'oxygen' contaminate the product via oxyhalide formation (§2.9.11.1).

The metal fluorides prepared by direct reaction are listed in Table 1. The preparation of  $TiF_4$  exemplifies the flow-line technique used. The reaction is carried out at 200°C, where  $TiF_4$  is volatile and therefore easily removed<sup>2</sup>. Preparation of  $ZrF_4$  is carried out similarly<sup>7-9</sup> but at 420°C. Less information is available on  $HfF_4$ , but it is reported to form during  $\Delta H_f$  measurements when Hf and fluorine are reacted in a bomb<sup>5</sup>.

Fluorination of metallic V at 150°C yields<sup>7</sup> a mixture of  $VF_5$ ,  $VF_4$  and  $VF_3$ . The tetrafluoride can be obtained from this reaction by subliming the resultant mixture at 200°C in a flow system. Fluorinating V at 300°C gives  $VF_5$  alone<sup>6</sup>.

TABLE 1. SYNTHESIS OF METAL FLUORIDES FROM THE ELEMENTS

Product	Reactants and conditions	T (°C)	Refs.
$TiF_4$	$F_2$ + Ti sponge, flow system	200	2
$ZrF_4$	$F_2$ + Zr, flow system	420	2-4
$HfF_4$	$F_2$ + Hf, bomb		5
$VF_5$	V + $F_2$ , flow system	300	6
$VF_4$	V + $F_2$ - $N_2$ , 2 h	150-200	7
$NbF_5$	Nb + $F_2$ - $N_2$ , flow system, 3 h	250-300	8, 9
$TaF_5$	Ta + $F_2$ - $N_2$ , flow system, 3 h	250-300	9, 10
$CrF_6$	Cr-Mn powder + $F_2$ (350 atm)	400	11
$CrF_5$	Cr + $F_2$ (200 atm); Ni autoclave	300	12, 15
$MoF_6$	Mo + $F_2$	100	16-18
$WF_6$	W + $F_2$	RT	9
$MnF_4$	Mn powder + $F_2$ , fluidized bed	700	19, 20
$ReF_7$	Re + $F_2$ (250 mm Hg)	300-400	21-23
$ReF_6$	Obtained with $ReF_7$ as above		
$TcF_6$	Tc + $F_2$ , static system	400	24, 25
$TcF_5$	Tc + $F_2$ - $N_2$ , flow system		26, 27
$FeF_3$	$F_2$ + electrolytic Fe powder	500	28
$RuF_6$	Ru powder + $F_2$ (300 atm)		29, 30
$RuF_5$	Ru + $F_2$ , flow system	> 300	31, 32
$OsF_7$	Os + $F_2$ (350-400 atm)	500-600	33
$OsF_6$	Os + $F_2$ (250 mm Hg)	250-300	34-36
$RhF_6$	Rh + $F_2$		37
$RhF_3$	Rh wire + $F_2$	500-600	38
$IrF_6$	Ir + $F_2$	270	39
$IrF_5$	Ir + $F_2$ , Monel bomb	350-380	40
$NiF_2$	Ni (finely powdered) + $F_2$	550	41
$PtF_6$	Pt (wire) + $F_2$		42, 43
$PtF_6$	Pt sponge + $F_2$ (1:15)	200	44
$PdF_6$	Pd powder + atomic fluorine		8

Reaction between Re metal and  $F_2$  at 250 mm pressure and 300–400°C leads<sup>21–23</sup> to a mixture of  $ReF_7$  and  $ReF_6$ . Lower T favors formation of  $ReF_6$  but it is not possible to separate the two fluorides. To obtain pure  $ReF_7$ , the mixture is heated with  $F_2$  at 300 atm and 400°C for several hours; the hexafluoride is converted to the heptafluoride. If pure  $ReF_6$  is required the mixture should be heated with Re metal in a closed Ni can at 250–400°C for several hours<sup>22</sup>.

Early reports<sup>45,46</sup> suggest the halides  $RuF_8$  and  $OsF_8$  can be prepared by reacting the metal and  $F_2$ . However the existence of these octahalides has not been convincingly proved. Magnetic susceptibility measurements<sup>34</sup> on  $OsF_8$  show it to be  $OsF_6$ . The heptafluoride has been prepared<sup>33</sup> under 350–400 atm of  $F_2$  at 500–600°C in a Ni reactor. The compound is unstable and decomposes to  $OsF_6$  and  $F_2$ . The analogous  $RuF_7$  has not been reported.

Direct fluorination is reported<sup>41</sup> as a preparative route to  $NiF_2$ , but the method involves repeated fluorinations, followed by grinding of the sample after each fluorination. Far simpler methods are available (§2.9.3).

By electrically heating a Pt wire in  $F_2$  close to a surface cooled by liq  $N_2$ ,  $PtF_6$  is prepared<sup>42,43</sup>.  $PtF_6$  is also prepared by heating thoroughly dried platinum sponge in an atmosphere of fluorine at 200°C for several hours<sup>44</sup>. Another technique involves heating Pd powder with F atoms<sup>8</sup>. The product is extremely unstable and decomposes at 273 K to  $PdF_4$  and  $F_2$ .

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### 2.9.2.2. of Metal Chlorides from the Elements.

Direct chlorination of the metal in a flow system is widely used to prepare transition-metal chlorides. The flow system is made of silica or quartz glass, depending on the reaction T. The technique of flow-line reactions is simple; the metal is heated inside the reaction tube through which the halogen vapor is passed. The product is sufficiently volatile at the reaction temperature to sublime out into a cooler section of the tube for collection. The reaction conditions, e.g., T, flow rate, carrier gases and their dilutions, are varied to obtain maximum yield of the desired halide. However, most metal chlorides prepared by this technique are air and moisture sensitive, so rigorous drying and degassing procedures must be carried out before the reaction is commenced. Once formed the halide is allowed to cool in a stream of air-free dried nitrogen and then sealed and transferred to a dry box or a vacuum line.

The product formed by direct  $\text{Cl}_2$  reactions is usually the highest stable chloride; for second- and third-row elements on the left side of the d block this generally contains the metal in its maximum oxidation state. As the atomic number increases along each row the oxidation state of the metal in its highest stable chloride decreases (Table 1).

Conditions for preparing  $\text{TiCl}_4$ ,  $\text{ZrCl}_4$  and  $\text{HfCl}_4$  from the elements are given in Table 1, but these compounds are best prepared by chlorinating the oxides in the presence of C (§2.9.4.1).

Chlorination of Cr should be carried out in porcelain tubes at  $T \leq 1200^\circ\text{C}$ <sup>5,7,8</sup>. High T, causing corrosion of the tube, are a major disadvantage of the method. Formation of solid  $\text{CrCl}_3$  is accompanied by a large increase in volume, so care must be taken that the tube not become plugged, creating a back pressure of chlorine. The  $\text{CrCl}_3$  formed should be sublimed in chlorine, then boiled with conc HCl and washed thoroughly before drying at  $200\text{--}250^\circ\text{C}$ .

Chlorination of Mo powder gives  $\text{MoCl}_5$  in good yields, but complete elimination of metal oxychlorides from the product is difficult<sup>9,10</sup>. Before reaction the metal powder should be heated to high T in a stream of  $\text{H}_2$ - or  $\text{O}_2$ -free  $\text{N}_2$  to remove any surface oxide. Great care should be taken to ensure the apparatus is completely flushed of air and

## 2.9. Formation of the Halogen-Transition-Metal Bond

## 2.9.2. by Direct Reaction of the Metals with Halogens

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TABLE 1. SYNTHESIS OF TRANSITION-METAL CHLORIDES FROM THE ELEMENTS

Product	Reaction and conditions	T (°C)	Refs.
TiCl <sub>4</sub>	Ti + Cl <sub>2</sub>	350	1
ZrCl <sub>4</sub>	Zr + Cl <sub>2</sub>		1, 2
HfCl <sub>4</sub>	Hf + Cl <sub>2</sub>		1
VCl <sub>4</sub>	Ferrovanadium + Cl <sub>2</sub>	200	3, 4
NbCl <sub>5</sub>	Nb powder + Cl <sub>2</sub>	400	5, 6
TaCl <sub>5</sub>	Ta + Cl <sub>2</sub>	300-350	5, 6
CrCl <sub>3</sub>	Cr powder + Cl <sub>2</sub>	960-1000	5, 7, 8
MoCl <sub>5</sub>	Mo + Cl <sub>2</sub>	300	5, 9, 10
WCl <sub>6</sub>	W + Cl <sub>2</sub>	500-600	5, 10, 11
MnCl <sub>2</sub>	Mn + Cl <sub>2</sub> in EtOH		12
TcCl <sub>6</sub>	Tc mirror + Cl <sub>2</sub>	400	13
TcCl <sub>4</sub>	Tc + Cl <sub>2</sub>	400	13
ReCl <sub>6</sub>	Re mirror + Cl <sub>2</sub>	650	14
ReCl <sub>5</sub>	Re sponge + Cl <sub>2</sub>	400-500	5, 14, 15
ReCl <sub>3</sub>	Re + Cl <sub>2</sub>	Red heat	5, 16, 17
FeCl <sub>3</sub>	Fe + Cl <sub>2</sub>	300-350	5, 18, 19
α-RuCl <sub>3</sub>	Ru + Cl <sub>2</sub> , 15 h	600	20
β-RuCl <sub>3</sub>	Ru + CO-Cl <sub>2</sub>	330-340	20
OsCl <sub>4</sub>	Os + Cl <sub>2</sub> (liq)	600	21
RhCl <sub>3</sub>	Rh + Cl <sub>2</sub>	300	5, 22, 23
IrCl <sub>3</sub>	Ir + Cl <sub>2</sub>	450-600	24, 25
NiCl <sub>2</sub>	Ni + Cl <sub>2</sub> , flow system	1000	26, 27
PdCl <sub>2</sub>	Pd + Cl <sub>2</sub>	300	23
PtCl <sub>4</sub>	Pt + Cl <sub>2</sub>	Very high	28
PtCl <sub>2</sub>	Pt + Cl <sub>2</sub>	1100	28, 29

moisture before reaction. Chlorine is introduced to the apparatus through wash bottles of conc H<sub>2</sub>SO<sub>4</sub> and passes through a H<sub>2</sub>SO<sub>4</sub> trap on exit. Reaction is carried out at ca. 300°C; MoCl<sub>5</sub> is formed as a red vapor that condenses to gray/black crystalline leaflets on the cooler parts of the tube. Any MoCl<sub>4</sub>O formed can be sublimed out at ca. 80-90°C. Reaction is complete after 2-3 h; the system is allowed to cool in O<sub>2</sub>-free N<sub>2</sub> to remove xs Cl<sub>2</sub>. The receptor bulb containing MoCl<sub>5</sub> is sealed off under a pressure of N<sub>2</sub> and should be opened and handled in a good dry box. Contamination of MoCl<sub>5</sub> by MoCl<sub>4</sub>O is indicated by a greenish layer on the surface of the glass MoCl<sub>5</sub> storage container. Early preparations of MoCl<sub>5</sub> described the product as a green-black crystalline solid<sup>30</sup> but the green is now known to come from MoCl<sub>4</sub>O present as an impurity<sup>9</sup>.

By reacting W powder and Cl<sub>2</sub> in a quartz tube at 600°C WCl<sub>6</sub> is similarly prepared<sup>5,10,11</sup>. The first product is orange-red WCl<sub>4</sub>O, which can be removed by flaming it along to a collector at the far end of the tube. The pure hexachloride is obtained as a blue-black crystalline powder. Reaction is complete after 3-4 h; the flow line is allowed to cool in O<sub>2</sub>-free N<sub>2</sub> and the tube is sealed and reopened in a dry box.

The product obtained by chlorinating Re depends on T and the physical state of the Re. Chlorination at 600°C of Re mirror, obtained by H<sub>2</sub> reduction of NH<sub>4</sub>[ReO<sub>4</sub>],



yields<sup>19</sup> dark green  $\text{ReCl}_6$ . If the reaction is carried out at  $500^\circ\text{C}$  using Re powder or sponge, the major product<sup>5,15,31,32</sup> is brownish-black  $\text{ReCl}_5$ . The trichloride is also reported<sup>5,16</sup> from the reaction of Re metal and chlorine at  $500^\circ\text{C}$ . It is collected as the less volatile sublimate from the reaction and probably forms<sup>5,17</sup> via thermal decomposition of  $\text{ReCl}_5$ .  $\text{ReCl}_3$  is prepared<sup>17</sup> more conveniently by thermal decomposition of  $\text{ReCl}_5$  in  $\text{N}_2$ .

Early work on Tc chlorides claimed there was no reaction between the metal and  $\text{Cl}_2$ , even when heated<sup>33</sup>. However, when the reaction is carried out in a flow system the gas removes the products on formation, allowing the metal to react further<sup>13</sup>. In this manner at  $400^\circ\text{C}$ , chlorinating Tc obtained by reducing  $\text{NH}_4[\text{TcO}_4]$ , yields two products,  $\text{TcCl}_6$  and  $\text{TcCl}_4$ . The hexachloride is more volatile and is extremely unstable, decomposing to the tetrachloride and chlorine on gentle heating. It can be separated from the tetrachloride by distilling at RT under a steady stream of nitrogen into an ice-cooled tube. It is nevertheless extremely difficult to obtain pure because of its instability and its tendency to dissolve chlorine gas. The major product of chlorinating Tc is  $\text{TcCl}_4$ , which is obtained as a stable red compound after sublimation at  $300^\circ\text{C}$ .

Iron trichloride,  $\text{FeCl}_3$ , is prepared<sup>18,19,34</sup> by reacting  $\text{Cl}_2$  gas with very pure Fe wire at  $200\text{--}400^\circ\text{C}$ . The  $\text{Cl}_2$  must be dried carefully by first passing it through conc  $\text{H}_2\text{SO}_4$  and  $\text{P}_4\text{O}_{10}$  and then liquefying it to  $-40^\circ\text{C}$  before allowing it to volatilize onto the Fe.

Two forms of ruthenium trichloride,  $\alpha\text{-RuCl}_3$  and  $\beta\text{-RuCl}_3$ , are obtained by chlorinating Ru metal<sup>20</sup>. Contamination of  $\beta\text{-RuCl}_3$  by  $\alpha\text{-RuCl}_3$  is avoided by heating small quantities of Ru sponge in a  $\text{CO-Cl}_2$  mixture at  $330\text{--}340^\circ\text{C}$ . The product is then ground and reheated to achieve maximum yield of  $\beta\text{-RuCl}_3$ . Localized overheating results in the formation of  $\alpha\text{-RuCl}_3$ ; this form is also prepared by heating the metal in  $\text{CO-Cl}_2$  at  $600^\circ\text{C}$  for 15 h, although a simpler route is to convert the  $\beta\text{-RuCl}_3$  to  $\alpha\text{-RuCl}_3$  by heating in  $\text{Cl}_2$  or Ar at  $450\text{--}600^\circ\text{C}$ .

Although chlorination of Ni metal at high  $T$ <sup>26,27</sup>  $\text{NiCl}_2$ , this can be prepared more conveniently by direct reaction of the elements in ethanol at RT<sup>12</sup> and by various other methods<sup>35,36</sup> involving dehydration of the hexahydrate,  $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$ .

Chlorination of Pt metal at elevated  $T$  to form  $\text{PtCl}_4$  is slow and is inhibited by the formation of a surface halide layer<sup>28</sup>. Reaction can be accelerated by adding some aluminum chloride, which removes the halide layer<sup>37</sup>.

Reaction of a glowing Pt filament with molecular chlorine under equilibrium conditions at 1300 K forms<sup>29</sup>  $\text{PtCl}_2$ .

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### 2.9.2.3. of Metal Bromides from the Elements.

Preparation of transition-metal bromides from the elements closely parallels that of the chlorides, although the bromide usually contains the metal in a lower oxidation state. Direct bromination reactions can be carried out either in a flow system, often employing  $N_2$  as a carrier gas, or in sealed tubes using a measured amount of liq  $Br_2$ . Bromination T are generally higher than those for the analogous chlorination reactions (Table 1).

Bromine reacts at RT with metallic Ti in a sealed quartz tube to form<sup>1,2</sup>  $TiBr_4$ . However, because of the high pressures generated<sup>4</sup>, it is generally considered safer to carry out this reaction in a flow system at 300–600°C<sup>4,5,39,40</sup>.

Vanadium tribromide is obtained by brominating ferrovanadium<sup>1,7,8,9</sup>. Bromine vapor is carried over the metal by a stream of dry  $CO_2$ . Air and moisture must first be eliminated and the metal heated to red heat; reaction forms  $VBr_3$  and  $FeBr_3$ . A little  $VBr_3O$  is usually obtained first and is removed by subliming through the tube. The  $VBr_3$  sublimes out from the hot end of the tube, leaving the  $FeBr_3$  behind. Repeated sublimations remove all the  $FeBr_3$ <sup>8</sup>. Reaction of V and  $Br_2$  can also be carried out<sup>3</sup> in a sealed tube at 400°C.

Niobium and Ta pentabromides are prepared<sup>1,10–12</sup> by reacting the elements in a flow system at around 250°C. However, they can also be prepared in a sealed tube with high yields free from hydrolysis products<sup>13</sup>.

Tungsten pentabromide is obtained by brominating W metal in a sealed tube. Contamination by hexabromide occurs unless the reaction T is maintained at 1000°C, where virtually pure  $WBr_5$  is obtained<sup>21</sup>. If the reaction is carried out at around 700°C

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Niobium and Ta pentabromides are prepared<sup>1,10–12</sup> by reacting the elements in a flow system at around 250°C. However, they can also be prepared in a sealed tube with high yields free from hydrolysis products<sup>13</sup>.

Tungsten pentabromide is obtained by brominating W metal in a sealed tube. Contamination by hexabromide occurs unless the reaction T is maintained at 1000°C, where virtually pure WBr<sub>5</sub> is obtained<sup>21</sup>. If the reaction is carried out at around 700°C

TABLE 1. SYNTHESIS OF METAL BROMIDES FROM THE ELEMENTS

Product	Reaction conditions	T (°C)	Refs.
TiBr <sub>4</sub>	Ti + Br <sub>2</sub> , sealed tube	RT	1-3
TiBr <sub>4</sub>	Ti + Br <sub>2</sub> , flow system	300-600	4-6
VBr <sub>3</sub>	V + Br <sub>2</sub> , flow system	>400	1, 7-9
VBr <sub>3</sub>	V + Br <sub>2</sub> , sealed tube	400	3
NbBr <sub>5</sub> , TaBr <sub>5</sub>	M + Br <sub>2</sub> -N <sub>2</sub> , flow system	230-250	1, 10-12
NbBr <sub>5</sub> , TaBr <sub>5</sub>	M + Br <sub>2</sub>	400-450	12, 13
CrBr <sub>3</sub>	Cr + Br <sub>2</sub> -N <sub>2</sub> or Ar	1000	1, 14
MoBr <sub>3</sub>	Mo + Br <sub>2</sub>	450-500	15-18
MoBr <sub>3</sub>	Mo + Br <sub>2</sub> in ether	RT	19
MoBr <sub>2</sub>	Mo + Br <sub>2</sub>	600-650	20
WBr <sub>5</sub>	W + Br <sub>2</sub> -N <sub>2</sub>	1000	21, 22
WBr <sub>5</sub>	W + Br <sub>2</sub>	450-500	23, 24
ReBr <sub>5</sub>	Re + Br <sub>2</sub>	650	25
Re <sub>3</sub> Br <sub>9</sub>	Re + Br <sub>2</sub>	450	26, 27
FeBr <sub>3</sub>	Fe + Br <sub>2</sub> , sealed tube	175-200	1, 28
FeBr <sub>3</sub>	Fe + Br <sub>2</sub> , flow system	450	29
FeBr <sub>2</sub>	Fe + Br <sub>2</sub> , flow system	200	30
RuBr <sub>3</sub>	Ru + Br <sub>2</sub>	500	31, 32
OsBr <sub>4</sub>	Os + Br <sub>2</sub> , sealed tube	>450	33
NiBr <sub>2</sub>	Ni + Br <sub>2</sub> -ether, 12 h	RT	34,35
PtBr <sub>4</sub>	Pt + Br <sub>2</sub> , flow system	150	36
PtBr <sub>4</sub>	Pt + Br <sub>2</sub> -conc HBr, sealed tube	150	37
PtBr <sub>2</sub>	Pt + Br <sub>2</sub> , then thermal decomp		36
PdBr <sub>2</sub>	Pd + Br <sub>2</sub> or Br <sub>2</sub> in HNO <sub>3</sub>		38

WBr<sub>6</sub> is formed along with WBr<sub>5</sub>; if the mixture is sublimed, WBr<sub>6</sub> is decomposed<sup>22</sup> to WBr<sub>5</sub> and Br<sub>2</sub>.

Iron tribromide is best prepared in a bent borosilicate tube in which Br<sub>2</sub> is condensed onto degassed Fe powder, held on the left side of the tube. The vessel is then sealed and the Br<sub>2</sub> is condensed from the iron powder to the right side of the tube, which is heated to 120°C. The left side is heated to 175-200°C, which produces a pressure of 5 atm; FeBr<sub>3</sub> then condenses out of the 200°C zone and can be purified by sublimation in Br<sub>2</sub><sup>1,28</sup>.

Allowing Ni powder to react with Br<sub>2</sub> in dry ether for 12 h gives<sup>1,41</sup> NiBr<sub>2</sub>. After unreacted bromine and ether are removed the product is heated to 130°C under vacuum and then resublimed, yielding pure dry NiBr<sub>2</sub>.

Platinum tetrabromide, PtBr<sub>4</sub>, can be prepared by passing Br<sub>2</sub> vapor over Pt metal at 150°C, but the reaction is slow<sup>36</sup>. It is better prepared by allowing Pt to react with Br<sub>2</sub> in conc HBr at 150°C in a sealed tube<sup>37</sup>. Thermal decomposition of the product obtained by brominating platinum metal yields PtBr<sub>2</sub>, but it is difficult to keep it pure because of its thermal instability<sup>36</sup>.

Direct bromination of Pd metal gives PdBr<sub>2</sub>, but the reaction is extremely slow. It can be obtained by reacting Pd and Br<sub>2</sub> ion HNO<sub>3</sub>, but the dibromide is not well documented in the literature<sup>37</sup>.

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#### 2.9.2.4 of Metal Iodides from the Elements.

Direct reaction with  $I_2$ , usually in a sealed tube, is a principal method of preparing transition-metal iodides (Table 1). Iodine tends to stabilize the lower oxidation states of the transition metals and only group-IVA and -VA elements give metal iodides in their maximum oxidation states.

Reaction of Ti metal and  $x$ s  $I_2$  near  $500^\circ\text{C}$  yields<sup>1,2</sup>  $TiI_4$  but  $TiI_3$  is the major product<sup>5,6</sup> at higher T. Direct reaction of equimolar Ti and  $I_2$  in a sealed quartz tube at only slightly elevated T yields<sup>5,6</sup>  $TiI_2$ .

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## 2.9.2. by Direct Reaction of the Metals with Halogens

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## 2.9.2.4 of Metal Iodides from the Elements.

Direct reaction with  $I_2$ , usually in a sealed tube, is a principal method of preparing transition-metal iodides (Table 1). Iodine tends to stabilize the lower oxidation states of the transition metals and only group-IVA and -VA elements give metal iodides in their maximum oxidation states.

Reaction of Ti metal and  $x$ s  $I_2$  near  $500^\circ\text{C}$  yields<sup>1,2</sup>  $TiI_4$  but  $TiI_3$  is the major product<sup>5,6</sup> at higher T. Direct reaction of equimolar Ti and  $I_2$  in a sealed quartz tube at only slightly elevated T yields<sup>5,6</sup>  $TiI_2$ .

TABLE 1. PREPARATION OF TRANSITION-METAL IODIDES FROM THE ELEMENTS

Product	Reactants	Reaction conditions	T (°C)	Refs.
TiI <sub>4</sub>	Ti + I <sub>2</sub>	Sealed tube	525	1, 2
TiI <sub>4</sub>	Ti + I <sub>2</sub>		400-425	3
TiI <sub>4</sub>	Ti + I <sub>2</sub>	CCl <sub>4</sub> solvent, reflux		4
TiI <sub>3</sub>	Ti + I <sub>2</sub>	Sealed tube	700	5, 6
TiI <sub>2</sub>	Ti + I <sub>2</sub>	Sealed tube	Slight heat	5, 6
ZrI <sub>4</sub>	Zr + I <sub>2</sub>	Sealed tube, 25 h	450	7, 8
VI <sub>3</sub>	V + I <sub>2</sub>	Sealed tube	150-280	5, 9, 10
NbI <sub>5</sub>	Nb + I <sub>2</sub>	Sealed tube	270	11, 14
TaI <sub>5</sub>	Ta + I <sub>2</sub>	Sealed tube	340-370	15
TaI <sub>5</sub>	Ta + I <sub>2</sub>	Metal heated by high-frequency induction currents	1500	11, 12
CrI <sub>3</sub>	Cr + I <sub>2</sub>	3 atm, 24 h	225-475	16
CrI <sub>2</sub>	Cr + I <sub>2</sub>		550-700	17
MoI <sub>3</sub>	Mo + I <sub>2</sub>		300	18, 19
MnI <sub>2</sub>	Mn + I <sub>2</sub>	Ether solvent	RT	20
FeI <sub>2</sub>	Fe + I <sub>2</sub>		180-530	5, 21, 22
CoI <sub>2</sub>	Co + I <sub>2</sub>	Flow system	Red heat	23, 24
PtI <sub>4</sub>	Pt + I <sub>2</sub> (1:2)		150	25
PtI <sub>4</sub>	Pt + I <sub>2</sub> (xs)		240	26

In a convenient synthesis<sup>3</sup> for TiI<sub>4</sub> I<sub>2</sub> vapor is allowed to sublime over Ti sponge at 400-425°C. The route gives 80% yields of very pure product at low cost. Refluxing Ti and I<sub>2</sub> in CCl<sub>4</sub> also gives TiI<sub>4</sub>; this method uses lower T but the yield is smaller (50%) and rigorously dried CCl<sub>4</sub> is required<sup>4</sup>.

The general method of preparing other group-IVA tetrahalides, i.e., passing I<sub>2</sub> vapor over a heated mixture of MO and C, does not yield<sup>27</sup> ZrI<sub>4</sub>. However, reacting I<sub>2</sub> vapor with heated Zr metal forms ZrI<sub>4</sub><sup>7,8</sup>.

Reacting V with I<sub>2</sub> yields<sup>5,9,10</sup> VI<sub>3</sub>, whereas Nb and Ta give<sup>11-13</sup> pentaiodides. The reaction occurs when I<sub>2</sub> vapor (1-2 atm) is passed over the heated metal in a sealed tube. The metal may be heated<sup>11</sup> by high-frequency induction currents. Triclinic NbI<sub>5</sub> is prepared<sup>14</sup> from Nb and a 3-4 bar pressure of I<sub>2</sub> in a T gradient of 400-230°C. Molecules of Nb<sub>2</sub>I<sub>10</sub> have been found by solid-state crystallography.

The iodination of Cr depends on T, CrI<sub>3</sub> being formed<sup>16</sup> at T 200-225°C and CrI<sub>2</sub> at T ≤ 700°C<sup>17</sup>.

Manganese diiodide is prepared<sup>20</sup> by direct reaction of the elements in ether at RT.

The reaction between iron and iodine is well documented<sup>5,21,22</sup>. The optimum conditions for preparing FeI<sub>2</sub> involve a T gradient of 530-180°C; the FeI<sub>2</sub> sublimes out of the reaction mixture into the cooler zone.

Reaction of Ru metal and I<sub>2</sub> at 350°C may yield<sup>28</sup> RuI<sub>3</sub>, but it is possible that the product is an oxy- or hydroxyhalide<sup>29</sup>.

Reacting stoichiometric quantities of the elements in a sealed tube at 150°C<sup>25</sup> or by heating xs I<sub>2</sub> with Pt metal to 240°C gives<sup>26</sup> PtI<sub>4</sub>.

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## 2.9.3 Synthesis of Metal Halides from the Metals

### 2.9.3.1. by Halogenation.

Reactions of transition metals and halogens that give transition-metal halides are described in §2.9.2.

### 2.9.3.2. from the Metal and Anhydrous Hydrogen Halides.

Direct reaction of the metal and anhydrous HX is used to prepare many transition-metal halides, particularly those of the first-row elements. The route is especially useful for preparing lower oxidation state fluorides. Hydrogen halides tend to be slightly weaker oxidizing agents than the elemental halogen; e.g., reacting Ti and F<sub>2</sub> yields TiF<sub>4</sub>, whereas TiF<sub>3</sub> is obtained with HF.

Metal fluorides produced by reacting the metal and hydrogen halide at elevated temperatures in a sealed bomb<sup>1</sup> are given in Table 1.



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### 2.9.3. Synthesis of Metal Halides from the Metals

#### 2.9.3.2. from the Metal and Anhydrous Hydrogen Halides.

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Metal fluorides produced by reacting the metal and hydrogen halide at elevated temperatures in a sealed bomb<sup>1</sup> are given in Table 1.

TABLE 1. SYNTHESIS OF TRANSITION-METAL HALIDES FROM THE METAL AND ANHYDROUS HYDROGEN HALIDE

Product	Reactants	Time (h)	T (°C)	Refs.
TiF <sub>3</sub>	Ti + HF, bomb	200		1
TiF <sub>3</sub>	Ti + HF + H <sub>2</sub> , flow system	700		2
TiF <sub>4</sub>	Ti + HF			3
ZrF <sub>4</sub>	Zr + HF, bomb	24	225	1
HfF <sub>4</sub>	Hf + HF, bomb	24	225	1
VF <sub>3</sub>	V + HF, bomb	24	225	1
VF <sub>2</sub>	V + HF		1250	4
VCl <sub>2</sub>	V + HCl, flow system		950	5
NbF <sub>3</sub> , TaF <sub>3</sub>	Nb, Ta + HF, bomb	12	225	1
TaF <sub>3</sub>	Ta + HF + H <sub>2</sub> , flow system		300	6
NbF <sub>5</sub> , TaF <sub>5</sub>	M + HF, flow system		300	6
TaCl <sub>5</sub>	Ta + HCl, flow system		350-700	7-9
TaBr <sub>5</sub>	Ta + HBr, flow system		550	8
CrF <sub>3</sub>	Cr + HF, bomb	96	300	1
CrF <sub>2</sub>	Cr + HF, flow system	3	225	1
CrCl <sub>2</sub>	Cr + HCl-Cl <sub>2</sub>		1150	10
CrCl <sub>2</sub>	Cr + HCl, flow		1150-1200	11-15
CrBr <sub>2</sub>	Cr + HBr, flow		750	16, 17
CrBr <sub>2</sub>	Cr + HBr-Br <sub>2</sub> , flow		890	10
MoF <sub>3</sub>	Mo + HF, bomb	24	225	1
MnF <sub>2</sub>	Mn + HF, bomb	24	180	1
FeF <sub>2</sub>	Fe + HF, flow system		900	18
FeF <sub>2</sub>	Fe + HF, bomb	24	180	1
FeCl <sub>2</sub>	Fe + HCl, flow		Red heat	19
FeCl <sub>2</sub>	Fe + HCl + Cl <sub>2</sub> , flow		700	10
FeBr <sub>2</sub>	Fe + HBr + Br <sub>2</sub> , flow		690	10
CoF <sub>2</sub>	Co + HF, bomb	24	180	1
CoBr <sub>2</sub>	Co + HBr, flow		Red heat	17
CoI <sub>2</sub>	Co + HI, sealed tube		500	11, 20
NiF <sub>2</sub>	Ni + HF, bomb	48	225	1
NiBr <sub>2</sub>	Ni + HBr, flow		Red heat	17

Vanadium difluoride is given<sup>4</sup> by reacting V and HF at 1250°C, followed by controlled reduction of the VF<sub>3</sub> obtained by a mixture of H<sub>2</sub> and HF.

Although the reaction between Nb and HF was claimed<sup>1</sup> to yield NbF<sub>3</sub>, this material has since been proved an oxide fluoride and it is doubtful whether an oxygen-free trifluoride exists<sup>21</sup>. For similar reasons the TaF<sub>3</sub> reported by this method<sup>1</sup> is likely an oxyfluoride, although the x-ray crystal structure of the compound has been determined<sup>22</sup>.

The preparation of CrCl<sub>2</sub> by action of anhyd HCl on the metal above the melting point of the dihalide (1200°C) is well documented<sup>11-15</sup> but the use of a mixture of H<sub>2</sub> and HCl allows the reaction to be carried out at a lower T<sup>12,13</sup>.

Chromium dibromide,  $\text{CrBr}_2$ , is prepared in an analogous manner using slightly lower T<sup>10,17,23</sup>.

Small amounts of  $\text{MoF}_3$  can be prepared<sup>1</sup> by heating Mo powder in anhyd HF in a bomb at 225°C for 24 h.

No second- or third-row transition-metal halide has been prepared by this method for elements in groups d<sup>5</sup> to d<sup>8</sup>.

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### 2.9.3.3. by Hydrohalic Acids.

The reaction of concentrated hydrohalic acids with metals usually does not give transition-metal halides, chiefly because most anhydrous transition-metal halides are very reactive with moisture, forming oxy- and hydroxyhalides. The few metal halides for which the method is successful are listed in Table 1.

Manganese dichloride can be prepared, via the hydrated salt, by the action of conc HCl on spectroscopically pure Mn metal<sup>1</sup>. The hydrated salt is precipitated by saturating the solution with HCl gas and filtering. Repeated concentration of the solution by evaporation gives good yields of hydrated  $\text{MnCl}_2$ . Heating the hydrate in a stream of dry HCl gas at 560–580°C gives anhyd  $\text{MnCl}_2$ .

Both  $\text{ReI}_4$  and  $\text{ReI}_3$  have been prepared<sup>3</sup> by the action of conc HI on perrhenic acid, obtained from Re metal and 30%  $\text{H}_2\text{O}_2$ . In the case of  $\text{ReI}_4$  the perrhenic acid is evaporated to dryness with xs conc HI and allowed to stand for 3 d in a dessicator over

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## 2.9.3. Synthesis of Metal Halides from the Metals

## 2.9.3.3. by Hydrohalic Acids.

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## 2.9.3.3. by Hydrohalic Acids.

The reaction of concentrated hydrohalic acids with metals usually does not give transition-metal halides, chiefly because most anhydrous transition-metal halides are very reactive with moisture, forming oxy- and hydroxyhalides. The few metal halides for which the method is successful are listed in Table 1.

Manganese dichloride can be prepared, via the hydrated salt, by the action of conc HCl on spectroscopically pure Mn metal<sup>1</sup>. The hydrated salt is precipitated by saturating the solution with HCl gas and filtering. Repeated concentration of the solution by evaporation gives good yields of hydrated  $\text{MnCl}_2$ . Heating the hydrate in a stream of dry HCl gas at 560–580°C gives anhyd  $\text{MnCl}_2$ .

Both  $\text{ReI}_4$  and  $\text{ReI}_3$  have been prepared<sup>3</sup> by the action of conc HI on perrhenic acid, obtained from Re metal and 30%  $\text{H}_2\text{O}_2$ . In the case of  $\text{ReI}_4$  the perrhenic acid is evaporated to dryness with xs conc HI and allowed to stand for 3 d in a dessicator over

TABLE 1. SYNTHESIS OF METAL HALIDES BY HYDROHALIC ACIDS

Product	Reactants	Refs.
MnCl <sub>2</sub>	Mn + conc HCl	1
CoCl <sub>2</sub>	Co + conc HCl	2
ReI <sub>4</sub>	Re in H <sub>2</sub> O <sub>2</sub> + conc HI	3
ReI <sub>3</sub>	Re in H <sub>2</sub> O <sub>2</sub> followed by HI + ethanol	3, 4, 5

P<sub>2</sub>O<sub>5</sub> and solid NaOH. In preparing ReI<sub>3</sub> the perrhenic acid is evaporated to dryness with 55% HI and EtOH and allowed to cool; black crystals of ReI<sub>3</sub> form<sup>4</sup>. Heating unstable ReI<sub>4</sub> with I<sub>2</sub> in a sealed tube at 355°C for 6 h also gives ReI<sub>3</sub>.

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#### 2.9.3.4. by Fluorination with Interhalogens.

Fluorination of the metal by interhalogens is an alternate way to form the transition-metal-fluorine bond. Reaction of the metal with interhalogens occurs with only a few elements (Table 1). The method is more widely applicable to halogen-exchange reactions with metal halides.

One major disadvantage of the method is removing xs reactant, especially in reactions involving BrF<sub>3</sub> which forms adducts with the fluoride. In some cases, e.g., reactions between Nb or Ta and BrF<sub>3</sub>, the adducts formed, MF<sub>5</sub>·BrF<sub>3</sub>, are extremely stable and even prolonged heating removes only 70% of them<sup>4</sup>. Adduct formation also occurs when BrF<sub>3</sub> reacts with PdX<sub>2</sub>. The PdX<sub>2</sub>·BrF<sub>3</sub> adducts are obtained and must be decomposed by heating in vacuo to obtain the metal halide<sup>10-12</sup>.

TABLE 1. SYNTHESIS OF METAL FLUORIDES BY FLUORINATION BY INTERHALOGENS

Product	Metal	Interhalogen	Conditions	Refs.
TiF <sub>4</sub>	Ti	ClF <sub>3</sub>	Flow system, 350°C	1
ZrF <sub>4</sub>	Zr	BrF <sub>3</sub>	High T	2
NbF <sub>5</sub>	Nb	ClF <sub>3</sub> , BrF <sub>3</sub>		3
TaF <sub>5</sub>	Ta	BrF <sub>3</sub>		4
MoF <sub>6</sub>	Mo	ClF <sub>3</sub>	RT	5
WF <sub>6</sub> , MoF <sub>6</sub>	W, Mo	BrF <sub>3</sub>	RT	6, 7
ReF <sub>6</sub>	Re	ClF <sub>3</sub>	300°C	8
RuF <sub>5</sub>	Ru	BrF <sub>3</sub>	10-15°C	9

## 2.9. Formation of the Halogen-Transition-Metal Bond

## 2.9.3. Synthesis of Metal Halides from the Metals

## 2.9.3.4. by Fluorination with Interhalogens.

TABLE 1. SYNTHESIS OF METAL HALIDES BY HYDROHALIC ACIDS

Product	Reactants	Refs.
MnCl <sub>2</sub>	Mn + conc HCl	1
CoCl <sub>2</sub>	Co + conc HCl	2
ReI <sub>4</sub>	Re in H <sub>2</sub> O <sub>2</sub> + conc HI	3
ReI <sub>3</sub>	Re in H <sub>2</sub> O <sub>2</sub> followed by HI + ethanol	3, 4, 5

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ZrF <sub>4</sub>	Zr	BrF <sub>3</sub>	High T	2
NbF <sub>5</sub>	Nb	ClF <sub>3</sub> , BrF <sub>3</sub>		3
TaF <sub>5</sub>	Ta	BrF <sub>3</sub>		4
MoF <sub>6</sub>	Mo	ClF <sub>3</sub>	RT	5
WF <sub>6</sub> , MoF <sub>6</sub>	W, Mo	BrF <sub>3</sub>	RT	6, 7
ReF <sub>6</sub>	Re	ClF <sub>3</sub>	300°C	8
RuF <sub>5</sub>	Ru	BrF <sub>3</sub>	10-15°C	9

Reactions of the metal and  $\text{ClF}_3$  are usually carried out in a flow system, as in the preparation<sup>1</sup> of  $\text{TiF}_4$ . When the interhalogen is  $\text{BrF}_3$  or  $\text{IF}_5$  the reaction can be done under reflux.

Molybdenum hexafluoride can be obtained by reacting  $\text{ClF}_3$  on Mo powder<sup>5</sup>, which occurs spontaneously at RT, the metal burning vigorously in the gas. The product must be washed well with anhyd HF to remove xs  $\text{ClF}_3$ . Both  $\text{MoF}_6$  and  $\text{WF}_6$  are obtained by action of  $\text{BrF}_3$  on the metal powders, but the products must be separated from bromine elements which is soluble in the hexafluorides<sup>6,7</sup>.

The  $\text{ReF}_6 \cdot \text{ClF}_3$  adduct is obtained<sup>8</sup> by reacting  $\text{ClF}_3$  and Re metal at 300°C. Decomposition of this adduct by distillation in a Pt tube at 50°C under  $\text{H}_2$  yields  $\text{ReF}_6$ .

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### 2.9.3.5. of Transition-Metal Halides by Chlorination of the Metal by Sulfuryl Chloride.

Chlorination of transition metals by  $\text{S}_2\text{Cl}_2$  and other nonmetal chlorides, e.g.,  $\text{CCl}_4$ , is not generally used to prepare metal halides. However, there are reactions of metal oxides with chlorinating agents, e.g.,  $\text{S}_2\text{Cl}_2$ ,  $\text{SOCl}_2$ ,  $\text{CCl}_4$ , that are convenient methods for synthesizing metal halides (§2.9.4.5, 2.9.4.6).

Rhenium trichloride,  $\text{ReCl}_3$ , is prepared<sup>1</sup> by reacting Re powder and  $\text{S}_2\text{Cl}_2$  with and without traces of  $\text{AlCl}_3$ . Poor yields are obtained even after boiling for 48 h, heating in a sealed tube for 6 h at 150°C or refluxing in ether for 60 h. This route is not recommended.

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Few reactions between transition metals and non-transition-metal halides form pure transition-metal halides. Using non-transition-metal halides to halogenate transition-metal oxides is a much more widespread preparation of transition-metal halides, especially iodides (§2.9.4.7).

## 2.9. Formation of the Halogen-Transition-Metal Bond

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## 2.9.3. Synthesis of Metal Halides from the Metals

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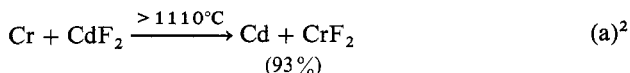
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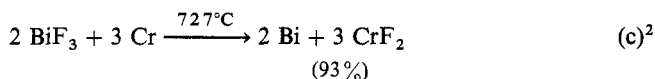
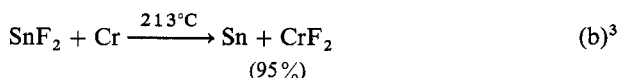
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Chromium difluoride,  $\text{CrF}_2$ , is given<sup>1</sup> by reacting Cr metal and the molten fluorides of a series of metals, all more noble than Cr (see Eqs. d-e).

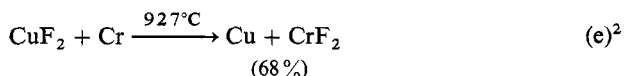
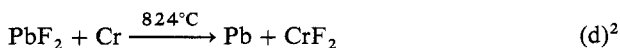
The reactions are carried out at a  $T > m_p$  of the reacting metal fluoride. The reactions prepare pure  $\text{CrF}_2$ , providing it is easily separable from the noble metal. In the reaction with  $\text{CdF}_2$ :



The Cd is removed so efficiently that less than 0.2% remains in the  $\text{CrF}_2$  residue.



When the reaction mixture is maintained in the molten state ( $900^\circ\text{C}$ ) for 2 h  $\text{CrF}_2$  is separated from Bi and Sn, the denser liquid metal settling out. Molten Cu and Pb do not separate as readily, so yields are much lower with these fluorides:



A similar reaction between Nb metal and tin  $\text{SnF}_2$  gives<sup>4,5</sup>  $\text{NbF}_5$ ; the reactants are heated in a bomb at  $375$ – $500^\circ\text{C}$ .

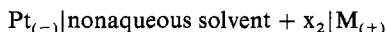
Reacting Re metal and  $\text{SbCl}_5$  in a sealed tube at  $600^\circ\text{C}$  gives<sup>6</sup>  $\text{ReCl}_4$ ; xs  $\text{SbCl}_5$  and  $\text{SbCl}_3$  produced distill out, leaving a black residue of  $\text{ReCl}_4$  in 95% yield.

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### 2.9.3.7. of Transition-Metal Halides Electrochemically.

An electrochemical technique can synthesize certain anhydrous metal halides; the metals are mainly first-row transition elements and the halides are Cl, Br and I. Electrochemical oxidation of the metal occurs at RT by the halogen dissolved in a mixture of organic solvents. The electrochemical cell is represented by:



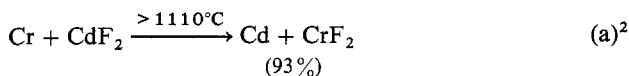
## 2.9. Formation of the Halogen-Transition-Metal Bond

## 2.9.3. Synthesis of Metal Halides from the Metals

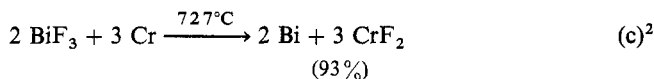
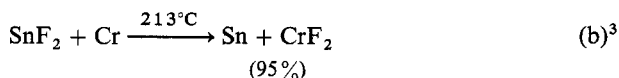
## 2.9.3.7. of Transition-Metal Halides Electrochemically.

Chromium difluoride,  $\text{CrF}_2$ , is given<sup>1</sup> by reacting Cr metal and the molten fluorides of a series of metals, all more noble than Cr (see Eqs. d-e).

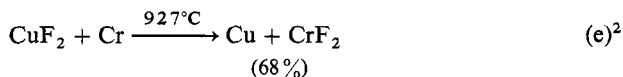
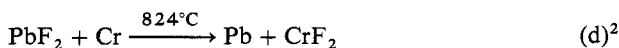
The reactions are carried out at a  $T > \text{mp}$  of the reacting metal fluoride. The reactions prepare pure  $\text{CrF}_2$ , providing it is easily separable from the noble metal. In the reaction with  $\text{CdF}_2$ :



The Cd is removed so efficiently that less than 0.2% remains in the  $\text{CrF}_2$  residue.



When the reaction mixture is maintained in the molten state ( $900^\circ\text{C}$ ) for 2 h  $\text{CrF}_2$  is separated from Bi and Sn, the denser liquid metal settling out. Molten Cu and Pb do not separate as readily, so yields are much lower with these fluorides:



A similar reaction between Nb metal and tin  $\text{SnF}_2$  gives<sup>4,5</sup>  $\text{NbF}_5$ ; the reactants are heated in a bomb at  $375\text{--}500^\circ\text{C}$ .

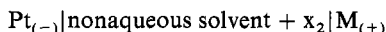
Reacting Re metal and  $\text{SbCl}_5$  in a sealed tube at  $600^\circ\text{C}$  gives<sup>6</sup>  $\text{ReCl}_4$ ; xs  $\text{SbCl}_5$  and  $\text{SbCl}_3$  produced distill out, leaving a black residue of  $\text{ReCl}_4$  in 95% yield.

(E.M. PAGE)

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## 2.9.3.7. of Transition-Metal Halides Electrochemically.

An electrochemical technique can synthesize certain anhydrous metal halides; the metals are mainly first-row transition elements and the halides are Cl, Br and I. Electrochemical oxidation of the metal occurs at RT by the halogen dissolved in a mixture of organic solvents. The electrochemical cell is represented by:



The procedure for the synthesis is well documented<sup>1</sup> for main-group elements and is described in detail for chromium (III) bromide<sup>2</sup>.

The cell is set up in a tall-form beaker with a rubber stopper supporting the electrodes. The cathode is a Pt wire connected to a  $2 \times 2$  cm Pt sheet; the anode is a piece of high-purity foil of the metal to be oxidized. The liquid phase is generally  $\text{CH}_3\text{CN}$  or a  $\text{C}_6\text{H}_6$ - $\text{CH}_3\text{OH}$  (3:1) mixture. In chlorination reactions the diluted gas is bubbled through the solution. In synthesizing the bromides or iodides the halogen is added to the solution before electrolysis. The electrodes are connected, about 1-2 cm apart, to a dc power supply capable of delivering up to 100 V and 500 mA.

**Caution: Care is required during the operation of cells at high voltages.**

In a typical experiment 42 V is applied for about 3 h. The metal halide is obtained as either the anhydrous compound or the acetonitrile or methanol adduct, which is subsequently decomposed thermally<sup>3</sup>.

Metal halides that have been prepared by this method<sup>3,4</sup> are shown in Table 1.

Electrochemical oxidation of Ti, Zr and Hf in a solution of  $\text{Cl}_2$  or  $\text{Br}_2$  in  $\text{CH}_3\text{CN}$  leads to the direct synthesis of  $\text{MX}_4 \cdot 2 \text{CH}_3\text{CN}$  in good yield within a few hours. In the reported syntheses the  $\text{MX}_4 \cdot 2 \text{CH}_3\text{CN}$  compounds were not decomposed to give the anhydrous metal halides but used to prepare further  $\text{MX}_4$  adducts.

Vanadium metal dissolves rapidly in a  $\text{Pt-X}_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) cell in  $\text{CH}_3\text{CN}$  and the solution phase yields crystalline  $\text{VCl}_2 \cdot 2 \text{CH}_3\text{CN}$ ,  $\text{VBr}_2 \cdot \text{CH}_3\text{CN}$  and  $\text{VI}_2$ . The acetonitrile adducts decompose easily to the anhydrous metal halide on heating in vacuo

TABLE 1. SYNTHESIS OF TRANSITION-METAL HALIDES BY ELECTROCHEMICAL METHODS

Halide	Solution phase	Time (h)	Yield (%)	Refs.
$\text{TiX}_4$ ( $\text{X} = \text{Cl}, \text{Br}$ )	$\text{CH}_3\text{CN-X}_2$	8		4, 5
$\text{TiBr}_4$	$\text{CH}_3\text{CN-Br}_2$	4.5		4, 5
$\text{ZrX}_4$ ( $\text{X} = \text{Cl}, \text{Br}$ )	$\text{CH}_3\text{CN-Cl}_2$	6		4, 5
	$\text{CH}_3\text{CN-Br}_2$	4.5		4, 5
$\text{HfX}_4$ ( $\text{X} = \text{Cl}, \text{Br}$ )	$\text{CH}_3\text{CN-Cl}_2$	8		4, 5
	$\text{CH}_3\text{CN-Br}_2$	3		4, 5
$\text{VCl}_2$	$\text{CH}_3\text{CN-Cl}_2$	1	90	6
$\text{VBr}_2$	$\text{CH}_3\text{CN-Br}_2$	8	84	6
$\text{VI}_2$	$\text{CH}_3\text{CN-I}_2$		26	6
$\text{CrBr}_3$	$\text{C}_6\text{H}_6\text{-CH}_3\text{OH-Br}_2$	3	93	2
$\text{MnBr}_2$	$\text{C}_6\text{H}_6\text{-CH}_3\text{OH-Br}_2$	18		4
	$\text{CH}_3\text{CN-Br}_2$	19.5	75	4
$\text{FeCl}_2$	$\text{CH}_3\text{CN-Cl}_2$	1		4
$\text{FeBr}_2$	$\text{C}_6\text{H}_6\text{-CH}_3\text{CN-Br}_2$	19	90	4
$\text{FeI}_2$	$\text{CH}_3\text{CN-I}_2$	24.5		4
$\text{CoBr}_2$	$\text{C}_6\text{H}_6\text{-CH}_3\text{OH-Br}_2$	6	95	4
$\text{NiCl}_2$	$\text{CH}_3\text{CN-Cl}_2$	1	97	4
$\text{NiBr}_2$	$\text{C}_6\text{H}_6\text{-CH}_3\text{OH-Br}_2$	13.4		4
$\text{NiI}_2$	$\text{CH}_3\text{CN-I}_2$	25	22	4

and yields of 80-90% are achieved. The electrochemical technique stabilizes the V(II) oxidation state directly without reduction via higher halides.

Synthesis of  $\text{CrBr}_3$  in this way has many advantages over the thermal route, which involves heating chromium in a stream of  $\text{Br}_2$  (§2.9.2) at  $850^\circ\text{C}$ . The electrochemical method avoids the need for high T and yields a reactive product from which complexes of the type  $[\text{CrL}_6]\text{Br}_3$  can be obtained.

Electrolytic oxidation of manganese in  $\text{CH}_3\text{OH}-\text{C}_6\text{H}_6-\text{Br}_2$  yield a precipitate thought to be  $\text{MnBr}_2 \cdot 2 \text{MeOH}$ ; removal of the solvent was not attempted<sup>4</sup>. When  $\text{CH}_3\text{CN}$  is used as the solvent oxidation forms  $\text{MnBr}_2 \cdot \text{CH}_3\text{CN}$ , which yields pink  $\text{MnBr}_2$  when heated at  $240^\circ\text{C}$ .

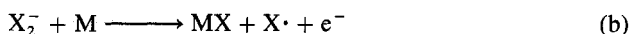
The  $\text{FeCl}_2 \cdot \text{CH}_3\text{CN}$  adduct forms at relatively low voltages by the oxidation of Fe wire in  $\text{CH}_3\text{CN}-\text{Cl}_2$  and yields  $\text{FeCl}_2$  on heating at  $220^\circ\text{C}$ . The bromide is obtained analogously by decomposing  $\text{FeBr}_2 \cdot 2 \text{CH}_3\text{CN}$  and the iodide by decomposing  $\text{FeI}_2 \cdot \text{CH}_3\text{CN}$ .

Several factors are specific to these electrochemical oxidative reactions<sup>3,4</sup>. The product obtained contains the metal in a low oxidation state, e.g., V(II), Cr(III), Fe(II), despite the presence of free halogen. The electrochemical route yields a different product in some cases from the thermal combination of the elements (cf.  $\text{VX}_2$  rather than  $\text{VX}_3$ ), and complexes of differing oxidation states are obtained depending upon the conditions [viz. Ti(III) and Ti(IV), Cu(I) and Cu(II)]. Finally, the current efficiencies suggest that some chain reaction follows the initial electrochemical step. The proposed<sup>3,4</sup> mechanism is:

Cathode:



Anode:



then



The chain process is given by steps (d) and (e) and the nature of the final product  $\text{MX}_n$  depends on the specific interactions of M with the halide.

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## 2.9. Formation of the Halogen-Transition-Metal Bond

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## 2.9.3. Synthesis of Metal Halides from the Metals

## 2.9.3.8. of Transition-Metal Halides by Oxidative Addition.

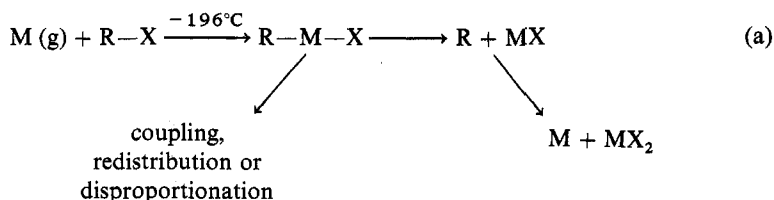
**2.9.3.8. of Transition-Metal Halides by Oxidative Addition by Alkyl Halides.**

Insertion of highly reactive metal atoms into the carbon-halogen bond of an alkyl or aryl halide provides transition-metal halides directly from the metal. The technique prepares binary halides only of metals on the right side of the d block.

The most common method of producing reactive metal atoms is the thermal vaporization of the metal under vacuum<sup>1</sup>, with T of vaporization depending on the metal used. The metal atoms formed are allowed to react with the alkyl halide.

Vaporization of the metal is done at a controlled rate (0.2–2.0 g h<sup>-1</sup>) by heating under vacuum (<10<sup>-3</sup> Torr). The metal atoms then pass to the cooled walls of the vacuum chamber where they condense with the excess alkyl halide vapor. Temperature < -100°C is needed to restrict the vapor pressure of the components to below 10<sup>-3</sup> Torr.

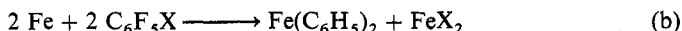
With this technique Ni and Pd atoms insert into the R–X bond of a range of alkyl and aryl halides. The insertion product, RMX, decomposes on warming to yield the metal halide:



Yields of insertion products with Ni or Pd from such oxidative addition reactions<sup>2</sup> are low, even with a large xs of RX. Yields are highest with iodides and lowest with chlorides.

Reduction of anhydrous metal halide with lithium in about 5% naphthalene, which acts as an electron carrier, also gives highly reactive metal powders<sup>3,4</sup>. The reaction is carried out in a slurry of ethereal solvent, e.g., glyme or THF. The reaction, complete in –20 h, yields finely divided black metal powders of Ni, Co and Fe that react readily with pentafluorophenylhalides. This technique is designed to prepare organometallic compounds, but transition-metal halides are formed as side products.

Iron slurry has the greatest reactivity, reacting at 0°C:



where X = Br, I.

Reaction at RT of a Co slurry and 1 equiv C<sub>6</sub>F<sub>5</sub>I is mildly exothermic and gives a blue-green solution of Co(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> and CoI<sub>2</sub>.

Similarly reaction of a Ni slurry obtained from NiX<sub>2</sub> (X = Cl, Br, I) with C<sub>6</sub>F<sub>5</sub>I proceeds via formation of Ni(C<sub>6</sub>F<sub>5</sub>)I, which redistributes to Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> and NiI<sub>2</sub>.

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2. K. J. Klabunde, *Angew. Chem., Int. Ed. Engl.*, **14**, 287 (1975).
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## 2.9.4. Synthesis of Metal Halides from Metal Oxides

### 2.9.4.1 by Halogenation.

Direct halogenation of transition-metal oxides (Table 1) is widely applicable to the early transition metals of groups IVA and VA, which give binary halides; with groups VIA and VIIA, oxychlorides are obtained. In many cases the metal halide is formed along with the oxyhalide and if they cannot be separated the method is not useful for preparing pure halide. The amount of oxyhalide formed can be reduced if the metal oxide is mixed with charcoal or carbon black, e.g.:



Reaction is carried out in a flow system and provides a useful route to the tetrahalides of group IVA (Table 1). Reaction T for preparing  $\text{TiCl}_4$  and  $\text{TiBr}_4$  can be reduced if the  $\text{TiO}_2$  is finely ground and mixed with  $\text{MnO}_2$ , which acts as a catalyst<sup>2</sup>.

Reaction of  $\text{V}_2\text{O}_5$ -C mixtures and  $\text{Cl}_2$  at  $800^\circ\text{C}$  forms<sup>6</sup>  $\text{VCl}_4$ , but this is produced more conveniently by direct chlorination of the metal (§2.9.2) or  $\text{VCl}_3$ .

The action of  $\text{Cl}_2$  on  $\text{Nb}_2\text{O}_5$  and  $\text{TaCl}_5$ -C mixtures, the original method<sup>7</sup> of preparing  $\text{NbCl}_5$  and  $\text{TaCl}_5$ , is now seldom used because the product is heavily contaminated by oxychlorides<sup>8</sup>. For  $\text{NbCl}_5$ , especially, the reaction between  $\text{Nb}_2\text{O}_5$  and  $\text{Cl}_2$  below  $500^\circ\text{C}$  gives mainly  $\text{NbOCl}_3$ ; even at  $T \leq 1000^\circ\text{C}$  a mixture of products is obtained. Although reaction of  $\text{Ta}_2\text{O}_5$ -C and  $\text{Cl}_2$  is less likely to give product containing oxychlorides, higher reaction T are required. Direct reaction between the group-VA metal and  $\text{Cl}_2$  provides a simpler method and a purer product (§2.9.2).

TABLE 1. SYNTHESIS OF METAL HALIDES BY HALOGENATION OF METAL OXIDES

Product	Oxide	Halogen	T ( $^\circ\text{C}$ ) and conditions	Refs.
$\text{TiF}_4$	$\text{TiO}_2$	$\text{F}_2$	350	1
$\text{TiCl}_4$	$\text{TiO}_2 + \text{C}$	$\text{Cl}_2$	400-600	2
$\text{TiBr}_4$	$\text{TiO}_2 + \text{C}$	$\text{Br}_2$	450-650	2-4
$\text{ZrF}_4, \text{HfF}_4$	$\text{ZrO}_2, \text{HfO}_2$	$\text{F}_2$		1
$\text{ZrCl}_4, \text{HfCl}_4$	$\text{ZrO}_2, \text{HfO}_2$	$\text{Cl}_2$	700	2
$\text{ZrBr}_4, \text{HfBr}_4$	$\text{Mo}_2 + \text{C}$	$\text{Br}_2$	700	2
$\text{VF}_5$	$\text{V}_2\text{O}_5$	$\text{F}_2$	200-475, bomb	5
$\text{VCl}_4$	$\text{V}_2\text{O}_5 + \text{C}$	$\text{Cl}_2$	800	6
$\text{NbCl}_5$	$\text{Nb}_2\text{O}_5 + \text{C}$	$\text{Cl}_2$	> 500	7, 8
$\text{TaCl}_5$	$\text{Ta}_2\text{O}_5 + \text{C}$	$\text{Cl}_2$	> 700	7, 8
$\text{NbBr}_5, \text{TaBr}_5$	$\text{M}_2\text{O}_5 + \text{C}$	$\text{Br}_2$	700-860	9
$\text{CrF}_6, \text{CrF}_5$	$\text{CrO}_3$	$\text{F}_2, 25 \text{ atm}$	170	10, 11
$\text{CrCl}_3$	$\text{CrO}_3 + \text{C}$	$\text{Cl}_2$	800, flow system	12
$\text{MnF}_3$	$\text{MnO}_2$	$\text{F}_2$	100-150, flow system	13
$\text{ReI}_2$	$\text{ReO}_4$	$\text{I}_2\text{-CO}_2$	350, sealed tube	14
$\text{NiF}_2$	$\text{NiO}$	$\text{F}_2$	375, flow system	15
$\text{NiCl}_2$	$\text{NiO} + \text{C}$	$\text{Cl}_2$	> 300	16
$\text{PtCl}_2$	$\text{PtO}_2$	$\text{Cl}_2$	550	17

Although reacting  $\text{MnO}_2$  and  $\text{F}_2$  reportedly yields  $\text{MnF}_3$ , some  $\text{MnF}_2$  is formed also<sup>13</sup> and a purer product can be obtained by fluorinating the difluoride.

(E.M. PAGE)

1. H. M. Haendler, S. F. Bartram, R. S. Becker, W. J. Bernard, S. W. Bukatay, *J. Am. Chem. Soc.*, **76**, 2177 (1954).
2. G. Brauer, *A Handbook of Preparative Inorganic Chemistry*, Vol. 2, 2nd ed., Academic Press, New York, 1965.
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11. E. G. Hope, P. J. Jones, W. Levason, J. S. Ogden, M. Tajik, *J. Chem. Soc., Chem. Commun.*, 1355 (1984).
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17. J. M. Lutton, R. W. Parry, *J. Am. Chem. Soc.*, **76**, 4271 (1954).

### 2.9.4.2 and Hydrogen Halide.

Reaction of transition-metal oxides and anhyd HX gives the transition-metal halides shown in Table 1. The HX is passed over the heated oxide in a flow system; except in the preparation of  $\text{MnCl}_3$ , which is carried out in anhyd EtOH at  $-63^\circ\text{C}$ . The method yields<sup>1</sup> black  $\text{MnCl}_3$ , which is thermally unstable and decomposes above  $-40^\circ\text{C}$ .

TABLE 1. SYNTHESIS OF METAL HALIDES BY HYDROHALOGENATION REACTIONS

Product	Oxide	HX	T ( $^\circ\text{C}$ ) and conditions	Refs.
$\text{MnCl}_3$	$\text{MnO}_2$	HCl	$-63$ , anhyd EtOH	1
$\text{FeCl}_3$	$\text{Fe}_2\text{O}_3$	HCl	300-1000, flow system	2
$\text{FeF}_2$	$\text{Fe}_2\text{O}_3\text{-C}$	HF	950-1000, flow system	3
$\text{FeBr}_2$	$\text{Fe}_2\text{O}_3$	HBr	200-325, flow system	4
$\text{IrBr}_2$	$\text{IrO}_2\cdot\text{H}_2\text{O}$	HBr	440	5

Reaction between  $\text{IrO}_2\cdot\text{H}_2\text{O}$  and HBr at  $440^\circ\text{C}$  is claimed to produce  $\text{IrBr}_2$  as a red-brown graphite-like powder that decomposes to the monobromide, IrBr, at  $485^\circ\text{C}$ . However, there is no recent confirmation of this method<sup>5</sup>.

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2.9. Formation of the Halogen-Transition-Metal Bond  
 2.9.4. Synthesis of Metal Halides from Metal Oxides  
 2.9.4.2. and Hydrogen Halide.

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Although reacting  $\text{MnO}_2$  and  $\text{F}_2$  reportedly yields  $\text{MnF}_3$ , some  $\text{MnF}_2$  is formed also<sup>13</sup> and a purer product can be obtained by fluorinating the difluoride.

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$\text{FeF}_2$	$\text{Fe}_2\text{O}_3\text{-C}$	HF	950-1000, flow system	3
$\text{FeBr}_2$	$\text{Fe}_2\text{O}_3$	HBr	200-325, flow system	4
$\text{IrBr}_2$	$\text{IrO}_2\cdot\text{H}_2\text{O}$	HBr	440	5

Reaction between  $\text{IrO}_2\cdot\text{H}_2\text{O}$  and HBr at  $440^\circ\text{C}$  is claimed to produce  $\text{IrBr}_2$  as a red-brown graphite-like powder that decomposes to the monobromide,  $\text{IrBr}$ , at  $485^\circ\text{C}$ . However, there is no recent confirmation of this method<sup>5</sup>.

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1. J. H. Krepelka, *Coll. Czech. Chem. Commun.*, **7**, 105 (1935).
2. H. Schafer, *Z. Anorg. Allg. Chem.*, **259**, 53 (1949).
3. M. Kestigian, F. D. Leipzig, W. J. Croft, R. Guidoboni, *Inorg. Chem.*, **5**, 1462 (1966).
4. J. D. Christian, N. W. Gregory, *J. Phys. Chem.*, **71**, 1583 (1967).
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### 2.9.4.3 and Hydrohalic Acid.

Treatment of transition-metal oxides with hydrohalic acids is of limited use because hydrated or hydrolyzed products form; e.g.,  $V_2O_5$  and HF form<sup>1</sup>  $VF_3 \cdot H_2O$  (Table 1). This can be dehydrated by treating with anhyd HF at 300°C, but the reaction is complex and rarely goes to completion. Pure anhyd  $VF_3$  is better prepared by the thermal decomposition of ammonium hexafluorovanadate(III) in an inert atmosphere. The ammonium hexafluorovanadate is formed by fusing  $V_2O_5$  with excess ammonium hydrogen fluoride at 250°C; the product then decomposes at T ca. 500–600°C<sup>10</sup>.

Many early reports of reactions of metal oxides of elements in the Ru, Os, Rh, Ir block with HX claim production of the metal halide. However, most of this work was carried out at the beginning of the 20th century and has not been confirmed by more recent techniques.

Osmium diiodide,  $OsI_2$ , is reported<sup>2</sup> from the reduction of  $OsO_4$  with 50% HI solution. The black diiodide was obtained pure by treating the solution with EtOH to remove xs I. The monoiodide may be prepared<sup>2</sup> by prolonged treatment of  $OsO_4$  with HI.

Early reports<sup>3,4</sup> on the reaction of  $RuO_4$  and conc HCl claim the formation of hydrated ruthenium tetrachloride,  $RuCl_4 \cdot 5 H_2O$ . However, more recent studies<sup>5</sup> have shown that the product is most likely to be ruthenium(IV)hydroxy chloride,  $Ru(OH)Cl_3$ , or water-soluble ruthenium trichloride. Reaction of  $RuO_4$  with HBr is claimed<sup>6</sup> to yield  $RuBr_3$ , but the product does not exhibit the properties of the  $RuBr_3$  prepared by direct reaction between Ru and  $Br_2$  (§2.9.2) and so is also likely an oxybromide.

Although early work reports the formation of  $IrBr_4$  via reacting the dioxide and HBr, it is likely that the aquated free acid is formed<sup>8</sup>. The reported preparation of  $IrI_3$  from  $IrIO_2$  and aq HI also is not confirmed<sup>9</sup>.

(E.M. PAGE)

TABLE 1. SYNTHESIS OF METAL HALIDES FROM THE METAL OXIDE AND HYDROHALIC ACIDS

Product	Oxide	Acid	Conditions	Refs.
$VF_3 \cdot 3 H_2O$	$V_2O_5$	HF		1
$OsI_2$	$OsO_4$	HI (55%)–EtOH; boil for 3 h		2
$OsI$	$OsO_4$	HI (55%)–EtOH; boil for 48 h		2
$RuCl_4 \cdot 5 H_2O$	$RuO_4$	HCl		3, 4
$Ru(OH)Cl_3$	$RuO_4$	Conc HCl		5
$RuBr_3$	$RuO_4$	Conc HBr		6
$CoCl_2$	$Co_3O_4$	Conc HCl		7
$IrBr_4$	$IrO_2$	HBr (aq)		8
$IrI_3$	$IrO_2$	HI (aq)		9

## 2.9. Formation of the Halogen-Transition-Metal Bond

## 2.9.4. Synthesis of Metal Halides from Metal Oxides

## 2.9.4.3. and Hydrohalic Acid.

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$OsI_2$	$OsO_4$	HI (55%)–EtOH; boil for 3 h		2
$OsI$	$OsO_4$	HI (55%)–EtOH; boil for 48 h		2
$RuCl_4 \cdot 5 H_2O$	$RuO_4$	HCl		3, 4
$Ru(OH)Cl_3$	$RuO_4$	Conc HCl		5
$RuBr_3$	$RuO_4$	Conc HBr		6
$CoCl_2$	$Co_3O_4$	Conc HCl		7
$IrBr_4$	$IrO_2$	HBr (aq)		8
$IrI_3$	$IrO_2$	HI (aq)		9

1. J. R. Long, H. A. Wilhelm, AEC Report No. ISC-244, 1951 pp. 32-35.
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#### 2.9.4.4. by Fluorination by Interhalogens.

Fluorination of transition-metal oxides by interhalogens is of restricted use in preparing metal halides (Table 1). The more reactive halogen fluorides,  $\text{ClF}_3$ ,  $\text{BrF}_3$  and  $\text{IF}_5$ , react<sup>1</sup> with anhyd  $\text{MoO}_3$  or  $\text{WO}_3$  to give the metal hexafluoride,  $\text{MF}_6$ . At  $350^\circ\text{C}$  in a bomb, the hexafluorides can also be obtained<sup>2</sup> from the trioxides and  $\text{SF}_4$ .

TABLE 1. SYNTHESIS OF METAL HALIDES BY FLUORINATION BY INTERHALOGENS

Product	Oxide	Interhalogen	Conditions	Refs.
$\text{WF}_6$	$\text{WO}_3$	$\text{BrF}_3$ , $\text{ClF}_3$ , $\text{IF}_5$		1
$\text{MoF}_6$	$\text{MoO}_3$	$\text{BrF}_3$ , $\text{ClF}_3$ , $\text{IF}_5$		1
$\text{MoF}_6$ , $\text{WF}_6$	$\text{MO}_3$	$\text{SF}_4$	Bomb, $350^\circ\text{C}$	2
$\text{NiF}_2$	$\text{NiO}_2$	$\text{ClF}_3$	Flow system, $200^\circ\text{C}$	3

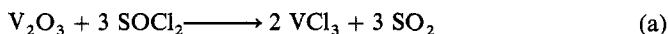
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#### 2.9.4.5 by Chlorination by Thionyl Chloride.

Heating thionyl chloride and  $\text{S}_2\text{Cl}_2$  chlorinates transition-metal oxides together in a bomb with care or under reflux (Table 1).

Reaction occurs between  $\text{VO}_3$  powder and  $\text{SOCl}_2$  at  $200^\circ\text{C}$  in a bomb tube<sup>3,4</sup>:



Unreacted  $\text{SOCl}_2$  is removed by vacuum distillation.

Great care must be exercised on opening the tube as the reaction proceeds with the formation of  $\text{SO}_2$ .

2.9. Formation of the Halogen–Transition–Metal Bond  
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Product	Oxide	Interhalogen	Conditions	Refs.
$\text{WF}_6$	$\text{WO}_3$	$\text{BrF}_3$ , $\text{ClF}_3$ , $\text{IF}_5$		1
$\text{MoF}_6$	$\text{MoO}_3$	$\text{BrF}_3$ , $\text{ClF}_3$ , $\text{IF}_5$		1
$\text{MoF}_6$ , $\text{WF}_6$	$\text{MO}_3$	$\text{SF}_4$	Bomb, 350°C	2
$\text{NiF}_2$	$\text{NiO}_2$	$\text{ClF}_3$	Flow system, 200°C	3

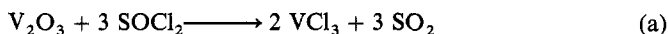
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Unreacted  $\text{SOCl}_2$  is removed by vacuum distillation.

Great care must be exercised on opening the tube as the reaction proceeds with the formation of  $\text{SO}_2$ .

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TABLE 1. SYNTHESIS OF METAL HALIDES BY FLUORINATION BY INTERHALOGENS

Product	Oxide	Interhalogen	Conditions	Refs.
$\text{WF}_6$	$\text{WO}_3$	$\text{BrF}_3$ , $\text{ClF}_3$ , $\text{IF}_5$		1
$\text{MoF}_6$	$\text{MoO}_3$	$\text{BrF}_3$ , $\text{ClF}_3$ , $\text{IF}_5$		1
$\text{MoF}_6$ , $\text{WF}_6$	$\text{MO}_3$	$\text{SF}_4$	Bomb, 350°C	2
$\text{NiF}_2$	$\text{NiO}_2$	$\text{ClF}_3$	Flow system, 200°C	3

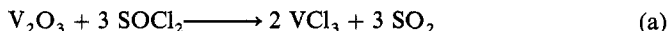
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Unreacted  $\text{SOCl}_2$  is removed by vacuum distillation.

Great care must be exercised on opening the tube as the reaction proceeds with the formation of  $\text{SO}_2$ .

TABLE 1. SYNTHESIS OF METAL HALIDES BY CHLORINATION BY THIONYL CHLORIDE

Product	Metal	Oxide Chlorinating agent	Conditions	Refs.
ZrCl <sub>4</sub>	ZrO <sub>2</sub> + C	S <sub>2</sub> Cl <sub>2</sub> , PCl <sub>5</sub>		1
HfCl <sub>4</sub>	HfO <sub>2</sub> + C	S <sub>2</sub> Cl <sub>2</sub> , PCl <sub>5</sub>		1
VCl <sub>3</sub>	VO <sub>2</sub>	SOCl <sub>2</sub>	Reflux	2
VCl <sub>3</sub>	V <sub>2</sub> O <sub>3</sub>	SOCl <sub>2</sub>	Bomb, 24 h, 200°C	3, 4
VCl <sub>3</sub>	V <sub>2</sub> O <sub>5</sub>	S <sub>2</sub> Cl <sub>2</sub>	Reflux, 8 h	3, 5
NbCl <sub>5</sub>	Nb <sub>2</sub> O <sub>5</sub>	SOCl <sub>2</sub>	Reflux	6, 7
NbCl <sub>5</sub>	Nb <sub>2</sub> O <sub>5</sub>	SOCl <sub>2</sub>	Flow system, 100–150°C	2
NbCl <sub>5</sub>	Nb <sub>2</sub> O <sub>5</sub>	SOCl <sub>2</sub>	Sealed tube, 3 h at 200°C	3, 4, 8
TaCl <sub>5</sub>	Ta <sub>2</sub> O <sub>5</sub>	SOCl <sub>2</sub>	Sealed tube, 6 h at 230–240°C	3, 4, 8
TaCl <sub>5</sub>	Ta <sub>2</sub> O <sub>5</sub>	SOCl <sub>2</sub>	Flow system, >150°C	2
CrCl <sub>3</sub>	CrO <sub>3</sub>	SOCl <sub>2</sub>	Reflux	9
CrCl <sub>3</sub>	CrO <sub>3</sub>	S <sub>2</sub> Cl <sub>2</sub>	Reflux	9, 10
MoF <sub>6</sub>	MoO <sub>3</sub>	SF <sub>4</sub>	Bomb, 350°C	11
ReCl <sub>4</sub>	ReO <sub>2</sub>	SOCl <sub>2</sub>	Reflux	12
OsCl <sub>5</sub>	OsO <sub>4</sub>	SCl <sub>2</sub>		13

An alternative route to VCl<sub>3</sub> is the reaction between V<sub>2</sub>O<sub>5</sub> powder and S<sub>2</sub>Cl<sub>2</sub> under reflux<sup>3,5</sup>. Here, production of SO<sub>2</sub> is not a problem but the product must be thoroughly washed by continuous recycling extraction with CS<sub>2</sub>, to remove impurities of sulfur and S<sub>2</sub>Cl<sub>2</sub>, and then vacuum heated; despite extended purification the VCl<sub>3</sub> produced cannot be completely freed from sulfur.

Niobium and Ta pentachlorides can be prepared by treating the pentoxide (obtained from the precipitated hydrated oxide) with SOCl<sub>2</sub>. The reaction can be carried out either in a bomb tube at elevated T<sup>4,6,8</sup>, or under reflux<sup>6,7</sup>. The latter method does not generate high P<sub>SO<sub>2</sub></sub>. One of the simplest methods to niobium pentachloride is reacting niobium hydroxide and thionyl chloride at RT. The hydroxide dissolves completely in <24 h and after vacuum sublimation the yield of pentachloride can be 95%. This method also avoids the NbOCl<sub>3</sub> that forms in many of the other routes to NbCl<sub>5</sub> and that is very difficult to remove. The reaction is not as successful for synthesizing tantalum pentachloride<sup>14</sup>.

Chlorination of CrO<sub>3</sub> with sulfur monochloride<sup>9,10</sup> or thionyl chloride<sup>9</sup>, either in sealed tubes or in flow systems at high T, is a route to CrCl<sub>3</sub>. The product must be purified by vacuum sublimation in a stream of chlorine at 850°C or under vacuum at higher T.

Rhenium tetrachloride is prepared by treating ReO<sub>2</sub>, formed by hydrolyzing ReCl<sub>5</sub>, with SOCl<sub>2</sub>. The reactants are heated under reflux and the green product solution evaporated to dryness; ReCl<sub>4</sub> is obtained as a black solid<sup>12</sup>.

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### 2.9.4.6. by Chlorination with $\text{CCl}_4$ and Other Chlorocarbons.

Reaction of the transition-metal oxide with  $\text{CCl}_4$  provides a straightforward route to anhydrous metal chlorides (Table 1). This method, first reported<sup>18</sup> in 1910, suffered from

TABLE 1. CHLORINATION OF METAL OXIDES BY  $\text{CCl}_4$  AND OTHER CHLOROCARBONS

Halide	Reactants	Conditions and T (°C)	Refs.
$\text{TiCl}_4$	$\text{TiO}_2 + \text{CCl}_4$	Flow system, 600	1
$\text{TiCl}_4$	$\text{TiO}_2 + \text{C}_6\text{H}_4\text{Cl}_6$ (1,3-bis-trichloromethylbenzene)	Bomb, 200-300	2
$\text{TiCl}_4$	$\text{TiO}_2 + \text{C}_5\text{Cl}_8$ (octachlorocyclopentene)	Reflux	3
$\text{TiCl}_4$	$\text{TiO}_2 + \text{CHCl}_3$	440	
$\text{VCl}_4$	$\text{V}_2\text{O}_5 + \text{CCl}_4$		4
$\text{VCl}_4$	$\text{V}_2\text{O}_5 + \text{COCl}_2$		4
$\text{VCl}_4$	$\text{V}_2\text{O}_5 + \text{C}_6\text{H}_5\text{CCl}_3$	Bomb, 200-300	2
$\text{VCl}_3$	$\text{V}_2\text{O}_5 + \text{C}_5\text{Cl}_8$	Reflux	3
$\text{NbCl}_5$	$\text{Nb}_2\text{O}_5 + \text{CCl}_4$	Flow system, 200-225	5
$\text{NbCl}_5$	$\text{Nb}_2\text{O}_5 + \text{CCl}_4$	Sealed tube, 270-300	4, 6
$\text{NbCl}_5$	$\text{Nb}_2\text{O}_5 + \text{Cl}_2$	Reflux in $\text{C}_4\text{Cl}_6$ (hexachlorobutadiene)	7
$\text{NbCl}_5$	$\text{Nb}_2\text{O}_5 + \text{C}_5\text{Cl}_8$	Reflux	3
$\text{NbBr}_5$	$\text{Nb}_2\text{O}_5 + \text{CBr}_4$	Sealed tube, 370	8
$\text{TaCl}_5$	$\text{Ta}_2\text{O}_5 + \text{CCl}_4$	Sealed tube, 400	4, 6
$\text{TaBr}_5$	$\text{Ta}_2\text{O}_5 + \text{CBr}_4$	24 h at 200	9
$\text{CrCl}_3$	$\text{CrO}_3 + \text{CCl}_4$	Reflux	10
$\text{CrCl}_3$	$\text{CrO}_3 + \text{CCl}_4$	Flow system, 630	11, 12
$\text{MoCl}_5$	$\text{MoO}_3 + \text{CCl}_4$	Sealed tube, 400	4
$\text{MoCl}_4$	$\text{MoO}_2 + \text{C}_6\text{Cl}_6 + \text{Cl}_2$	Reflux, 24 h	7
$\text{WCl}_6$	$\text{WO}_3 + \text{CCl}_4$	Sealed tube, 400	4, 13, 14
$\text{WBr}_6$	$\text{WO}_3 + \text{CBr}_4$	Sealed tube, 200	15
$\text{MnCl}_2$	$\text{MnO}_2 + \text{CH}_3\text{C(O)Cl}$	RT	16
$\text{ReCl}_5$	$\text{Re}_2\text{O}_7 + \text{CCl}_4$	Bomb, 400	4
$\text{TeCl}_4$	$\text{Te}_2\text{O}_7 + \text{CCl}_4$	Bomb, 400	4
$\text{FeCl}_3$	$\text{Fe}_2\text{O}_3 + \text{CCl}_4$	Flow system, 500	1
$\text{FeCl}_3$	$\text{Fe}_2\text{O}_3 + \text{C}_6\text{Cl}_6 + \text{Cl}_2$	Reflux	7
$\text{FeCl}_3$	$\text{Fe}_2\text{O}_3 + \text{C}_5\text{Cl}_8$	Reflux	3
$\text{CoCl}_2$	$\text{Co}_3\text{O}_4 + \text{CCl}_4$	Flow system, 300-900	17



## 2.9. Formation of the Halogen-Transition-Metal Bond

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## 2.9.4. Synthesis of Metal Halides from Metal Oxides

2.9.4.6. by Chlorination with  $\text{CCl}_4$  and Other Chlorocarbons.

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**2.9.4.6. by Chlorination with  $\text{CCl}_4$  and Other Chlorocarbons.**

Reaction of the transition-metal oxide with  $\text{CCl}_4$  provides a straightforward route to anhydrous metal chlorides (Table 1). This method, first reported<sup>18</sup> in 1910, suffered from

TABLE 1. CHLORINATION OF METAL OXIDES BY  $\text{CCl}_4$  AND OTHER CHLOROCARBONS

Halide	Reactants	Conditions and T (°C)	Refs.
$\text{TiCl}_4$	$\text{TiO}_2 + \text{CCl}_4$	Flow system, 600	1
$\text{TiCl}_4$	$\text{TiO}_2 + \text{C}_8\text{H}_4\text{Cl}_6$ (1,3-bis-trichloromethylbenzene)	Bomb, 200–300	2
$\text{TiCl}_4$	$\text{TiO}_2 + \text{C}_5\text{Cl}_8$ (octachlorocyclopentene)	Reflux	3
$\text{TiCl}_4$	$\text{TiO}_2 + \text{CHCl}_3$	440	
$\text{VCl}_4$	$\text{V}_2\text{O}_5 + \text{CCl}_4$		4
$\text{VCl}_4$	$\text{V}_2\text{O}_5 + \text{COCl}_2$		4
$\text{VCl}_4$	$\text{V}_2\text{O}_5 + \text{C}_6\text{H}_5\text{CCl}_3$	Bomb, 200–300	2
$\text{VCl}_3$	$\text{V}_2\text{O}_5 + \text{C}_5\text{Cl}_8$	Reflux	3
$\text{NbCl}_5$	$\text{Nb}_2\text{O}_5 + \text{CCl}_4$	Flow system, 200–225	5
$\text{NbCl}_5$	$\text{Nb}_2\text{O}_5 + \text{CCl}_4$	Sealed tube, 270–300	4, 6
$\text{NbCl}_5$	$\text{Nb}_2\text{O}_5 + \text{Cl}_2$	Reflux in $\text{C}_4\text{Cl}_6$ (hexachlorobutadiene)	7
$\text{NbCl}_5$	$\text{Nb}_2\text{O}_5 + \text{C}_5\text{Cl}_8$	Reflux	3
$\text{NbBr}_5$	$\text{Nb}_2\text{O}_5 + \text{CBr}_4$	Sealed tube, 370	8
$\text{TaCl}_5$	$\text{Ta}_2\text{O}_5 + \text{CCl}_4$	Sealed tube, 400	4, 6
$\text{TaBr}_5$	$\text{Ta}_2\text{O}_5 + \text{CBr}_4$	24 h at 200	9
$\text{CrCl}_3$	$\text{CrO}_3 + \text{CCl}_4$	Reflux	10
$\text{CrCl}_3$	$\text{CrO}_3 + \text{CCl}_4$	Flow system, 630	11, 12
$\text{MoCl}_5$	$\text{MoO}_3 + \text{CCl}_4$	Sealed tube, 400	4
$\text{MoCl}_4$	$\text{MoO}_2 + \text{C}_6\text{Cl}_6 + \text{Cl}_2$	Reflux, 24 h	7
$\text{WCl}_6$	$\text{WO}_3 + \text{CCl}_4$	Sealed tube, 400	4, 13, 14
$\text{WBr}_6$	$\text{WO}_3 + \text{CBr}_4$	Sealed tube, 200	15
$\text{MnCl}_2$	$\text{MnO}_2 + \text{CH}_3\text{C(O)Cl}$	RT	16
$\text{ReCl}_5$	$\text{Re}_2\text{O}_7 + \text{CCl}_4$	Bomb, 400	4
$\text{TeCl}_4$	$\text{Te}_2\text{O}_7 + \text{CCl}_4$	Bomb, 400	4
$\text{FeCl}_3$	$\text{Fe}_2\text{O}_3 + \text{CCl}_4$	Flow system, 500	1
$\text{FeCl}_3$	$\text{Fe}_2\text{O}_3 + \text{C}_6\text{Cl}_6 + \text{Cl}_2$	Reflux	7
$\text{FeCl}_3$	$\text{Fe}_2\text{O}_3 + \text{C}_5\text{Cl}_8$	Reflux	3
$\text{CoCl}_2$	$\text{Co}_3\text{O}_4 + \text{CCl}_4$	Flow system, 300–900	17

the high gas pressures produced that could not be circumvented at that time. The problem has been overcome by balancing the high pressures generated by an external pressure of  $\text{CCl}_4$  or water in a high-pressure steel reaction vessel.

The reaction of  $\text{TiO}_2$  with chlorinated hydrocarbons prepares  $\text{TiCl}_4$ . A variety of chlorinated hydrocarbons are used, including  $\text{CCl}_4$ <sup>1</sup>,  $\text{C}_8\text{H}_4\text{Cl}_3$ <sup>2</sup> and  $\text{CHCl}_3$ <sup>19</sup>. Octachlorocyclopentene,  $\text{C}_5\text{Cl}_8$  (bp  $285^\circ\text{C}$ , is an efficient means to  $\text{TiCl}_4$  as it is self-drying, the chlorine atoms in the organic molecule being replaced by oxygen atoms<sup>3</sup>.

Allowing  $\text{V}_2\text{O}_5$  and  $\text{CCl}_4$  to react under reflux<sup>4</sup> or reacting stoichiometric amounts of  $\text{V}_2\text{O}_5$  with  $\text{C}_8\text{H}_4\text{Cl}_6$  or  $\text{C}_7\text{H}_5\text{Cl}_3$  in a sealed tube<sup>2</sup> gives  $\text{VCl}_4$ . However, it is best prepared by direct reaction of the elements (§2.9.2).

Both  $\text{Nb}_2\text{O}_5$  and  $\text{Ta}_2\text{O}_5$  can be chlorinated by  $\text{CCl}_4$  in a bomb at around  $400^\circ\text{C}$  but the reaction produces high pressures of  $\text{COCl}_2$  so **care should be taken opening the tube**. A more convenient method is to use high-bp chlorinated hydrocarbons at atmospheric pressure.

Anhydrous  $\text{CrCl}_3$  is prepared from  $\text{CrO}_3$  and  $\text{CCl}_4$  under reflux, or from hydrated  $\text{CrO}_3$  ( $\text{CrO}_3 \cdot 6 \text{H}_2\text{O}$ ) and  $\text{CCl}_4$  in a flow system at high T ( $300$ – $650^\circ\text{C}$ ). **Caution: phosgene is produced in the reaction.**

Reaction of  $\text{Re}_2\text{O}_7$  with  $\text{CCl}_4$  gives<sup>4</sup>  $\text{ReCl}_5$ ;  $\text{CCl}_4$  dissolves the gases formed and reduces the pressure. The reactants are sealed together in a bomb and heated to  $400^\circ\text{C}$  for a few hours. At this T **pressures of up to 100 atm are produced**; when cooled they reduce to 1–2 atm. The tube is finally **opened with care** by gently heating the tip with a gas flame until the tip blows out due to the excess pressure inside the tube. **CAUTION: The tube should be pointed in a safe direction inside a fume hood.** Yields of about 90% of large black crystals of  $\text{ReCl}_5$  are obtained after washing with  $\text{CCl}_4$ . A similar method can be used to obtain  $\text{TeCl}_4$ ,  $\text{WCl}_6$  and  $\text{MoCl}_5$ .

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### 2.9.4.7. by Phosgene Chlorination.

Phosgene is of limited use for synthesizing transition-metal halides. Zirconium tetrachloride,  $\text{ZrCl}_4$ , is the only halide prepared this way<sup>1</sup>, which involves treating  $\text{ZrO}_2$  with  $\text{CoCl}_2$  in  $\text{CCl}_4$ .

(E.M. PAGE)

1. W. B. Blumental, *The Chemical Behavior of Zirconium*, Van Nostrand, New Jersey, 1958.

### 2.9.4.8. by Halogenation by Aluminum Halides.

Aluminum halides, especially the triiodide, are excellent halogenating agents for transition-metal oxides (Table 1)<sup>1,2</sup>.

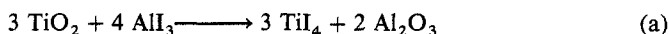


TABLE 1. PREPARATION OF METAL HALIDES FROM THE METAL OXIDE AND ALUMINUM HALIDE

Product	Reactants	Conditions	Extraction	Refs.
$\text{TiI}_4$	$\text{TiO}_2 + \text{AlI}_3$	230°C, 24 h	Sublime at 400°C	1
$\text{ZrI}_4$	$\text{ZrO}_2 + \text{AlI}_3$	400°C, 48 h	Sublime at 250°	1
$\text{Vl}_2$	$\text{V}_2\text{O}_3 + \text{AlI}_3$	230°C, 24 h	Sublime at 800°C	1
$\text{TaCl}_5$	$\text{Ta}_2\text{O}_5 + \text{AlCl}_3$	300°C		2
$\text{NbBr}_5$	$\text{Nb}_2\text{O}_5 + \text{AlBr}_3$	200°C		2, 3
$\text{TaBr}_5$	$\text{Ta}_2\text{O}_5 + \text{AlBr}_3$			2, 3
$\text{NbI}_3$	$\text{Nb}_2\text{O}_5 + \text{AlI}_3$	230°C, 24 h	Sublime at 230°C	1, 4
$\text{TaI}_5$	$\text{Ta}_2\text{O}_5 + \text{AlI}_3$	230°C		1, 4
$\text{MoI}_2$	$\text{MoO}_3 + \text{AlI}_3$	230°C, 48 h	Extract in $\text{C}_2\text{H}_5\text{I}$	1
$\text{WI}_4$	$\text{WO}_3 + \text{AlI}_3$	230°C, 24 h	Extract in $\text{C}_2\text{H}_5\text{OH}$	1
$\text{MnI}_2$	$\text{MnO}_2 + \text{AlI}_3$	230°C, 48 h	Extract in $\text{H}_2\text{O}$	1, 5
$\text{FeI}_2$	$\text{Fe}_2\text{O}_3 + \text{AlI}_3$	300°C, 24 h	Sublime at 550°C	1
$\text{CoI}_2$	$\text{Co}_3\text{O}_4 + \text{AlI}_3$	230°C, 24 h	Sublime at 600°C	1, 4
$\text{NiI}_2$	$\text{Ni}_2\text{O}_3 + \text{AlI}_3$	230°C, 24 h	Sublime at 800°C	1, 4

The reactions are carried out in sealed tubes using stoichiometric amounts of metal oxide and aluminum trihalide.

In most cases the metal halide is separated from the  $\text{Al}_2\text{O}_3$  by sublimation. If the metal halide is involatile it is extracted into a suitable solvent, e.g., water for  $\text{MnI}_2$ ,  $\text{C}_2\text{H}_5\text{I}$

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## 2.9.4. Synthesis of Metal Halides from Metal Oxides

## 2.9.4.8. by Halogenation by Aluminum Halides.

18. A. Michael, A. Murphy, *J. Am. Chem. Soc.*, **44**, 365 (1910).19. D. L. Kepert, *The Early Transition Metals*, Academic Press, New York, 1972.

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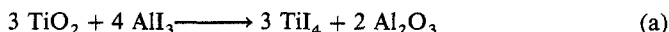


TABLE 1. PREPARATION OF METAL HALIDES FROM THE METAL OXIDE AND ALUMINUM HALIDE

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$\text{Vl}_2$	$\text{V}_2\text{O}_3 + \text{AlI}_3$	230°C, 24 h	Sublime at 800°C	1
$\text{TaCl}_5$	$\text{Ta}_2\text{O}_5 + \text{AlCl}_3$	300°C		2
$\text{NbBr}_5$	$\text{Nb}_2\text{O}_5 + \text{AlBr}_3$	200°C		2, 3
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$\text{NbI}_3$	$\text{Nb}_2\text{O}_5 + \text{AlI}_3$	230°C, 24 h	Sublime at 230°C	1, 4
$\text{TaI}_5$	$\text{Ta}_2\text{O}_5 + \text{AlI}_3$	230°C		1, 4
$\text{MoI}_2$	$\text{MoO}_3 + \text{AlI}_3$	230°C, 48 h	Extract in $\text{C}_2\text{H}_5\text{I}$	1
$\text{WI}_4$	$\text{WO}_3 + \text{AlI}_3$	230°C, 24 h	Extract in $\text{C}_2\text{H}_5\text{OH}$	1
$\text{MnI}_2$	$\text{MnO}_2 + \text{AlI}_3$	230°C, 48 h	Extract in $\text{H}_2\text{O}$	1, 5
$\text{FeI}_2$	$\text{Fe}_2\text{O}_3 + \text{AlI}_3$	300°C, 24 h	Sublime at 550°C	1
$\text{CoI}_2$	$\text{Co}_3\text{O}_4 + \text{AlI}_3$	230°C, 24 h	Sublime at 600°C	1, 4
$\text{NiI}_2$	$\text{Ni}_2\text{O}_3 + \text{AlI}_3$	230°C, 24 h	Sublime at 800°C	1, 4

The reactions are carried out in sealed tubes using stoichiometric amounts of metal oxide and aluminum trihalide.

In most cases the metal halide is separated from the  $\text{Al}_2\text{O}_3$  by sublimation. If the metal halide is involatile it is extracted into a suitable solvent, e.g., water for  $\text{MnI}_2$ ,  $\text{C}_2\text{H}_5\text{I}$

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## 2.9.4. Synthesis of Metal Halides from Metal Oxides

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1. W. B. Blumental, *The Chemical Behavior of Zirconium*, Van Nostrand, New Jersey, 1958..

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Aluminum halides, especially the triiodide, are excellent halogenating agents for transition-metal oxides (Table 1)<sup>1,2</sup>.

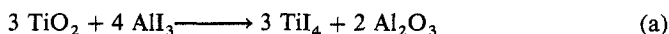


TABLE 1. PREPARATION OF METAL HALIDES FROM THE METAL OXIDE AND ALUMINUM HALIDE

Product	Reactants	Conditions	Extraction	Refs.
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$\text{ZrI}_4$	$\text{ZrO}_2 + \text{AlI}_3$	400°C, 48 h	Sublime at 250°	1
$\text{Vl}_2$	$\text{V}_2\text{O}_3 + \text{AlI}_3$	230°C, 24 h	Sublime at 800°C	1
$\text{TaCl}_5$	$\text{Ta}_2\text{O}_5 + \text{AlCl}_3$	300°C		2
$\text{NbBr}_5$	$\text{Nb}_2\text{O}_5 + \text{AlBr}_3$	200°C		2, 3
$\text{TaBr}_5$	$\text{Ta}_2\text{O}_5 + \text{AlBr}_3$			2, 3
$\text{NbI}_3$	$\text{Nb}_2\text{O}_5 + \text{AlI}_3$	230°C, 24 h	Sublime at 230°C	1, 4
$\text{TaI}_5$	$\text{Ta}_2\text{O}_5 + \text{AlI}_3$	230°C		1, 4
$\text{MoI}_2$	$\text{MoO}_3 + \text{AlI}_3$	230°C, 48 h	Extract in $\text{C}_2\text{H}_5\text{I}$	1
$\text{Wl}_4$	$\text{WO}_3 + \text{AlI}_3$	230°C, 24 h	Extract in $\text{C}_2\text{H}_5\text{OH}$	1
$\text{MnI}_2$	$\text{MnO}_2 + \text{AlI}_3$	230°C, 48 h	Extract in $\text{H}_2\text{O}$	1, 5
$\text{FeI}_2$	$\text{Fe}_2\text{O}_3 + \text{AlI}_3$	300°C, 24 h	Sublime at 550°C	1
$\text{CoI}_2$	$\text{Co}_3\text{O}_4 + \text{AlI}_3$	230°C, 24 h	Sublime at 600°C	1, 4
$\text{NiI}_2$	$\text{Ni}_2\text{O}_3 + \text{AlI}_3$	230°C, 24 h	Sublime at 800°C	1, 4

The reactions are carried out in sealed tubes using stoichiometric amounts of metal oxide and aluminum trihalide.

In most cases the metal halide is separated from the  $\text{Al}_2\text{O}_3$  by sublimation. If the metal halide is involatile it is extracted into a suitable solvent, e.g., water for  $\text{MnI}_2$ ,  $\text{C}_2\text{H}_5\text{I}$

for  $\text{MoI}_2$ . An analogous method prepares the halides of  $\text{CrI}_3$ ,  $\text{MnI}_2$  and  $\text{CoI}_2$  from the sulfides<sup>5</sup> (§2.9.5).

(E. M. PAGE)

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2. M. Chaigneau, *Compt. Rend.*, 243, 957 (1956).
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4. M. Chaigneau, *Compt. Rend.*, 242, 263 (1956).
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## 2.9.5. Synthesis of Metal Halides from Metal Sulfides.

The preparation of metal halides from metal sulfides has a number of advantages<sup>1</sup>:

1. Anhydrous metal chlorides can be prepared directly from the sulfides, whether natural or synthetic.
2. The metal is converted to a single chloride.
3. In minerals where sand is the only impurity and the metal chloride is to be carried through further reaction steps, no additional purification is required. The pure metal chloride can be separated by sublimation or extraction with  $\text{CCl}_4$ .
4. Sulfides can be converted as readily to the chloride as the corresponding oxide.
5. Sulfides are more readily available than the oxides, which simplifies the process for attaining the anhydrous chloride.

TABLE 1. PREPARATION OF METAL HALIDES FROM METAL SULFIDES

Product	Reactants	Conditions	Ref.
$\text{WCl}_6$	$\text{WS}_2 + \text{CCl}_4$	400°C-bomb, 2-4 h	1
$\text{MoCl}_5$	$\text{MoS}_3 + \text{CCl}_4$	400°C-bomb, 12 h	1
$\text{MoCl}_5$	$\text{MoS}_2 + \text{Cl}_2$	Heat	2
$\text{MoF}_4$	$\text{MoS}_2 + \text{SF}_4$	350 °C, 8 h	3
$\text{ReCl}_5$	$\text{Re}_2\text{S}_7 + \text{CCl}_4$	400°C-bomb, 10 h	1
$\text{FeF}_3$	$\text{FeS}_2 + \text{SF}_4$	350°C-8 h	3
$\text{FeCl}_3$	$\text{FeS}_2 + \text{CCl}_4$	400°C-bomb	1
$\text{FeCl}_3$	$\text{FeS} + \text{CCl}_4$	400°C-bomb, 8 h	1
$\text{FeCl}_2$	$\text{Fe}_2\text{S}(\text{FeS}) + \text{Cl}_2$	8 h, 25°C	4
$\text{CrCl}_3$	$\text{Cr}_2\text{S}_3 + \text{Cl}_2$	Heat	5
$\text{CrI}_3$	$\text{Cr}_2\text{S}_3 + \text{AlI}_3$	350°C	6
$\text{WCl}_6$	$\text{WS}_3 + \text{Cl}_2$	Heat	7
$\text{ReCl}_5$	$\text{Re}_2\text{S}_7 + \text{Cl}_2$	Heat	8
$\text{ReCl}_5$	$\text{ReS}_2 + \text{Cl}_2$	Heat	8
$\text{TaI}_4$	$\text{TaS}_2 + \text{I}_2$	Adjust heat for equilibrium	9
$\text{UBr}_4$	$\text{U}_3\text{O}_2\text{S}_4 + \text{Br}_2$	400°C	10

## 2.9. Formation of the Halogen-Transition-Metal Bond

### 2.9.5. Synthesis of Metal Halides from Metal Sulfides.

for  $\text{MoI}_2$ . An analogous method prepares the halides of  $\text{CrI}_3$ ,  $\text{MnI}_2$  and  $\text{CoI}_2$  from the sulfides<sup>5</sup> (§2.9.5).

(E. M. PAGE)

1. M. Chaigneau, *Bull. Soc. Chim. Fr.*, 886 (1957).
2. M. Chaigneau, *Compt. Rend.*, 243, 957 (1956).
3. G. Brauer, *A Handbook of Preparative Inorganic Chemistry*, Vol. 2, 2nd Ed. Academic Press, New York, 1965, p. 131.
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TABLE 1. PREPARATION OF METAL HALIDES FROM METAL SULFIDES

Product	Reactants	Conditions	Ref.
$\text{WCl}_6$	$\text{WS}_2 + \text{CCl}_4$	400°C-bomb, 2-4 h	1
$\text{MoCl}_5$	$\text{MoS}_3 + \text{CCl}_4$	400°C-bomb, 12 h	1
$\text{MoCl}_5$	$\text{MoS}_2 + \text{Cl}_2$	Heat	2
$\text{MoF}_4$	$\text{MoS}_2 + \text{SF}_4$	350 °C, 8 h	3
$\text{ReCl}_5$	$\text{Re}_2\text{S}_7 + \text{CCl}_4$	400°C-bomb, 10 h	1
$\text{FeF}_3$	$\text{FeS}_2 + \text{SF}_4$	350°C-8 h	3
$\text{FeCl}_3$	$\text{FeS}_2 + \text{CCl}_4$	400°C-bomb	1
$\text{FeCl}_3$	$\text{FeS} + \text{CCl}_4$	400°C-bomb, 8 h	1
$\text{FeCl}_2$	$\text{Fe}_2\text{S}(\text{FeS}) + \text{Cl}_2$	8 h, 25°C	4
$\text{CrCl}_3$	$\text{Cr}_2\text{S}_3 + \text{Cl}_2$	Heat	5
$\text{CrI}_3$	$\text{Cr}_2\text{S}_3 + \text{AlI}_3$	350°C	6
$\text{WCl}_6$	$\text{WS}_3 + \text{Cl}_2$	Heat	7
$\text{ReCl}_5$	$\text{Re}_2\text{S}_7 + \text{Cl}_2$	Heat	8
$\text{ReCl}_5$	$\text{ReS}_2 + \text{Cl}_2$	Heat	8
$\text{TaI}_4$	$\text{TaS}_2 + \text{I}_2$	Adjust heat for equilibrium	9
$\text{UBr}_4$	$\text{U}_3\text{O}_2\text{S}_4 + \text{Br}_2$	400°C	10

6. Halogenation of the sulfide leads to the anhydrous halide unless a thio-halo compound is obtained.
7. This preparation is a straightforward, single-step method for extracting metals from their sulfide ores.

One method involves the conversion of the sulfide to the anhydrous chloride by  $\text{CCl}_4$  at high pressure and T; e.g.,  $\text{WS}_2$ ,  $\text{WS}_3$ ,  $\text{MoS}_3$  and  $\text{Re}_2\text{S}_7$  give  $\text{WCl}_6$ ,  $\text{MoCl}_5$  and  $\text{ReCl}_5$ , respectively, and  $\text{FeS}$ ,  $\text{FeS}_2$  and  $\text{MoS}_2$  give  $\text{FeCl}_3$  and  $\text{MoCl}_3$ , respectively. Direct chlorination is also possible, e.g., for the group-VI and group-VII elements. The use of  $\text{CCl}_4$  has the advantage of an easily handled reagent rather than the more corrosive  $\text{Cl}_2$ .

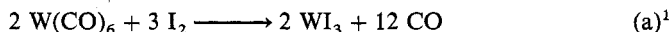
Typical conversions of sulfides to halides are given in Table 1.

(T.M. BROWN)

1. A. B. Bardawil, F. N. Collier, S. Y. Tyree, *Inorg. Chem.* 3, 149 (1964).
2. C. W. Blomstrand, *J. Prakt. Chem.*, 71, 449 (1857).
3. A. L. Oppegard, W. C. Smith, E. L. Muetterties, V. A. Engelhardt, *J. Am. Chem. Soc.*, 82, 3835 (1960).
4. T. Ishikawa, S. Yoshizawa, *Kogyo Kagaku Zasshi*, 66 (3), 642 (1963); *Chem. Abstr.*, 59, 12,429 (1963).
5. M. J. Udy, *Chemistry of Chromium and Its Compounds*, Reinhold, New York, 1956.
6. M. Chaigneau, M. Chastagnier, *Bull. Soc. Chim. Fr.*, 1192 (1958).
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8. R. D. Peacock, *The Chemistry of Technetium and Rhenium*, Elsevier, New York, 1966.
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10. D. Brown, ed., *Halides of the Transition Elements. Halides of the Lanthanides and Actinides*, John Wiley and Sons, New York, 1968, p. 190.

## 2.9.6. Synthesis of Metal Halides from Metal Carbonyls.

The action of halogens on the group-VIB elements is useful for preparing iodides since relatively low T are required; e.g.,  $\text{MoI}_3$  and  $\text{WI}_3$  are prepared by heating the hexacarbonyl with  $\text{I}_2$ :



Gaseous  $\text{F}_2$  can act on Mo hexacarbonyl in two different ways<sup>2</sup> depending on the T. In dil  $\text{F}_2$  the carbonyl remains unchanged at RT, but by raising or lowering the T, two different reactions can be induced. Above  $50^\circ\text{C}$ , where Mo hexacarbonyl is volatile, a vigorous reaction occurs resulting in Mo hexafluoride,  $\text{MoF}_6$ , carbonyl fluoride,  $\text{COF}_2$ , and impure Mo dioxide. But if the T is lowered to  $-75^\circ\text{C}$ , only a small amount of the hexafluoride and an olive-green solid results along with free CO. If the solid is heated to  $170^\circ\text{C}$  in a vacuum, two fluorides of Mo,  $\text{MoF}_5$  and  $\text{MoF}_4$ , result.

Intermediate halides may be prepared by the action of a high oxidation state metal halide on the carbonyl, e.g., in the preparation of  $\text{WCl}_4$ :





## 2.9. Formation of the Halogen-Transition-Metal Bond

### 2.9.6. Synthesis of Metal Halides from Metal Carbonyls.

195

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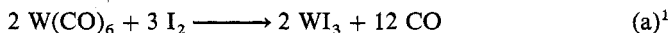
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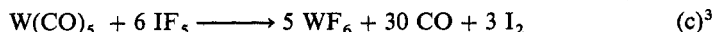
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TABLE 1. PREPARATION OF METAL HALIDES  
FROM METAL CARBONYLS

Product	Reactants	Ref.
CrCl <sub>3</sub>	Cr(CO) <sub>6</sub> + Cl <sub>2</sub>	4
MoF <sub>6</sub>	Mo(CO) <sub>6</sub> + F <sub>2</sub> (high T)	2
MoF <sub>5</sub>	Mo(CO) <sub>6</sub> + F <sub>2</sub> (low T)	2
MoF <sub>5</sub>	Mo(CO) <sub>6</sub> + MoF <sub>6</sub>	9
MoF <sub>4</sub>	Mo(CO) <sub>6</sub> + F <sub>2</sub> (low T)	2
MoBr <sub>4</sub>	Mo(CO) <sub>6</sub> + Br <sub>2</sub>	4
MoBr <sub>3</sub>	Mo(CO) <sub>6</sub> + MoBr <sub>4</sub>	5
MoI <sub>3</sub>	Mo(CO) <sub>6</sub> + I <sub>2</sub>	1
WF <sub>6</sub>	W(CO) <sub>6</sub> + ReF <sub>6</sub>	6
WF <sub>5</sub>	W(CO) <sub>6</sub> + IF <sub>5</sub>	3
WCl <sub>5</sub>	W(CO) <sub>6</sub> + WCl <sub>6</sub>	7
WCl <sub>4</sub>	W(CO) <sub>6</sub> + WCl <sub>5</sub>	7
WBr <sub>5</sub>	W(CO) <sub>6</sub> + Br <sub>2</sub>	8
WBr <sub>4</sub>	W(CO) <sub>6</sub> + WBr <sub>5</sub>	7
ReF <sub>5</sub>	ReF <sub>6</sub> + WF <sub>6</sub> + W(CO) <sub>6</sub>	6
WI <sub>3</sub>	W(CO) <sub>6</sub> + I <sub>2</sub>	1
FeI <sub>2</sub>	Heat Fe(CO) <sub>4</sub> I <sub>2</sub>	10

Iodine pentafluoride is also used for preparing fluorides from the carbonyl, e.g., in the preparation of W hexafluoride:



Halides prepared from metal carbonyls are given in Table 1.

(T.M. BROWN)

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4. W. Hieber, E. Romberg, *Z. Anorg. Allg. Chem.*, 221, 321 (1935).
5. R. E. Robinson, U.S. Pat. 3,298,778; *Chem. Abstr.*, 66, 77,856 (1967).
6. J. B. Hargreaves, R. D. Peacock, *J. Chem. Soc.*, 1099 (1960).
7. M. A. S. King, R. E. McCarley, *Inorg. Chem.*, 12, 1972 (1973).
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10. G. Brauer, *Preparative Inorganic Chemistry*, Vol. 2, 2nd ed. Academic Press, New York, 1965, p. 1496.

### 2.9.7. Synthesis of Metal Halides from Metal Carboxylates by Reaction with Acetyl Halide or Hydrohalogenation Reactions.

Pure anhydrous halides may be produced quantitatively by the interaction of the anhydrous metal carboxylate and acetyl halide or hydrogen halide in a nonaqueous

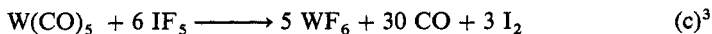
## 2.9. Formation of the Halogen-Transition-Metal Bond

## 2.9.7. Synthesis of Metal Halides from Metal Carboxylates.

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MoF <sub>5</sub>	Mo(CO) <sub>6</sub> + F <sub>2</sub> (low T)	2
MoF <sub>5</sub>	Mo(CO) <sub>6</sub> + MoF <sub>6</sub>	9
MoF <sub>4</sub>	Mo(CO) <sub>6</sub> + F <sub>2</sub> (low T)	2
MoBr <sub>4</sub>	Mo(CO) <sub>6</sub> + Br <sub>2</sub>	4
MoBr <sub>3</sub>	Mo(CO) <sub>6</sub> + MoBr <sub>4</sub>	5
MoI <sub>3</sub>	Mo(CO) <sub>6</sub> + I <sub>2</sub>	1
WF <sub>6</sub>	W(CO) <sub>6</sub> + ReF <sub>6</sub>	6
WF <sub>5</sub>	W(CO) <sub>6</sub> + IF <sub>5</sub>	3
WCl <sub>5</sub>	W(CO) <sub>6</sub> + WCl <sub>6</sub>	7
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WBr <sub>4</sub>	W(CO) <sub>6</sub> + WBr <sub>5</sub>	7
ReF <sub>5</sub>	ReF <sub>6</sub> + WF <sub>6</sub> + W(CO) <sub>6</sub>	6
WI <sub>3</sub>	W(CO) <sub>6</sub> + I <sub>2</sub>	1
FeI <sub>2</sub>	Heat Fe(CO) <sub>4</sub> I <sub>2</sub>	10

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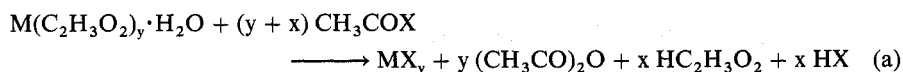
### 2.9.7. Synthesis of Metal Halides from Metal Carboxylates by Reaction with Acetyl Halide or Hydrohalogenation Reactions.

Pure anhydrous halides may be produced quantitatively by the interaction of the anhydrous metal carboxylate and acetyl halide or hydrogen halide in a nonaqueous

TABLE 1. PREPARATION METAL HALIDES FROM METAL CARBOXYLATES (X = Cl, Br, I)

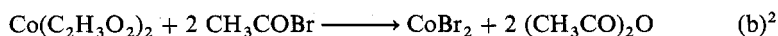
Metal halide	Precursor	Ref.
MnX <sub>2</sub>	Mn(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ·4 H <sub>2</sub> O + CH <sub>3</sub> COX	1
CoX <sub>2</sub>	Co(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ·4 H <sub>2</sub> O + CH <sub>3</sub> COX	1
NiX <sub>2</sub>	Ni(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ·4 H <sub>2</sub> O + CH <sub>3</sub> COX	1
CuX <sub>2</sub>	Cu(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ·H <sub>2</sub> O + CH <sub>3</sub> COX	1
CrX <sub>3</sub>	Cr(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ·x H <sub>2</sub> O + CH <sub>3</sub> COX	1
NdX <sub>3</sub>	Nd(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ·x H <sub>2</sub> O + CH <sub>3</sub> COX	1
SmX <sub>3</sub>	Sm(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ·x H <sub>2</sub> O + CH <sub>3</sub> COX	1
CrCl <sub>2</sub>	Cr <sub>2</sub> (C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>4</sub> + 4 HCl	2
CrBr <sub>2</sub>	Cr <sub>2</sub> (C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>4</sub> + HBr	2
CoBr <sub>2</sub>	Co(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> + CH <sub>3</sub> COBr	
MoCl <sub>2</sub>	Mo(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> + HCl(g)	3

solvent such as benzene or ether. With hydrated metal acetates the anhydrous metal halide is obtained using acetyl halide in benzene<sup>1</sup>:

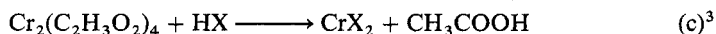


where M is a metal and X is Cl, Br or I. All products except the halide are volatile and can be removed under vacuum. Some of the halides that may be prepared via this method are given in Table 1. Acetyl iodide is not stable and should be prepared as required.

The anhydrous halides may also be obtained from anhydrous acetates as illustrated in the following reaction:



Dimeric metal complexes of the carboxylates are cleaved with anhydrous hydrogen halides to give MX<sub>2</sub> compounds:



where X = Cl, Br.

The acetate of Mo(II) reacts with dry, oxygen-free HCl at ca. 250°C to afford a compound that analyzes as ca. 98% MoCl<sub>2</sub>. This is not the yellow molybdenum dichloride, Mo<sub>6</sub>Cl<sub>12</sub><sup>4</sup>. Some reactions occur that are expected of the true chloride; e.g., the compound dissolves, leaving a small residue, in hot pyridine and hot isoquinoline to give air-sensitive yellow and blood-red solutions, respectively.

(T.M. BROWN)

1. G. W. Watt, P. S. Gentile, E. P. Helvenstan, *J. Am. Chem. Soc.*, **77**, 2752 (1955).
2. G. Brauer, *Handbook of Preparative Inorganic Chemistry*, Vol. 2, 2nd ed., Academic Press, New York, 1965, p. 1337.
3. T. A. Stephenson, E. Bannister, G. Wilkinson, *J. Chem. Soc.*, 2538 (1964).

## 2.9. Formation of the Halogen-Transition-Metal Bond

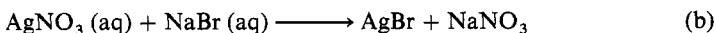
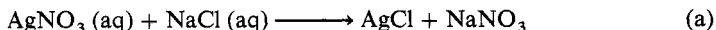
## 2.9.9. Dehydration of Metal Halide Hydrates

## 2.9.9.1. by Dehydration or Hydrohalogenation Reactions.

**2.9.8. Synthesis of Metal Halides from Other Metal Salts.**

Most halides can be prepared using the methods outlined in earlier sections. Halides on the right side of the periodic table are also afforded via exchange of the transition-metal salt and the halide ion in solution.

Silver monofluoride is prepared by dissolving Ag carbonate in aq HF and evaporating the solution to dryness. Silver chloride and bromide are produced from concentrated solutions of their constituent ions:



The reaction is forced to completion by the precipitation of the halide in solution.

Acidic solutions of Cu(II) salts and Au result in Cu(I) chloride or bromide upon heating, but Cu(II) solutions with iodide ion afford CuI.

(T.M. BROWN)

**2.9.9. Dehydration of Metal Halide Hydrates**

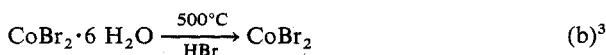
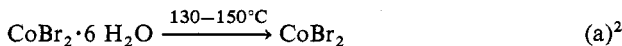
Metal halide hydrates may be heated with or without a hydrogen halide in order to drive off H<sub>2</sub>O to yield the anhydrous metal halides. With many of the less basic metal halides, the halides may be crystallized from H<sub>2</sub>O and dehydrated thermally; e.g., the lanthanides may be dehydrated in a stream of HCl<sup>1</sup>. Often, chemical dehydrating agents such as thionyl chloride are needed to insure complete dehydration. Halides of Ti(III), Cu, Fe(III) and Ni(II) can be dehydrated by heating in carbonyl or thionyl chloride. Chromium(III) chloride hydrate is heated in CCl<sub>4</sub> to produce the anhydrous halide.

(T.M. BROWN)

1. S. Y. Tyree, *Inorg. Synth.*, 4, 108 (1953).

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Transition-metal halides may be dehydrated with heat in either the absence or the presence of hydrogen halides:

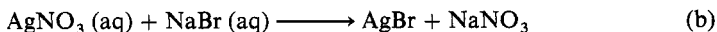
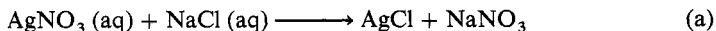


Problems arise where hydrogen halide is lost in preference to H<sub>2</sub>O, resulting in the formation of oxyhalides or oxides at the T required for dehydration. Thus dehydration in

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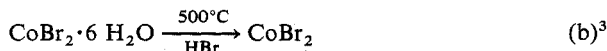
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TABLE 1. PREPARATION OF TRANSITION  
 METAL HALIDES BY THERMAL METHODS

Product	Reactant(s)	Ref.
CoCl <sub>2</sub>	CoCl <sub>2</sub> ·6 HCl + HCl	2
CoBr <sub>2</sub>	CoBr <sub>2</sub> ·6 H <sub>2</sub> O + HCl	2
NiBr <sub>2</sub>	NiBr <sub>2</sub> ·6 H <sub>2</sub> O	2
LaCl <sub>3</sub>	LaCl <sub>3</sub> ·6 H <sub>2</sub> O + HCl	4
CeCl <sub>3</sub>	CeCl <sub>3</sub> ·6 H <sub>2</sub> O + HCl	4
PrCl <sub>3</sub>	PrCl <sub>3</sub> ·6 H <sub>2</sub> O + HCl	4
NdCl <sub>3</sub>	NdCl <sub>3</sub> ·6 H <sub>2</sub> O + HCl	4
SmCl <sub>3</sub>	SmCl <sub>3</sub> ·6 H <sub>2</sub> O + HCl	4
DyCl <sub>3</sub>	DyCl <sub>3</sub> ·6 H <sub>2</sub> O + HCl	4
YtCl <sub>3</sub>	YtCl <sub>3</sub> ·6 H <sub>2</sub> O + HCl	4
HoCl <sub>3</sub>	HoCl <sub>3</sub> ·6 H <sub>2</sub> O + HCl	4
TmCl <sub>3</sub>	TmCl <sub>3</sub> ·6 H <sub>2</sub> O + HCl	4

the presence of HX or other halogenating agents ensures the formation of the anhydrous halide. Some anhydrous halides prepared by thermal methods are illustrated in Table 1.

(T.M. BROWN)

1. G. Brauer, *Preparative Inorganic Chemistry*, Vol. 2, 2nd ed. Academic Press, New York, 1965, p. 1515.
2. G. Crut, *Bull. Soc. Chim. Fr.*, 4, 35, 550 (1924).
3. J. H. Kleinheksel, H. C. Kremers, *J. Am. Chem. Soc.*, 50, 959 (1928).

### 2.9.9.2. by Chemical Methods.

Anhydrous halides may be prepared from a readily available hydrated halide, since many hydrated halides are commercially available and most anhydrous halides are hygroscopic, e.g., via treatment with thionyl chloride:



This simple method requires no special apparatus, and other than the chloride, the products are gaseous and easily removed. The method is useful regardless of the metal.

TABLE 1. PREPARATION OF ANHYDROUS METAL CHLORIDES USING  
 THIONYL CHLORIDE

Chloride	Starting material	Ref.
CrCl <sub>3</sub>	CrCl <sub>3</sub> ·6 H <sub>2</sub> O	2
FeCl <sub>3</sub>	FeCl <sub>3</sub> ·6 H <sub>2</sub> O	2
CoCl <sub>2</sub>	CoCl <sub>2</sub> ·6 H <sub>2</sub> O	2
NiCl <sub>2</sub>	NiCl <sub>2</sub> ·6 H <sub>2</sub> O	2
CuCl <sub>2</sub>	CuCl <sub>2</sub> ·2 H <sub>2</sub> O	2
NdCl <sub>2</sub>	NdCl <sub>2</sub> ·6 H <sub>2</sub> O	2
ThCl <sub>4</sub>	ThCl <sub>4</sub> ·8 H <sub>2</sub> O	2

## 2.9. Formation of the Halogen–Transition–Metal Bond

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NiBr <sub>2</sub>	NiBr <sub>2</sub> ·6 H <sub>2</sub> O	2
LaCl <sub>3</sub>	LaCl <sub>3</sub> ·6 H <sub>2</sub> O + HCl	4
CeCl <sub>3</sub>	CeCl <sub>3</sub> ·6 H <sub>2</sub> O + HCl	4
PrCl <sub>3</sub>	PrCl <sub>3</sub> ·6 H <sub>2</sub> O + HCl	4
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SmCl <sub>3</sub>	SmCl <sub>3</sub> ·6 H <sub>2</sub> O + HCl	4
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YtCl <sub>3</sub>	YtCl <sub>3</sub> ·6 H <sub>2</sub> O + HCl	4
HoCl <sub>3</sub>	HoCl <sub>3</sub> ·6 H <sub>2</sub> O + HCl	4
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CoCl <sub>2</sub>	CoCl <sub>2</sub> ·6 H <sub>2</sub> O	2
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ThCl <sub>4</sub>	ThCl <sub>4</sub> ·8 H <sub>2</sub> O	2



Where heating the hydrate alone may lead to an oxychloride as with  $\text{Th}^{1}$ , the dehydration can be achieved by refluxing with thionyl chloride. The chlorides of the lanthanides Sc and Yb lose  $\text{HCl}$  more readily than  $\text{H}_2\text{O}$ , resulting in the formation of  $\text{MoCl}$ , with Sc and Ce going all the way to their oxides  $\text{Sc}_2\text{O}_3$  and  $\text{CeO}_2$ , respectively.

Anhydrous chlorides prepared using thionyl chloride are shown in Table 1.

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## 2.9.10. Synthesis of Complex Halo Anions

Complex halo anions are known for all of the transition-metal elements as well as for the lanthanides and actinides. Because of their structural simplicity, they are of theoretical interest. Their electronic and vibrational spectra as well as their magnetic properties relate their electronic structures to their stereochemistry. Complex halo anions can be prepared by reacting the metal halide with non-transition-metal halides, which may be an alkali, alkaline-earth, or organic (usually quaternary ammonium) halide. Owing to the variety of oxidation states exhibited by the early transition elements, these elements receive the most attention.

(T.M. BROWN)

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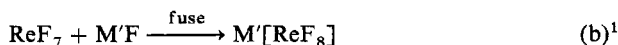
The ability of metal halides to function as electron-pair acceptor acids toward halide ions provides a route to the halo anions. Fusing the metal halide with a non-transition-metal halide (usually an alkali-metal halide) affords the anion. The fluorides and chlorides work, but the bromides and iodides are not obtained owing to their instability at higher T.

The early transition elements have high affinity for oxygen, and the reactions should be carried out in the absence of  $\text{O}_2$  or  $\text{H}_2\text{O}$ . The remaining transition-metal halo anions may be prepared from their oxides or aqueous solutions of the element.

Most halo anions exhibit coordination numbers of 6, but in fused melts of the metal fluorides with an alkali-metal fluoride, fluoroanions have coordination numbers of 7 or 8. This point is illustrated in the preparation of  $\text{M}'_3[\text{MF}_8]$  and  $\text{M}'[\text{ReF}_8]$ :



Where  $\text{M}' = \text{Nb}, \text{Ta}$ ;  $\text{M} = \text{alkali metal}$ :



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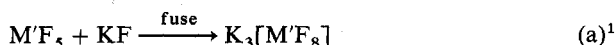
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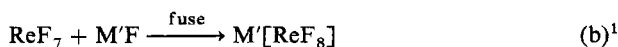
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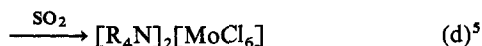
Where M' = Nb, Ta; M = alkali metal:



Chlorides, bromides and iodides rarely form halo complexes having a coordination number greater than 6.

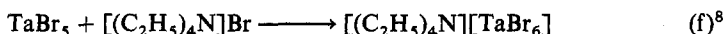
While most of the halo anions are stable in all of the oxidation states exhibited by the metal (e.g., groups IVA and VA), there are exceptions (especially, groups VIA and VIIA). The hexahalides  $\text{WCl}_6$ ,  $\text{WBr}_6$  and  $\text{ReCl}_6$  do not give complex chlorides but are reduced to lower oxidation state species. However,  $\text{MoF}_6$ ,  $\text{WF}_6$  and  $\text{ReF}_6$  are stabilized in salts such as  $(\text{NO})\text{MF}_7$  ( $\text{M} = \text{Mo}, \text{W}, \text{Re}$ ) and  $(\text{NO})_2\text{MF}_8$  ( $\text{M} = \text{W}, \text{Re}$ )<sup>2,3</sup>.

A second method of preparation involves the interaction of the parent binary halide with a halide in an inert solvent. A quaternary ammonium derivative is used as the cation, as are pyridinium and tetraphenylarsonium salts, for solubility reasons. The choice of solvent can dictate the product formed as in the reactions of Mo pentachloride:

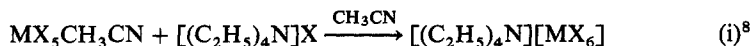
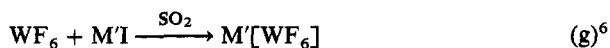


Thionyl chloride is a solvent that can function both as a dehydrating agent and as an oxidizing agent. The transition metal tends toward its highest oxidation state in this solvent.

The lower T for reactions utilizing a solvent often allow complex bromides and iodides to form that are unstable at the higher T used in the fused-melt preparations. Thus  $[(\text{C}_2\text{H}_5)_4\text{N}][\text{NbBr}_6]$  and  $[(\text{C}_2\text{H}_5)_4\text{N}][\text{TaBr}_6]$  are prepared in acetonitrile:



The pentahalides of Nb, T, Mo and W react with halide ions to afford octahedral  $[\text{MX}_6]^-$  anions:

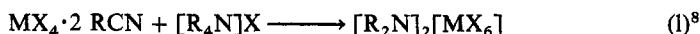


where  $\text{M} = \text{Nb}, \text{Ta}$ ;  $\text{X} = \text{Cl}, \text{Br}$ ;



where  $\text{M} = \text{Nb}, \text{Ta}$ ;  $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$ .

The  $[\text{MX}_6]^{2-}$  halo anions can be prepared using similar methods. In addition to alkali halide melts, the use of  $\text{ICl}$ , thionyl chloride,  $\text{CH}_3\text{CN}$ ,  $\text{CHCl}_3$ , etc., as reaction solvents gives rise to complex halo anions:



where  $\text{M} = \text{Ti}, \text{Zr}, \text{Th}, \text{U}$ ;  $\text{X} = \text{Cl}, \text{Br}$ ;  $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7$ ;

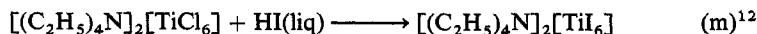


TABLE 1. FORMATION OF COMPLEX HALO ANIONS BY REACTIONS OF TRANSITION-METAL HALIDES WITH NON-TRANSITION-METAL AND ORGANIC HALIDES

Product	Reactants	Conditions	Ref.
$M_2[TiF_6]$	$TiF_4 + MF$	Aq HF	22
$M_2[TiCl_6]$	$TiCl_4 + MCl$	Fused $SbCl_3$	23
$[C_2H_5)_4N]_2[TiCl_6]$	$TiCl_4 \cdot 2 CH_3CN$	$CH_3CN$ solvent	8
$(C_2H_5NH)_3[TiCl_6]$	$TiCl_3 \cdot 3 CH_3CN + [C_2H_5NH]Cl$	$CHCl_3$	15
$Cs_2[Ti_2Cl_9]$	$TiCl_3 + CsCl$		16
$M[TiBr_6]$	$TiBr_4 + MBr$	Fused $SbBr_3$	24
$[C_2H_5)_4N]_2[TiBr_6]$	$TiBr_4 \cdot 2 CH_3CN + [C_2H_5)_4N]Br$	$CH_3CN$ solvent	8
$[C_2H_5NH)_3[TiBr_6]$	$TiBr_3 \cdot 3 CH_3CN + [C_2H_5NH]Br$	$CHCl_3$	15
$[C_2H_5)_4N]_2[TiH_6]$	$[C_2H_5)_4N][TiCl_6] + HI$	Liq HI	12
$Cs_3[TiI_6]$	$TiI_4 + CsI$	Fuse	66
$M_3[ZrF_7]$	$ZrF_4 + MF$	Fuse	1
$M_2[ZrF_6]$	$ZrF_4 + MF$	Fuse	25
$M_2[ZrCl_6]$	$ZrCl_4 + MCl$	Fuse	26, 27
$Cs_2[ZrCl_6]$	$ZrCl_4 + CsCl$	Fuse	28
$[C_2H_5)_4N]_2[ZrCl_6]$	$ZrCl_4 \cdot 2 CH_3CH + [(C_2H_5)_4N]Cl$	$CH_3CN$ solvent	8
$[C_2H_5)_4N]_2[ZrBr_6]$	$ZrBr_4 \cdot 2 CH_3CN + [(C_2H_5)_4N]Cl$	$CH_3CN$ solvent	8
$Cs_2[ZrI_6]$	$ZrI_4 + CsI$	Fuse	66
$M_3[HfF_7]$	$HfF_4 + MF$	Fuse	1
$M_2[HfF_6]$	$HfF_4 + MF$	Fuse	1
$[C_2H_5)_4N]_2[HfCl_6]$	$HfCl_4 + [(C_2H_5)_4N]Cl$	$SOCl_2$	28
$Cs_2[HfCl_6]$	$HfCl_4 + CsCl$	$ICl-SOCl_2$	28
$[C_2H_5)_4N]_2[HfBr_6]$	$HfBr_4 + [(C_2H_5)_4N]Br$	$SOCl_2$	28
$Cs_2[HfI_6]$	$HfI_4 + CsI$	Fuse	66
$M[VF_6]$	$VF_5 + MF$	Anhyd HF	6
$K[VF_6]$	$VCl_3 + KCl$	$BF_3$	29
$[C_2H_5)_2N]_2[VCl_6]$	$VCl_4 + [(C_2H_5)_4N]Cl$	$SOCl_2$ solvent	30
$[C_2H_5NH)_3[VCl_6]$	$VCl_3 + [C_2H_5NH]Cl$	$150^\circ C$	15
$M_2[VCl_6]$	$M_2VOCl_4 + SOCl_2$	Heat	31
$[C_2H_5NH)_3[VCl_6]$	$VCl_3 + [C_2H_5NH]Cl$	$150^\circ C$	15

$\text{Cs}_3[\text{V}_2\text{Cl}_9]$	$\text{VCl}_3 + \text{CsCl}$	$\text{SOCl}_2$	16
$[(\text{C}_2\text{H}_5)_4\text{N}]_3[\text{V}_2\text{Cl}_9]$	$\text{VCl}_3 + [(\text{C}_2\text{H}_5)_4\text{N}]\text{Cl}$	$\text{CHCl}_3$	32
$[\text{C}_5\text{H}_5\text{NH}]_3[\text{VBr}_6]$	$\text{VBr}_3 + [\text{C}_5\text{H}_5\text{NH}]\text{Br}$	Fuse	15
$\text{M}_3[\text{NbF}_8]$	$\text{NbF}_5 + \text{MF}$	Fuse	1
$\text{M}_2[\text{NbF}_7]$	$\text{NbF}_5 + \text{MF}$	Fuse	33
$\text{M}[\text{NbF}_6]$	$\text{MF}_5 + \text{MF}$	Fuse	1
$\text{M}[\text{NbCl}_6]$	$\text{NbCl}_5 + \text{MCl}$	Fuse	34
$[(\text{C}_2\text{H}_5)_4\text{N}][\text{NbCl}_6]$	$\text{NbCl}_5 \cdot \text{CH}_3\text{CN} + [(\text{C}_2\text{H}_5)_4\text{N}]\text{Cl}$	$\text{CH}_3\text{CN}$	8
$\text{M}_2[\text{NbCl}_6]$	$\text{NbCl}_5 + \text{MCl}$	Fuse	35
$\text{M}_2[\text{NbCl}_5]$	$\text{NbCl}_3 + \text{MCl}$	Fuse	36
$[(\text{C}_2\text{H}_5)_4\text{N}][\text{NbCl}_{12}]\text{Cl}_6]$	$\text{NbCl}_{12} \cdot n \text{H}_2\text{O} + [(\text{C}_2\text{H}_5)_4\text{N}]\text{Cl}$	$\text{C}_2\text{H}_5\text{OH}$	19
$[(\text{C}_2\text{H}_5)_4\text{N}][\text{NbBr}_6]$	$\text{NbBr}_5 \cdot \text{CH}_3\text{CN} + [(\text{C}_2\text{H}_5)_4\text{N}]\text{Br}$	$\text{CH}_3\text{CN}$	8
$\text{Cs}[\text{Nb}_6\text{Br}_{11}]$	$\text{Nb}_3\text{Br}_6 + \text{Nb} + \text{CsBr}$	$630^\circ\text{--}610^\circ\text{C}$	21
$\text{M}_3[\text{TaF}_8]$	$\text{TaF}_5 + \text{MF}$	Fuse	1
$\text{M}_2[\text{TaF}_7]$	$\text{TaF}_5 + \text{MF}$	Fuse	33
$\text{K}[\text{TaF}_6]$	$\text{TaF}_5 + \text{KF}$	Aq HF	1
$\text{M}[\text{TaCl}_6]$	$\text{TaCl}_5 + \text{MCl}$	Fuse	34
$[(\text{C}_2\text{H}_5)_4\text{N}][\text{TaCl}_6]$	$\text{TaCl}_5 \cdot \text{CH}_3\text{CN} + [(\text{C}_2\text{H}_5)_4\text{N}]\text{Cl}$	$\text{CH}_3\text{CN}$	8
$\text{M}_2[\text{TaCl}_6]$	$\text{TaCl}_4 + \text{MCl}$	Fuse	35
$\text{M}_2[\text{TaCl}_5]$	$\text{TaCl}_3 + \text{MCl}$	Fuse	37
$\text{K}_4[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_6]$	$\text{TaCl}_5 + \text{Al} + \text{KCl}$	$550^\circ\text{C}$	20
$[(\text{C}_2\text{H}_5)_4\text{N}][\text{TaBr}_6]$	$\text{TaBr}_5 \cdot \text{CH}_3\text{CN} + [(\text{C}_2\text{H}_5)_4\text{N}]\text{Br}$	$\text{CH}_3\text{CN}$	8
$\text{M}[\text{CrF}_5]$	$\text{CrF}_4 + \text{MCl}$	$\text{BF}_3$	38
$[\text{NH}_4]_3[\text{CrF}_6]$	$\text{CrCl}_3 \cdot 6 \text{H}_2\text{O} + \text{NH}_4\text{F}$	Water	39
$\text{M}_3[\text{CrF}_6]$	$\text{CrCl}_3 + \text{MCl} + \text{F}_2$		33
$\text{M}_3[\text{CrCl}_6]$	$\text{CrCl}_3 + \text{MCl}$	Fuse	40
$[\text{C}_5\text{H}_5\text{NH}]_3[\text{CrCl}_6]$	$\text{CrCl}_3 + \text{C}_5\text{H}_5\text{NHCl}$	Fuse	15
$\text{Cs}_3[\text{Cr}_2\text{Cl}_9]$	$\text{CrCl}_3 + \text{CsCl}$	$200^\circ\text{C}$	17
$[(\text{C}_2\text{H}_5)_4\text{N}]_4[\text{Cr}_3\text{Cl}_{10}]$	$\text{CrCl}_2 + [(\text{C}_2\text{H}_5)_4\text{N}]\text{Cl}$	$\text{CH}_2\text{Cl}_2$	60
$[(\text{C}_2\text{H}_5)_4\text{N}]_3[\text{Cr}_2\text{Br}_9]$	$\text{CrBr}_3 + [(\text{C}_2\text{H}_5)_4\text{N}]\text{Br}$	$\text{CH}_3\text{COBr}$ reflux	17
$\text{M}_2[\text{MoF}_8]$	$\text{MoF}_6 + \text{MF}$	Aq HF	41
$\text{M}[\text{MoF}_6]$	$\text{MoF}_6 + \text{M}$	Liq $\text{SO}_2$	6, 42
$\text{M}[\text{MoF}_6]$	$\text{MoF}_6 + \text{MI}$	$\text{IF}_5$	33
$[(\text{C}_2\text{H}_5)_4\text{N}][\text{MoCl}_6]$	$\text{MoCl}_5 + [(\text{C}_2\text{H}_5)_4\text{N}]\text{Cl}$	$\text{CH}_2\text{Cl}_2$ reflux	4

TABLE 1. (Continued)

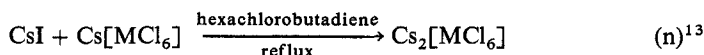
Product	Reactants	Conditions	Ref.
$[R_4N]_2[MoCl_6]$	$MoCl_4 \cdot 2 RCN + [R_4N]Cl$	$CHCl_3$	44
$K_2[MoCl_6]$	$MoCl_5 + KCl$	$200^\circ C$	11
$Cs_2[MoCl_6]$	$MoCl_5 + CsCl$	Liq $SO_2$	44
$Cs_3[Mo_2Cl_9]$	$MoCl_5 + CsCl$	Fuse	18
$[(C_2H_5)_4N]_3[MoCrCl_9]$	$[(C_2H_5)_4N]_4[Cr_3Cl_{10}] + [(C_2H_5)_4N]_2[MoCl_6]$	$CH_2Cl_2$	60
$M_2[MoBr_6]$	$MoBr_3 + MBr$	$IBr$	11
$Cs_3[Mo_2Br_9]$	$MoBr_3 + CsCl$	Fuse	18
$M_2[WF_8]$	$WF_6 + MF$		45
$M[WF_7]$	$WF_6 + MF$	$IF_5$	45
$(Cs \text{ or } Rb)$			
$M[WF_6]$	$WF_6 + MI$		6, 42
$M[WCl_6]$	$WCl_6 + MCl$	Liq $SO_2$	47
$[(C_2H_5)_4N][WCl_6]$	$WCl_5 + [(C_2H_5)_4N]Cl$	Fuse	4
$M_2[WCl_6]$	$WCl_6 + M$	$CHCl_3$ reflux	46
$M_2[WBr_6]$	$WBr_6 + MI$	$130^\circ C$	46
$[(C_2H_5)_4N][WBr_6]$	$WBr_5 + (C_2H_5)_4NBr$	$290^\circ C$	48
$M_2[MnF_6]$	$MnCl_2 + MCl + F_2$	$CHCl_3$ reflux	33
$M_2[MnF_4]$	$MnF_2 + MF$		49
$M_2[MnCl_4]$	$MnCl_2 + MCl$	Fuse	50
$M_2[MnCl_6]$	$MnCl_2 + MCl$	Fuse	50
$[(C_2H_5)_4N][MnCl_4]$	$MnCl_2 \cdot 4 H_2O + (C_2H_5)_4NCl$	$SOCl_2$	9
$[(C_2H_5)_4N]_2[MnCl_4]$	$MnCl_2 + C_2H_5NHCN$	Conc $HCl$	51
$[R_4N]_2[MnBr_4]$	$MnBr_2 + R_4NBr$	$C_2H_5OH$	52, 53
$[R_4N]_2[MnI_4]$	$MnI_2 + R_4NI$	$C_2H_5OH$	52, 53
$M[TcF_6]$	$TcF_6 + MCl$	$IF_5$	54
$K[ReF_8]$	$ReF_7 + KF$	Low T	1
$K[ReF_6]$	$ReF_6 + KI$	Liq $SO_2$	55
$M_3[ReCl_6]$	$ReCl_5 + MCl$	Fuse	56
$[(C_2H_5)_2NH_2]_2[Re_2Cl_8]$	$Re_3Cl_9 + (C_2H_5)_2NH_2Cl$	Fuse	57

## 2.9.10. Synthesis of Complex Halo Anions

## 2.9.10.1. by Reaction of Metal Halides.

$M_3[FeF_6]$	$FeCl_3 + MCl + F_2$	Conc HCl	33
$[CH_3NH_3]_4[FeCl_7]$	$FeCl_3 + [CH_3NH_3]Cl$		58
$K_3[CoF_6]$	$CoF_3 + KF$ in HF		33
$[C_2H_5]_4[N]_2[CoCl_4]$	$CoCl_2 + [(C_2H_5)_4N]Cl$	Ethanol	61
$[C_2H_5]_4[N]_2[CoBr_4]$	$CoBr_2 + [(C_2H_5)_4N]Br$	Ethanol	61
$[C_2H_5]_4[N]_2[CoI_4]$	$CoI_2 + [(C_2H_5)_4N]I$	Ethanol	61
$K_3[NiF_6]$	$NiCl_2 + KCl + F_2$		33
$K_2[NiF_6]$	$NiCl_2 + K(OCl) + F_2$		33
$[C_2H_5]_4[N]_2[NiCl_4]$	$NiCl_2 + [(C_2H_5)_4N]Cl$	Ethanol	61
$[C_2H_5]_4[N]_2[NiBr_4]$	$NiBr_2 + [(C_2H_5)_4N]Br$	Ethanol	61
$[C_2H_5]_4[N]_2[NiI_4]$	$NiI_2 + [(C_2H_5)_4N]I$	Ethanol	61
$K_3[CuF_6]$	$CuCl + KCl + F_2$		33
$Cs_2[CuCl_4]$	$CuCl_2 + CsCl$	Water	63
$[C_6H_5]_4[As]_2[CuCl_4]$	$CuCl_2 + [(C_6H_5)_4As]Cl$	Ethanol	61
$[C_6H_5]_4[As]_2[CuBr_4]$	$CuBr_2 + [(C_6H_5)_4As]Br$	Ethanol	61
$M_3[YF_6]$	$YCl_3 + MCl + F_2$		33
$M[IrF_6]$	$IrBr_3 + MCl$	$BrF_3$	33
$Cs[RhF_6]$	$RhF_5 + CsF$	$IF_5$	58
$Na_3[RhCl_6] \cdot 12 H_2O$	$RhCl_3 + NaCl + Cl_2$		62
$M[OsF_6]$	$OsBr_4 + MCl$	$BrF_3$	33
$K_2[PdCl_4]$	$PdCl_2 + KCl$	Water	62
$K_2[PdCl_6]$	$PdCl_2 + KCl + Cl_2$	Water	62
$K_2[PtCl_6]$	$H_2PtCl_6 + KCl$	Water	62
$M_4[ThCl_6]$	$ThCl_4 + MCl$	Fuse	64
$M_2[ThCl_6]$	$ThCl_4 + MCl$	Fuse	64
$[CH_3]_4[N]_2[ThCl_6]$	$ThCl_4 \cdot 4 CH_3CN + [(CH_3)_4N]Cl$	$CH_3CN$	65
$[CH_3]_4[N]_2[ThBr_6]$	$ThBr_4 \cdot 4 CH_3CN + [(CH_3)_4N]Br$	$CH_3CN$	65
$M_2[ThI_6]$	$ThI_4 + MI$	Fuse	67
$M_2[UCl_6]$	$ThCl_4 + MCl$	Fuse	64
$[CH_3]_4[N]_2[UCl_6]$	$ThCl_4 \cdot 4 CH_3CN + [(CH_3)_4N]Cl$	$CH_3CN$	65
$[CH_3]_4[N]_2[UBr_6]$	$ThBr_4 \cdot 4 CH_3CN + [(CH_3)_4N]Br$	$CH_3CN$	65
$[CH_3]_4[N]_2[NpCl_6]$	$NpCl_4 \cdot 4 CH_3CN + [(CH_3)_4N]Cl$	$CH_3CN$	65
$[CH_3]_4[N]_2[NpBr_6]$	$NpBr_4 \cdot 4 CH_3CN + [(CH_3)_4N]Br$	$CH_3CN$	65

Reduction of higher oxidation state species can lead to hexahalo salts:



where M = Nb, Ta. By adjusting the reactants, complex halides other than  $[\text{MX}_6]^{n-}$  can be isolated. The reaction of  $\text{TiCl}_4$  with tetraethylammonium chloride in  $\text{CH}_2\text{Cl}_2$  using  $[(\text{C}_2\text{H}_5)_4\text{N}]\text{Cl}:\text{TiCl}_4$  proportions of 1:1 and 1:2 affords  $[(\text{C}_2\text{H}_5)_4\text{N}][\text{TiCl}_5]$  and  $[(\text{C}_2\text{H}_5)_4\text{N}][\text{Ti}_2\text{Cl}_9]$  with the former compound containing the  $\text{TiCl}_5$  anion and the latter containing bridging halogen atoms<sup>14</sup>.

The trihalides of the early transition elements with fused alkali-metal halides or substituted ammonium halides form complex halo anions:



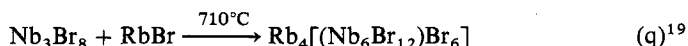
where M = Ti, V, Cr.



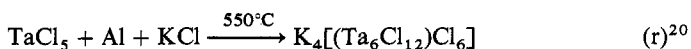
where M = Ti, V, Cr. The resulting complexes may be monomeric or dimeric.

The direct, stoichiometric reaction of  $\text{MoCl}_3$  and  $\text{MoBr}_3$  with the cesium halide affords the crystalline  $\text{Cs}_3\text{Mo}_2\text{X}_9$  at ca. 700–800°C<sup>18</sup>.

Anionic complexes containing the metal clusters of Nb and Ta can be obtained by fusing the metal cluster with alkali-metal halides:



reduction of the higher halide with Al:



or the reaction of the metal halide with the metal in the presence of an alkali-metal halide:

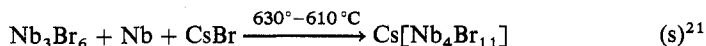


Table 1 indicates the ways in which complex halo anions may be prepared. The tabulation is not exhaustive, but represents the methods available to obtain these salts from transition-metal halides and alkali-metal halides (in some cases alkaline-earth halides may be used) or organic halides, either fused or in solution.

(T.M. BROWN)

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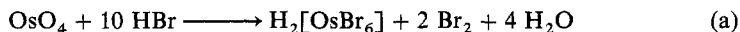
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### 2.9.10.2. by Reaction of Metal Oxides with Hydrohalic Acids.

Complex chlorides can be prepared by the reduction of an oxide or an oxygen complex of a transition metal in conc HCl.

Bromine and iodine stabilize the lower oxidation states of transition-metal complex bromides and iodides. Owing to their instability, many cannot be prepared from the melt; hence, most preparations are carried out in hydrobromic or hydroiodic acid. The complex iodides are more prevalent for elements to the right of the periodic table.

Hexahalometallates of Re, Rh and Os are prepared by starting with the oxide or oxy anion of the metal, e.g., in the preparation of  $(\text{NH}_4)_2\text{OsBr}_6$ :



Although the lanthanides form weak complexes, complex halo anions with all of the halogens are known, e.g.:



The hexachlorolanthanides are then used to prepare the salts of the bromo or iodo complexes:

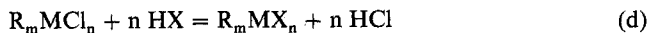


TABLE 1. PREPARATION OF COMPLEX HALO ANIONS FROM METAL OXIDES AND HYDROHALIC ACIDS

Product	Reactants	Ref.
$\text{K}_3[\text{W}_2\text{Cl}_9]$	$\text{K}_2[\text{WO}_4] + \text{HCl} + \text{Sn}$	3
$\text{K}_2[\text{ReCl}_6]$	$\text{K}[\text{ReO}_4] + \text{KCl} + \text{HCl} + \text{H}_3\text{PO}_2$	4
$\text{K}_2[\text{ReBr}_6]$	$\text{K}[\text{ReO}_4] + \text{KBr} + \text{HBr}$	4
$\text{M}_2[\text{ReBr}_6]$	$\text{ReO}_2 + \text{MBr} + \text{HBr}$	5
$\text{K}[\text{ReI}_6]$	$\text{K}[\text{ReO}_4] + \text{HI}$	6
$\text{M}_2[\text{RuBr}_6]$	$\text{RuO}_4 + \text{MBr} + \text{HBr}$	7
$[\text{NH}_4]_2[\text{OsCl}_6]$	$\text{OsO}_4 + \text{NH}_4\text{Cl} + \text{HCl} + \text{FeCl}_2$	1
$[\text{NH}_4]_2[\text{OsBr}_6]$	$\text{OsO}_4 + \text{NH}_4\text{Br} + \text{HBr}$	1
$\text{K}_2[\text{OsI}_6]$	$\text{OsO}_4 + \text{KI} + \text{HI}$	8
$\text{M}_2[\text{IrCl}_6]$	$\text{IrO}_2 + \text{MCl} + \text{HCl}$	9
$[\text{Ph}_3\text{PH}]_3[\text{LnCl}_6]^a$	$\text{Ln}_2\text{O}_3 + [\text{Ph}_3\text{PH}]\text{Cl} + \text{HCl}^a$	2

<sup>a</sup>Ln = Pr, Nd, Sm, Dy, Er, Yb.

## 2.9. Formation of the Halogen-Transition-Metal Bond

## 2.9.10. Synthesis of Complex Halo Anions

## 2.9.10.2. by Reaction of Metal Oxides with Hydrohalic Acids.

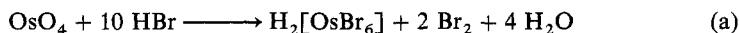
61. N. A. Gill, R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).
62. G. Brauer, *Preparative Inorganic Chemistry*, Vol. 2, 2nd ed., Academic Press, New York, 1965.
63. L. Helmoltz, R. F. Kruh, *J. Am. Chem. Soc.*, 74, 1176 (1952).
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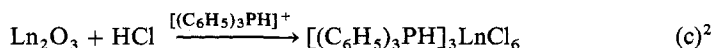
Complex chlorides can be prepared by the reduction of an oxide or an oxygen complex of a transition metal in conc HCl.

Bromine and iodine stabilize the lower oxidation states of transition-metal complex bromides and iodides. Owing to their instability, many cannot be prepared from the melt; hence, most preparations are carried out in hydrobromic or hydroiodic acid. The complex iodides are more prevalent for elements to the right of the periodic table.

Hexahalometallates of Re, Rh and Os are prepared by starting with the oxide or oxy anion of the metal, e.g., in the preparation of  $(\text{NH}_4)_2\text{OsBr}_6$ :



Although the lanthanides form weak complexes, complex halo anions with all of the halogens are known, e.g.:



The hexachlorolanthanides are then used to prepare the salts of the bromo or iodo complexes:

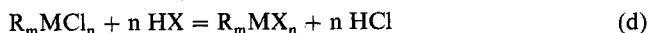


TABLE 1. PREPARATION OF COMPLEX HALO ANIONS FROM METAL OXIDES AND HYDROHALIC ACIDS

Product	Reactants	Ref.
$\text{K}_3[\text{W}_2\text{Cl}_6]$	$\text{K}_2[\text{WO}_4] + \text{HCl} + \text{Sn}$	3
$\text{K}_2[\text{ReCl}_6]$	$\text{K}[\text{ReO}_4] + \text{KCl} + \text{HCl} + \text{H}_3\text{PO}_2$	4
$\text{K}_2[\text{ReBr}_6]$	$\text{K}[\text{ReO}_4] + \text{KBr} + \text{HBr}$	4
$\text{M}_2[\text{ReBr}_6]$	$\text{ReO}_2 + \text{MBr} + \text{HBr}$	5
$\text{K}[\text{ReI}_6]$	$\text{K}[\text{ReO}_4] + \text{HI}$	6
$\text{M}_2[\text{RuBr}_6]$	$\text{RuO}_4 + \text{MBr} + \text{HBr}$	7
$[\text{NH}_4]_2[\text{OsCl}_6]$	$\text{OsO}_4 + \text{NH}_4\text{Cl} + \text{HCl} + \text{FeCl}_2$	1
$[\text{NH}_4]_2[\text{OsBr}_6]$	$\text{OsO}_4 + \text{NH}_4\text{Br} + \text{HBr}$	1
$\text{K}_2[\text{OsI}_6]$	$\text{OsO}_4 + \text{KI} + \text{HI}$	8
$\text{M}_2[\text{IrCl}_6]$	$\text{IrO}_2 + \text{MCl} + \text{HCl}$	9
$[\text{Ph}_3\text{PH}]_3[\text{LnCl}_6]^a$	$\text{Ln}_2\text{O}_3 + [\text{Ph}_3\text{PH}]\text{Cl} + \text{HCl}^a$	2

<sup>a</sup>Ln = Pr, Nd, Sm, Dy, Er, Yb.

in which X is Br or I. Equilibrium is established rapidly even at liq HX T if  $R_m$  is a large organic cation.

Examples of preparing complex halo anions from metal oxides are given in Table 1.

(T.M. BROWN)

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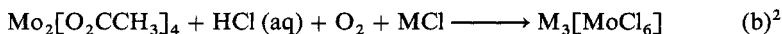
### 2.9.10.3. by Reaction of Metal Carboxylates with Hydrohalic Acids.

Transition-metal halo complexes can be synthesized from metal carboxylates using methods outlined for the preparation of metal halides from metal carboxylates followed by the addition of the appropriate non-transition-metal halide, in the appropriate hydrohalic acid. Acetyl halides can be used:



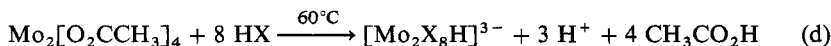
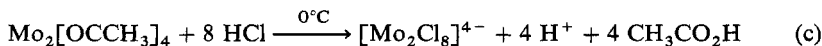
The reaction of  $\text{KHF}_2$  with anhyd  $\text{Cr}(\text{II})$  acetate in petroleum ether<sup>2</sup> yields  $\text{K}[\text{CrF}_3]$ .

Electrolytic reduction of  $\text{MoO}_3$  in  $\text{HCl}$ , which is time consuming and tedious, yields  $\text{K}_3\text{MoCl}_6$ . Furthermore, potassium is used, which is a problem because potassium chloride is insoluble in hydrochloric acid and therefore contaminates the product. However, this compound may be prepared, using  $[\text{NH}_4]^+$ ,  $\text{Rb}^+$  or  $\text{Cs}^+$  as the counterion, by employing tetrakis(acetate)dimolybdenum, which is readily prepared from  $\text{Mo}(\text{CO})_6$ . By saturating the solution with  $\text{HCl}$  in the presence of  $[\text{NH}_4]^+$ ,  $\text{Rb}^+$  or  $\text{Cs}^+$  chloride, the desired  $\text{M}_3\text{MoCl}_6$  salt is obtained<sup>3</sup>:



The compound  $[(\text{C}_6\text{H}_5)_4\text{As}]_2[\text{Re}_2\text{Cl}_8]$  is prepared by treating  $[\text{Re}(\text{O}_2\text{CCH}_3)_2\text{Cl}]_2$  with conc  $\text{HCl}$  and propionic acid<sup>4</sup>. The addition of  $[(\text{C}_6\text{H}_5)_4\text{As}]\text{Cl}$  precipitates  $[(\text{C}_6\text{H}_5)_4\text{As}]_2[\text{Re}_2\text{Cl}_8]$ . Similar compounds can also be prepared by this method.

Another example is the preparation of  $[\text{Mo}_2\text{Cl}_8]^{4-}$  and  $[\text{Mo}_2\text{Br}_8\text{H}]^{3-5}$ . High yields of  $[\text{Mo}_2\text{Cl}_8]^{4-}$  or  $[\text{Mo}_2\text{Br}_8\text{H}]^{3-}$  involve the interaction of  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$  and hydrochloric acid or 48% hydrobromic acid, respectively, under  $\text{N}_2$ :



where  $\text{X} = \text{Cl}, \text{Br}$ . After flushing with  $\text{N}_2$ ,  $\text{CsCl}$  or  $\text{CsBr}$  is added and the precipitate collected by suction filtration and washed with ethanol and  $\text{H}_2\text{O}$ . The dimeric anions

## 2.9. Formation of the Halogen-Transition-Metal Bond

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## 2.9.10. Synthesis of Complex Halo Anions

## 2.9.10.3. by Reaction of Metal Carboxylates with Hydrohalic Acids.

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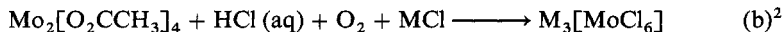
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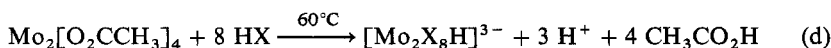
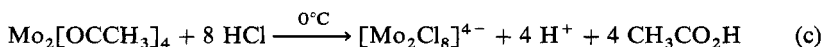
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$[\text{Mo}_2\text{X}_8]^{3-}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) are obtained from  $\text{Mo(II)}$  acetate in hydrochloric acid by the addition of a large cation. The reaction involves the oxidation of the metal, but this does not always go to completion as the  $\text{Mo(II)}$  complexes  $[\text{Mo}_2\text{X}_4]^{4-}$  are also obtained from the same solutions. Salts of the dinuclear  $\text{Mo}$  halides are precursors for the preparation of complexes of  $\text{Mo(II)}$ .

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#### 2.9.10.4. by Electrochemical methods.

Complex halo anions can be prepared using electrochemical synthesis; e.g., the tetraethylammonium salts of the anionic bromo complexes of  $\text{Fe(III)}$ ,  $\text{Co(II)}$ ,  $\text{Ni(II)}$ ,  $\text{Cu(II)}$  and  $\text{Au(III)}$  are prepared by direct electrochemical oxidation of the metal<sup>1</sup>. The products are easily and rapidly prepared in high purity. The metal forms the anode of the electrochemical cell in which the solution phase is benzene, containing a small amount (20%) of methanol plus a suitable solute. The cathode is a Pt wire. The choice of solute depends on whether the ligand to be attached to the metal is in itself a current carrier. With the bromides of the metals indicated above,  $[\text{Et}_4\text{N}]\text{Br}$  and  $\text{Br}_2$  in ca. equimolar quantities are used with applied voltages of ca. 500 (see Table 1, §2.9.10.1). Chloro complexes can be prepared, but complications occur in solvent attack by  $\text{Cl}_2$ .

When halo anions of high purity are required, electrochemical preparation of the anhydrous halides may be carried out<sup>2</sup>, followed by the reaction of the anhydrous halide with an alkali metal or organic halide.

Electrolytic reductions of metal compounds are also known, e.g., the prolonged electrolytic reduction of  $\text{Mo(VI)}$  in chloro complexes allows for the precipitation of  $[\text{MoCl}_6]^{3-}$  by the larger alkali metals<sup>3</sup>:

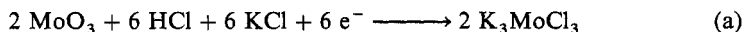


TABLE 1. PREPARATION OF COUPLES HALO ANIONS USING ELECTROCHEMICAL TECHNIQUES

Product	Reactants	Ref.
$[(\text{C}_2\text{H}_5)_4\text{N}][\text{FeBr}_4]$	$\text{Fe} + \text{Br}_2 + [(\text{C}_2\text{H}_5)_4\text{N}]\text{Br}$	1
$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{CoBr}_4]$	$\text{Co} + \text{Br}_2 + [(\text{C}_2\text{H}_5)_4\text{N}]\text{Br}$	1
$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{NiBr}_4]$	$\text{Ni} + \text{Br}_2 + [(\text{C}_2\text{H}_5)_4\text{N}]\text{Br}$	1
$[(\text{C}_2\text{H}_5)_4\text{N}]_3[\text{CuBr}_5]$	$\text{Cu} + \text{Br}_2 + [(\text{C}_2\text{H}_5)_4\text{N}]\text{Br}$	1
$[(\text{C}_2\text{H}_5)_4\text{N}][\text{AuBr}_4]$	$\text{Au} + \text{Br}_2 + [(\text{C}_2\text{H}_5)_4\text{N}]\text{Br}$	1
$\text{K}_3[\text{MoCl}_6]$	$\text{MoO}_3 + \text{HCl} + \text{KCl}$	3
$\text{K}_3[\text{W}_2\text{Cl}_9]$	$\text{WO}_3 + \text{K}_2\text{CO}_3 + \text{HCl}$	4
$\text{K}_3[\text{TiF}_6]$	$\text{K}_2[\text{TiF}_6] + \text{KCl melt}$	5

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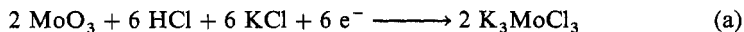


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$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{NiBr}_4]$	$\text{Ni} + \text{Br}_2 + [(\text{C}_2\text{H}_5)_4\text{N}]\text{Br}$	1
$[(\text{C}_2\text{H}_5)_4\text{N}]_3[\text{CuBr}_5]$	$\text{Cu} + \text{Br}_2 + [(\text{C}_2\text{H}_5)_4\text{N}]\text{Br}$	1
$[(\text{C}_2\text{H}_5)_4\text{N}][\text{AuBr}_4]$	$\text{Au} + \text{Br}_2 + [(\text{C}_2\text{H}_5)_4\text{N}]\text{Br}$	1
$\text{K}_3[\text{MoCl}_6]$	$\text{MoO}_3 + \text{HCl} + \text{KCl}$	3
$\text{K}_3[\text{W}_2\text{Cl}_9]$	$\text{WO}_3 + \text{K}_2\text{CO}_3 + \text{HCl}$	4
$\text{K}_3[\text{TiF}_6]$	$\text{K}_2[\text{TiF}_6] + \text{KCl melt}$	5

Smooth Pt, Hg or amalgamated Pb is used for the cathode. Carbon serves as the anode. Similarly, W in the form of  $\text{WO}_3$  in a KCl-conc HCl solution is electrolytically reduced to  $\text{K}_3\text{W}_2\text{Cl}_9$ <sup>4</sup> (see Table 1).

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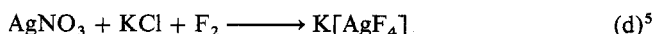
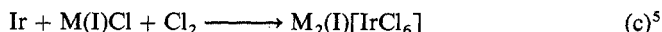
### 2.9.10.5. by Other Methods.

Complex halo anions are prepared by halogen exchange, e.g., the hexachlorolanthanides undergo exchange in hydrobromic and hydroiodic acid to yield the hexabromides and hexaiodides, respectively<sup>1</sup>. This method is also common among transition-metal halides; e.g.,  $[\text{W}_2\text{Br}_9]^{3-}$  can be prepared from  $[\text{W}_2\text{Cl}_9]^{3-}$  and HBr with the addition of a cation<sup>2</sup> such as  $\text{K}^+$  or  $\text{Rb}^+$ . Most chlorides will undergo halogen exchange in HBr or HI.

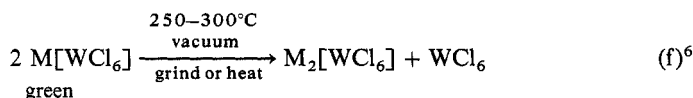
Fluorination of other halo salts or the metal or its salt gives rise to complex fluorides:



with large cations, salts of  $[\text{Rh}_2\text{Cl}_9]^{3-}$  can be isolated<sup>4</sup>:



Still another method involves thermal decomposition of halo salts where the metal exhibits a variety of oxidation states. Tungsten(V) complexes can be decomposed to the W(IV) complex, viz:



where M = Cs, K.

(T.M. BROWN)

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2. J. H. Hayden, R. A. D. Wentworth, *J. Am. Chem. Soc.*, **90**, 5291 (1968).
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## 2.9. Formation of the Halogen-Transition-Metal Bond

211

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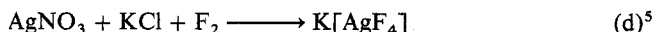
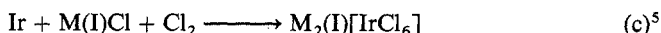
**2.9.10.5. by Other Methods.**

Complex halo anions are prepared by halogen exchange, e.g., the hexachlorolanthanides undergo exchange in hydrobromic and hydroiodic acid to yield the hexabromides and hexaiodides, respectively<sup>1</sup>. This method is also common among transition-metal halides; e.g.,  $[\text{W}_2\text{Br}_9]^{3-}$  can be prepared from  $[\text{W}_2\text{Cl}_9]^{3-}$  and HBr with the addition of a cation<sup>2</sup> such as  $\text{K}^+$  or  $\text{Rb}^+$ . Most chlorides will undergo halogen exchange in HBr or HI.

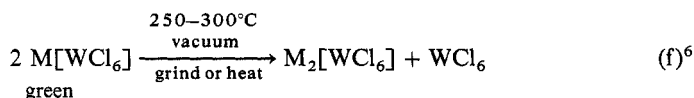
Fluorination of other halo salts or the metal or its salt gives rise to complex fluorides:



with large cations, salts of  $[\text{Rh}_2\text{Cl}_9]^{3-}$  can be isolated<sup>4</sup>:



Still another method involves thermal decomposition of halo salts where the metal exhibits a variety of oxidation states. Tungsten(V) complexes can be decomposed to the W(IV) complex, viz:



where  $\text{M} = \text{Cs}, \text{K}$ .

(T.M. BROWN)

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## 212 2.9. Formation of the Halogen-Transition-Metal Bond

## 2.9.11. Synthesis of Metal Oxohalides from the Metals

## 2.9.11.2. by Direct Reaction of the Metal with Halogen-Oxygen Mixtures.

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The majority of oxohalides are formed by the elements in groups IVA, VA, VIA, VIIA and VIII, with those formed by group-VA and -VIA elements receiving most attention<sup>1-4</sup>.

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TABLE 1. FORMATION OF OXYHALIDES BY DIRECT REACTION OF THE METAL WITH HALOGENS

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OsO <sub>4</sub> O	Os	F <sub>2</sub>			3

Astatine in the 1- oxidation state coprecipitates with PdI<sub>2</sub>, presumably<sup>4</sup> as PdAtI. "Zero-state" astatine is strongly adsorbed on metallic Pt, which may indicate formation of a compound on the surface<sup>5</sup>.

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WOF <sub>4</sub>	W	F <sub>2</sub> , O <sub>2</sub>	3:1		4
ReOF <sub>3</sub>	Re	F <sub>2</sub> , O <sub>2</sub>	3:1	300-150	4, 5
MoO <sub>2</sub> Cl <sub>2</sub>	Mo	Cl <sub>2</sub> :O <sub>2</sub>	1:1	250-300	6
MoO <sub>2</sub> Br <sub>2</sub>	Mo	Br <sub>2</sub> :O <sub>2</sub>	Trace O <sub>2</sub>	300	6
WOBBr <sub>4</sub>	W	Br <sub>2</sub> :O <sub>2</sub>	6:1	250-300	1
WO <sub>2</sub> Br <sub>2</sub>	W	Br <sub>2</sub> :O <sub>2</sub>	2:1	250-300	1
OsOCl <sub>4</sub>	Os	Cl <sub>2</sub> :O <sub>2</sub>	8:1	400	7
OsO <sub>3</sub> F <sub>2</sub>	Os	F <sub>2</sub> :O <sub>2</sub>	2:1		7
ReOBr <sub>4</sub> O	Re	Br <sub>2</sub> , O <sub>2</sub>		400	2

1). The halogen-oxygen ratio must be controlled to ensure that the desired product is obtained, e.g., for the oxobromides of tungsten(VI) a 6:1 Br<sub>2</sub> to O<sub>2</sub> ratio produces mainly WOBBr<sub>4</sub>, whereas a 2:1 ratio yields WO<sub>2</sub>Br<sub>2</sub> as the major product<sup>1</sup>. Similar reactions with O<sub>2</sub>-Cl<sub>2</sub> mixtures over Mo and W yield MOCl<sub>4</sub> (M = Mo or W), but these species are more easily prepared by the chlorination of the trioxides MO<sub>3</sub> (M = Mo or W). The reaction of metallic Re with Br<sub>2</sub> in the presence of traces of air produces a blue compound previously thought to be ReO<sub>2</sub>Br<sub>3</sub><sup>2</sup>. However, later studies show it to be ReOBr<sub>4</sub> which is best prepared by the bromination of ReO<sub>2</sub> at 150°C<sup>3</sup>.

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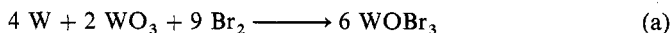
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Product	Reactants	T (°C)	Time (h)	Yield (%)	Ref.
WO <sub>2</sub> Br <sub>2</sub>	W + 2 WO <sub>3</sub> + 3 Br <sub>2</sub>	450-325 <sup>a</sup>	5		1
WOBr <sub>4</sub>	2 W + WO <sub>3</sub> + 6 Br <sub>2</sub>	425-250 <sup>a</sup>	15	96	1
WOBr <sub>3</sub>	2 W + WO <sub>3</sub> + 4.5 Br <sub>2</sub>	450-350 <sup>a</sup>	30	98	1, 2
WOBr <sub>2</sub>	2 W + WO <sub>3</sub> + 3 Br <sub>2</sub>	580-450 <sup>a</sup>	100		1, 3
WO <sub>2</sub> I <sub>2</sub>	W + 2 WO <sub>3</sub> + 3 I <sub>2</sub>	800-300 <sup>b</sup>	70	60	1, 4
WO <sub>2</sub> I	W + 2 WO <sub>3</sub> + 1.5 I <sub>2</sub>	720-200 <sup>b</sup>	4		5
NbOI <sub>3</sub>	3 Nb + 7.5 I <sub>2</sub> + Nb <sub>2</sub> O <sub>5</sub>	500-450 <sup>b</sup>	24		6, 7
NbOI <sub>2</sub>	3 Nb + I <sub>2</sub> + Nb <sub>2</sub> O <sub>5</sub>	400-275 <sup>b</sup>	48		6, 7

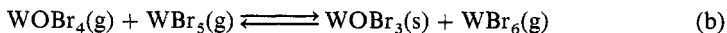
<sup>a</sup> Initial temperature gradient of 400-40°C.

<sup>b</sup> Initial temperature gradient of 100-25°C.

solid species formed under the reaction conditions and thus sublimes to the cooler zone. This point is illustrated by the preparation of WOBr<sub>3</sub>:



Reaction takes place via the formation of a mixture of bromides and oxobromides that are in equilibrium



Thus the WOBr<sub>3</sub> is removed by deposition and the reaction proceeds to the right. By variation of the W:WO<sub>3</sub> ratio in W-WO<sub>3</sub>-Br<sub>2</sub> experiments either WO<sub>2</sub>Br<sub>2</sub> or WOBr<sub>4</sub> can be obtained, while by varying the W:Br<sub>2</sub> ratio W(VI), (V) or (IV) species can be obtained (Table 1)<sup>1-3</sup>.

(E.M. PAGE, D.A. RICE)

1. J. Tillack, *Inorg. Synth.*, 14, 109 (1968).
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#### 2.9.11.4. by Reaction of the Metal with Metal Oxide-Metal Halide Mixtures.

Oxohalides can be prepared by heating a mixture consisting of the metal, one of its oxides and one of its halides. This method is particularly advantageous for oxochlorides where the metal-metal oxide-chlorine ratios (see §2.9.11.3) are difficult to control. Table 1 lists oxochlorides prepared by this route, together with the necessary reaction conditions. The reactants are usually held in evacuated, sealed quartz tubes at a suitable temperature. For NbOCl<sub>2</sub> Cl<sub>2</sub> is passed over Nb metal, forming NbCl<sub>5</sub>, which is in turn carried by chemical transport over a Nb-Nb<sub>2</sub>O<sub>5</sub> mixture at 350-370°C<sup>1</sup>. Small crystals of NbOCl<sub>2</sub> are deposited at 350°C, the position of the equilibrium:



Being governed by deposition of the NbCl<sub>2</sub>O.

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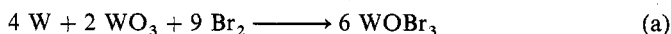
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WO <sub>2</sub> Br <sub>2</sub>	W + 2 WO <sub>3</sub> + 3 Br <sub>2</sub>	450–325 <sup>a</sup>	5		1
WOBr <sub>4</sub>	2 W + WO <sub>3</sub> + 6 Br <sub>2</sub>	425–250 <sup>a</sup>	15	96	1
WOBr <sub>3</sub>	2 W + WO <sub>3</sub> + 4.5 Br <sub>2</sub>	450–350 <sup>a</sup>	30	98	1, 2
WOBr <sub>2</sub>	2 W + WO <sub>3</sub> + 3 Br <sub>2</sub>	580–450 <sup>a</sup>	100		1, 3
WO <sub>2</sub> I <sub>2</sub>	W + 2 WO <sub>3</sub> + 3 I <sub>2</sub>	800–300 <sup>b</sup>	70	60	1, 4
WO <sub>2</sub> I	W + 2 WO <sub>3</sub> + 1.5 I <sub>2</sub>	720–200 <sup>b</sup>	4		5
NbOI <sub>3</sub>	3 Nb + 7.5 I <sub>2</sub> + Nb <sub>2</sub> O <sub>5</sub>	500–450 <sup>b</sup>	24		6, 7
NbOI <sub>2</sub>	3 Nb + I <sub>2</sub> + Nb <sub>2</sub> O <sub>5</sub>	400–275 <sup>b</sup>	48		6, 7

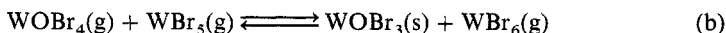
<sup>a</sup> Initial temperature gradient of 400–40°C.

<sup>b</sup> Initial temperature gradient of 100–25°C.

solid species formed under the reaction conditions and thus sublimes to the cooler zone. This point is illustrated by the preparation of WOBr<sub>3</sub>:



Reaction takes place via the formation of a mixture of bromides and oxobromides that are in equilibrium



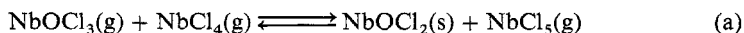
Thus the WOBr<sub>3</sub> is removed by deposition and the reaction proceeds to the right. By variation of the W:WO<sub>3</sub> ratio in W–WO<sub>3</sub>–Br<sub>2</sub> experiments either WO<sub>2</sub>Br<sub>2</sub> or WOBr<sub>4</sub> can be obtained, while by varying the W:Br<sub>2</sub> ratio W(VI), (V) or (IV) species can be obtained (Table 1)<sup>1–3</sup>.

(E.M. PAGE, D.A. RICE)

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#### 2.9.11.4. by Reaction of the Metal with Metal Oxide–Metal Halide Mixtures.

Oxohalides can be prepared by heating a mixture consisting of the metal, one of its oxides and one of its halides. This method is particularly advantageous for oxochlorides where the metal–metal oxide–chlorine ratios (see §2.9.11.3) are difficult to control. Table 1 lists oxochlorides prepared by this route, together with the necessary reaction conditions. The reactants are usually held in evacuated, sealed quartz tubes at a suitable temperature. For NbOCl<sub>2</sub> Cl<sub>2</sub> is passed over Nb metal, forming NbCl<sub>5</sub>, which is in turn carried by chemical transport over a Nb–Nb<sub>2</sub>O<sub>5</sub> mixture at 350–370°C<sup>1</sup>. Small crystals of NbOCl<sub>2</sub> are deposited at 350°C, the position of the equilibrium:



Being governed by deposition of the NbCl<sub>2</sub>O.



TABLE 1. FORMATION OF OXYHALIDES BY REACTION OF THE METAL WITH METAL OXIDE AND METAL HALIDE MIXTURES

Product	Reactants	T (°C)	Time	Ref.
WOCl <sub>3</sub>	W + 2 WO <sub>3</sub> + 3 WCl <sub>6</sub>	450–230	40 h	2
WOCl <sub>2</sub>	W + WO <sub>3</sub> + WCl <sub>6</sub>	450–250		2
NbOCl <sub>2</sub>	Nb + 2 NbCl <sub>5</sub> + Nb <sub>2</sub> O <sub>5</sub>	370–350		1, 3
TaOCl <sub>2</sub>	Ta + 2 TaCl <sub>5</sub> + Ta <sub>2</sub> O <sub>5</sub>	500–400	9 d	1, 3
TaOCl <sub>2</sub>	2 Ta + 8 TaCl <sub>5</sub> + 5 SiO <sub>2</sub>	550–450	4 d	1, 3

(E.M. PAGE, D.A. RICE)

1. H. Schafer, E. Sibbing, R. Gerkin, *Z. Anorg. Allg. Chem.*, **307**, 163 (1961).
2. J. Tillack, *Inorg. Synth.*, **14**, 109 (1968).
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## 2.9.12. Synthesis of Metal Oxohalides from Metal Oxides

The use of metal oxide rather than metal powders obviates the problem of obtaining pure metal powders, which often contain oxides, and the metal oxide powders are cheaper. Numerous halogen-containing species as well as the pure halogens have been employed to halogenate oxides, so only the most useful are discussed here.

(E.M. PAGE, D.A. RICE)

### 2.9.12.1. by Metal Oxide–Halogen Reactions.

Table 1 lists the metal oxohalides prepared by direct halogenation of the oxide. All the oxohalides listed contain the metal in its maximum oxidation state. Interesting aspects of this route are illustrated by the preparation of VOX<sub>3</sub> (X = F, Cl or Br). The reaction of V<sub>2</sub>O<sub>3</sub> with F<sub>2</sub> at 475°C yields VF<sub>3</sub>O as a pale yellow solid, which must be resublimed to remove impurities<sup>1</sup>. The oxochloride and oxobromide are prepared from V<sub>2</sub>O<sub>5</sub> by first reducing the pentoxide to V<sub>2</sub>O<sub>3</sub> with hydrogen at 500°C, followed by the reaction of V<sub>2</sub>O<sub>3</sub>–C mixtures with the halogen:



Thus in this process the oxidation state of the vanadium is unchanged while the halogen is reduced and the carbon oxidized. The V<sub>2</sub>O<sub>5</sub>–C mixtures used to produce VOB<sub>3</sub> can be obtained by heating V<sub>2</sub>O<sub>5</sub>–sucrose mixtures until carbonization is complete. The resulting powder is then reduced by H<sub>2</sub> at 500°C. From this reduced product VOB<sub>3</sub> can be obtained by bromination<sup>2</sup>. The species VOX<sub>3</sub> (X = Cl or Br) obtained by the halogenation of V<sub>2</sub>O<sub>3</sub>–C powders must be distilled to remove an excess of halogen and vanadium halides. In early preparations of VOCl<sub>3</sub>, VCl<sub>4</sub> was removed by addition of sodium and distilling the VOCl<sub>3</sub>. **This process is dangerous, and the last few cm<sup>3</sup> of VOCl<sub>3</sub> should not be distilled because of the risk of explosion<sup>3</sup>.**

In contrast to the halogenation by Cl<sub>2</sub> or Br<sub>2</sub> of Nb<sub>2</sub>O<sub>5</sub>–C mixtures, which leads to the isolation of NbOX<sub>3</sub> (X = Cl or Br)<sup>4</sup>, the analogous reactions intended to yield

2.9. Formation of the Halogen–Transition–Metal Bond  
 2.9.12. Synthesis of Metal Oxohalides from Metal Oxides  
 2.9.12.1. by Metal Oxide–Halogen Reactions.

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TABLE 1. FORMATION OF OXYHALIDES BY REACTION OF THE METAL WITH METAL OXIDE AND METAL HALIDE MIXTURES

Product	Reactants	T (°C)	Time	Ref.
WOCl <sub>3</sub>	W + 2 WO <sub>3</sub> + 3 WCl <sub>6</sub>	450–230	40 h	2
WOCl <sub>2</sub>	W + WO <sub>3</sub> + WCl <sub>6</sub>	450–250		2
NbOCl <sub>2</sub>	Nb + 2 NbCl <sub>5</sub> + Nb <sub>2</sub> O <sub>5</sub>	370–350		1, 3
TaOCl <sub>2</sub>	Ta + 2 TaCl <sub>5</sub> + Ta <sub>2</sub> O <sub>5</sub>	500–400	9 d	1, 3
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Thus in this process the oxidation state of the vanadium is unchanged while the halogen is reduced and the carbon oxidized. The V<sub>2</sub>O<sub>5</sub>–C mixtures used to produce VOBr<sub>3</sub> can be obtained by heating V<sub>2</sub>O<sub>5</sub>–sucrose mixtures until carbonization is complete. The resulting powder is then reduced by H<sub>2</sub> at 500°C. From this reduced product VOBr<sub>3</sub> can be obtained by bromination<sup>2</sup>. The species VOX<sub>3</sub> (X = Cl or Br) obtained by the halogenation of V<sub>2</sub>O<sub>3</sub>–C powders must be distilled to remove an excess of halogen and vanadium halides. In early preparations of VOCl<sub>3</sub>, VCl<sub>4</sub> was removed by addition of sodium and distilling the VOCl<sub>3</sub>. **This process is dangerous, and the last few cm<sup>3</sup> of VOCl<sub>3</sub> should not be distilled because of the risk of explosion<sup>3</sup>.**

In contrast to the halogenation by Cl<sub>2</sub> or Br<sub>2</sub> of Nb<sub>2</sub>O<sub>5</sub>–C mixtures, which leads to the isolation of NbOX<sub>3</sub> (X = Cl or Br)<sup>4</sup>, the analogous reactions intended to yield

TABLE 1. FORMATION OF OXYHALIDES BY HALOGENATION OF THE METAL OXIDE

Product	Oxide	Halogen	T (°C)	Time (h)	Yield (%)	Ref.
VOF <sub>3</sub>	V <sub>2</sub> O <sub>5</sub>	F <sub>2</sub>	475			1
VOCl <sub>3</sub>	V <sub>2</sub> O <sub>3</sub>	Cl <sub>2</sub>	500-600		71	2, 3, 10
VOBr <sub>3</sub>	V <sub>2</sub> O <sub>3</sub>	Br <sub>2</sub> , N <sub>2</sub>	200			2, 2, 11, 12
NbOCl <sub>3</sub>	Nb <sub>2</sub> O <sub>5</sub> -C	Cl <sub>2</sub>	500			4
NbOBr <sub>3</sub>	Nb <sub>2</sub> O <sub>5</sub> -C	Br <sub>2</sub> , N <sub>2</sub>	540			4
CrO <sub>2</sub> F <sub>2</sub>	CrO <sub>3</sub>	F <sub>2</sub>	150	41		5
CrOF <sub>4</sub>	CrO <sub>3</sub>	F <sub>2</sub>				5, 21
MoO <sub>2</sub> Cl <sub>2</sub>	MoO <sub>2</sub>	Cl <sub>2</sub>	650			13, 14
WO <sub>2</sub> Cl <sub>2</sub>	WO <sub>2</sub>	Cl <sub>2</sub>	500			15
WO <sub>2</sub> Cl <sub>2</sub>	WO <sub>3</sub> -C	Cl <sub>2</sub>	600			16
WOCl <sub>4</sub>	WO <sub>3</sub>	Cl <sub>2</sub> in CCl <sub>4</sub>	200	3		17
TeO <sub>3</sub> F	TcO <sub>2</sub>	F <sub>2</sub>	150		56	6, 7
TcOCl <sub>3</sub>	TcO <sub>2</sub>	Cl <sub>2</sub>	200			18
TcOBr <sub>3</sub>	TcO <sub>2</sub>	Br <sub>2</sub>	300-350	4-5		18
ReOF <sub>5</sub> , ReO <sub>2</sub> F <sub>3</sub>	ReO <sub>2</sub>	F <sub>2</sub> , N <sub>2</sub>				8, 9
ReO <sub>3</sub> Cl	ReO <sub>3</sub>	Cl <sub>2</sub>	160-190		70	19
ReOBr <sub>4</sub>	ReO <sub>2</sub>	Br <sub>2</sub> -N <sub>2</sub>	150			20

TaOX<sub>3</sub> (X = Cl or Br) are unsuccessful, although bromination of Ta<sub>2</sub>O<sub>5</sub> yields small amounts of TaOBr<sub>3</sub>.

Direct halogenation of group-VIA metal oxides is not commonly used for the preparation of oxohalides. An exception is the fluorination of CrO<sub>3</sub> in Ni vessels, which by control of the reaction conditions can be made to yield CrO<sub>2</sub>F<sub>2</sub> and CrOF<sub>4</sub><sup>5</sup>. Better yields of CrOF<sub>4</sub> have been obtained from CrO<sub>3</sub>-F<sub>2</sub> mixtures held at 140°C and 40 atm.

Reaction of WO<sub>3</sub> with Cl<sub>2</sub> in the presence of CCl<sub>4</sub> in a sealed tube at 200°C yields WOCl<sub>4</sub>:



but simpler methods are available for the preparation of this oxochloride. **Phosgene is produced in this reaction, and high pressures may be generated in the sealed tube.**

Differences in reactivity between the 4d and 5d transition elements as seen with Nb and Ta are also observed between Tc and Re; e.g., while fluorination of TcO<sub>2</sub> produces TcO<sub>3</sub>F<sup>6,7</sup>, similar reactions with ReO<sub>2</sub> give ReOF<sub>5</sub> and ReO<sub>2</sub>F<sub>3</sub> mixtures<sup>8,9</sup>.

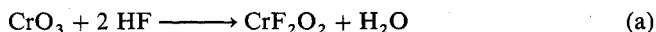
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### 2.9.12.2. by Reaction of Metal Oxides with Hydrogen Halides.

The reaction of metal oxides with hydrogen halides proceeds as in this chromium example:



To prevent hydrolysis of the products the reactions are carried out either in the presence of drying agents or in a large flow of dry hydrogen halide. Typical reactions are listed in Table 1, e.g., those to form the  $\text{CrO}_2\text{X}_2$  ( $\text{X} = \text{F}, \text{Cl}$  or  $\text{Br}$ ) species. The chloride,  $\text{CrO}_2\text{Cl}_2$ , is prepared using a mixture of conc  $\text{HCl-H}_2\text{SO}_4$ , and the product is formed as a hydrolyzable, red fuming liquid that must be distilled in vacuo to remove traces of  $\text{HCl}$ <sup>1,2</sup>. The bromide,  $\text{CrO}_2\text{Br}_2$ , is prepared by hydrobromination of  $\text{CrO}_3\text{-P}_2\text{O}_5\text{-CCl}_4$  mixtures and purified by vacuum distillation at  $-135^\circ\text{C}$ <sup>3</sup>. **The  $\text{CrO}_2\text{X}_2$  species are powerful oxidizing agents and should be handled with extreme care.**

The chemically inert  $\text{WF}_2\text{O}$  is produced in attempts to prepare  $\text{WF}_4$  by heating  $\text{WO}_2$  with anhyd  $\text{HF}$  at  $500\text{-}600^\circ\text{C}$ <sup>4</sup>.

TABLE 1. FORMATION OF OXYHALIDES BY REACTIONS OF METAL OXIDES WITH HYDROGEN HALIDES

Product	Oxide	Hydrogen halide <sup>a</sup>	T (°C)	Ref.
$\text{CrO}_2\text{F}_2$	$\text{CrO}_3$	$\text{HF}^a$	25	6
$\text{CrO}_2\text{Cl}_2$	$\text{CrO}_3$	Conc $\text{HCl-H}_2\text{SO}_4$	0	1, 2
$\text{CrO}_2\text{Br}_2$	$\text{CrO}_3$	$\text{HBr}^a$	-20	3
$\text{WOF}_2$	$\text{WO}_2$	$\text{HF}^a$	500-600	4
$\text{ReO}_3\text{F}$	$\text{Re}_2\text{O}_7$	$\text{HF}^a$		5
$\text{NbO}_2\text{F}$	$\text{Nb}_2\text{O}_5$	$\text{HF}^b$	250	7
$\text{TaO}_2\text{F}$	$\text{Ta}_2\text{O}_5$	$\text{HF}^b$	250	7

<sup>a</sup> Anhydrous hydrogen halides must be employed.

<sup>b</sup> 48% aq  $\text{HF}$  is required.

## 2.9. Formation of the Halogen-Transition-Metal Bond

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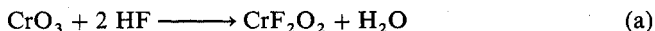
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## 2.9.12.2. by Reaction of Metal Oxides with Hydrogen Halides.

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$\text{CrO}_2\text{Br}_2$	$\text{CrO}_3$	$\text{HBr}^a$	-20	3
$\text{WOF}_2$	$\text{WO}_2$	$\text{HF}^a$	500-600	4
$\text{ReO}_3\text{F}$	$\text{Re}_2\text{O}_7$	$\text{HF}^a$		5
$\text{NbO}_2\text{F}$	$\text{Nb}_2\text{O}_5$	$\text{HF}^b$	250	7
$\text{TaO}_2\text{F}$	$\text{Ta}_2\text{O}_5$	$\text{HF}^b$	250	7

<sup>a</sup> Anhydrous hydrogen halides must be employed.

<sup>b</sup> 48% aq  $\text{HF}$  is required.

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 2.9.12. Synthesis of Metal Oxohalides from Metal Oxides  
 2.9.12.3. by Fluorination by Interhalogens and Other Nonmetal Fluorides

Treatment of  $\text{Nb}_2\text{O}_5$  or  $\text{Ta}_2\text{O}_5$  with 48% aq HF yields  $\text{NbFO}_2$  and  $\text{TaFO}_2$ , respectively. The resulting solutions are evaporated and heated at  $250^\circ\text{C}$  to remove  $\text{H}_2\text{O}$  and xs HF. Table 1 lists the preparation of  $\text{ReO}_3\text{F}$ , but it is best prepared by other routes<sup>5</sup>.

(E.M. PAGE, D.A. RICE)

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### 2.9.12.3. by Fluorination by Interhalogens and Other Nonmetal Fluorides

Some fluorinterhalogens react more readily than  $\text{F}_2$  with metal oxides to yield oxofluorides. The oxofluoride  $\text{CrO}_2\text{F}_2$ , is prepared by fluorination of the trioxide  $\text{CrO}_3$ , using a whole range of fluorinating agents, listed in Table 1. From this it can be seen that two interhalogens,  $\text{IF}_5$  and  $\text{ClF}_3$ , are among the best fluorinating agents. However, Table 2 reveals that the reactions of  $\text{IF}_5$  with oxides other than  $\text{CrO}_3$  are not straightforward, there being no replacement of oxygen with the compounds  $\text{MoO}_3$  and  $\text{WO}_3$  while with  $\text{V}_2\text{O}_5$  an adduct  $2\text{VOF}_3 \cdot 3\text{IOF}_5$  is formed<sup>1</sup>. However, reaction of  $\text{IF}_5$  with  $\text{KMO}_4$  ( $\text{M} = \text{Mn}$  or  $\text{Re}$ ) leads to the formation of  $\text{MO}_3\text{F}$  ( $\text{M} = \text{Mn}^{2+}$  or  $\text{Re}^{3+}$ ) and these volatile oxofluorides are distilled out of the reaction mixture and trapped at low temperature.

The bromo analogs  $\text{BrF}_5$  and  $\text{BrF}_3$  are useful fluorinating agents (see Table 2). Although reaction of  $\text{OsO}_4$  with  $\text{BrF}_5$  yields  $\text{OsO}_3\text{F}$ , reaction with  $\text{RuO}_4$  leads to the isolation of  $\text{RuF}_5$ <sup>4</sup>. The reactions of  $\text{BrF}_3$  and  $\text{BrF}_5$  with the  $\text{Cr(VI)}$  species  $\text{KO}_4\text{Cr}$  and  $\text{CrO}_3$  yield  $\text{Cr(V)}$  products, the oxide yielding  $4\text{CrOF}_3 \cdot \text{L}$  ( $\text{L} = \text{BrF}_3$  or  $\text{BrF}_5$  according to fluorinating agent), while with  $[\text{CrO}_4]^-$ ,  $4\text{KCrOF}_4 \cdot \text{BrF}_5$  and  $\text{KCrOF}_4$  are obtained<sup>5</sup> (from  $\text{BrF}_5$ ).

TABLE 1. PREPARATIONS OF  $\text{CrO}_2\text{F}_2$  BY REACTION OF  $\text{CrO}_3$  WITH FLUORINATING AGENTS

Fluorinating agent	T ( $^\circ\text{C}$ )	Time (h)	Yield (%)	Ref.
$\text{IF}_5$	100			1
$\text{ClF}_3$	0	12	100	6
$\text{COF}_2$	185	12	100	6
$\text{CoF}_3$	450			7
$\text{SF}_4$	5		62	8
$\text{SeF}_4$	40			9

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## 2.9.12. Synthesis of Metal Oxohalides from Metal Oxides

## 2.9.12.3. by Fluorination by Interhalogens and Other Nonmetal Fluorides

Treatment of  $\text{Nb}_2\text{O}_5$  or  $\text{Ta}_2\text{O}_5$  with 48% aq HF yields  $\text{NbFO}_2$  and  $\text{TaFO}_2$ , respectively. The resulting solutions are evaporated and heated at  $250^\circ\text{C}$  to remove  $\text{H}_2\text{O}$  and xs HF. Table 1 lists the preparation of  $\text{ReO}_3\text{F}$ , but it is best prepared by other routes<sup>5</sup>.

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The bromo analogs  $\text{BrF}_5$  and  $\text{BrF}_3$  are useful fluorinating agents (see Table 2). Although reaction of  $\text{OsO}_4$  with  $\text{BrF}_5$  yields  $\text{OsO}_3\text{F}$ , reaction with  $\text{RuO}_4$  leads to the isolation of  $\text{RuF}_5$ <sup>4</sup>. The reactions of  $\text{BrF}_3$  and  $\text{BrF}_5$  with the  $\text{Cr(VI)}$  species  $\text{KO}_4\text{Cr}$  and  $\text{CrO}_3$  yield  $\text{Cr(V)}$  products, the oxide yielding  $4\text{CrOF}_3 \cdot \text{L}$  ( $\text{L} = \text{BrF}_3$  or  $\text{BrF}_5$  according to fluorinating agent), while with  $[\text{CrO}_4]^-$ ,  $4\text{KCrOF}_4 \cdot \text{BrF}_5$  and  $\text{KCrOF}_4$  are obtained<sup>5</sup> (from  $\text{BrF}_5$ ).

TABLE 1. PREPARATIONS OF  $\text{CrO}_2\text{F}_2$  BY REACTION OF  $\text{CrO}_3$  WITH FLUORINATING AGENTS

Fluorinating agent	T ( $^\circ\text{C}$ )	Time (h)	Yield (%)	Ref.
$\text{IF}_5$	100			1
$\text{ClF}_3$	0	12	100	6
$\text{COF}_2$	185	12	100	6
$\text{CoF}_3$	450			7
$\text{SF}_4$	5		62	8
$\text{SeF}_4$	40			9

TABLE 2. FORMATION OF OXY HALIDES BY REACTIONS OF INTERHALOGENS AND RELATED COMPOUNDS WITH METAL OXIDES

Product	Oxide	Interhal.	T (°C)	Time (h)	Yield (%)	Ref.
CrO <sub>2</sub> F <sub>2</sub>	CrO <sub>3</sub>	IF <sub>5</sub>	100			1
2 MoO <sub>3</sub> ·3 IF <sub>5</sub>	MoO <sub>3</sub>	IF <sub>5</sub>				1
WO <sub>3</sub> ·2 IF <sub>5</sub>	WO <sub>3</sub>	IF <sub>5</sub>				1
2 VOF <sub>3</sub> ·3 IOF <sub>5</sub>	V <sub>2</sub> O <sub>5</sub>	IF <sub>5</sub>				1
MnO <sub>3</sub> F	KMnO <sub>4</sub>	IF <sub>5</sub>	>40			2
ReO <sub>3</sub> F	KReO <sub>4</sub>	IF <sub>5</sub>	97			3
CrO <sub>2</sub> F <sub>2</sub>	CrO <sub>3</sub>	ClF	0	12	100	6
CrO <sub>2</sub> F <sub>2</sub>	CrO <sub>3</sub>	COF <sub>2</sub>	185	12	100	6
CrOF <sub>3</sub> ·0.3 ClF <sub>3</sub>	CrO <sub>3</sub>	ClF <sub>3</sub>	120			5
CrO <sub>2</sub> F <sub>2</sub>	CrO <sub>3</sub>	CoF <sub>3</sub>	450			7
CrOF <sub>3</sub> ·0.25 BrF <sub>5</sub>	CrO <sub>3</sub>	BrF <sub>5</sub>	25			5
CrOF <sub>3</sub> ·0.25 BrF <sub>3</sub>	CrO <sub>3</sub>	BrF <sub>3</sub>	25	24		5
CrOF <sub>3</sub>	CrO <sub>3</sub>	BrF <sub>3</sub> , then F <sub>2</sub>	120			10
K[CrOF <sub>4</sub> ]·0.25 BrF <sub>3</sub>	KCrO <sub>4</sub>	BrF <sub>5</sub>				5
K[CrOF <sub>4</sub> ]	KCrO <sub>4</sub>	BrF <sub>3</sub>				5
OsO <sub>3</sub> F	OsO <sub>4</sub>	BrF <sub>3</sub>	100			4
RuF <sub>5</sub> ·BrF <sub>5</sub>	RuO <sub>4</sub>	BrF <sub>5</sub> , BrF <sub>3</sub>				4
CrO <sub>2</sub> F <sub>2</sub>	CrO <sub>3</sub>	SF <sub>4</sub> -N <sub>2</sub>	5		62	8
CrO <sub>2</sub> F <sub>2</sub>	CrO <sub>3</sub>	SeF <sub>4</sub>	40			9
MoO <sub>2</sub> F <sub>2</sub> ·SeF <sub>4</sub>	MoO <sub>3</sub>	SeF <sub>4</sub>	50			9
SeF <sub>4</sub> ·WOF <sub>4</sub>	WO <sub>3</sub>	3 SeF <sub>4</sub>				9
SeOF <sub>2</sub> ·WOF <sub>4</sub>	WO <sub>3</sub>	2 SeF <sub>4</sub>				9

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#### 2.9.12.4. the Reaction of Metal Oxides with Halocarbons

Halocarbons can be used to produce oxohalides from oxides. It is sometimes necessary to control the metal oxide-halocarbon ratio to prevent total halogenation of the oxide and the halocarbons must be of the perhalo type, i.e., with no carbon-hydrogen bonds. Most frequently used are CCl<sub>4</sub> and CBr<sub>4</sub> and the reactions are carried out in steel



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 2.9.12. Synthesis of Metal Oxohalides from Metal Oxides  
 2.9.12.4. the Reaction of Metal Oxides with Halocarbons

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TABLE 2. FORMATION OF OXY HALIDES BY REACTIONS OF INTERHALOGENS AND RELATED COMPOUNDS WITH METAL OXIDES

Product	Oxide	Interhal.	T (°C)	Time (h)	Yield (%)	Ref.
CrO <sub>2</sub> F <sub>2</sub>	CrO <sub>3</sub>	IF <sub>5</sub>	100			1
2 MoO <sub>3</sub> ·3 IF <sub>5</sub>	MoO <sub>3</sub>	IF <sub>5</sub>				1
WO <sub>3</sub> ·2 IF <sub>5</sub>	WO <sub>3</sub>	IF <sub>5</sub>				1
2 VOF <sub>3</sub> ·3 IOF <sub>5</sub>	V <sub>2</sub> O <sub>5</sub>	IF <sub>5</sub>				1
MnO <sub>3</sub> F	KMnO <sub>4</sub>	IF <sub>5</sub>	> 40			2
ReO <sub>3</sub> F	KReO <sub>4</sub>	IF <sub>5</sub>	97			3
CrO <sub>2</sub> F <sub>2</sub>	CrO <sub>3</sub>	ClF	0	12	100	6
CrO <sub>2</sub> F <sub>2</sub>	CrO <sub>3</sub>	COF <sub>2</sub>	185	12	100	6
CrOF <sub>3</sub> ·0.3 ClF <sub>3</sub>	CrO <sub>3</sub>	ClF <sub>3</sub>	120			5
CrO <sub>2</sub> F <sub>2</sub>	CrO <sub>3</sub>	CoF <sub>3</sub>	450			7
CrOF <sub>3</sub> ·0.25 BrF <sub>5</sub>	CrO <sub>3</sub>	BrF <sub>5</sub>	25			5
CrOF <sub>3</sub> ·0.25 BrF <sub>3</sub>	CrO <sub>3</sub>	BrF <sub>3</sub>	25	24		5
CrOF <sub>3</sub>	CrO <sub>3</sub>	BrF <sub>3</sub> , then F <sub>2</sub>	120			10
K[CrOF <sub>4</sub> ]·0.25 BrF <sub>3</sub>	KCrO <sub>4</sub>	BrF <sub>5</sub>				5
K[CrOF <sub>4</sub> ]	KCrO <sub>4</sub>	BrF <sub>3</sub>				5
OsO <sub>3</sub> F	OsO <sub>4</sub>	BrF <sub>3</sub>	100			4
RuF <sub>5</sub> ·BrF <sub>5</sub>	RuO <sub>4</sub>	BrF <sub>5</sub> , BrF <sub>3</sub>				4
CrO <sub>2</sub> F <sub>2</sub>	CrO <sub>3</sub>	SF <sub>4</sub> -N <sub>2</sub>	5		62	8
CrO <sub>2</sub> F <sub>2</sub>	CrO <sub>3</sub>	SeF <sub>4</sub>	40			9
MoO <sub>2</sub> F <sub>2</sub> ·SeF <sub>4</sub>	MoO <sub>3</sub>	SeF <sub>4</sub>	50			9
SeF <sub>4</sub> ·WOF <sub>4</sub>	WO <sub>3</sub>	3 SeF <sub>4</sub>				9
SeOF <sub>2</sub> ·WOF <sub>4</sub>	WO <sub>3</sub>	2 SeF <sub>4</sub>				9

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TABLE 1. FORMATION OF OXYHALIDES BY REACTION OF OXIDES WITH HALOCARBONS

Product	Oxide	Halocarbon	T (°C)	Time (h)	Yield (%)	Ref.
CrO <sub>2</sub> F <sub>2</sub>	CrO <sub>3</sub>	COF <sub>2</sub>	185	9		
NbOCl <sub>3</sub>	Nb <sub>2</sub> O <sub>5</sub>	CCl <sub>4</sub>	200			1, 7
NbOBr <sub>3</sub>	Nb <sub>2</sub> O <sub>5</sub>	CBr <sub>4</sub>	200	24	100	2
TaOBr <sub>3</sub>	Ta <sub>2</sub> O <sub>5</sub>	CBr <sub>4</sub>	> 200	24	Low	2
MoO <sub>2</sub> Cl <sub>2</sub>	MoO <sub>3</sub>	CCl <sub>4</sub> -O <sub>2</sub>	550	$\frac{3}{4}$	100	3
WO <sub>2</sub> Cl <sub>2</sub>	WO <sub>3</sub>	CCl <sub>4</sub> -O <sub>2</sub>	370	1	100	3
WOCl <sub>4</sub>	WO <sub>3</sub>	CCl <sub>4</sub>	250	3-4	100	4
WO <sub>2</sub> Cl <sub>2</sub>	WO <sub>3</sub>	CCl <sub>4</sub>	300-320			4
WOBr <sub>4</sub>	WO <sub>3</sub>	CBr <sub>4</sub>	200	24		8 <sup>a</sup>
WO <sub>2</sub> Br <sub>2</sub>	WO <sub>3</sub>	CBr <sub>4</sub>	200	24		8
VOCl <sub>3</sub>	V <sub>2</sub> O <sub>5</sub>	ocp <sup>b</sup>	Reflux	$\frac{1}{4}$	80	5
MoOCl <sub>3</sub>	MoO <sub>2</sub>	ocp	Reflux	$\frac{1}{4}$	80	5
WOCl <sub>4</sub>	WO <sub>3</sub>	ocp	Reflux	2	91	5, 6
WOCl <sub>4</sub>	WO <sub>3</sub>	hcp <sup>c</sup>	Reflux	2	88	5

<sup>a</sup> In this reaction xs CBr<sub>4</sub> produced mainly WOBr<sub>4</sub> and xs WO<sub>3</sub> produced WO<sub>2</sub>Br<sub>2</sub>.

<sup>b</sup> ocp = octachlorocyclopentane.

<sup>c</sup> hcp = hexachloropentadiene.

bombs at high temperatures and under pressure. **The reactions proceed with formation of COF<sub>2</sub>, COCl<sub>2</sub> and COBr<sub>2</sub>, care must be taken in opening up the reaction vessel.** In Table 1 is a list of oxohalides that can be prepared from halocarbons. The reactions of Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub> with CCl<sub>4</sub> are contrasting<sup>1,2</sup>. The former readily yields NbOCl<sub>3</sub>, but care has to be taken to prevent the formation of NbCl<sub>5</sub>; with Ta<sub>2</sub>O<sub>5</sub>, however, the yield of TaOCl<sub>3</sub> is low. This could be caused by the decomposition of the oxohalide to give TaCl<sub>5</sub> and TaO<sub>2</sub>Cl.

The complex nature of this type of halogenation is illustrated by the WO<sub>3</sub>-CCl<sub>4</sub> reaction where a mixture of WO<sub>2</sub>Cl<sub>2</sub>, WOCl<sub>4</sub>, WCl<sub>6</sub> and WCl<sub>4</sub> is easily obtained, although with careful control of the stoichiometry WOCl<sub>4</sub> or WO<sub>2</sub>Cl<sub>2</sub> can be obtained<sup>3,4</sup>. The best method of obtaining pure WO<sub>2</sub>Cl<sub>2</sub> from CCl<sub>4</sub> is by heating the oxide in a rapid stream of CCl<sub>4</sub> vapor and O<sub>2</sub>. A similar procedure produces MoO<sub>2</sub>Cl<sub>2</sub><sup>3</sup>. The chlorocarbons octachlorocyclopentene and hexachloropentadiene can be used under reflux conditions with oxides to produce oxohalides. The conditions for the reaction of these halocarbons obviate the need for bomb techniques<sup>5,6</sup>.

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## 2.9.12. Synthesis of Metal Oxohalides from Metal Oxides

2.9.12.5. by Reaction of Oxides with  $\text{SOCl}_2$  and Nonmetal Chlorides**2.9.12.5. by Reaction of Oxides with  $\text{SOCl}_2$  and Other Nonmetal Chlorides**

Thionyl chloride's action as both a dehydrating and chlorinating agent makes it suitable for converting certain metal oxides to metal oxochlorides. The side product,  $\text{SO}_2$ , is easily removed leaving a pure oxochloride (see Table 1).

**TABLE 1. FORMATION OF OXYHALIDES BY REACTION OF METAL OXIDES WITH  $\text{SOCl}_2$  AND OTHER NONMETAL CHLORIDES**

Product	Oxide	Halide	T (°C)	Time	Ref.
$\text{VOCl}_3$	$\text{V}_2\text{O}_5$	$\text{SOCl}_2$	Reflux	6-8 h	1
$\text{NbOCl}_3$	$\text{Nb}_2\text{O}_5$	$\text{SOCl}_2$	200	3 h	1, 12
$\text{WOCl}_4$	$\text{WO}_3, \text{WO}_2$	$\text{SOCl}_2$	200	6 h	1, 12
$\text{MoOCl}_4$	$\text{MoO}_3$	$\text{SOCl}_2$	Reflux	30 min	2
$\text{CrOCl}_3$	$\text{CrO}_3$	$\text{SOCl}_2$	0	8 d	3
$\text{MoOCl}_3$	$\text{MoO}_3$	$\text{S}_2\text{Cl}_2$	120-140	6-7 h	4
$\text{MoO}_2\text{Br}_2$	$\text{MoO}_3$	$\text{BBr}_3$			5
$\text{NbOBr}_3$	$\text{Nb}_2\text{O}_5$	$\text{BBr}_3$			5
$\text{CrO}_2\text{Cl}_2$	$\text{CrO}_3$	$\text{AlCl}_3$	25		7
$\text{VOCl}_3$	$\text{V}_2\text{O}_5$	$\text{AlCl}_3$	400		8
$\text{VOBr}_2$	$\text{V}_2\text{O}_5$	$\text{BBr}_3$	120-160	4 h	6
$\text{WOBr}_4$	$\text{WO}_3$	$\text{BBr}_3$	130-160	3 h	6
$\text{MnO}_3\text{F}$	$\text{KMnO}_4$	$\text{HSO}_3\text{F}$	-60		9
$\text{MnO}_3\text{Cl}$	$\text{KMnO}_4$	$\text{HSO}_3\text{Cl}$	-60		9
$\text{MnOCl}_3$	$\text{KMnO}_4$	$\text{HSO}_3\text{Cl}$	0	15 min	9
$\text{MnO}_2\text{Cl}_2$	$\text{KMnO}_4$	$\text{HSO}_3\text{Cl}-\text{H}_2\text{SO}_4-\text{SO}_2$	0		9
$\text{OSOCl}_4$	$\text{OsO}_4$	$\text{BCl}_3$		25	14

Vanadium pentoxide<sup>1</sup> and  $\text{MoO}_3$ <sup>2</sup> react smoothly with refluxing  $\text{SOCl}_2$  to yield  $\text{VOCl}_3$  and  $\text{MoOCl}_4$ , respectively. Heating thionyl chloride with  $\text{Nb}_2\text{O}_5$  (1:3 mol ratio) or  $\text{WO}_3$  (1:4 mol ratio) in a high-pressure bomb yields  $\text{NbOCl}_3$  and  $\text{WOCl}_4 \cdot \text{SOCl}_2$ , respectively<sup>1</sup>. Boiling a mixture of  $\text{MoO}_3$  and  $\text{S}_2\text{Cl}_2$  yields initially a mixture of  $\text{MoO}_2\text{Cl}_2$ ,  $\text{MoOCl}_4$ ,  $\text{MoOCl}_3$  and  $\text{MoCl}_5$ . If the mixture is boiled until no further  $\text{SO}_2$  or  $\text{SCl}_2$  is given off,  $\text{MoOCl}_3$  is the major product, and it can be separated from the other species by vacuum sublimation<sup>4</sup>.

Among the other nonmetal halogens used to partially halogenate metal oxides is  $\text{BBr}_3$ <sup>5,6</sup>. With  $\text{WO}_3$   $\text{BBr}_3$  gives  $\text{WOBr}_4$ , while with  $\text{MoO}_3$ ,  $\text{MoO}_2\text{Br}_2$  is formed. The increased stability of the highest oxidation state on going down group VA is reflected in the products of the  $\text{BBr}_3-\text{M}_2\text{O}_5$  reaction. Thus with  $\text{M} = \text{V}$ ,  $\text{VOBr}_2$  is formed and with  $\text{M} = \text{Nb}$ , the product is  $\text{NbOBr}_3$ <sup>5,6</sup>. The oxochlorides  $\text{CrO}_2\text{Cl}_2$  and  $\text{VOCl}_3$  are prepared by reacting the appropriate oxides with  $\text{AlCl}_3$ <sup>7,8</sup>.

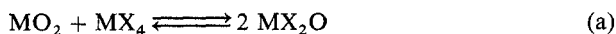
Manganese oxohalides are prepared by treating potassium permanganate with halogenosulfonic acids. However, **these reactions are dangerous as the oxohalides and the acids form potentially explosive mixtures**<sup>9</sup>.

A specialized route to a whole range of oxohalides of group VIA is the heating of the metal trioxides with alkali halides. The oxohalides sublime from the reaction mixture<sup>10,11</sup>.

1. H. Hecht, G. Jander, H. Schlapmann, *Z. Anorg. Allg. Chem.*, **254**, 255 (1947).
2. R. Colton, I. B. Tomkins, P. W. Wilson, *Aust. J. Chem.*, **17**, 496 (1964).
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### 2.9.12.6. by the Interaction of a Metal Oxide with Its Halide.

The thermal combination of a metal oxide with its halide is an important method for the preparation of metal oxohalides, e.g., for a metal in oxidation state four:



The decomposition or sublimation temperature of the oxide or halide must be lower than the reaction temperature. When the oxidation state is the same in oxide and halide there is only one product.

The oxohalides prepared by this route are listed in Table 1. The range of compounds produced is enormous, from layer compounds such as  $\text{FeOCl}^{1,2}$ ,  $\text{CrOCl}^3$  to compounds that readily volatilize giving molecular species such as  $\text{WOCl}_4^4$ . Time and temperature conditions are given in Table 1. The reactions are carried out in sealed quartz tubes, the product collecting in the coolest zone.

TABLE 1. FORMATION OF METAL OXY HALIDES BY THE INTERACTION OF A METAL OXIDE WITH ITS HALIDES

Product	Reaction mixture	T (°C)	Time	Yield (%)	Ref.
TiOCl	TiO <sub>2</sub> + 2 TiCl <sub>3</sub>	550-650	12 h		7
VOC1 <sub>2</sub>	V <sub>2</sub> O <sub>5</sub> + 3 VCl <sub>6</sub> + VCl <sub>3</sub> O	600	4-5 d		8-10
VOC1	V <sub>2</sub> O <sub>3</sub> + VCl <sub>3</sub>	650-750	1-2 d		10, 11
NbOCl <sub>3</sub>	Nb <sub>2</sub> O <sub>5</sub> + NbCl <sub>5</sub> (xs)	210-350			12, 19
TaOCl <sub>3</sub>	Ta <sub>2</sub> O <sub>5</sub> + 3 TaCl <sub>5</sub>	600-1000			5, 6, 19
CrOCl	Cr <sub>2</sub> O <sub>3</sub> + CrCl <sub>3</sub>	840-1040			3
MoOCl <sub>2</sub>	MoO <sub>3</sub> + 2 MoCl <sub>3</sub>	300-350	6 d		13, 14
MoO <sub>2</sub> Cl	MoO <sub>3</sub> + MoCl <sub>5</sub> (or MoCl <sub>3</sub> )				20
WOCl <sub>4</sub>	WO <sub>3</sub> + 2 WCl <sub>6</sub>	175-200	10 h	98	4
WO <sub>2</sub> Cl <sub>2</sub>	2 WO <sub>3</sub> + WCl <sub>6</sub>	275-350		98	4
ReOCl <sub>4</sub>	ReO <sub>3</sub> + 3 ReCl <sub>5</sub>	180	12 h		15
ReOCl <sub>4</sub>	Re <sub>2</sub> O <sub>7</sub> + ReCl <sub>5</sub>	70			16
ReOCl <sub>2</sub>	ReO <sub>3</sub> + ReCl <sub>5</sub>	400	5 d		17
ReOCl <sub>2</sub>	ReO <sub>3</sub> + ReCl <sub>4</sub> O	120-280	72 h		17
ReO <sub>2</sub> Cl	ReO <sub>3</sub> + ReCl <sub>2</sub> O				21
FeOCl	Fe <sub>2</sub> O <sub>3</sub> + FeCl <sub>3</sub>	300-350			1, 2
CrO <sub>2</sub> F <sub>2</sub>	CrO <sub>3</sub> + MoF <sub>6</sub> (or WF <sub>6</sub> )	125	12 h		18

## 2.9. Formation of the Halogen-Transition-Metal Bond

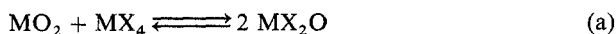
## 2.9.12. Synthesis of Metal Oxohalides from Metal Oxides

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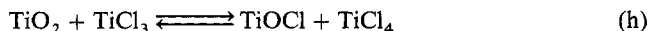
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The complexity of these reactions is illustrated by the synthesis of  $\text{TaOCl}_3$  from  $\text{Ta}_2\text{O}_5$  and  $\text{TaCl}_5$ <sup>5,6</sup>. Although gaseous  $\text{TaOCl}_3$  is readily formed above  $500^\circ\text{C}$ , on cooling the compound disproportionates, reverting to starting materials<sup>6</sup>. The use of metal oxides and halides having the metal in differing oxidation states is also employed. In these reactions two products are often formed, and so it is helpful if they differ in their volatility, thus allowing ready separation by vacuum sublimation, e.g., in the reaction of  $\text{TiO}_2$  and  $\text{TiCl}_3$  where the volatile halide,  $\text{TiCl}_4$ , is distilled from the reaction mixture<sup>7</sup>:



An excess of  $\text{TiCl}_3$  is used, and this is removed by treating the  $\text{TiOCl-TiCl}_4$  mixture with DMF, in which the halide is soluble. A more complex product mixture ( $\text{ReOCl}_4$ ,  $\text{ReO}_3\text{Cl}$ ,  $\text{Re}_3\text{Cl}_9$  and  $\text{ReOCl}_2$ ) is obtained from  $\text{ReO}_3$  and  $\text{ReCl}_5$ . If  $\text{ReOCl}_2$  is the desired product, the volatile oxohalides  $\text{ReOCl}_4$  and  $\text{ReO}_3\text{Cl}$  are distilled from the reaction mixture, followed by extraction with  $\text{CH}_3\text{CN}$ , which removes the  $\text{Re}_3\text{Cl}_9$ .

(E.M. PAGE, D.A. RICE)

1. H. Schafer-Stahl, R. Abele, *Angew. Chem.*, **19**, 477 (1980).
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### 2.9.12.7. by the Use of Group-IVb and -Vb Oxides with Transition-Metal Halides

This route provides a simple, low-T preparative technique that can be carried out either in sealed glass tubes or in the presence of a solvent such as  $\text{CS}_2$ . The usefulness of this technique is illustrated by the preparation of  $\text{TaOCl}_3$ . As stated in §2.9.12.6,  $\text{TaOCl}_3$  can be prepared from  $\text{Ta}_2\text{O}_5$ - $\text{TaCl}_5$  mixtures, disproportionation occurs but at the T necessary to promote reaction. However, by the reaction of  $\text{TaCl}_5$  in a stream of  $\text{Cl}_2$  with  $\text{Sb}_2\text{O}_3$  at  $180$ – $250^\circ\text{C}$ ,  $\text{TaOCl}_3$  can be obtained<sup>1</sup>:



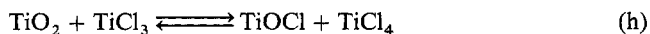
## 2.9. Formation of the Halogen-Transition-Metal Bond

223

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TABLE 1. FORMATION OF OXY HALIDES BY THE REACTION OF GROUP-VB OXIDES WITH TRANSITION-METAL HALIDES

Product	Reactants	T (°C)	Ref.
TiOCl <sub>2</sub>	TiCl <sub>4</sub> + M <sub>2</sub> O <sub>3</sub> (M = As, Sb or Bi)		2
VOCl <sub>2</sub>	VCl <sub>3</sub> O + As <sub>2</sub> O <sub>3</sub>		3
WOCl <sub>4</sub>	WCl <sub>6</sub> + Sb <sub>2</sub> O <sub>3</sub> , As <sub>2</sub> O <sub>3</sub>	100	4
WOCl	WCl <sub>3</sub> + Sb <sub>2</sub> O <sub>3</sub>	250	6
WOB <sub>4</sub>	WBr <sub>6</sub> + Sb <sub>2</sub> O <sub>3</sub>	25	5
MoOCl <sub>3</sub>	MoCl <sub>5</sub> + Sb <sub>2</sub> O <sub>3</sub>		5
WOCl <sub>3</sub>	WCl <sub>5</sub> + Sb <sub>2</sub> O <sub>3</sub>		5
WOB <sub>3</sub>	WBr <sub>5</sub> + Sb <sub>2</sub> O <sub>3</sub>		5
WO <sub>2</sub> Cl <sub>2</sub>	WCl <sub>4</sub> O + Sb <sub>2</sub> O <sub>3</sub>	50	4

At 25°C in CS<sub>2</sub>, TaOCl<sub>3</sub> is rapidly formed, and the SbCl<sub>3</sub> is soluble in CS<sub>2</sub>; thus anerobic filtration leads to the isolation of TaOCl<sub>3</sub>.

In Table 1 are listed oxy halides that are prepared by this type of reaction. In most cases either Sb<sub>2</sub>O<sub>3</sub> or As<sub>2</sub>O<sub>3</sub> can be used and the side product, the group-VB(III) halide, can be separated by use of its differing volatility or solubility from the desired oxy halide. The requirement for pure Sb<sub>2</sub>O<sub>3</sub> is met by subliming commercially available Sb<sub>2</sub>O<sub>3</sub> at high T under a dynamic vacuum. A related reaction is the isolation of MF<sub>4</sub>O from MF<sub>4</sub>-SiO<sub>2</sub> mixtures (M = Mo, W)<sup>7,8</sup>.

(E.M. PAGE, D.A. RICE)

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## 2.9.13. Synthesis of Complex Halo Anions of Metal Oxohalides

Transition-metal complex halo anions are formed by elements belonging to groups IVA, VA, VIA, VIIA and VIII, as with the metal oxohalides. The complex anions formed, especially those of group-VA and -VIA elements, are extensive, as are the preparative routes. To maintain the consistency of the rest of §2.9 the syntheses of complex halo anions is subdivided according to the transition metal. Reviews of oxohalo anions are largely devoted to vibrational spectroscopy<sup>1-5</sup>.

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TABLE 1. FORMATION OF OXY HALIDES BY THE REACTION OF GROUP-VB OXIDES WITH TRANSITION-METAL HALIDES

Product	Reactants	T (°C)	Ref.
TiOCl <sub>2</sub>	TiCl <sub>4</sub> + M <sub>2</sub> O <sub>3</sub> (M = As, Sb or Bi)		2
VOCl <sub>2</sub>	VCl <sub>3</sub> O + As <sub>2</sub> O <sub>3</sub>		3
WOCl <sub>4</sub>	WCl <sub>6</sub> + Sb <sub>2</sub> O <sub>3</sub> , As <sub>2</sub> O <sub>3</sub>	100	4
WOCl	WCl <sub>3</sub> + Sb <sub>2</sub> O <sub>3</sub>	250	6
WOB <sub>4</sub>	WBr <sub>6</sub> + Sb <sub>2</sub> O <sub>3</sub>	25	5
MoOCl <sub>3</sub>	MoCl <sub>5</sub> + Sb <sub>2</sub> O <sub>3</sub>		5
WOCl <sub>3</sub>	WCl <sub>5</sub> + Sb <sub>2</sub> O <sub>3</sub>		5
WOB <sub>3</sub>	WBr <sub>5</sub> + Sb <sub>2</sub> O <sub>3</sub>		5
WO <sub>2</sub> Cl <sub>2</sub>	WCl <sub>4</sub> O + Sb <sub>2</sub> O <sub>3</sub>	50	4

At 25°C in CS<sub>2</sub>, TaOCl<sub>3</sub> is rapidly formed, and the SbCl<sub>3</sub> is soluble in CS<sub>2</sub>; thus anaerobic filtration leads to the isolation of TaOCl<sub>3</sub>.

In Table 1 are listed oxy halides that are prepared by this type of reaction. In most cases either Sb<sub>2</sub>O<sub>3</sub> or As<sub>2</sub>O<sub>3</sub> can be used and the side product, the group-VB(III) halide, can be separated by use of its differing volatility or solubility from the desired oxy halide. The requirement for pure Sb<sub>2</sub>O<sub>3</sub> is met by subliming commercially available Sb<sub>2</sub>O<sub>3</sub> at high T under a dynamic vacuum. A related reaction is the isolation of MF<sub>4</sub>O from MF<sub>4</sub>-SiO<sub>2</sub> mixtures (M = Mo, W)<sup>7,8</sup>.

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## 2.9.13. Synthesis of Complex Halo Anions of Metal Oxohalides

225

## 2.9.13.1. from Metal Oxides

## 2.9.13.1.1. with Oxofluoro Anions.

## 2.9.13.1. from Metal Oxides

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The solubility of transition-metal oxides in HF solutions makes possible the isolation of oxofluoro anions of varying stoichiometries (see Table 1). Alkali-metal fluorides react with the metal oxide-HF soln in polyethylene or metal vessels, e.g., NaF, KF AF-V<sub>2</sub>O<sub>5</sub>-HF-H<sub>2</sub>O (A = alkali metal), the anion formed depending upon the metal

TABLE 1. PREPARATION OF COMPLEX FLUORO ANIONS FROM THE METAL OXIDE

Element	Anion	Cations	Reaction	Ref.
Ti(IV)	[TiOF <sub>3</sub> ] <sup>-</sup> ·H <sub>2</sub> O	NH <sub>4</sub> <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup> , [Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup> , [Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup> , Ba <sup>2+</sup>	TiO <sub>2</sub> in HF (40%) + cation in aq ethanol (anhyd)	11
V(V)	[TiOF <sub>4</sub> ] <sup>2-</sup> [Ti <sub>4</sub> O <sub>3</sub> F <sub>16</sub> ] <sup>6-</sup> [V <sub>2</sub> O <sub>4</sub> F <sub>5</sub> ] <sup>3-</sup> [V <sub>3</sub> O <sub>3</sub> F <sub>14</sub> ] <sup>5-</sup> [VO <sub>2</sub> F <sub>3</sub> ] <sup>2-</sup>	K <sup>+</sup> , Rb <sup>+</sup> K <sup>+</sup> , Rb <sup>+</sup> , Cs <sup>+</sup> K <sup>+</sup> K <sup>+</sup> , Rb <sup>+</sup> , Cs <sup>+</sup>	V <sub>2</sub> O <sub>5</sub> in 40% HF + AF V <sub>2</sub> O <sub>5</sub> + in HF (xs) + KF V <sub>2</sub> O <sub>5</sub> in 40% HF + AF or AF-V <sub>2</sub> O <sub>5</sub> mixtures heated at 650-750°C in vacuum	1, 2, 3 1 2
	[VO <sub>2</sub> F <sub>4</sub> ] <sup>3-</sup>	[A <sub>2</sub> A'] <sup>3+</sup> A = K <sup>+</sup> , Rb <sup>+</sup> , Cs <sup>+</sup> A' = Na <sup>+</sup> , K <sup>+</sup> , Rb <sup>+</sup>	V <sub>2</sub> O <sub>5</sub> in 40% HF + AF	2, 3
	[VOF <sub>5</sub> ] <sup>2-</sup> [VOF <sub>4</sub> ] <sup>-</sup>	K <sup>+</sup> , [NH <sub>4</sub> ] <sup>+</sup> Cs <sup>+</sup>	V <sub>2</sub> O <sub>5</sub> in 40% HF + A <sub>2</sub> CO <sub>3</sub> V <sub>2</sub> O <sub>5</sub> + CsF in anhyd HF at -30°C	4 12
V(IV)	[V <sub>2</sub> O <sub>2</sub> F <sub>7</sub> ] <sup>3-</sup> [VOF <sub>5</sub> ] <sup>3-</sup> [VOF <sub>4</sub> ] <sup>2-</sup> [VOF <sub>4</sub> ] <sup>2-</sup>	Cs <sup>+</sup> Na <sup>+</sup> K <sup>+</sup> , Rb <sup>+</sup> [C <sub>5</sub> H <sub>5</sub> NH] <sup>+</sup> , [C <sub>6</sub> H <sub>7</sub> NH] <sup>+</sup> , [C <sub>9</sub> H <sub>7</sub> NH] <sup>+</sup>	CsF-VO <sub>2</sub> -HF-H <sub>2</sub> O NaF-VO <sub>2</sub> -HF-H <sub>2</sub> O AF-VO <sub>2</sub> -HF-H <sub>2</sub> O V <sub>2</sub> O <sub>5</sub> -HF + organic base in HF (20%)	3 3 3 4
Nb(V)	[NbOF <sub>6</sub> ] <sup>3-</sup>	[NH <sub>4</sub> ] <sup>+</sup>	Nb <sub>2</sub> O <sub>5</sub> + H <sub>2</sub> O <sub>2</sub> + NH <sub>4</sub> OH	13
Ta(V)	[TaOF <sub>6</sub> ] <sup>3-</sup> [Ta <sub>4</sub> F <sub>4</sub> O <sub>9</sub> ] <sup>2-</sup>	[NH <sub>4</sub> ] <sup>+</sup> K <sup>+</sup>	Ta <sub>2</sub> O <sub>5</sub> in HF + NH <sub>4</sub> OH + NH <sub>4</sub> F K <sub>2</sub> TaF <sub>7</sub> -KTaO <sub>3</sub> -Ta <sub>2</sub> O <sub>5</sub> + KCl heated at 1173 K for 3 h in Pt tube	13 14
	[Ta <sub>15.5</sub> F <sub>18.5</sub> O <sub>35.5</sub> ] <sup>12-</sup>	K <sup>+</sup>	K <sub>2</sub> TaF <sub>7</sub> -KTaO <sub>3</sub> -Ta <sub>2</sub> O <sub>5</sub> heated at 973-1173 K in Au tube	15
Mo(VI)	[Mo <sub>4</sub> O <sub>13</sub> F] <sup>3-</sup> ·3 H <sub>2</sub> O [MoO <sub>3</sub> F <sub>2</sub> ] <sup>2-</sup> ·H <sub>2</sub> O [MoO <sub>3</sub> F <sub>3</sub> ] <sup>3-</sup> ·H <sub>2</sub> O [MoO <sub>2</sub> F <sub>4</sub> ] <sup>2-</sup> ·H <sub>2</sub> O	K <sup>+</sup> K <sup>+</sup> K <sup>+</sup> , Rb <sup>+</sup> , Cs <sup>+</sup> K <sup>+</sup> , (QH <sup>+</sup> )[picH] <sup>+</sup>	MoO <sub>3</sub> + KF heated at 110°C MoO <sub>3</sub> + KF in H <sub>2</sub> O MoO <sub>3</sub> + KF in H <sub>2</sub> O at 90°C MoO <sub>3</sub> + KHF <sub>2</sub> (1:3) MoO <sub>3</sub> in HF + organic base (1:5) MoO <sub>3</sub> in 5 mol L <sup>-1</sup> HF MoO <sub>3</sub> in HF + organic base (1:1)	5 6, 7 6, 7, 8 5 16 17 16
	cis[MoO <sub>2</sub> F <sub>3</sub> ] <sup>-</sup> ·H <sub>2</sub> O [MoO <sub>2</sub> F <sub>3</sub> ] <sup>-</sup>	[bipyH] <sup>+</sup> [1, 10-phen] <sup>+</sup>		
W(VI)	[WOF <sub>5</sub> ] <sup>-</sup>	K <sup>+</sup>	WO <sub>3</sub> + KF in boiling SeF <sub>4</sub>	9
Os(VIII)	[OsO <sub>3</sub> F <sub>3</sub> ] <sup>-</sup>	K <sup>+</sup> , Cs <sup>+</sup> , Ag <sup>+</sup>	OsO <sub>4</sub> + BF <sub>3</sub> condensed into KBr, CsBr or AgIO <sub>3</sub>	10
	[OsO <sub>4</sub> F <sub>2</sub> ] <sup>2-</sup>	Cs <sup>+</sup> , Rb <sup>+</sup>	OsO <sub>4</sub> + CsF	18

to fluorine ratio<sup>1-4</sup>. The most stable oxofluoro salt in this series is  $K_3V_2O_4F_5$ , which is the final product from the decomposition of any of the other oxofluorovanadates. The salts  $K_3[V_2O_4F_5]$  and  $K_2[VO_2F_3]$  cocrystallize from HF to give polyhedral pneumatic crystals of  $K_5[V_3O_3F_{14}]$ . If  $VO_2$  is substituted for  $V_2O_5$ , salts of V(IV) are formed.

Other fluorinating agents employed include  $KF$ ,  $KHF_2$ <sup>5-8</sup>,  $SeF_4$ <sup>9</sup> and  $BF_3$ <sup>10</sup>.

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### 2.9.13.1.2. with Oxochloro and Oxobromo Anions.

Use of the metal oxide as a starting reagent in the synthesis of oxohalo anions avoids the need to prepare the intermediate oxohalide, a process that can involve complex handling techniques (Table 1). Oxochloro salts of V(V) can be prepared by the reaction of ethanolic  $V_2O_5$  saturated with HCl and an appropriate cation at 0°C<sup>1</sup>. Such reactions yield V(IV) salts if T is allowed to rise or if a reducing agent, e.g., pyridine is employed instead of the pyridinium salt<sup>2</sup>.

The electrolytic reduction of Mo or W(VI) oxides in conc HCl produces Mo(V) and W(V) solutions from which salts of  $[MOX_3]^{2-}$  can be obtained by addition of the appropriate cation<sup>3-6</sup>. Reduction can also be induced by addition of hydroquinone<sup>7,8</sup>.

Oxohalo anions of Ru(VI) and Os(VI) can be obtained from the oxides  $RuO_4$  and  $OsO_4$ , which are readily reduced in the presence of hydrohalic acids to give the anions<sup>9-11</sup>  $[RuO_2X_4]^{2-}$  and  $[OsO_2X_4]^{2-}$ .

The complex oxoanion of Ru,  $[Ru_2OCl_{10}]^{4-}$ , is best prepared from Ru metal, using finely powdered Ru and  $KO_3Cl$  with fused KOH in an Ag crucible. **Potassium chlorate should be ground with caution in a clean mortar free from organic matter.**

The powdered mixture is added slowly to the melt and heated for ca. 30 min. The resulting mass is cooled and dissolved in 5 mol L<sup>-1</sup> HCl. Filtration and evaporation of the solution yields<sup>12</sup>  $K_4[Ru_2OCl_{10}]$ .

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## 2.9. Formation of the Halogen-Transition-Metal Bond

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(E.M. PAGE, D.A. RICE)

TABLE I. PREPARATION OF COMPLEX OXOCHLORO + BROMO ANIONS FROM THE METAL OXIDE

Element	Anion	Cation	Reaction	Ref.
V(V)	$[\text{VOCl}_4]^-$	$[\text{pyH}]^+$ , $[\text{quinH}]^+$ $[\text{Et}_4\text{N}]^+$ , $[\text{isoquinH}]^+$	$\text{V}_2\text{O}_5$ in $\text{EtOH}$ -satd $\text{HCl}$ gas + cation at $0^\circ\text{C}$ , 4 h	1
V(IV)	$[\text{VOCl}_4]^{2-} \cdot 2 \text{H}_2\text{O}$	$[\text{pyH}]^+$ , $[\text{quinH}]^+$	$\text{V}_2\text{O}_5$ in $\text{EtOH}$ :conc $\text{HCl}$ (1:1) + py at $0^\circ\text{C}$ satd with $\text{HCl}$	2
Cr(V)	$[\text{VOCl}_3]^{2-} \cdot 2 \text{H}_2\text{O}$ $[\text{CrOCl}_3]^{2-}$	$[\text{Me}_4\text{N}]^+$ , $[\text{Et}_4\text{N}]^+$ , $\text{Cs}^+$	$\text{V}_2\text{O}_5$ in $\text{EtOH}$ :conc $\text{HCl}$ (1:1) + $\text{R}_4\text{NCl}$ $\text{CrO}_3$ in $\text{CH}_3\text{COOH}$ -satd $\text{HCl}$ + $\text{CsCl}$ in $\text{CH}_3\text{COOH}-\text{HCl}$	13
Cr(V)	$[\text{CrOCl}_3]^{2-}$	$[\text{Me}_4\text{N}]^+$ , $[\text{Et}_4\text{N}]^+$	$\text{CrO}_3$ in $\text{CH}_3\text{COOH}-\text{HCl}$ (g) + base	17
Cr(V)	$[\text{CrOCl}_4]^-$ $[\text{CrOCl}_3]^{2-}$	$\text{K}^+$ , $\text{Rb}^+$ $[\text{Pr}_4\text{M}]^+$ , $[\text{Bu}_4\text{P}]^+$ $[\text{Ph}_4\text{As}]^+$	$\text{CrO}_3$ in $\text{CH}_3\text{COOH}$ -satd $\text{HCl}$ + $\text{RCl}$ $\text{CrO}_3$ in $\text{CH}_3\text{COOH}$ -sat $\text{HCl}$ in $\text{CH}_3\text{COOH}-\text{HCl}$	14, 15 18
Cr(V)	$[\text{CrOCl}_4]^-$ $[\text{MoOCl}_3]^{2-}$	$[\text{pyH}]^+$ $[\text{NH}_4]^+$	$\text{CrO}_3$ in glacial $\text{CH}_3\text{COOH}$ + $\text{CH}_3\text{COCl}$ $\text{MoO}_3$ in conc $\text{HCl}$ reduced electrolytically and $\text{NH}_4\text{Cl}$ added	19 3, 4
Mo(V)	$[\text{MoOBr}_5]^{2-}$	$[\text{NH}_4]^+$ , $\text{K}^+$ $\text{Rb}^+$ , $[\text{pyH}]^+$ $[\text{quinH}]^+$	$\text{MoO}_3$ in conc $\text{HBr}$ reduced at Pt cathode + $\text{MCl}$ added	5
W(V)	$[\text{WOCl}_3]^{2-}$ $[\text{MoOCl}_3]^{2-}$	$\text{Rb}^+$ , $[\text{C}_6\text{H}_5\text{NH}_3]^+$ $[\text{quinH}]^+$	$\text{WO}_3$ reduced at Pt cathode $\text{MoO}_3$ in conc $\text{HCl}$ reduced by hydroquinone and $\text{NH}_4\text{Cl}$ added	6 7
	$[\text{MoOBr}_4]^-$ $[\text{MoO}_3\text{Cl}]^-$	$[\text{C}_9\text{H}_8\text{N}]^+$ $[\text{Ph}_4\text{P}]^+$ , $[\text{Ph}_4\text{As}]^+$	$\text{MoO}_3$ in $\text{HBr}$ + quinoline $\text{MoO}_3$ + $[\text{Ph}_4\text{E}]\text{Cl}$ at $250-280^\circ\text{C}$ under $\text{N}_2$ 1 h	8 16
Ru(VI)	$[\text{RuO}_2\text{X}_4]^{2-}$ (X = Cl, Br)	$\text{K}^+$ , $\text{Cs}^+$ , $\text{Rb}^+$	$\text{RuO}_4$ + MX in HX	9,10
Os(VI)	$[\text{OsO}_2\text{Cl}_4]^{2-}$ $[\text{OsO}_2\text{Br}_4]^{2-}$	$\text{K}^+$ , $\text{Cs}^+$ , $[\text{NH}_4]^+$ $\text{K}^+$	$\text{OsO}_4$ + $\text{HCl}$ with $\text{MCl}$ $\text{OsO}_4$ + $\text{HBr}$ + $\text{KBr}$	11 12

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### 2.9.13.2. from Metaloxo Anions (Metallates)

Treatment of metaloxo anions (i.e., metallates, e.g., vanadates, chromates, molybdates, tungstates and rhenates) with concentrated hydrohalic acids provides solutions of complex halo anions. Oxohalide salts having the metal in its highest oxidation state can be obtained by precipitation with an appropriate cation (see Table 1). An exception is the oxofluoride  $\text{NH}_4[\text{V}_3\text{O}_6\text{F}]$  which is prepared by reaction, at  $450^\circ\text{C}$  and  $1.35 \times 10^5 \text{ Nm}^{-2}$ , of  $\text{NH}_4[\text{VO}_3]$ , vanadium metal and ammonium hydrogen fluoride in a thin-walled Au tube. The product is obtained after ca. 10 d<sup>1</sup>. One method for the preparation of  $\text{KCrO}_3\text{X}$  (X = Cl, F) involves heating  $\text{K}_2\text{Cr}_2\text{O}_7$  and conc HX in  $\text{H}_2\text{O}$  to yield crystals of the salt after 1-2 d<sup>2</sup>. The product can then be dissolved in dil HX and other salts of  $[\text{CrO}_3\text{X}]^-$  obtained by cation exchange<sup>3</sup>.

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TABLE 1. PREPARATION OF COMPLEX HALO ANIONS FROM THE METALLATE

Element	Anion	Cations	Reaction	Ref.
V(V)	$[\text{VO}_2\text{F}_2]^-$	$[\text{NH}_4]^+$ , $\text{Na}^+$	$\text{MVO}_3 + \text{HF}$ (40%), 3–4 d	11
	$[\text{VO}_2\text{F}_2]^-$	$[\text{Ph}_4\text{E}]^+$	$\text{NaVO}_3$ in $\text{HF}$ (40%) + $[\text{Ph}_4\text{E}]^+$	12, 13
	$[\text{VO}_2\text{Cl}_2]^-$	$[\text{Ph}_4\text{E}]^+$ (E = P, As)		
V(IV)	$[\text{V}_3\text{O}_6\text{F}]^-$	$[\text{NH}_4]^+$	$\text{NaVO}_3$ in $\text{HCl}$ (25%) + $[\text{Ph}_4\text{E}]^+$ $[\text{NH}_4][\text{VO}_3] + \text{V} + \text{NH}_4 \cdot \text{HF}_2$ [1:0 to 1:4] at 450°C 1–10 d	12, 13 1
	$[\text{VOF}_4]^{2-}$	$[\text{NH}_4]^+$	$[\text{NH}_4][\text{VO}_3]$ in $\text{HF}$ (35%) reduced by $\text{SO}_2$ from $[\text{NH}_4]_2[\text{VOF}_4]$ in $\text{HF}$ (35%) + $\text{Ni}(\text{NO}_3)_2$	4
	$[\text{VOF}_4]^{2-}$	$\text{Ni}^{2+}$		
Cr(VI)	$[\text{VOCl}_4]^{2-} \cdot 2 \text{H}_2\text{O}$	$[\text{NH}_4]^+$	$[\text{NH}_4][\text{VO}_3]$ in $\text{HCl}$ -EtOH	14
	$[\text{CrO}_3\text{X}]^-$	$\text{K}^+$	From $\text{K}_2\text{Cr}_2\text{O}_7$ + conc HX	2, 15, 16
	$[\text{CrO}_3\text{X}]^-$ (X = Cl, F)	$[\text{Ph}_4\text{E}]^+$ (E = As, P)		
	$[\text{CrOF}_4]^-$	$\text{K}^+$	From $\text{KCrO}_3\text{X}$ in dil HX + $[\text{Ph}_4\text{E}]\text{Cl}$ $\text{K}_2\text{Cr}_2\text{O}_7 + \text{BrF}_3$	3 17
Cr(V)	$[\text{CrOBr}_5]^{2-}$	$[\text{bipy}]^+$	From $\text{K}_2\text{Cr}_2\text{O}_7$ in $\text{HBr}$ at 0°C + 2,2'-bipyridinium bromide	10
	$\text{cis}[\text{WO}_2\text{F}_3(\text{H}_2\text{O})]$	$\text{Na}^+$	From $\text{Na}_2\text{WO}_4$ in 5 mol $\text{L}^{-1}$ HF	18
W(VI)	$[\text{MO}_2\text{Cl}_4]^{2-}$	$\text{Cs}^+$	From $\text{Na}_2\text{MO}_4$ in conc $\text{HCl}$ satd with $\text{HCl}$ , $\text{CsCl}$ added to solution	19
	(M = Mo, W)			
W(V)	$[\text{MoOBr}_5]^{2-}$	$[\text{NH}_4]^+$	From $[\text{NH}_4]_6[\text{Mo}_7\text{O}_{24}] \cdot 4 \text{H}_2\text{O}$ in $\text{HBr}$	20
	$[\text{WOCls}]^{2-}$	$[\text{NH}_4]^+$ , $\text{Rb}^+$ , $\text{K}^+$ $[\text{C}_6\text{H}_5\text{NH}_3]^+$	From $\text{M}_2(\text{C}_2\text{O}_4) + [\text{NH}_4]_2[\text{WO}_4] + \text{tin}$	5
W(V)	$[\text{MoOCl}_5]^{2-}$	$[\text{NH}_4]^+$	Electrolytic reduction of $[\text{NH}_4]_2[\text{MoO}_4]$ in conc $\text{HCl}$	21
	$[\text{MoOCl}_5]^{2-}$	$[\text{NH}_4]^+$	Reduction of $[\text{NH}_4]_2[\text{MoO}_4]$ in conc $\text{HCl}$ by $\text{HI}$ or hydroquinone	6, 7, 8
Re(VI)	$[\text{MoOBr}_5]^{2-}$	$[\text{NH}_4]^+$	Reduction of $[\text{NH}_4]_2[\text{MoO}_4]$ in 9 mol $\text{L}^{-1}$ $\text{HBr}$ by $\text{HBr}$	8
	$[\text{MoOCl}_5]^{2-}$	$[\text{pyH}]^+$	Reduction $\text{Na}_2\text{MoO}_4 \cdot 2 \text{H}_2\text{O}$ by hydrazine in $\text{HCl}$ + $\text{py}$	22
	$[\text{MoOBr}_5]^{2-}$	$[\text{pyH}]^+$	Reduction of $\text{Na}_2\text{MoO}_4 \cdot 2 \text{H}_2\text{O}$ in $\text{HBr}$ + $\text{py}$	8
	$[\text{ReOCl}_5]^-$	$[\text{Ph}_4\text{E}]^+$	From $\text{KReO}_4$ in acetic acid-acetic-anhydride satd with $\text{HCl}$ + $[\text{Ph}_4\text{E}]\text{Cl}$	23
Re(V)	$[\text{ReOCl}_5]^{2-}$	$\text{Cs}^+$ , $\text{Rb}^+$	Reduction of $\text{KReO}_4$ by $\text{HI}$ or $\text{HCl}$ at $-10^\circ\text{C}$	9



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### 2.9.13.3 from Metal Halides

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An alternative method is illustrated by the reaction of molybdenum pentahalide with alkali-metal salt in liq SO<sub>2</sub> in a sealed ampule<sup>1</sup> to form the [MoOCl<sub>4</sub>]<sup>-</sup> anion. However, as this anion is the favored product from solutions containing Mo(V), chloride ions and traces of H<sub>2</sub>O, simpler routes are available for its preparation. The reaction between MoCl<sub>5</sub> and SeCl<sub>4</sub> at 200°C in a sealed tube yields [MoOCl<sub>4</sub>]<sup>-</sup>, despite the use of vacuum line and dry box techniques, indicating the ease with which oxygen attack occurs<sup>2</sup>. The reaction between MoCl<sub>5</sub> and Ph<sub>3</sub>AsO, originally thought to yield the adduct MoCl<sub>5</sub>·Ph<sub>3</sub>AsO<sup>3</sup>, yields a salt, [Ph<sub>3</sub>AsCl][MoOCl<sub>4</sub>]<sub>4</sub>, via oxygen abstraction.

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TABLE 1. PREPARATION OF COMPLEX OXO ANIONS FROM THE METAL HALIDE

Element	Anion	Cation	Reaction	Ref.
V(IV)	$[\text{VOCl}_4]^{2-}$ , $-2 \text{ H}_2\text{O}$	$\text{K}^+$ , $\text{Rb}^+$ , $\text{Cs}^+$ , $[\text{NH}_4]^+$	$\text{VCl}_4 + \text{MCl}$ in conc HCl satd with HCl at $0^\circ\text{C}$	5
Nb(V)	$[\text{NbOCl}_5]^{2-}$	$\text{Cs}^+$ , $\text{Rb}^+$	$\text{NbCl}_5 + \text{MCl}$ in conc HCl satd with HCl at $0^\circ\text{C}$	6, 7, 8
	$[\text{NbOBr}_5]^{2-}$	$\text{Cs}^+$ , $\text{Rb}^+$	$\text{NbBr}_5 + \text{MBr}$ in aq HBr	7
Ta(V)	$[\text{NbOCl}_4]^-$	$[\text{pyH}]^+$ , $[\text{quinH}]^+$	$\text{NbCl}_5 + [\text{ArH}]\text{Cl}$ in HCl satd HCl gas	9
Mo(VI)	$[\text{TaO}_2\text{Cl}_5]^-$	$\text{K}^+$ , $\text{Rb}^+$ , $\text{Cs}^+$ , $\text{NH}_4^+$	$\text{TaCl}_5 + \text{MCl}$ in HCl satd with HCl	10
	$[\text{MoOF}_5]^-$	$\text{Rb}^+$ , $\text{Cs}^+$	$\text{MoF}_6 + \text{MF}$ with $\text{SO}_2$ or $\text{AsF}_3$	11
	$[\text{MoO}_3\text{F}_2]^{2-}$		$\text{MoF}_6$ in HF (17.2–34.7%)	12
W(VI)	$[\text{WO}_2\text{Cl}_4]^{2-}$	$\text{NH}_4^+$ , $\text{Rb}^+$ , $\text{Cs}^+$	$\text{WCl}_6 + \text{MCl}$ in conc HCl	13
		$[\text{Me}_4\text{N}]^+$ , $[\text{Et}_4\text{N}]^+$		
M(V)	$[\text{MOCl}_5]^{2-}$ (M = Mo or W)	$\text{M}' = \text{alkali metal}$	$\text{MCl}_5 + \text{M}'\text{Cl}$ (1:2) in conc HCl satd with HCl gas at $0^\circ\text{C}$	1
	$[\text{MOBr}_5]^{2-}$ (M = Mo or W) <sup>1</sup>	$\text{M}' = \text{alkali metal}$	$\text{MBr}_5 + \text{M}'\text{Br}$ (1:2) in HBr (46–48%) satd with HBr gas at $0^\circ\text{C}$	1
	$[\text{MoOCl}_4]^-$	$\text{Rb}^+$ , $\text{Cs}^+$ , $[\text{pyH}]^+$	$\text{MoCl}_5 + \text{M}'\text{Cl}$ or $[\text{ArH}]\text{Cl}$ in liq $\text{SO}_2$	1
		$[\text{quinH}]^+$ , $[\text{Et}_4\text{N}]^+$		
	$[\text{MoOCl}_4]^-$	$[\text{Ph}_3\text{AsCl}]^+$	$\text{MoCl}_5 + \text{Ph}_3\text{AsO}$ in $\text{CCl}_4\text{--CH}_2\text{Cl}_2$ or	4, 3
			$\text{MoCl}_5 + \text{Ph}_3\text{AsCl}_2$ in $\text{SO}_2$	4
	$[\text{MoOCl}_4]^-$	$\text{SeCl}_4^+$	$\text{MoCl}_5 + \text{SeCl}_4$ (1:1) at $200^\circ\text{C}$ for 24 h	2
	$[\text{Mo}_2\text{O}_4\text{F}_6]^{2-}$	$[\text{NH}_4]^+$ , $\text{Na}^+$	$\text{MoCl}_5$ in THF + NaF or $[\text{NH}_4]\text{F}$ in $\text{H}_2\text{O}$ (12–15 h)	14
	$[\text{Mo}_2\text{O}_4\text{F}_4]^{2-}$	$[\text{Me}_4\text{N}]^+$	$\text{MoCl}_5$ in EtOH + KHF <sub>2</sub> and $[\text{Me}_4\text{N}]\text{Cl}$ at $70^\circ\text{C}$ for 20 h	14
	$[\text{MoO}_2\text{F}_3]^{2-}$	$[\text{NH}_4]^+$	$\text{MoCl}_5$ in EtOH– $\text{H}_2\text{O}$ or THF + $[\text{NH}_4]\text{F}$ or $[\text{Me}_4\text{N}]\text{F}$	15
Re(VI)	$[\text{MoO}_2\text{F}_2]^-$	$[\text{CH}_3)_4\text{N}]^+$	$\text{ReCl}_5$ in conc HCl + CsCl in conc HCl or $\text{ReCl}_5$ in $\text{SOCl}_2\text{--ICl}$ (1:3) + CsCl	16
	$[\text{ReOCl}_5]^{2-}$	$\text{Cs}^+$	$\text{ReCl}_5$ in 12 mol L <sup>-1</sup> HCl CsCl in conc HCl added after evolution of HCl ceases	16
Re(V)	$[\text{ReOCl}_5]^{2-}$	$\text{Cs}^+$	$\text{RuCl}_3$ in conc HCl + IKCl	17
Ru(IV)	$[\text{Ru}_2\text{OCl}_{10}]^{4-}$	$\text{K}^+$ , $\text{Cs}^+$		

## 2.9. Formation of the Halogen-Transition-Metal Bond

## 2.9.13. Synthesis of Complex Halo Anions of Metal Oxohalides

## 2.9.13.4. from Oxohalides

## 2.9.13.3.2. with Complex Metal Halides

Anionic  $[MX_n]^{m-}$  halo complexes are infrequently used to prepare oxohalo anions. The salt  $K_3[TiF_5O]$  is obtained by heating powdered mixtures of  $K_2[TiF_6]$ ,  $TiO_2$  and  $KF$  contained in a Pt crucible under high vacuum at  $T$  shown in Table 1<sup>1</sup>. Zirconium and hafnium hexafluorides,  $K_2[ZrF_6]$ ,  $K_2[HfF_6]$ , obtained from  $ZrOCl_2$  and  $HfOCl_2$  in  $HF$ , are used to prepare the oxytrifluoro anions  $[MF_3O]^-$  by treatment with  $KOH$ <sup>2</sup>. Another route to oxohalo anions for the group-VA metals is reacting the hexahalide salt ( $MM'X_6$ ) with antimony oxide in sealed tubes at high  $T$ <sup>3,4</sup>. The side product,  $SbCl_3$ , is removed by sublimation.

TABLE 1. PREPARATION OF COMPLEX OXOHALO ANIONS FROM HALO SALTS

Element	Anion	Cations	Reaction	Ref.
Ti(IV)	$[TiOF_5]^{3-}$	$K^+$	$K_2[TiF_6]$ , $TiO_2$ + $KF$ at 150–180°C for 12 h, then 880°C for 8 h	1
Zr(IV)	$[ZrOCl_4]^{2-}$ $[ZrOF_3]^- \cdot 2 H_2O$	$K^+$ , $Rb^+$ , $Cs^+$	$M_2[ZrCl_6] + O_2$ at 400–550°C	5
		$K^+$	$K_2[MF_6] + KF$ ( $M = Zr, Hf$ ) (boiled) + $KOH$	2
Hf(IV)	$[HfOF_5]^- \cdot 2 H_2O$	$K^+$	$K_3[VCl_6] + \frac{1}{3} Sb_2O_3$ at 340–430°C 7 h	3
V(III)	$[VOCl_4]^{3-}$	$Rb^+$	$Rb_3[VCl_6] + \frac{1}{3} Sb_2O_3$ at 350–450°C 8 h	
		$Cs^+$	$Cs_3[VCl_6] + \frac{1}{3} Sb_2O_3$ at 450–480°C 20 h	
Ta(IV)	$[TaOCl_4]^{2-}$	$K^+$ , $Rb^+$	$M_2[TaCl_6] + \frac{1}{3} Sb_2O_3$ at 280–520°C (for 10–25 h in Ar)	4
		$Cs^+$	$Cs_2[TaCl_6] + \frac{1}{3} Sb_2O_3$ at 430–580°C (for 10–25 h in Ar)	4
Mo(V)	$[MoOF_5]^{2-}$	$K^+$	$K[MoF_6] + xs KHF_2$ fused in $CO_2$	6

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## 2.9.13.4. from Oxohalides

## 2.9.13.4.1. with Neutral Oxohalides

The reaction between ionic chlorides and  $VOCl_3$  in hydrochloric acid saturated with  $HCl$  at 0°C is used to prepare salts of both  $[VOCl_4]^-$  and  $[VOCl_5]^{2-}$  (see Table 1) depending upon the cation and its concentration<sup>1–3</sup>. The  $V(IV)$  species  $VOCl_2$  is used similarly to prepare  $M'[VOCl_3] \cdot x H_2O$  or  $M_2[VOCl_4] \cdot x H_2O$  salts<sup>2,4,5</sup>. Pale yellow salts of Nb(V),  $M_2[NbOCl_5]$  ( $M = [NH_4]^+$ ,  $K^+$ ,  $Rb^+$ ,  $Cs^+$ ) are obtained in aq  $HCl$

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## 2.9. Formation of the Halogen-Transition-Metal Bond

## 2.9.13. Synthesis of Complex Halo Anions of Metal Oxohalides

## 2.9.13.4. from Oxohalides

## 2.9.13.3.2. with Complex Metal Halides

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TABLE 1. PREPARATION OF COMPLEX OXOHALO ANIONS FROM HALO SALTS

Element	Anion	Cations	Reaction	Ref.
Ti(IV)	$[\text{TiOF}_5]^{3-}$	$\text{K}^+$	$\text{K}_2[\text{TiF}_6]$ , $\text{TiO}_2$ + $\text{KF}$ at 150–180°C for 12 h, then 880°C for 8 h	1
Zr(IV)	$[\text{ZrOCl}_4]^{2-}$ $[\text{ZrOF}_3]^- \cdot 2 \text{H}_2\text{O}$	$\text{K}^+$ , $\text{Rb}^+$ , $\text{Cs}^+$	$\text{M}_2[\text{ZrCl}_6] + \text{O}_2$ at 400–550°C	5
		$\text{K}^+$	$\text{K}_2[\text{MF}_6] + \text{KF}$ ( $\text{M} = \text{Zr}, \text{Hf}$ ) (boiled) + $\text{KOH}$	2
Hf(IV)	$[\text{HfOF}_3]^- \cdot 2 \text{H}_2\text{O}$	$\text{K}^+$	$\text{K}_3[\text{VCl}_6] + \frac{1}{3} \text{Sb}_2\text{O}_3$ at 340–430°C 7 h	3
V(III)	$[\text{VOCl}_4]^{3-}$	$\text{Rb}^+$	$\text{Rb}_3[\text{VCl}_6] + \frac{1}{3} \text{Sb}_2\text{O}_3$ at 350–450°C 8 h	
Ta(IV)	$[\text{TaOCl}_4]^{2-}$	$\text{Cs}^+$	$\text{Cs}_3[\text{VCl}_6] + \frac{1}{3} \text{Sb}_2\text{O}_3$ at 450–480°C 20 h	4
		$\text{K}^+$ , $\text{Rb}^+$	$\text{M}_2[\text{TaCl}_6] + \frac{1}{3} \text{Sb}_2\text{O}_3$ at 280–520°C (for 10–25 h in Ar)	
Mo(V)	$[\text{MoOF}_5]^{2-}$	$\text{Cs}^+$	$\text{Cs}_2[\text{TaCl}_6] + \frac{1}{3} \text{Sb}_2\text{O}_3$ at 430–580°C (for 10–25 h in Ar)	4
		$\text{K}^+$	$\text{K}[\text{MoF}_6] + \text{xs KHF}_2$ fused in $\text{CO}_2$	6

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## 2.9.13.4.1. with Neutral Oxohalides

The reaction between ionic chlorides and  $\text{VOCl}_3$  in hydrochloric acid saturated with  $\text{HCl}$  at 0°C is used to prepare salts of both  $[\text{VOCl}_4]^-$  and  $[\text{VOCl}_5]^{2-}$  (see Table 1) depending upon the cation and its concentration<sup>1–3</sup>. The V(IV) species  $\text{VOCl}_2$  is used similarly to prepare  $\text{M}'[\text{VOCl}_3] \cdot x \text{H}_2\text{O}$  or  $\text{M}_2[\text{VOCl}_4] \cdot x \text{H}_2\text{O}$  salts<sup>2,4,5</sup>. Pale yellow salts of Nb(V),  $\text{M}_2[\text{NbOCl}_5]$  ( $\text{M} = [\text{NH}_4]^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ) are obtained in aq  $\text{HCl}$

TABLE 1. PREPARATION OF COMPLEX OXOHALO ANIONS FROM OXY HALIDES

Element	Anion	Cations	Reaction	Ref.
V(V)	$[\text{VOCl}_5]^{2-}$	$\text{K}^+, \text{Cs}^+, \text{Rb}^+, [\text{NH}_4]^+, [\text{quinH}]^+$	$\text{VOCl}_3$ in HCl satd with HCl gas + M'Cl at $0^\circ\text{C}$ (1:2)	2
	$[\text{VOCl}_5]^{2-}$	$\text{Cs}^+, \text{Rb}^+, [\text{Et}_4\text{N}]^+$	$\text{VOCl}_3 + \text{M}'\text{Cl}$ (1:2) in liq $\text{SO}_2$ at $0^\circ\text{C}$	1, 15
	$[\text{VOCl}_4]^-$	$[\text{pyH}]^+, [\text{Ph}_4\text{As}]^+, [\text{quinH}]^+$	$\text{VOCl}$ in $\text{EtOH-HCl} + \text{RCl}$ in HCl at $0^\circ\text{C}$	1, 3
	$[\text{VOCl}_4]^-$	$[\text{PCl}_4]^+$	$\text{VOCl}_3 + \text{PCl}_5$ (1:1) in dry $\text{CH}_2\text{Cl}_2$ at RT	16
V(IV)	$[\text{VOCl}_4]^{2-}$	$[\text{Et}_2\text{NH}_2]^{2+}, [\text{pyH}]^+, [\text{quinH}]^+, [\text{Et}_4\text{N}]^+$	$\text{VOCl}_2 + [\text{Et}_2\text{NH}_2]\text{Cl}$ (1:2)	1
	$[\text{VOCl}_4]^{2-} \cdot x \text{H}_2\text{O}$	$\text{K}^+$	$\text{VOCl}_2 + \text{KOH}$ in $\text{EtOH}$ satd with HCl at $0^\circ\text{C}$	4
	$[\text{VOCl}_4]^{2-} \cdot x \text{H}_2\text{O}$	$\text{Cs}^+$	$\text{VOCl}_2 + \text{CsCl}$ satd with HCl at $0^\circ\text{C}$	4
	$[\text{VOBr}_4]^{2-}$	$[\text{pyH}]^+, [\text{quinH}]^+, [\text{Et}_4\text{N}]^+, [\text{pyH}]^+$	$\text{VOCl}_2$ in $\text{EtOH} + [\text{pyH}]\text{Cl}$ or $[\text{quinH}]\text{Cl}$ $\text{VOBr}_3 + \text{RBr}$ in $\text{CH}_3\text{CN}$ at $0^\circ\text{C}$ for 2 h	5
Nb(V)	$[\text{NbO}_2\text{F}_2]^-$	$\text{Na}^+$	$\text{NbO}_2\text{F} + \text{NaF}$ (1:1) $600^\circ\text{C}$ for 1 d	17, 18
	$[\text{NbOCl}_4]^-$	$[\text{pyH}]^+, [\text{quinH}]^+$	$\text{NbOCl}_3 + [\text{ArH}]\text{Cl}$ (aq) in HCl gas satd HCl	19
	$[\text{NbOCl}_3]^{2-}$	$[\text{pyH}]^+, [\text{quinH}]^+ (= [\text{ArH}]\text{Cl})$	$\text{NbOCl}_3 + [\text{ArH}]$ in ethanolic HQ satd with HCl gas	6
Cr(VI)	$[\text{CrO}_2\text{F}_4]^{2-}$	$\text{Na}^+, \text{K}^+, \text{Cs}^+, \text{Ca}^{2+}, \text{Mg}^{2+}$	$\text{CrO}_2\text{F}_2 + \text{MF}$ or $\text{MF}_2$	20
	$[\text{CrO}_3\text{Cl}]^-$	$\text{K}^+$	$\text{K}_2\text{CrO}_4 + \text{CrO}_2\text{Cl}_2$ at $90-100^\circ\text{C}$ for 1 h.	21
Cr(V)	$[\text{CrOCl}_4]^-$	$[\text{Ph}_4\text{E}]^+$	$\text{CrO}_2\text{Cl}_2$ in glacial acetic acid + dry HCl gas at $0^\circ\text{C} + [\text{Ph}_4\text{E}]\text{Cl}$	7
W(VI)	$[\text{WOX}_3]^- (\text{X} = \text{Cl}, \text{Br})$	$[\text{Et}_4\text{N}]^+, [\text{quinH}]^+$	$\text{WOX}_4 + \text{RX}$ in $\text{CHCl}_3$	8
Mo(V)	$[\text{WOCl}_5]^-$	$[\text{Ph}_4\text{P}]^+$	$\text{WOCl}_4 + [\text{Ph}_4\text{P}]\text{Cl}$ in $\text{SOCl}_2$	9
	$[\text{MoOCl}_5]^{2-}$	$\text{Cs}^+$	$\text{MoOCl}_3 + \text{HCl}$ (10 mol $\text{L}^{-1}$ ) + $\text{CsCl}$	22
Re(VII)	$[\text{MoOCl}_4\text{Br}]^{2-}$	$[\text{Et}_4\text{N}]^+$	$\text{MoOCl}_4 + [\text{Et}_4\text{N}]\text{Br}$ (1:3) in $\text{CH}_2\text{Cl}_2$	23
	$[\text{ReO}_3\text{Cl}_3]^{2-}$	$[\text{Me}_4\text{N}]^+, [\text{Et}_4\text{N}]^+, [\text{pyH}]^+, [\text{quinH}]^+$	$\text{ReO}_3\text{Cl}$ in $\text{CCl}_4\text{-CHCl}_3\text{-CH}_2\text{Cl}_2 + \text{RCl}$ (1:2)	24
Re(VI)	$[\text{ReOX}_5]^-$	$[\text{Ph}_4\text{E}]^+, [\text{Et}_4\text{N}]^+$	$\text{ReOX}_4$ in $\text{CHCl}_3 + [\text{R}_4\text{N}]\text{Cl}$	10, 11
	$[\text{ReOCl}_5]^-$	$\text{Cs}^+$	$\text{ReOCl}_4$ in $\text{SOCl}_2 + \text{CsCl}$	12

saturated with gaseous HCl, but analogous reactions with py[HCl] and quin[HCl] lead to salts of  $[\text{NbOCl}_4]^-$ . The complexes  $[\text{pyH}]_2[\text{NbOCl}_5]$  and  $[\text{quinH}]_2[\text{NbOCl}_5]$  are obtained<sup>6</sup> from ethanolic HCl.

Chromyl chloride,  $\text{CrO}_2\text{Cl}_2$ , can be reduced in glacial acetic acid by anhyd HCl at  $0^\circ\text{C}$  to yield the Cr(V) anion<sup>7</sup>  $[\text{CrOCl}_4]^-$ .

Salts of  $[\text{WOCl}_5]^-$  are obtained by treating solutions of  $\text{WOCl}_4$  in  $\text{CHCl}_3$  or  $\text{SOCl}_2$  with the appropriate cation<sup>8,9</sup>. The dehydrating properties of thionyl chloride make it a useful solvent for this reaction as the W(VI) salts formed decompose to tungsten blues if left in contact with air. The orange salts can be precipitated from thionyl chloride solution by addition of hydrocarbon solvents such as 2-methylbutane. The oxopentachloride  $[\text{Ph}_4\text{P}][\text{WOCl}_5]$  is converted to the oxobromide by passing HBr through solutions of the chloride in dry  $\text{CH}_2\text{Cl}_2$ . Salts of  $[\text{ReOCl}_5]^-$  can also be prepared from  $\text{ReOCl}_4$  by reaction with the cation chloride in  $\text{SOCl}_2$  or dry  $\text{CHCl}_3$ <sup>10-12</sup>.

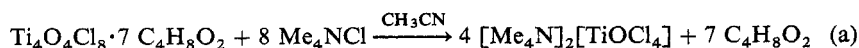
Cation exchange is used to prepare different salts of oxy halides, e.g., in the preparation of  $[\text{Et}_4\text{N}]_2[\text{VOCl}_4]$  and  $[\text{NH}_4]_2[\text{VOCl}_4]$  from solutions of  $\text{M}_2[\text{VOCl}_4]$  and  $[\text{Et}_4\text{N}]\text{Cl}$  or  $[\text{NH}_4]\text{Cl}$  in  $\text{CH}_3\text{CN}$ <sup>13</sup>. Cation-exchange resins can be employed, e.g., in the formation of  $[\text{NH}_4]_2[\text{VO}_2\text{F}_3]$  from  $\text{K}_2[\text{VO}_2\text{F}_3]$  on a resin in the  $[\text{NH}_4]^+$  form<sup>14</sup>.

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#### 2.9.13.4.2. with Anionic Oxohalides.

Salts of  $[\text{TiOCl}_4]^{2-}$  are best prepared by reaction of a Ti oxy halide adduct with an ionic chloride<sup>1,2</sup>:



## 2.9. Formation of the Halogen-Transition-Metal Bond

## 2.9.13. Synthesis of Complex Halo Anions of Metal Oxohalides

## 2.9.13.4. from Oxohalides

saturated with gaseous HCl, but analogous reactions with py[HCl] and quin[HCl] lead to salts of  $[\text{NbOCl}_4]^-$ . The complexes  $[\text{pyH}]_2[\text{NbOCl}_5]$  and  $[\text{quinH}]_2[\text{NbOCl}_5]$  are obtained<sup>6</sup> from ethanolic HCl.

Chromyl chloride,  $\text{CrO}_2\text{Cl}_2$ , can be reduced in glacial acetic acid by anhyd HCl at  $0^\circ\text{C}$  to yield the  $\text{Cr(V)}$  anion<sup>7</sup>  $[\text{CrOCl}_4]^-$ .

Salts of  $[\text{WOCl}_5]^-$  are obtained by treating solutions of  $\text{WOCl}_4$  in  $\text{CHCl}_3$  or  $\text{SOCl}_2$  with the appropriate cation<sup>8,9</sup>. The dehydrating properties of thionyl chloride make it a useful solvent for this reaction as the  $\text{W(VI)}$  salts formed decompose to tungsten blues if left in contact with air. The orange salts can be precipitated from thionyl chloride solution by addition of hydrocarbon solvents such as 2-methylbutane. The oxopentachloride  $[\text{Ph}_4\text{P}][\text{WOCl}_5]$  is converted to the oxobromide by passing  $\text{HBr}$  through solutions of the chloride in dry  $\text{CH}_2\text{Cl}_2$ . Salts of  $[\text{ReOCl}_5]^-$  can also be prepared from  $\text{ReOCl}_4$  by reaction with the cation chloride in  $\text{SOCl}_2$  or dry  $\text{CHCl}_3$ <sup>10-12</sup>.

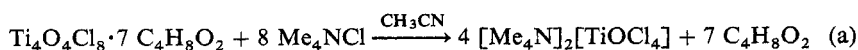
Cation exchange is used to prepare different salts of oxy halides, e.g., in the preparation of  $[\text{Et}_4\text{N}]_2[\text{VOCl}_4]$  and  $[\text{NH}_4]_2[\text{VOCl}_4]$  from solutions of  $\text{M}'_2[\text{VOCl}_4]$  and  $[\text{Et}_4\text{N}]\text{Cl}$  or  $[\text{NH}_4]\text{Cl}$  in  $\text{CH}_3\text{CN}$ <sup>13</sup>. Cation-exchange resins can be employed, e.g., in the formation of  $[\text{NH}_4]_2[\text{VO}_2\text{F}_3]$  from  $\text{K}_2[\text{VO}_2\text{F}_3]$  on a resin in the  $[\text{NH}_4]^+$  form<sup>14</sup>.

(E.M. PAGE, D.A. RICE)

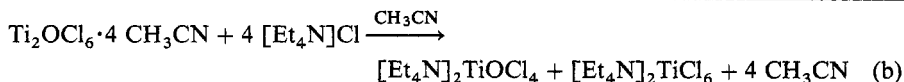
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18. D. Nicholls, K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 2747 (1973).
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## 2.9.13.4.2. with Anionic Oxohalides.

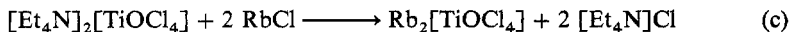
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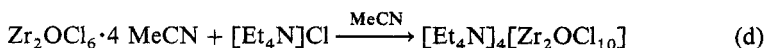




The salts formed undergo cation exchange in liq  $\text{SO}_2$  at  $0^\circ\text{C}$  to give alkali-metal oxotetrachlorotitanates(IV):



Complex oxohalides of Zr are also prepared from methyl cyanide adducts of zirconium oxohalides<sup>3</sup>:



Reaction of the  $\text{VOCl}_2 \cdot 2 \text{C}_4\text{H}_8\text{O}_2$  and  $\text{VOCl}_2 \cdot 2 \text{CH}_3\text{CN} \cdot 0.5 \text{C}_4\text{H}_8\text{O}_2$  adducts of vanadyl chloride, with alkali-metal chlorides in liq  $\text{SO}_2$  at  $-15^\circ\text{C}$  leads to salts of  $[\text{VOCl}_4]^-$  when the solid precipitate is heated at  $150^\circ\text{C}$  under vacuum<sup>4,5</sup>. Salts such as  $\text{M}_2[\text{VOCl}_4]$  ( $\text{M} = [\text{pyH}]^+$ ,  $[\text{Et}_4\text{N}]^+$ ,  $[\text{Ph}_4\text{As}]^+$ ) are prepared by reaction of  $\text{VOCl}_2 \cdot 2 \text{MeCN}$  with  $\text{RCl}$  in  $\text{CH}_3\text{CN}$  at 243 K. The salts precipitate as green solids after several days<sup>5</sup>. The adduct  $[\text{enH}_2][\text{ReOCl}_5]$  is prepared from  $\text{trans}[\text{ReO}_2\text{en}_2]\text{Cl}$  in  $10 \text{ mol L}^{-1} \text{HCl}$ , and when heated with  $\text{CsCl}$  in  $5 \text{ mol L}^{-1} \text{HCl}$  crystals of  $\text{Cs}_2[\text{ReOCl}_5]$  are obtained<sup>6</sup>.

(E.M. PAGE, D.A. RICE)

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## 2.9.14. Synthesis of Metal Sulfido-, Seleno- and Tellurohalides

Transition metal oxohalides are better known than their S, Se and Te counterparts. However, although for some metallic elements the pure oxohalides have eluded synthesis, or at times claimed compounds have been poorly characterized. However, other chalcogenide halides have been isolated, e.g., with Cu, for which structures of  $\text{CuTe}_2\text{X}$  ( $\text{X} = \text{Cl, Br or I}$ ) and  $\text{CuTeX}$  ( $\text{X} = \text{Cl, Br or I}$ ) and the synthesis of  $\text{CuSe}_2\text{Cl}$  and  $\text{CuSe}_3\text{X}$  ( $\text{X} = \text{Br or I}$ ) are available (see §2.9.14.3).

Reviews of the chalcogenide halides relevant to this section with emphasis on the preparation of the transition element species<sup>1,2</sup>, the lanthanide chemistry<sup>2,3</sup> and the p-block elements are available.

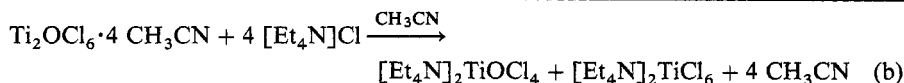
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## 2.9. Formation of the Halogen-Transition-Metal Bond

235

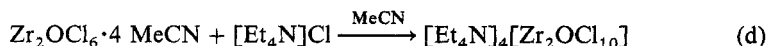
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Reviews of the chalcogenide halides relevant to this section with emphasis on the preparation of the transition element species<sup>1,2</sup>, the lanthanide chemistry<sup>2,3</sup> and the p-block elements are available.

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## 2.9. Formation of the Halogen-Transition-Metal Bond

## 2.9.14. Synthesis of Metal Sulfido-, Seleno- and Tellurohalides

## 2.9.14.1. from the Metals

**2.9.14.1. from the Metals****2.9.14.1.1. To Form Group-IIIa and Lanthanide Compounds.**

Many of these compounds exist in more than one solid phase, and so the conditions of preparation (T, pressure, reaction time, etc.) are particularly important (Table 1)<sup>1</sup>.

TABLE 1. KNOWN METAL CHALCOGENIDE HALIDES

Metal	Product	Ref.
Y	YSF	2
	YSBr	
La	LaSX (X = Cl, Br or I)	3
	LaSF	2, 4
Ce	CeSX (X = Cl, Br or I)	3
	CeSF	4
Pr	PrSBr	5
Nd	NdSBr	5
Sm	SmSBr	5
	SmSI	2
Eu	EuSF	4
Gd	GdSBr	5
	GdSI	2
Tb	TbSBr	5
Dy	DySBr	5
Ho	HoSF	2
	HoSBr	5
Er	ErSF	2
	ErSBr	5
Yb	YbSF	2
	YbSBr	5
Lu	LuSF	2
	LuSBr	5

The metal is successively reacted with the halogen and then with sulfur vapor, the reactants being contained in individual ampoules inside a sealed glass tube. In the preparation of sulfidofluorides the metal trifluoride can be used rather than the metal<sup>1</sup>.

(E.M. PAGE, D.A. RICE)

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**2.9.14.1.2. To Form the Transition-Metal Compounds.**

The sulfido-, selenido- and telluridohalides of the transition metals prepared directly from the metals are listed in Table 1. Some of the preparations are not feasible for the production of large quantities of materials (e.g., the reactions between SF<sub>6</sub> and W in a

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Nd	NdSBr	5
Sm	SmSBr	5
	SmSI	2
Eu	EuSF	4
Gd	GdSBr	5
	GdSI	2
Tb	TbSBr	5
Dy	DySBr	5
Ho	HoSF	2
	HoSBr	5
Er	ErSF	2
	ErSBr	5
Yb	YbSF	2
	YbSBr	5
Lu	LuSF	2
	LuSBr	5

The metal is successively reacted with the halogen and then with sulfur vapor, the reactants being contained in individual ampoules inside a sealed glass tube. In the preparation of sulfidofluorides the metal trifluoride can be used rather than the metal<sup>1</sup>.

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TABLE 1. PREPARATION OF TRANSITION-METAL SPECIES DIRECTLY FROM THE METAL

Element	Product	Reactants	Ref.
Nb	NbS <sub>2</sub> Cl <sub>2</sub>	Nb + S + NbCl <sub>5</sub>	5-7
		Nb + S <sub>2</sub> Cl <sub>2</sub>	6, 7
		Nb + S + NbCl <sub>4</sub> (480-475°C)	4
	NbSe <sub>2</sub> Cl <sub>2</sub>	Nb + Se + NbCl <sub>5</sub>	6, 7
		Nb + Se + NbCl <sub>4</sub> (410-405°C)	4
	NbY <sub>2</sub> Br <sub>2</sub> (Y = S or Se)	Nb + Y + Br <sub>2</sub>	6
		Nb + Y + NbBr <sub>4</sub> (460-480°C)	6
	NbY <sub>2</sub> I <sub>2</sub> (Y = S or Se)	Nb + Y + I <sub>2</sub>	6
		Nb + Y + NbI <sub>4</sub> (380-470°C)	4
Mo	MoS <sub>2</sub> Cl <sub>2</sub>	Mo + S <sub>2</sub> Cl <sub>2</sub> (510-515°C)	4, 8
	MoS <sub>2</sub> Br <sub>2</sub>	Mo + S <sub>2</sub> Br <sub>2</sub> (500°C)	8
	MoSX (X = Cl, Br or I)	Mo + S + [Mo <sub>6</sub> X <sub>8</sub> ]X <sub>4</sub> (1000°C) (appropriate molar ratio)	9, 10
	Mo <sub>6</sub> S <sub>6</sub> X <sub>2</sub>	[MoX <sub>8</sub> ]X <sub>4</sub> + Mo + S (1050°C) (appropriate molar ratio)	11
W	WF <sub>2</sub> S	W + SF <sub>6</sub> in mass spectrometer	1
	WF <sub>3</sub> S		
	WF <sub>2</sub> OS		
	W <sub>2</sub> S <sub>3</sub> Cl <sub>4</sub>		
Au	AuSeBr	Au + Se + Br <sub>2</sub> (in anhyd HBr at 230°C for 9 d)	13
	AuSeCl	Au + Se + Cl <sub>2</sub> (in anhyd HCl at 200°C for 12 d)	13, 14
	AuTeI	Au + Te + I <sub>2</sub> (in HI heated to 400°C allowed to cool to 150°C over 10 d)	13, 15
	AuTe <sub>2</sub> I	as above omitting I <sub>2</sub>	3, 15, 16
	AuTe <sub>2</sub> Cl	Au + Te + Cl <sub>2</sub> (in anhyd HCl heated to 400°C allowed to cool to 100°C over 10 d)	3, 15, 16
	AuTe <sub>2</sub> Br	Au + Te + Br <sub>2</sub> (in anhyd HBr heated to 350°C allowed to cool to 150°C over 10 d)	3, 15

mass spectrometer<sup>1</sup>). The routes involve high temperatures and sealed systems in which high pressures are attained. **CAUTION is required in these experiments**, and the details in the literature should be examined; e.g., in the hydrothermal synthesis of Cu and Au compounds, an autoclave is used and a pressure of approximately  $2.5 \times 10^8$  Pa is developed at the high temperature used. **Explosions of the glass ampule in which the reactants are sealed can be prevented<sup>2,3</sup>.**

The difficulties in the reactions under discussion here are highlighted by the preparation of the niobium(IV) compounds NbY<sub>2</sub>X<sub>2</sub> (Y = S or Se, X = Cl, Br or I). In the preparation of NbSe<sub>2</sub>I<sub>2</sub> a grey coating forms on the surface of the crystals<sup>4</sup> which is NbOI obtained as an impurity. Poor agreement between the x-ray powder pattern<sup>4</sup> and the single-crystal data<sup>5</sup> for NbS<sub>2</sub>Cl<sub>2</sub> is attributed to other ternary compounds present in the powdered NbS<sub>2</sub>Cl<sub>2</sub>, and reactions leading to NbY<sub>2</sub>X<sub>2</sub> produce other phases, e.g., Nb<sub>3</sub>Se<sub>5</sub>Cl<sub>7</sub> from the NbSe<sub>2</sub>Cl<sub>2</sub> preparation<sup>4</sup>.

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### 2.9.14.2. from the Metal Chalcogenides.

Unlike oxohalides, which can be synthesized from the metal oxides (with the exception of f-block species), few sulfido, selenido or tellurido species are synthesized from the metal chalcogenides.

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Compounds that are claimed to be synthesized from transition-metal chalcogenides are listed in Table 2. Some are well characterized and are the subject of single-crystal x-ray studies, but others are at best poorly characterized. The uncertain nature of some is illustrated by a consideration of group VIIa. The Mn compounds  $\gamma$ -MnSCl<sub>2</sub>,  $\gamma$ -MnSBr and  $\gamma$ -MnSI and  $\alpha$ -MnSCl<sub>2</sub>,  $\alpha$ -MnSBr and  $\alpha$ -MnSI are isolated by heating either  $\gamma$ -MnS or  $\alpha$ -MnS with the appropriate Mn halide. Although these compounds and the related

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ELEMENT SPECIES PREPARED FROM METAL  
CHALCOGENIDES

Reactants: MF <sub>3</sub> + M <sub>2</sub> Y <sub>3</sub> (Y = S or Se)			
Compounds	Ref.	Compounds	Ref.
YSeF	2	La <sub>2</sub> SeF <sub>4</sub>	5
YSF	2, 3	Ce <sub>2</sub> SeF <sub>4</sub>	5
LaSF	3, 4	Pr <sub>2</sub> SeF <sub>4</sub>	5
LaSeF	5	Nd <sub>2</sub> SeF <sub>4</sub>	5
CeSeF	5	ErSeF	6
PrSeF	5	TmSeF	6
NdSeF	5	YbSeF	6
SmSeF	5	LuSeF	6
GdSeF	5		

## 2.9. Formation of the Halogen-Transition-Metal Bond

## 2.9.14. Synthesis of Metal Sulfido-, Seleno- and Tellurohalides

## 2.9.14.2. from the Metal Chalcogenides.

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LaSeF	5	Nd <sub>2</sub> SeF <sub>4</sub>	5
CeSeF	5	ErSeF	6
PrSeF	5	TmSeF	6
NdSeF	5	YbSeF	6
SmSeF	5	LuSeF	6
GdSeF	5		

TABLE 2. PREPARATION OF TRANSITION-METAL SPECIES DIRECT FROM CHALCOGENIDE

Element	Product	Reactant	Ref.
Cr	CrSBr	$\text{Cr}_2\text{S}_3 + \text{CrBr}_3$ at $870^\circ\text{C}$	7
	CrSeI	$\text{CrSe} + \text{CrI}_3$ at $400^\circ\text{C}$	7
	$\text{CrSi}_{0.83}$	$\text{CrS} + \text{CrI}_3$ at $420^\circ\text{C}$	7
	$\text{CrTeI}_{0.73}$	$\text{CrTe} + \text{CrI}_3$ at $315^\circ\text{C}$	7
Mo	$\text{MoSCl}_2$	$\text{MoS}_2 + \text{Cl}_2$ at $400^\circ\text{C}$	8
	$\text{MoTe}_2\text{Br}_{10}$	$\text{MoTe}_2 + \text{Br}_2$ at RT	9
	$\text{Mo}_2\text{S}_4\text{Br}_3$	$\text{MoS}_3 + \text{S}_2\text{Br}_2$ at $420^\circ\text{C}$	10
	$\text{Mo}_2\text{S}_4\text{Cl}_5$	$\text{MoS}_3 + \text{S}_2\text{Cl}_2$ at $350\text{--}400^\circ\text{C}$	10
Re	$\text{ReSCl}_2$	$\text{ReS}_2 + \text{Cl}_2$ at $400\text{--}450^\circ\text{C}$	11
	$\text{ReSeCl}_2$	$\text{ReSe}_2 + \text{Cl}_2$ at $480\text{--}500^\circ\text{C}$	12
	$\text{Re}_2\text{S}_3\text{Cl}_4$	$\text{Re}_2\text{S}_7 + \text{Cl}_2\text{--CO}_2$ (1:5) at $120^\circ\text{C}$	13
	$\text{Re}_3\text{Se}_2\text{Cl}_5$	3 $\text{ReSe}_2 + 2 \text{Re}_3\text{Cl}_9$ at $700\text{--}750^\circ\text{C}$ for 10–15 h	12
	$\text{Re}_3\text{Se}_2\text{Br}_5$	3 $\text{ReSe}_2 + 2 \text{Re}_3\text{Br}_9$ at $700\text{--}750^\circ\text{C}$	12
		$\text{ReSe}_2 + \text{Br}_2$ at $580^\circ\text{C}$	14
Ag	$\text{Re}_3\text{Te}_2\text{Br}_5$	$\text{Re}_2\text{Te}_5 + \text{Br}_2$ at $155\text{--}160^\circ\text{C}$	12
	$\text{Ag}_3\text{SBr}$	$\text{Ag}_2\text{S} + \text{AgBr}$ at $280^\circ\text{C}$	15
	$\text{Ag}_3\text{SI}$	$\text{Ag}_2\text{S} + \text{AgI}$ at $235^\circ\text{C}$ for 100 h	15
		$\text{Ag}_2\text{S} + \text{AgI} + \text{S}$ at $550^\circ\text{C}$ . Enough S must be present to give a pressure of 1 atm at $550^\circ\text{C}$ in the sealed tube	16
Ag	$\text{Ag}_3\text{TeBr}$		17
	$\text{Ag}_6\text{TeBr}_4$	These species are prepared by heating	18
	$\text{Ag}_5\text{Te}_2\text{Cl}$	stoichiometric quantities of $\text{Ag}_2\text{Te}$ and $\text{AgX}$	19

selenides are examined by density, refractive index and x-ray powder measurements, they remain largely uncharacterized<sup>1</sup>. Similarly, in view of the difficulties experienced in isolating  $\text{ReOCl}_3$  (although its adducts are well characterized) many reports concerning Re sulfido- or selenido halides have to be treated with caution.

The routes involving sulfides and selenides are best avoided if alternative routes exist. These chalcogenides are often unreactive and frequently impure. Also, direct chlorination of a sulfide or selenide frequently yields  $\text{S}_2\text{Cl}_2$  or  $\text{Se}_2\text{Cl}_2$  and the metal halide unless great care is taken.

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### 2.9.14.3. from Transition-Metal Halides with Chalcogens.

Synthetic routes to the chalcogenide halides via the reaction of transition-metal halides with chalcogens involve reactants that are well characterized and easy to purify, but species such as  $S_2Cl_2$  can be produced which themselves react with transition-metal halides to give chalcogenide halides. However, unlike, e.g., the chlorination of chalcogenides discussed in §2.9.14.1 and §2.9.14.2, the stoichiometry of the reaction can be controlled.

Chalcogenide halides prepared from the chalcogen/transition metal halide are listed in Table 1.

Some of the syntheses listed require further investigation; e.g., attempts to repeat the synthesis of  $NbS_2Cl$  and  $TaS_2Cl_2$  from the pentahalide and sulfur<sup>1</sup> show that these routes are not straightforward<sup>2</sup>. Also, the Mo trihalides react with chalcogens to synthesize compounds of stoichiometry  $Mo_3Y_7X_4$  ( $Y = S$  or  $Se$ ,  $X = Br$  or  $Cl$ ). The "d" spacings of these compounds<sup>3</sup> correspond not with the data for  $Mo_3S_7Cl_4$ <sup>4</sup> but with those of  $Mo_2S_5Cl_3$  instead<sup>5,6</sup>. The nature of  $Mo_3S_7Cl_4$  is revealed by single-crystal x-ray study<sup>7</sup>.

The cluster Mo halides,  $[Mo_6X_8]X_4$ , yield mixtures when treated with S or Se. The product depends upon the molar ratio of the reactants and the temperature<sup>8-10</sup>. For  $WScI_4$  the synthesis from  $WCl_6$  and S is the best route<sup>11</sup>. Commercial samples of  $WCl_6$  should be resublimed in  $Cl_2$  or  $WCl_6$  should be synthesized from the elements. This procedure eliminates contamination by  $WOCl_4$  found in commercial  $WCl_6$ .

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TABLE 1. THE PREPARATION OF CHALCOGENIDE HALIDES FROM THE REACTION OF METAL HALIDES AND A CHALCOGEN

Halide	Product	Reaction conditions	Ref.
NbCl <sub>5</sub>	NbS <sub>2</sub> Cl	NbCl <sub>5</sub> and S (1:8 molar ratio) in benzene	1
TaCl <sub>5</sub>	TaS <sub>2</sub> Cl <sub>2</sub>	TaCl <sub>5</sub> and S (1:8 molar ratio) in benzene	1
[Mo <sub>6</sub> I <sub>8</sub> ]I <sub>4</sub>	Mo <sub>2</sub> S <sub>5</sub> I <sub>3</sub>	[Mo <sub>6</sub> I <sub>8</sub> ]I <sub>4</sub> + S at 300°C	5
[Mo <sub>6</sub> Br <sub>8</sub> ]Br <sub>4</sub>	Mo <sub>2</sub> S <sub>5</sub> Br <sub>3</sub>	[Mo <sub>6</sub> Br <sub>8</sub> ]Br <sub>4</sub> + S at 350–400°C	5, 13
[Mo <sub>6</sub> Cl <sub>8</sub> ]Cl <sub>4</sub>	Mo <sub>2</sub> S <sub>5</sub> Cl <sub>3</sub>	[Mo <sub>6</sub> Cl <sub>8</sub> ]Cl <sub>4</sub> + S at 350–400°C.	5, 13
MoCl <sub>3</sub>	Mo <sub>3</sub> S <sub>7</sub> Cl <sub>4</sub>	MoCl <sub>3</sub> + S (1:10 molar ratio) at 450°C either with or without S <sub>2</sub> Cl <sub>2</sub> as solvent	4, 6
MoCl <sub>3</sub>	Mo <sub>3</sub> Se <sub>7</sub> Cl <sub>4</sub>	MoCl <sub>3</sub> + Se (molar ratio 1:10) at 400°C for 1 d	4
[Mo <sub>6</sub> Br <sub>8</sub> ]Br <sub>4</sub>	Mo <sub>3</sub> S <sub>7</sub> Br <sub>4</sub>	[Mo <sub>6</sub> Br <sub>8</sub> ]Br <sub>4</sub> + S (molar ratio 1:5) at 420°C for 10 h	14
MoBr <sub>3</sub>	Mo <sub>3</sub> S <sub>7</sub> Br <sub>4</sub>	MoBr <sub>3</sub> + S (molar ratio 1:5) at 360°C for 5 h	14
[Mo <sub>6</sub> Br <sub>8</sub> ]Br <sub>4</sub>	Mo <sub>3</sub> Se <sub>7</sub> Br <sub>4</sub>	[Mo <sub>6</sub> Br <sub>8</sub> ]Br <sub>4</sub> + Se (molar ratio 1:5) at 400°C for 10 h	14
MoBr <sub>3</sub>	Mo <sub>3</sub> Br <sub>4</sub> Se <sub>7</sub>	MoBr <sub>3</sub> + Se (molar ratio 1:5) at 340°C for 10 h	14
Wf <sub>6</sub>	WF <sub>4</sub> S	WF <sub>6</sub> + S	21
	WF <sub>4</sub> Se	WF <sub>6</sub> + Se	21
WCl <sub>6</sub>	WSCl <sub>4</sub>	WCl <sub>6</sub> + S (1:3 molar ratio) 170°C for 8 h	11
Re <sub>3</sub> Cl <sub>9</sub>	ReSCl <sub>2</sub>	Re <sub>3</sub> Cl <sub>9</sub> + S	15
Re <sub>3</sub> Cl <sub>9</sub>	ReSeCl <sub>2</sub>	Re <sub>3</sub> Cl <sub>9</sub> + Se	15
Re <sub>3</sub> Br <sub>9</sub>	ReSBr <sub>2</sub>	Re <sub>3</sub> Br <sub>9</sub> + S	15
Re <sub>3</sub> Br <sub>9</sub>	ReSeBr <sub>2</sub>	Re <sub>3</sub> Br <sub>9</sub> + Se	15
ReCl <sub>5</sub>	ReSCl <sub>4</sub>	2 ReCl <sub>5</sub> + 4 S 125°C	16
	Re <sub>2</sub> S <sub>3</sub> Cl <sub>4</sub>	2 ReCl <sub>5</sub> + 4 S 160°C	
	ReSCl <sub>2</sub>	2 ReCl <sub>5</sub> + 4 S 270°C	
ReF <sub>6</sub>	ReF <sub>4</sub> S	ReF <sub>6</sub> + S at 300°C	21
PdI <sub>2</sub>	Pd <sub>2</sub> SeI <sub>3</sub>	PdI <sub>2</sub> and Se with iodine present at 250°C	17
CuX	CuTe <sub>2</sub> X	An excess of CuX (15 g) with Te (5 g) in presence of HX heated to 350–440°C and allowed to cool to 150°C over 3 d	12, 18, 19
	CuTeX	As above but with CuX (20 g) and Te (1 g)	
CuCl	CuSe <sub>2</sub> Cl	CuCl (15 g) + Se (5 g) in presence of HCl. heated to 350°C and allowed to cool to 150°C over 10 d	12, 18, 19
CuBr	CuSe <sub>3</sub> Br	CuBr (15 g) + Se (5 g) in presence of HBr heated to 340°C and allowed to cool to 150°C	12, 18, 19
CuI	CuSe <sub>3</sub> I	CuI (10 g) + Se (5 g) in the presence of HI. heated to 390°C and allowed to cool to 200°C	12, 18, 19

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#### 2.9.14.4. from Transition-Metal Halides with Main-Group Chalcogenides

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From Table 1 it is apparent that sulfides and selenides of B and Sb are used more frequently than those of As. The reason is illustrated by attempts at preparing NbSCl<sub>2</sub> using NbCl<sub>5</sub>-As<sub>2</sub>S<sub>3</sub><sup>1</sup>, which result in incomplete reaction<sup>2</sup>. The choice of B<sub>2</sub>S<sub>3</sub> in place of Sb<sub>2</sub>S<sub>3</sub> is attractive as BCl<sub>3</sub> is more volatile than SbCl<sub>3</sub>. However, the ease with which B forms oxo compounds is such that B<sub>2</sub>S<sub>3</sub> often contains oxides. In contrast, a reactive and pure form of black Sb<sub>2</sub>S<sub>3</sub> is obtained by passing H<sub>2</sub>S through HCl solns of Sb(III).

TABLE 1

Element	Product	Reaction condition	Refs.
V	VSCl	VCl <sub>5</sub> + B <sub>2</sub> S <sub>3</sub>	6
Nb	NbYX <sub>3</sub> (Y = S or Se, X = Cl or Br)	NbX <sub>5</sub> + Sb <sub>2</sub> Y <sub>3</sub> (3:1 molar ratio) in CS <sub>2</sub> (see text)	3
	NbSCl <sub>3</sub>	NbCl <sub>5</sub> + B <sub>2</sub> S <sub>3</sub> (3:1 molar ratio) in a sealed tube at 90°C	7
	Nb <sub>2</sub> S <sub>3</sub> Cl <sub>4</sub>	NbCl <sub>5</sub> + Sb <sub>2</sub> S <sub>3</sub> (2:1 molar ratio) either in CS <sub>2</sub> solution (45°C for 10 d) or heated in a sealed tube	4
	Nb <sub>2</sub> S <sub>3</sub> Br <sub>4</sub>	NbBr <sub>5</sub> + Sb <sub>2</sub> S <sub>3</sub> (2:1 molar ratio) in CS <sub>2</sub> solution (45°C for 10 d)	4
	TaSX <sub>3</sub> (X = Cl or Br)	TaX <sub>5</sub> + Sb <sub>2</sub> S <sub>3</sub> (3:1 molar ratio) in CS <sub>2</sub> solution at 20°C.	3
Mo	MoSCl <sub>3</sub>	MoCl <sub>5</sub> + Sb <sub>2</sub> S <sub>3</sub> (3:1 molar ratio) either in CS <sub>2</sub> solution or heated in a sealed tube 140°C (see text)	8
	MoSeCl <sub>3</sub>	MoCl <sub>5</sub> + Sb <sub>2</sub> Se <sub>3</sub> (3:1 molar ratio) in a sealed tube 140°C (see text)	8
	W		
W	WSCl <sub>4</sub>	WCl <sub>6</sub> + Sb <sub>2</sub> S <sub>3</sub> (3:1 molar ratio) at 140°C for 3 d	8
	WYF <sub>4</sub>	WF <sub>6</sub> + Sb <sub>2</sub> Y <sub>3</sub> (3:1 molar ratio) at 300-350°C for 3 h (Y = S, Se)	9, 10
		WF <sub>6</sub> + B <sub>2</sub> S <sub>3</sub> (3:1 molar ratio) at 260°C followed by sublimation	10
	WYBr <sub>4</sub> (Y = S, Se)	WBr <sub>6</sub> + Sb <sub>2</sub> Y <sub>3</sub> (3:1 molar ratio) 120-140°C	8
	WYCl <sub>3</sub>	WCl <sub>5</sub> + Sb <sub>2</sub> Y <sub>3</sub> (3:1 molar ratio) at 120°C for 7 d	8
	WSCl <sub>3</sub>	WCl <sub>5</sub> + Sb <sub>2</sub> S <sub>3</sub> (3:1 molar ratio) in CS <sub>2</sub> solution	
	WSeBr <sub>3</sub>	WBr <sub>5</sub> + Sb <sub>2</sub> Se <sub>3</sub> (3:1 molar ratio) at 140°C for 14 d	8
	WCl <sub>2</sub> S <sub>2</sub>	WSCl <sub>4</sub> + Sb <sub>2</sub> S <sub>3</sub> (3:1 molar ratio) in CS <sub>2</sub>	3
	WCl <sub>2</sub> OS	WSCl <sub>4</sub> + Sb <sub>2</sub> O <sub>3</sub> (3:1 molar ratio) in CS <sub>2</sub>	3
	WCl <sub>2</sub> SSe	WSeCl <sub>4</sub> + Sb <sub>2</sub> S <sub>3</sub> (3:1 molar ratio) in CS <sub>2</sub>	3
Re	ReF <sub>5</sub> S	ReF <sub>7</sub> + Sb <sub>2</sub> S <sub>3</sub> or B <sub>2</sub> S <sub>3</sub>	11
	ReF <sub>3</sub> S	ReF <sub>5</sub> + Sb <sub>2</sub> S <sub>3</sub>	11

242    2.9. Formation of the Halogen–Transition–Metal Bond  
       2.9.14. Synthesis of Metal Sulfido-, Seleno- and Tellurohalides  
       2.9.14.4. from Transition-Metal Halides with Main-Group Chalcogenides

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From Table 1 it is apparent that sulfides and selenides of B and Sb are used more frequently than those of As. The reason is illustrated by attempts at preparing  $\text{NbSCl}_2$  using  $\text{NbCl}_4$ – $\text{As}_2\text{S}_3$ <sup>1</sup>, which result in incomplete reaction<sup>2</sup>. The choice of  $\text{B}_2\text{S}_3$  in place of  $\text{Sb}_2\text{S}_3$  is attractive as  $\text{BCl}_3$  is more volatile than  $\text{SbCl}_3$ . However, the ease with which B forms oxo compounds is such that  $\text{B}_2\text{S}_3$  often contains oxides. In contrast, a reactive and pure form of black  $\text{Sb}_2\text{S}_3$  is obtained by passing  $\text{H}_2\text{S}$  through  $\text{HCl}$  solns of  $\text{Sb(III)}$ .

TABLE 1

Element	Product	Reaction condition	Refs.
V	$\text{VSCl}$	$\text{VCl}_5 + \text{B}_2\text{S}_3$	6
Nb	$\text{NbYX}_3$ (Y = S or Se, X = Cl or Br)	$\text{NbX}_5 + \text{Sb}_2\text{Y}_3$ (3:1 molar ratio) in $\text{CS}_2$ (see text)	3
	$\text{NbSCl}_3$	$\text{NbCl}_5 + \text{B}_2\text{S}_3$ (3:1 molar ratio) in a sealed tube at $90^\circ\text{C}$	7
	$\text{Nb}_2\text{S}_3\text{Cl}_4$	$\text{NbCl}_5 + \text{Sb}_2\text{S}_3$ (2:1 molar ratio) either in $\text{CS}_2$ solution ( $45^\circ\text{C}$ for 10 d) or heated in a sealed tube	4
	$\text{Nb}_2\text{S}_3\text{Br}_4$	$\text{NbBr}_5 + \text{Sb}_2\text{S}_3$ (2:1 molar ratio) in $\text{CS}_2$ solution ( $45^\circ\text{C}$ for 10 d)	4
	$\text{TaSX}_3$ (X = Cl or Br)	$\text{TaX}_5 + \text{Sb}_2\text{S}_3$ (3:1 molar ratio) in $\text{CS}_2$ solution at $20^\circ\text{C}$ .	3
Mo	$\text{MoSCl}_3$	$\text{MoCl}_5 + \text{Sb}_2\text{S}_3$ (3:1 molar ratio) either in $\text{CS}_2$ solution or heated in a sealed tube $140^\circ\text{C}$ (see text)	8
	$\text{MoSeCl}_3$	$\text{MoCl}_5 + \text{Sb}_2\text{Se}_3$ (3:1 molar ratio) in a sealed tube $140^\circ\text{C}$ (see text)	8
W	$\text{WSCl}_4$	$\text{WCl}_6 + \text{Sb}_2\text{S}_3$ (3:1 molar ratio) at $140^\circ\text{C}$ for 3 d	8
	$\text{WYF}_4$	$\text{WF}_6 + \text{Sb}_2\text{Y}_3$ (3:1 molar ratio) at $300$ – $350^\circ\text{C}$ for 3 h (Y = S, Se)	9, 10
		$\text{WF}_6 + \text{B}_2\text{S}_3$ (3:1 molar ratio) at $260^\circ\text{C}$ followed by sublimation	10
	$\text{WYBr}_4$ (Y = S, Se)	$\text{WBr}_6 + \text{Sb}_2\text{Y}_3$ (3:1 molar ratio) $120$ – $140^\circ\text{C}$	8
	$\text{WYCl}_3$	$\text{WCl}_5 + \text{Sb}_2\text{Y}_3$ (3:1 molar ratio) at $120^\circ\text{C}$ for 7 d	8
	$\text{WSCl}_3$	$\text{WCl}_5 + \text{Sb}_2\text{S}_3$ (3:1 molar ratio) in $\text{CS}_2$ solution	
	$\text{WSeBr}_3$	$\text{WBr}_5 + \text{Sb}_2\text{Se}_3$ (3:1 molar ratio) at $140^\circ\text{C}$ for 14 d	8
	$\text{WCl}_2\text{S}_2$	$\text{WSCl}_4 + \text{Sb}_2\text{S}_3$ (3:1 molar ratio) in $\text{CS}_2$	3
	$\text{WCl}_2\text{OS}$	$\text{WSCl}_4 + \text{Sb}_2\text{O}_3$ (3:1 molar ratio) in $\text{CS}_2$	3
	$\text{WCl}_2\text{SSe}$	$\text{WSeCl}_4 + \text{Sb}_2\text{S}_3$ (3:1 molar ratio) in $\text{CS}_2$	3
Re	$\text{ReF}_3\text{S}$	$\text{ReF}_7 + \text{Sb}_2\text{S}_3$ or $\text{B}_2\text{S}_3$	11
	$\text{ReF}_3\text{S}$	$\text{ReF}_5 + \text{Sb}_2\text{S}_3$	11

The complications that can arise are illustrated by the  $\text{NbCl}_5\text{-Sb}_2\text{S}_3$  system. A 3:1 molar ratio of  $\text{NbCl}_5$  and  $\text{Sb}_2\text{S}_3$  in  $\text{CS}_2$  at RT readily yields the Nb(V) compound,  $\text{NbSCl}_3$ <sup>3</sup>; a 2:1 ratio in  $\text{CS}_2$  at 45°C for 10 d forms the Nb(IV) compound  $\text{Cl}_2\text{Nb-}\mu\text{-(S}_2\text{)-}\mu\text{-(S)-NbCl}_2$ <sup>4</sup>. Similar complications may occur in the formation of  $\text{MoSCl}_3$  and  $\text{MoSeCl}_3$ , for although samples having analyses close to those required for  $\text{MoSCl}_3$  and  $\text{MoSeCl}_3$  can be obtained, the possibility of reduction cannot be excluded.

Finally, no definite route to  $\text{TiSCl}_2$  exists. However, its MeCN adduct  $\text{TiSCl}_2\cdot(\text{NCMe})_2$  is isolated by treating  $\text{TiCl}_4$  with  $(\text{Me}_3\text{Si})_2\text{S}$  in MeCN<sup>5</sup>.

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## 2.9.15. Synthesis of Metal Carbonyl Halides and Nitrosyl Halides from the Metal Carbonyls and Their Derivatives

### 2.9.15.1. Synthesis of Metal Carbonyl Halides

Metal carbonyl halides, in which both CO and halogen are bonded to the central metal atom, are known for all elements of groups VIA–VIII and the group-IB metals. One method of preparation involves treating of the metal halide with CO, and another, the halogenation of the metal carbonyl itself. Since this section is concerned with forming transition-metal to halogen bonds, only carbonyl halides that are prepared by the second method are discussed.

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TABLE 1. PREPARATION OF TRANSITION-METAL CARBOONYLHALIDES FROM THE METAL CARBONYL

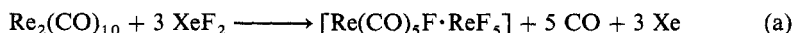
Carbonylhalide	Carbonyl	Halogenating agent	Solvent	T (°C)	Time	Color	Yield (%)	Refs.
$\text{Mo}(\text{CO})_4\text{F}_2$	$\text{Mo}(\text{CO})_6$	$\text{MoF}_6$	HF			Orange		5, 21
$\text{Mo}(\text{CO})_4\text{Cl}_2$	$\text{Mo}(\text{CO})_6$	$\text{Cl}_2(1)$		-78		Yellow		1
$\text{Mo}(\text{CO})_4\text{Br}_2^*$	$\text{Mo}(\text{CO})_6$	$\text{Br}_2$	$\text{CH}_2\text{Cl}_2$	-78				2
$\text{Mo}(\text{CO})_4\text{I}_2^*$	$\text{Mo}(\text{CO})_6$	$\text{I}_2 + \text{hv}$	$\text{CH}_2\text{Cl}_2$	RT		Dark brown		23
$[\text{Mo}(\text{CO})_4\text{I}]_2$	$\text{Mo}(\text{CO})_6$	$\text{SiI}_4 + \text{hv}$	Pet.ether		5 h			4
$\text{W}(\text{CO})_4\text{Cl}_2^*$	$\text{W}(\text{CO})_6$	$\text{Cl}_2$	$\text{CH}_2\text{Cl}_2$	-78		Yellow soln		3
$\text{W}(\text{CO})_4\text{Br}_2^*$	$\text{W}(\text{CO})_6$	$\text{Br}_2$	$\text{CH}_2\text{Cl}_2$			Red soln		3
$\text{W}(\text{CO})_4\text{I}_2$	$\text{W}(\text{CO})_6$	$\text{I}_2 + \text{hv}$	$\text{CH}_2\text{Cl}_2$	RT		Orange		23
$\text{W}(\text{CO})_4\text{I}$	$\text{W}(\text{CO})_6$	$\text{I}_2$	Hexane	RT		Orange		4
		$\text{Me}_2\text{SiI}_2$ , $\text{HgI}_2$ , $\text{Hg}_2\text{I}_2$ or $\text{Ag}_2\text{HgI}_4 + \text{hv}$						
$\text{Mn}(\text{CO})_3\text{F}_3$	$\text{Mn}(\text{CO})_5\text{Br}$	$\text{AgF (xs)}$	$\text{CH}_2\text{Cl}_2$	RT	20 min	Orange yellow	31	15
$[\text{Mn}(\text{CO})_4\text{F}]_2$	$\text{Mn}(\text{CO})_5\text{Br}$	$\text{AgF (1:2)}$	$\text{CH}_2\text{Cl}_2$	RT	75 min	Light orange yellow	31	15
$\text{Mn}(\text{CO})_5\text{Cl}$	$[\text{Mn}(\text{CO})_5]_2$	$\text{Cl}_2$	$\text{CCl}_4$	0		Yellow	64	6, 9

$\text{Mn}(\text{CO})_5\text{Br}$	$[\text{Mn}(\text{CO})_5]_2$	$\text{Br}_2$	$\text{CCl}_4$	40	1 h	Yellow	73	6
$\text{Te}(\text{CO})_5\text{Cl}$	$[\text{Te}(\text{CO})_5]_2$	$\text{Cl}_2$	$\text{CCl}_4$	25	1 h			7
$\text{Tc}(\text{CO})_5\text{Br}$	$[\text{Tc}(\text{CO})_5]_2$	$\text{Br}_2$	$\text{CCl}_4$	25	1 h			7
$\text{Tc}(\text{CO})_5\text{I}$	$[\text{Tc}(\text{CO})_5]_2$	$\text{I}_2$	—	100				7
$\text{Re}(\text{CO})_5\text{F} \cdot \text{ReF}_5$	$\text{Re}_2(\text{CO})_{10}$	$\text{ReF}_6$	$\text{HF}$			Orange	13	
$\text{Re}(\text{CO})_5\text{F} \cdot \text{ReF}_5$	$\text{Re}_2(\text{CO})_{10}$	$\text{XeF}_2$	$\text{CClF}_2\text{CCl}_2\text{F}$ or $\text{HF}$	RT		Orange yellow	14	
$\text{Re}(\text{CO})_3\text{F}_3$	$\text{Re}_2(\text{CO})_{10}$	$\text{ReF}_6$	$\text{HF}$	RT		Brown	11, 12	
$\text{Re}(\text{CO})_5\text{F}$	$\text{Re}_2(\text{CO})_{10}$	$\text{ReF}_6$	$\text{HF}$	RT		Brown	11, 12	
$\text{Re}(\text{CO})_5\text{F}$	$\text{Re}_2(\text{CO})_{10}$	$\text{XeF}_2$	$\text{HF}$		2-3 h	Brown	12	
$\text{Re}(\text{CO})_5\text{X}$ ( $\text{X} = \text{Cl}, \text{Br}$ )	$\text{Re}_2(\text{CO})_{10}$	$\text{X}_2$	Inert solvent				8	
$\text{Re}(\text{CO})_5\text{I}$	$\text{Re}_2(\text{CO})_{10}$	$\text{I}_2 + \text{h}\nu$		RT			8	
$\text{Re}(\text{CO})_5\text{I}$	$\text{Re}_2(\text{CO})_{10}$	$\text{I}_2$	—	130		Colorless	9	
$\text{Fe}(\text{CO})_4\text{X}_2$ ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ )	$\text{Fe}(\text{CO})_5$	$\text{X}_2$					16, 17	
$\text{Fe}_2(\text{CO})_8\text{I}_2$	$\text{Fe}_3(\text{CO})_{12}$	$\text{I}_2$	$\text{THF}$			White	20, 21	
$[\text{RuF}_2(\text{CO})_3]_4$	$\text{Ru}_3(\text{CO})_{12}$	$\text{XeF}_2$	Genetron 113 or $\text{HF}$	RT		Yellow	22	
$[\text{Ru}(\text{CO})_3\text{F}_3]$	$\text{Ru}_3(\text{CO})_{12}$	$\text{XeF}_2$ (1:4:5)	Genetron 113 or $\text{HF}$	RT		Buff	22	
$[\text{Ru}(\text{CO})_4\text{Br}_2]$	$\text{Ru}(\text{CO})_5$	$\text{X}_2$ (xs)	heptane	-40		Yellow	18	
$[\text{Ru}(\text{CO})_4\text{I}_2]$	$\text{Ru}(\text{CO})_5$	$\text{X}_2$ (xs)						
$\text{Os}(\text{CO})_4\text{Cl}_2$	$\text{Os}_3(\text{CO})_{12}$	UV	$\text{CCl}_4$	RT			19	
$[\text{Os}(\text{CO})_3\text{Cl}_2]_2$	$\text{Os}_3(\text{CO})_{12}$	UV	$\text{CCl}_4$	RT	long		19	

readily obtainable carbonyl, a criterion not met by Pt, Pd, Cu and Au. For Ni, Co and V the metal carbonyl reacts so rapidly with halogens that total loss of CO occurs with oxidation of the metal to the metal halide. For this reason reactions of carbonyls with Cl<sub>2</sub> are carried out at low T to reduce the rate of reaction and maintain the low oxidation state.

Reaction of Mo(CO)<sub>6</sub> with Cl<sub>2</sub> at –78°C yields Mo(CO)<sub>4</sub>Cl<sub>2</sub> as a thermally unstable yellow solid<sup>1</sup>. The corresponding bromo derivative is less stable, as it is only obtained in solution from which derivatives are precipitated by addition of the appropriate ligand<sup>2</sup>. Tungsten reactions have been attempted, but pure compounds are not isolated<sup>3</sup>. The dimeric iodides [M(CO)<sub>4</sub>I]<sub>2</sub> (M = Mo, W) are prepared by irradiation of solutions of the hexacarbonyl and SiI<sub>4</sub>, Me<sub>2</sub>SiI<sub>2</sub>, HgI<sub>2</sub>, etc<sup>4</sup>. The Mo compound, [Mo(CO)<sub>4</sub>I]<sub>2</sub>, is an iodine-bridged dimer. The carbonyl fluoride, Mo(CO)<sub>4</sub>F<sub>2</sub>, is prepared by an involved route in which anhyd HF is condensed onto Mo(CO)<sub>6</sub> and small successive additions of MoF<sub>6</sub> are made. A mixture of Mo(CO)<sub>4</sub>F<sub>2</sub>, MoF<sub>5</sub> and MoOF<sub>4</sub> is formed, which is separated by use of the differing solubilities of the components in WF<sub>6</sub>. The orange Mo(CO)<sub>4</sub>F<sub>2</sub> is polymeric<sup>5</sup>.

The monomeric species M(CO)<sub>5</sub>X (M = Mn, Tc, Re; X = Cl, Br, I) are best prepared by treating of the metal carbonyl with halogens<sup>6–10</sup>. In preparing Mn carbonyl halides some decomposition occurs, giving the metal halide, which can be removed by sublimation. The reactions of Tc<sub>2</sub>(CO)<sub>10</sub> with Cl<sub>2</sub> and I<sub>2</sub> yield mixtures of the desired Tc(CO)<sub>5</sub>X and the dimeric [Tc(CO)<sub>4</sub>X]<sub>2</sub>. Treatment of the products with CO at 6.9 × 10<sup>6</sup> N m<sup>–2</sup> at 100°C for 40 h converts the dimer to the monomeric Tc(CO)<sub>5</sub>X<sup>7</sup>. Rhenium carbonyl halides are prepared from Re<sub>2</sub>(CO)<sub>10</sub> and X<sub>2</sub> (X = Cl, Br) in inert solvents<sup>8</sup>. The iodide is best prepared by UV irradiation of mixtures of Re<sub>2</sub>(CO)<sub>10</sub> and I<sub>2</sub> at RT in the absence of solvent<sup>8</sup>. There are conflicting reports about the fluorination of Re<sub>2</sub>(CO)<sub>10</sub>. The reaction between Re<sub>2</sub>(CO)<sub>10</sub> and ReF<sub>6</sub> in anhyd HF yields a mixture of products including Re(CO)<sub>5</sub>F, Re(CO)<sub>3</sub>F<sub>3</sub>, ReF<sub>5</sub> and CO<sup>11,12</sup>, but Re(CO)<sub>5</sub>F, ReF<sub>5</sub> and [Re(CO)<sub>6</sub>][Re<sub>2</sub>F<sub>11</sub>] are also obtained<sup>13</sup>. The complex Re(CO)<sub>5</sub>F·ReF<sub>5</sub> is also prepared by the reaction between Re<sub>2</sub>(CO)<sub>10</sub> and XeF<sub>2</sub> (1:3 molar ratio) in CClF<sub>2</sub>CCl<sub>2</sub>F or anhyd HF at RT<sup>14</sup>:



Brown Re(CO)<sub>5</sub>F is formed<sup>12</sup>:

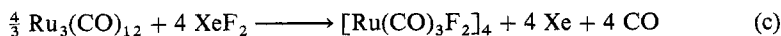


Carbonyl fluorides of Mn(III), Mn(CO)<sub>3</sub>F<sub>3</sub>, and Mn(I), [Mn(CO)<sub>4</sub>F]<sub>2</sub>, are prepared by halogen exchange between Mn(CO)<sub>5</sub>Br and AgF in varying stoichiometric amounts<sup>15</sup>.

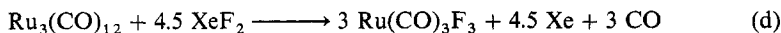
The action of halogens on Fe(CO)<sub>5</sub> yields Fe(CO)<sub>4</sub>X<sub>2</sub> (X = Cl, Br, I)<sup>16,17</sup>. The iodide Fe(CO)<sub>4</sub>I<sub>2</sub> is purified by sublimation, but the bromide and chloride are recrystallized because of their lower thermal stabilities. Although Ru carbonyl halides Ru(CO)<sub>4</sub>X<sub>2</sub> (X = Br, I) are prepared from RuX<sub>3</sub>, they can be obtained by the action of the halogen on Ru<sub>2</sub>(CO)<sub>10</sub> at –40 °C in heptane<sup>18</sup>. The UV irradiation of Os<sub>3</sub>(CO)<sub>12</sub> in CCl<sub>4</sub> at RT produces Os(CO)<sub>4</sub>Cl<sub>2</sub>. Prolonged photolysis of the solution yields [Os(CO)<sub>3</sub>Cl<sub>2</sub>]<sub>2</sub><sup>19</sup>. Reaction of the corresponding iron carbonyl, Fe<sub>3</sub>(CO)<sub>12</sub>, with I<sub>2</sub> in THF yields the dimeric Fe<sub>2</sub>(CO)<sub>8</sub>I<sub>2</sub><sup>20,21</sup> as a white solid, which melts at –5°C to give a red liquid.

The products formed from fluorination of Ru<sub>3</sub>(CO)<sub>12</sub> by XeF<sub>2</sub> in CClF<sub>2</sub>CCl<sub>2</sub>F or

HF depend upon the ratios of reactants. Using a 1:3 molar ratio, the yellow solid  $[(Ru(CO)_3F_2)_4]$ , is obtained:



When the molar ratio of  $XeF_2$  is greater than 4:5, buff colored  $Ru(CO)_3F_3$  is formed<sup>22</sup>:



(E.M. PAGE, D.A. RICE)

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### 2.9.15.1.2. Preparation of Anionic Carbonyl Halides from the Metal Carbonyl or its Derivative.

Table 1 lists carbonyl halide anions prepared directly from the metal carbonyl or carbonyl halide. Salts of the  $[Cr(CO)_5I]^-$  ion can be prepared by treating ice-cold solutions of  $Na_2[Cr_2(CO)_{10}]$  in acetic acid with  $KI-I_2$  mixtures. Addition of a cation, e.g.,  $[Me_4N]^+$ , precipitates the salts as orange solids. Iodine oxidation of  $Na[Cr(CO)_5I]$  yields  $Cr_2(CO)_{10}I$  and  $Cr(CO)_5I$  depending upon the amount of  $I_2$  used<sup>1</sup>. The series  $[MX(CO)_5]^-$  ( $M = Cr, Mo, W$ ;  $X = Cl, Br, I$ ) is prepared by reacting of the hexacarbonyl with tetraalkylammonium halide or  $KI$  in diglyme<sup>2,3</sup>:



The kinetics and mechanism of these reactions are known<sup>4</sup>. Excess tetraalkylammonium salt  $[M(CO)_6]:R_4NX > 1:2.9$  gives dimeric  $[(CO)_5M(\mu-X)_3M(CO)_5]^{2-}$  ions having a triple halogen bridge<sup>5,6</sup>.

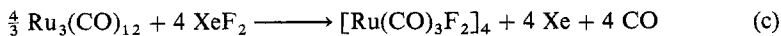
The anions  $[Mn(CO)_4X_2]^-$  ( $X = Cl, Br, I$ ) are isolated as  $[R_4N]^+$  salts by the action of halide ions on the pentacarbonylhalide  $Mn(CO)_5X$  at elevated  $T$ <sup>7,8</sup>. The

## 2.9.15. Synthesis of Metal Carbonyl Halides and Nitrosyl Halides 247

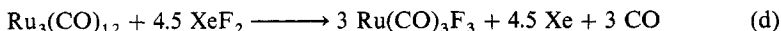
## 2.9.15.1. Synthesis of Metal Carbonyl Halides

## 2.9.15.1.2. Preparation of Anionic Carbonyl Halides.

HF depend upon the ratios of reactants. Using a 1:3 molar ratio, the yellow solid  $[(\text{Ru}(\text{CO})_3\text{F}_2)_4]$ , is obtained:



When the molar ratio of  $\text{XeF}_2$  is greater than 4:5, buff colored  $\text{Ru}(\text{CO})_3\text{F}_3$  is formed<sup>22</sup>:



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### 2.9.15.1.2. Preparation of Anionic Carbonyl Halides from the Metal Carbonyl or Its Derivative.

Table 1 lists carbonyl halide anions prepared directly from the metal carbonyl or carbonyl halide. Salts of the  $[\text{Cr}(\text{CO})_5\text{I}]^-$  ion can be prepared by treating ice-cold solutions of  $\text{Na}_2[\text{Cr}_2(\text{CO})_{10}]$  in acetic acid with KI- $\text{I}_2$  mixtures. Addition of a cation, e.g.,  $[\text{Me}_4\text{N}]^+$ , precipitates the salts as orange solids. Iodine oxidation of  $\text{Na}[\text{Cr}(\text{CO})_5\text{I}]$  yields  $\text{Cr}_2(\text{CO})_{10}\text{I}$  and  $\text{Cr}(\text{CO})_5\text{I}$  depending upon the amount of  $\text{I}_2$  used<sup>1</sup>. The series  $[\text{MX}(\text{CO})_5]^-$  (M = Cr, Mo, W; X = Cl, Br, I) is prepared by reacting of the hexacarbonyl with tetraalkylammonium halide or KI in diglyme<sup>2,3</sup>:



The kinetics and mechanism of these reactions are known<sup>4</sup>. Excess tetraalkylammonium salt  $[\text{M}(\text{CO})_6:\text{R}_4\text{NX} > 1:2.9]$  gives dimeric  $[(\text{CO})_3\text{M}(\mu\text{-X})_3\text{M}(\text{CO})_3]^{2-}$  ions having a triple halogen bridge<sup>5,6</sup>.

The anions  $[\text{Mn}(\text{CO})_4\text{X}_2]^-$  (X = Cl, Br, I) are isolated as  $[\text{R}_4\text{N}]^+$  salts by the action of halide ions on the pentacarbonylhalide  $\text{Mn}(\text{CO})_5\text{X}$  at elevated T<sup>7,8</sup>. The

TABLE 1. PREPARATION OF CARBONYL HALIDE ANIONS

Anion	Carbonyl or carbonyl halide	Reactant	Solvent	T (°C)	Time (h)	Yield (%)	Color	Refs.
$[\text{Cr}(\text{CO})_5\text{I}]^-$	$[\text{Cr}_2(\text{CO})_{10}]^{2-}$	$\text{I}_2\text{-Me}_4\text{NI}$	$\text{I}_2\text{-KI (aq)}$	Ice			Orange/yellow	1
$[\text{M}(\text{CO})_5\text{X}]^-$ (M = Cr, Mo, W; X = Cl, Br, I)	$\text{M}(\text{CO})_6$	$[\text{R}_4\text{N}]\text{X}$ (R = Et, Me, Bu)	Diglyme	120°C				2
$[\text{Mo}(\text{CO})_5\text{I}]^-$	$\text{Mo}(\text{CO})_6$	$[\text{R}_4\text{N}]\text{I}$ or KI	Diglyme	> 100 °C			Yellow	3
$[\text{Mo}_2(\mu\text{-Cl})_3(\text{CO})_6]^{3-}$	$\text{Mo}(\text{CO})_6$	$[\text{R}_4\text{N}]\text{Cl}$	Dioxan	Reflux	2			5
$[\text{W}_2(\mu\text{-Cl})_3(\text{CO})_6]^{3-}$	$\text{W}(\text{CO})_6$	$[\text{R}_4\text{N}]\text{Cl}$	Dioxan	Reflux	12			5
$[\text{M}_2(\mu\text{-X})_3(\text{CO})_6]^{3-}$ (M = Cr, Mo, W; X = Cl, Br)	$\text{M}(\text{CO})_6$	$[\text{Me}_4\text{N}]\text{X}$	EtOH	Reflux	6-12			6
$[\text{M}_2(\mu\text{-X})_3(\text{CO})_6]^{3-}$ (M = Cr, Mo, W)	$[\eta^6\text{-C}_6\text{H}_5\text{CH}_3]$	$[\text{R}_4\text{N}]\text{X}$ (R = CH <sub>3</sub> , C <sub>2</sub> H <sub>5</sub> )	EtOH	RT				6
$[\text{cis-Mn}(\text{CO})_4\text{Cl}_2]^-$	$\text{Mn}(\text{CO})_5$	$[\text{Et}_4\text{N}]\text{Cl}$	CH <sub>2</sub> Cl <sub>2</sub>	Reflux	1		Yellow	7
$[\text{cis-Mn}(\text{CO})_4\text{Br}_2]^-$	$\text{Mn}(\text{CO})_5$	$[\text{Et}_4\text{N}]\text{Br}$	MeOH	45-50°C	1		Yellow	7

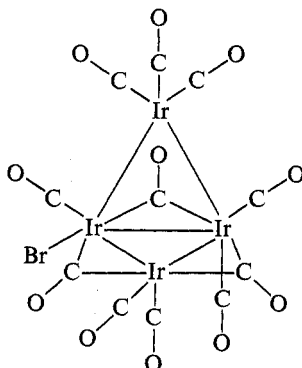
$[\text{Mn}(\text{CO})_4\text{XY}]^-$ (X, Y = Cl, Br, I)	$\text{Mn}(\text{CO})_5\text{X}$	$[\text{R}_4\text{N}]\text{Y}$	Diglyme	120°C		Yellow/red	8
$[\text{Re}(\text{CO})_4\text{X}_2]^-$ (X = Br, I)	$\text{Re}(\text{CO})_5\text{X}$	$[\text{Et}_4\text{N}]\text{X}$	Diglyme/EtOH	120°C reflux	3	Cream (Br)	9
$[\text{Mn}_2(\text{CO})_8\text{X}_2]^{2-}$ (X = Cl, I)	$\text{Mn}_2(\text{CO})_{10}$	$[\text{R}_4\text{N}]\text{X}$	Glycol	140°C	4	Yellow (I)	9
$[\text{Mn}_2(\text{CO})_6(\mu\text{-Cl})_3]^-$	$\text{Mn}_2(\text{CO})_{10}$	$[\text{Et}_4\text{N}]\text{Cl}$	$\text{CHCl}_3 + \text{h}\nu$		4	Yellow (Cl)	8
$[\text{Mn}_2(\text{CO})_6(\mu\text{-X})_3]^-$ (X = Cl, Br)	$\text{Mn}(\text{CO})_5\text{X}$	$[\text{Et}_4\text{N}]\text{X}$	$\text{CHCl}_3$	Reflux	5	Red (I)	8
$[\text{Re}_2(\text{CO})_6(\mu\text{-X})_3]^-$	$\text{Re}(\text{CO})_5\text{X}$	$[\text{Et}_4\text{N}]\text{X}$	Decalin	Reflux	18	Yellow	11
$[\text{H}_4\text{Re}_4(\text{CO})_{15}\text{I}]^-$	$[\text{H}_4\text{Re}_4(\text{CO})_{15}]^{2-}$	$\text{I}_2$	EtOH			91 (Cl)	10
$[\text{H}_3\text{Re}_3(\text{CO})_{10}\text{I}]^-$	$[\text{H}_3\text{Re}_3(\text{CO})_{10}]^{2-}$	$\text{I}_2$	EtOH			93 (Br)	10
$[\text{H}_2\text{Re}_3(\text{CO})_{10}\text{I}]^{2-}$	$[\text{H}_3\text{Re}_3(\text{CO})_{10}]^{2-}$	$\text{I}_2$				77 (Cl)	10
$[\text{H}_3\text{Re}_3(\text{CO})_{10}\text{I}]^-$	$[\text{H}_4\text{Re}_4(\text{CO})_{10}]^-$	$\text{I}_2$				68 (Br), 78 (I)	10
$[\text{CoNO}(\text{CO})_2\text{X}]^-$	$\text{CoNO}(\text{CO})_3$	$[\text{Bu}_4\text{N}]\text{X}$	EtOH				13
$[\text{Co}_4(\text{CO})_{11}\text{I}]^-$	$\text{Co}_4(\text{CO})_{12}$	$[\text{Et}_4\text{M}]\text{I}$	Diglyme	50–60°C	2	Yellow	14
$[\text{Ir}_4(\text{CO})_{11}\text{X}]^-$	$\text{Ir}_4(\text{CO})_{12}$	$[\text{Et}_4\text{N}]\text{X}(1:5)$	$\text{CH}_2\text{Cl}_2$	0°C	1	Violet	15
		$[\text{Ph}_4\text{P}]\text{X}$	THF	Reflux	3–4		16
$[\text{Ni}(\text{CO})_3\text{X}]^-$	$\text{Ni}(\text{CO})_4$	$[\text{Bu}_4\text{N}]\text{X}$	Ether/DMF				17

analogous Re anions,  $[\text{Re}(\text{CO})_4\text{X}_2]^-$  ( $\text{X} = \text{Br}, \text{I}$ ), can be obtained from similar reactions starting with  $\text{Re}(\text{CO})_5\text{X}$ <sup>9</sup>. Treatment of the dimeric carbonyl,  $\text{Mn}_2(\text{CO})_{10}$ , with 2 mol of  $[\text{R}_4\text{N}]\text{X}$  yields salts<sup>7</sup> of  $[\text{Mn}_2(\text{CO})_8\text{X}_2]^{2-}$ .



Triply bridged dimeric anions  $[\text{M}_2(\text{CO})_6(\mu\text{-X})_3]^-$  ( $\text{M} = \text{Mn}, \text{Re}$ ;  $\text{X} = \text{Cl}, \text{Br}$ ) obtained from  $\text{M}(\text{CO})_5\text{X}$  and  $\text{R}_4\text{NX}$  in a 2:1 mol ratio by refluxing for long periods<sup>10</sup>. The Mn anion  $[\text{Mn}_2(\text{CO})_6(\mu\text{-Cl})_3]^-$  can also be obtained by UV irradiation of mixtures of  $\text{Mn}_2(\text{CO})_{10}$  and  $[\text{Et}_4\text{N}]\text{Cl}$  in  $\text{CHCl}_3$ <sup>11</sup>. The reactions of  $\text{I}_2$  with the hydrido Re carbonyl cluster anions  $[\text{H}_4\text{Re}_3(\text{CO})_{10}]^-$ ,  $[\text{H}_3\text{Re}_3(\text{CO})_{10}]^{2-}$  and  $[\text{H}_4\text{Re}_4(\text{CO})_{15}]^{2-}$  incorporate iodide ions into the metal cluster, which remains intact<sup>12,13</sup>.

The nitrosylcarbonyls of Co are used to synthesize anionic carbonyl halides. Reaction of  $\text{Co}(\text{NO})(\text{CO})_3$  with  $[\text{Bu}_4\text{N}]\text{X}$  in diglyme yields the salts. The anion  $[\text{Co}_4(\text{CO})_{11}\text{I}]^-$  is obtained in good yield from  $[\text{Co}_4(\text{CO})_{12}]$  and  $[\text{Et}_4\text{N}]\text{I}$  at  $0^\circ\text{C}$ <sup>15</sup>. Analogous salts of Ir, e.g.,  $[\text{Ph}_4\text{P}][\text{Ir}_4(\text{CO})_{11}\text{X}]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ), are prepared from  $\text{Ir}_4(\text{CO})_{12}$  and  $[\text{Ph}_4\text{P}]\text{X}$  in THF. The structure of the orange  $[\text{PPh}_4][\text{Ir}(\text{CO})_{11}\text{Br}]$  is known and is depicted below. The anion contains a tetrahedral cluster bearing eight terminal and three edge bridging carbonyl groups. The bromine atom is terminally bonded to one of the iridium atoms<sup>16</sup>.



The  $[\text{Ni}(\text{CO})_3\text{X}]^-$  anion is prepared by reaction of  $\text{Ni}(\text{CO})_4$  with  $[\text{Bu}_4\text{N}]\text{I}$ , but decomposition of the product occurs on purification<sup>17</sup>.

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### 2.9.15.1.3. Halogenation of Substituted Metal Carbonyls.

Table 1 lists some of the better characterized substituted metal carbonyl halides prepared by halogen oxidation of the substituted carbonyl. Bromides and iodides are more common than chlorides because  $\text{Cl}_2$  promotes further oxidation and total displacement of CO groups.

The group-VIA substituted metal carbonyl halides are reviewed<sup>1</sup>.

Oxidation of  $\text{Cr}(\text{CO})_2(\text{diars})_2$  by  $\text{Br}_2$  or  $\text{I}_2$  leads to seven-coordinated  $\text{Cr}(\text{II})$  complexes<sup>2</sup>,  $[\text{Cr}(\text{CO})_2(\text{diars})_2\text{X}]\text{X}$ . Analogous  $\text{Mo}(\text{II})$  and  $\text{W}(\text{II})$  complexes can be prepared similarly<sup>3</sup>.

Reaction of  $[\text{Os}_4(\text{CO})_{12}\text{H}_4]$  in methanol with  $\text{KOH}$  gives  $[\text{Os}_4(\text{CO})_{12}\text{H}_3]^-$ . Treatment of this ion with 1 mol of  $\text{I}_2$  in methanol yields a yellow precipitate of  $[\text{Os}_4(\text{CO})_{12}(\mu_2\text{-I})(\mu_2\text{-H})(\mu_3\text{-H})_2]$ . The structure of this complex has been determined by x-ray and neutron diffraction<sup>4,5</sup>.

Although no stable, uncharged carbonyl halide of Co is known, halogenation of  $[\text{Co}(\text{PPh}_3)(\text{CO})_3]^-$  with  $\text{CF}_3\text{I}$  gives the triphenylphosphine-substituted carbonyl halide,  $\text{CoI}(\text{PPh}_3)(\text{CO})_3$ <sup>6</sup>. The analogous complexes,  $[\text{CoX}(\text{PPh}_3)_2(\text{CO})]$  ( $\text{X} = \text{Br}, \text{I}$ ), are also prepared<sup>7</sup>.

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TABLE 1. PREPARATION OF SUBSTITUTED METAL CARBONYL HALIDES

Derivative <sup>a</sup>	Substituted carbonyl <sup>a</sup>	Halogenating agent	Solvent	T (°C)	Time	Yield (%)	Color	Ref.
[Cr(CO) <sub>2</sub> (diars) <sub>2</sub> Br] <sup>b</sup> Br	[Cr(CO) <sub>2</sub> (diars) <sub>2</sub> ]	Br <sub>2</sub>	CCl <sub>4</sub>				Pale yellow	2
[Cr(CO) <sub>2</sub> (diars) <sub>2</sub> ][I]	[Cr(CO) <sub>2</sub> (diars) <sub>2</sub> ]	I <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>				Deep orange	2
[Cr(CO) <sub>2</sub> (diars) <sub>2</sub> Br] <sup>b</sup> Br <sub>3</sub>	[Cr(CO) <sub>2</sub> (diars) <sub>2</sub> ]	Br <sub>2</sub> (xs)	CH <sub>2</sub> Cl <sub>2</sub>				Yellow	2
[Cr(CO) <sub>2</sub> (diars) <sub>2</sub> ][I] <sub>3</sub>	[Cr(CO) <sub>2</sub> (diars) <sub>2</sub> ]	I <sub>2</sub> (xs)	CCl <sub>4</sub>				Brown	2
[Mo(CO) <sub>2</sub> (diars) <sub>2</sub> ][I] <sub>2</sub>	[Mo(CO) <sub>2</sub> (diars) <sub>2</sub> ]	I <sub>2</sub>	CCl <sub>4</sub>	Reflux	3 h		Red/brown	3
[Mo(CO) <sub>2</sub> (diars) <sub>2</sub> ][I] <sub>3</sub>	[Mo(CO) <sub>2</sub> (diars) <sub>2</sub> ]	I <sub>2</sub> (xs)	CHCl <sub>3</sub>		4 h		Dark brown	3
[W(CO) <sub>3</sub> (diars)Br <sub>2</sub> ]	[W(CO) <sub>4</sub> (diars)]	Br <sub>2</sub> (1:2)	CCl <sub>4</sub>	0°C			Yellow	3
[W(CO) <sub>3</sub> (diars)Br <sub>2</sub> ] <sup>b</sup> Br	[W(CO) <sub>4</sub> (diars)]	Br <sub>2</sub> (xs)	CCl <sub>4</sub>				Yellow-green	3
[W(CO) <sub>2</sub> (diars) <sub>2</sub> X] <sup>b</sup> X	[W(CO) <sub>2</sub> (diars) <sub>2</sub> ]	X <sub>2</sub>	CHCl <sub>3</sub> -CCl <sub>4</sub>				Yellow	3
(X = Br, I)								
[W(CO) <sub>2</sub> (diars) <sub>2</sub> X] <sup>b</sup> X <sub>3</sub>	[W(CO) <sub>2</sub> (diars) <sub>2</sub> ]	X <sub>2</sub> (xs)	CHCl <sub>3</sub> -CCl <sub>4</sub>				Deep yellow (Br)	3
							Orange (I)	
[W(CO) <sub>4</sub> (diars)][I] <sub>3</sub>	[W(CO) <sub>4</sub> (diars)]	I <sub>2</sub>	CHCl <sub>3</sub>				Orange	3
[Cr(CO) <sub>3</sub> (TTAS)][I] <sub>3</sub>	[Cr(CO) <sub>3</sub> (TTAS)]	I <sub>2</sub>	Benzene	Hot			Brown	8
[M(CO) <sub>3</sub> (triars)X] <sup>b</sup> X	[M(CO) <sub>3</sub> (triars)]	X <sub>2</sub>	CHCl <sub>3</sub>				Yellow (Br)	8
(M = Mo, W; X = Br, I)							Orange (I)	
[M(CO) <sub>3</sub> (dmpe)X <sub>2</sub> ]	[M(CO) <sub>4</sub> (dmpe)]	X <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	RT	40 min		Yellow orange	9
[M(CO) <sub>2</sub> (dmpe) <sub>2</sub> ][I] <sub>3</sub>	[M(CO) <sub>2</sub> (dmpe) <sub>2</sub> ]	I <sub>2</sub> (1:1:5)	CH <sub>2</sub> Cl <sub>2</sub>	RT			Red	9
(M = Mo, W)								
[M(CO) <sub>3</sub> (dpam)][I]	[M(CO) <sub>3</sub> (dpam)]	I <sub>2</sub> (1:2)	CH <sub>2</sub> Cl <sub>2</sub> -CHCl <sub>3</sub> 10°C	86 (Mo), 60 (W)			Yellow	10
[M(CO) <sub>3</sub> (Medpam)][I]	[M(CO) <sub>3</sub> (Medpam)]	I <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub> -CHCl <sub>3</sub> 10°C	67 (Mo), 46 (W)				10
[M(CO) <sub>3</sub> (dpea)][I]	[M(CO) <sub>3</sub> (dpea)]	I <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub> -CHCl <sub>3</sub> 10°C	65 (Mo), 63 (W)				10
(M = Mo, W)								

$[M(CO)_3(bipy)X_2]$ (M = Mo, W; X = Br, I)	$[M(CO)_4(bipy)]$	$X_2$	$CHCl_3-CCl_4$	Orange yellow	11
$[M(CO)_3(DTH)X_2]$ (X = Br, I; M = Mo, W)	$[M(CO)_4(DTH)]$	$X_2$	Benzene		12
$W(CO)_4(NO)Cl$	$H_2W_2(CO)_6NO$	$ONCl$			13
$W(CO)_4(NO)I$	$H_2W_2(CO)_6NO$	$I_2$	Benzene $CH_2Cl_2$	Yellow	13
$[Mn(CO)_3(dpam)][I]$	$[Mn(CO)_3(dpam)]$	$I_2$			10
$[Os(CO)_2(PPh_3)_2X_2]$ (X = Cl, Br, I)	$[Os(CO)_3(PPh_3)_2]$	$HX$	THF	Warm	14
$[Os(CO)_2(PPh_3)_2X][X]$ (X = Br, I)	$[Os(CO)_3(PPh_3)_2]$	$X_2$	Chlorobenzene	Yellow	14
$[Os_3(CO)_{10}(\mu_2-Br)_2]$	$[Os_3(CO)_{12}]$	2 Bromo-naphthalene			15
$[HOs_3(CO)_{11}X]$	$[CH_3CN]Os_3(CO)_{11}$	$HX$			16
$[HOs_3(CO)_{10}X]$ (X = Cl, Br)					
$[Os_4(CO)_{12}(\mu_2)(\mu_2H)(\mu_3H)_2]$	$[Os_4(CO)_{12}H_3]^-$	$I_2$	MeOH	Yellow	4
$[(Me_3Y)M(CO)_4X]$ (Y = Si, Ge; M = Os, Ru; X = Br, I)	$[(Me_3Y)M(CO)_4]_2$	$X_2$	hexane	15 min 5-15 min	17
$[Ru(CO)_3I_2(PPh_3)]$	$[Ru_3(CO)_9(PPh_3)_3]$	$I_2$	Chlorocarbon		18
$[Ru(CO)_3(IPMe_2)]_2$	$[Ru(CO)_3(PMe_2)]_2$	$I_2$	Chlorocarbon	Orange	18
$[Co(CO)_3(PPh_3)I]$	$[Co(PPh_3)(CO)_3]^-$	$CF_3I$	THF	Dark brown	6
$[Co(CO)_2(PPh_3)_2I]$	$[Co(CO)_3(PPh_3)_2]$	$I_2$	Acetone	Maroon	7
	$[Co(CO)_4]$				
$[IrHCl_2(CO)(PPh_3)_2]$	$[IrH_2Cl(CO)(PPh_3)_2]$	$HCl$	Ether	25°C	19
$[IrCl_3(CO)(PPh_3)_2]$	$[IrHCl_2(CO)(PPh_3)_3]$	$HCl$	DME	84°C	19
	or				
	$[IrHCl_2(CO)(PPh_3)_2]$	$Cl_2$		25°C	19

<sup>a</sup>TTAS = bis-(o-dimethylarsinophenyl)methylarsine; dpea = bis(2-pyridylethyl)amine.

**2.9.15.2. Preparation of Metal Nitrosyl Halides.**

This section is restricted to syntheses of nitrosyl halides that involve reaction of the metal carbonyl, carbonyl halide or substituted metal nitrosyl.

Metal carbonyls are especially used to prepare Mo and W nitrosyl halides. The ability of NOCl and NOBr to effect simultaneously nitrosylation and halogenation permits the formation of  $M(NO)_2X_2$  from  $M(CO)_6$  ( $M = Mo, W$ ;  $X = Cl, Br$ ). Carbon monoxide is displaced in reactions at RT. The solvent and excess metal carbonyl are removed by vacuum distillation<sup>1-3</sup>. There are several modes of reaction of NOCl with substituted metal carbonyls and nitrosyls<sup>4</sup>. Reaction of NOCl with  $[(\eta^5-Cp)M(CO)_3]_2$  ( $M = Mo, W$ ) yields an equimolar mixture of carbonyl halide,  $[(\eta^5-C_5H_5)M(CO)_3Cl]$ , and nitrosyl halide,  $[(\eta^5-Cp)M(NO)_2Cl]$ . With (o-xylene)Mo(CO)<sub>3</sub> the major product is the nitrosyl halide,  $[Mo(NO)_2Cl_2]_n$ . Similarly reaction of NOCl with  $(\eta^5-Cp)Co(CO)_2$  yields  $[Co(NO)_2Cl]_2$  as the only identifiable product.

Nitrosyl metal carbonyls are used to prepare nitrosyl halides by halogenation. Treating  $(\eta^5-Cp)Mo(NO)(CO)_2$  with  $Cl_2$  in  $CCl_4$  yields the orange  $[(\eta^5-Cp)Mo(NO)Cl_2]_2$ . The analogous reaction with  $Br_2$  yields the brown  $[(\eta^5-Cp)Mo(NO)Br_2]_2$ <sup>5</sup>.

Reaction of gaseous NO with metal carbonyl halides provides an alternative route to nitrosyl halides (see Table 1). Reaction involves displacement of CO by NO and is therefore accompanied by a decrease in oxidation state. Partial replacement of the CO in such carbonyl halides can lead to nitrosyl metal carbonyl halides. The complex  $Re_2(NO)(CO)_5Cl_3$  is prepared<sup>6</sup> by passing NO through  $[Re(CO)_4Cl]_2$  in boiling  $CCl_4$  for 11 h.

Halogenation of substituted metal nitrosyls provides a further route to metal nitrosyl halides. The hydrido derivative  $ReH_2(NO)(PPh_3)_3$  reacts with both halogens and hydrogen halides to give  $ReX_3(NO)(PPh_3)_2$ <sup>7</sup>. Reaction of  $[Ir(NO)_2(PPh_3)_2]ClO_4$  with LiX in EtOH gives the complexes  $[IrX(NO)_2(PPh_3)_2]$ . Reaction with hydrohalic acids yields the dihalo complexes  $[IrX_2(NO)(PPh_3)_2]$ <sup>2</sup>.

Complexes containing both NO and CO bonded to a transition metal are prepared by partial displacement of CO by NO in metal carbonyls. Halogenation of these complexes or their derivatives yields nitrosyl metal carbonyl halides. Reaction of  $HW_2(CO)_9NO$  with NOCl in benzene gives  $[trans-W(CO)_4(NO)Cl]$ . The iodide can be prepared by reaction of  $HW_2(CO)_9NO$  with  $I_2$  in  $CH_2Cl_2$ <sup>9</sup>.

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TABLE 1. PREPARATION OF TRANSITION-METAL NITROSYL HALIDES

Nitrosyl halide	Reaction	Solvent	T (°C)	Time	Color	Yield (%)	Refs.
$\text{M}(\text{NO})_2\text{Cl}_2$	$\text{M}(\text{CO})_6 + \text{NOCl}$	$\text{CH}_2\text{Cl}_2$	RT	1 h	Dark green		1, 2
$[\text{M}(\text{NO})_2\text{Br}_2]_n$	$\text{M}(\text{CO})_6 + \text{NOBr}$	$\text{CH}_2\text{Cl}_2$	RT		Dark green	90	3
$(\eta^5\text{-C}_5\text{H}_5)_3\text{M}(\text{NO})_2\text{Cl}$	$[(\eta^5\text{-C}_5\text{H}_5)_3\text{M}(\text{CO})_3]_2 + \text{NOCl}$	$\text{CH}_2\text{Cl}_2$	RT		Green Brown	35	4
$[\text{Mo}(\text{NO})_2\text{Cl}_2]_n$	Oxylene $\text{Mo}(\text{CO})_3 + \text{NOCl}$	$\text{CH}_2\text{Cl}_2$			Green		4
$[(\eta^5\text{-C}_5\text{H}_5)_3\text{Mo}(\text{NO})\text{Cl}_2]_2$	$(\eta^5\text{-C}_5\text{H}_5)_3\text{Mo}(\text{NO})(\text{CO})_2 + \text{Cl}_2$	$\text{CCl}_4$	RT	10 min	Orange	76	5
$[(\eta^5\text{-C}_5\text{H}_5)_3\text{Mo}(\text{NO})\text{Br}_2]_2$	$(\eta^5\text{-C}_5\text{H}_5)_3\text{Mo}(\text{NO})(\text{CO})_2 + \text{Br}_2$	$\text{CCl}_4$	RT	30 min	Brown	86	5
$[(\eta^5\text{-C}_5\text{H}_5)_3\text{Mo}(\text{NO})\text{I}_2]_2$	$(\eta^5\text{-C}_5\text{H}_5)_3\text{Mo}(\text{NO})(\text{CO})_2 + \text{I}_2$	$\text{CH}_2\text{Cl}_2$	Soxhlet	15 h	Purple black	92	5
$\text{Mn}(\text{NO})_2\text{L}_2\text{X}$	$\text{Mn}(\text{CO})_3\text{L}_2\text{X} + \text{NO (g)}$	$\text{C}_6\text{H}_6$	80	1 h			
[L = $\text{PPh}_3$ , $\text{PEt}_3$ , $\text{P(OPh)}_3$ $\text{P(OEt)}_3$ (X = Cl, Br, I)]							
$\text{Re}_2(\text{NO})(\text{CO})_5\text{Cl}_3$	$[\text{Re}(\text{CO})_4\text{Cl}]_2 + \text{NO (g)}$	$\text{CCl}_4$	77	11 h	Orange	51	11
$\text{Fe}(\text{NO})_3\text{X}$ (X = Br, I)	$\text{Fe}(\text{CO})_4\text{X}_2 + \text{Fe} + 6 \text{NO (g)}$						11
$[\text{Co}(\text{NO})_2\text{Cl}]_2$	$(\eta^5\text{-C}_5\text{H}_5)_3\text{Co}(\text{CO})_2 + \text{NOCl}$	$\text{CH}_2\text{Cl}_2$	-78		Black	51	4
$[\text{Co}(\text{NO})_2\text{X}]_2$	$\text{Co}(\text{CO})_3(\text{NO}) + \text{X}_2$						
$[\text{Rh}(\text{NO})_2\text{X}]$	$[\text{Rh}(\text{CO})_2\text{X}]_2 + \text{NO (g)}$	$\text{CCl}_4$ -pet. ether			Brown black		12

## 2.10. The Formation of the Halogen–Group 0 Element Bond

### 2.10.1. Introduction.

The halides are the noble-gas compounds most readily preparable from the elements and other noble-gas element bonds are derived from them, by ligand exchanges. The first ionization potentials of the noble gases, listed in Table 1, indicate that the removal of the outermost electrons increases as the size of the atom increases with increased atomic number. It is the increasing availability of electrons as group 0 is ascended from He to Rn that provides for the formation of bonds to highly electronegative atoms such as the halogens.

Since fluorine is the smallest and most electronegative halogen, fluorine is most effective in withdrawing electrons from the noble-gas atoms to form bonds. Fluorine therefore forms the greatest range of noble-gas compounds and fluorides of Rn, Xe and Kr are known. There are no known compounds (other than transient cationic species) of He, Ne or Ar.

The total bond energies of the difluorides of Kr and Xe, and what is believed to be Rn difluoride, are listed, together with the ionization potentials of the noble-gas atoms, in Table 1. The total bond energies increase monotonically with decrease in ionization potential. This is in accord with the rationale<sup>1</sup> that bond formation depends upon the net transfer of one electron from the noble-gas atom to the two fluorine ligands. This can be expressed by a formulation of the noble-gas difluoride  $\text{GF}_2$  as a resonance hybrid of the canonical forms  $[\text{F}-\text{G}]^+\text{F}^-$  and  $\text{F}^-[\text{G}-\text{F}]^+$  or as a noble-gas atom, single-electron bonded to each of the two F ligands. The latter simplistic representation, like the first, implies a formal charge of  $\frac{1}{2}-$  for each F ligand, viz:  $^{1/2-}\text{F}\cdot\text{G}^+\cdot\text{F}^{1/2-}$ . Much evidence supports this view<sup>2,3</sup>. It is therefore possible to think of the formation of  $\text{GF}_2(\text{g})$ , from  $\text{G}(\text{g}) + 2 \text{F}(\text{g})$ , in terms of the following sequence of steps:

- (1)  $\text{G}(\text{g}) \rightarrow \text{G}^+(\text{g}) + \text{e}^-$
- (2)  $\text{F}(\text{g}) + \text{e}^- \rightarrow \text{F}^-(\text{g})$
- (3)  $\text{G}^+(\text{g}) + \text{F}(\text{g}) \rightarrow (\text{G}-\text{F})^+(\text{g})$
- (4)  $(\text{G}-\text{F})^+(\text{g}) + \text{F}^-(\text{g}) \rightarrow [(\text{G}-\text{F})^+\text{F}^-](\text{g})$
- (5)  $[(\text{G}-\text{F})^+ - \text{F}^-](\text{g}) \rightarrow \text{GF}_2(\text{g})$

Step (1) is the ionization potential and is increasingly unfavorable to  $\text{GF}_2$  formation as the G atom becomes smaller (lighter). Step (2) is common to all  $\text{GF}_2$ , as is step (5), since the latter (the resonance energy) can be represented as the energy gained by delocalizing the electron given to the F atom in step (2) over two atoms instead of one. Step (3) is the electron-pair bond energy for the pseudo-halogen–fluoride diatomic. The bond energies for  $\text{I}-\text{F}$ ,  $\text{Br}-\text{F}$  and  $\text{Cl}-\text{F}$  are<sup>4</sup>, respectively, 251, 247 and 247  $\text{kJ mol}^{-1}$ . Since these values are close to one another, the isoelectronic  $[\text{G}-\text{F}]^+$  species similarly shows small variation. The electrostatic energy involved in the formation of the ion pair  $[(\text{G}-\text{F})^+\text{F}^-](\text{g})$  is also likely to be approximately constant, since the bigger the atom G,

**TABLE 1.** IONIZATION POTENTIALS FOR NOBLE-GAS ATOMS<sup>14</sup> AND TOTAL BOND ENERGIES FOR KrF<sub>2</sub><sup>15</sup>, XeF<sub>2</sub><sup>16</sup> AND RnF<sub>2</sub><sup>18</sup>

Noble gas	He	Ne	Ar	Kr	Xe	Rn
I(kJ·mol <sup>-1</sup> ) <sup>a</sup>	2373	2081	1521	1351	1171	1037
Total bond energy (kJ mol)				100 <sup>b</sup>	268 <sup>c</sup>	≤ 334 <sup>d</sup>

<sup>a</sup> Ref. 14, <sup>b</sup> Ref. 15, <sup>c</sup> Ref. 16, <sup>d</sup> Ref. 17.

the less electronegative it is and the smaller it becomes in interaction with F to form  $[G-F]^+$  (i.e., G more positive in such a cation, the lower its ionization potential). Thus, in the sequence (1)–(5) the one step in which significant variation occurs is step (1). The data in Table 1 support this view. The differences in the total bond energy for pairs of GF<sub>2</sub> are the same as the differences in the corresponding first ionization potentials of G. From this it follows that ArF<sub>2</sub> is most unlikely to be bound with respect to ground-state Ar and F<sub>2</sub> atoms, since the difference in the first ionization potentials of Kr and Ar exceeds the total bond energy of Kr difluoride. Neon and He fluorides are even less likely. Attempts to prepare fluorides (or other compounds) of Ar, Ne and He have failed.

Similar considerations for the other halides lead to the expectation that as the halogen becomes larger the electrostatic term (4) and the bond energy (5) become less favorable to G(X)<sub>2</sub> formation. The greater bond strength of Cl<sub>2</sub> compared with that of F<sub>2</sub> also contributes to the dramatically lower thermodynamic stability of the chlorides relative to the fluorides. Noble-gas-chlorine bonds are much weaker than the bonds to fluorine, and noble-gas-iodine bonds are unknown in neutral molecules. Thus Xe difluoride is a readily preparable, thermodynamically stable molecule, whereas Xe dichloride must be prepared and kept at low T because of its thermodynamic instability and lability. The stretching force constants for Xe—F in XeF<sub>2</sub> and Xe—Cl in XeCl<sub>2</sub> are 2.6 and 1.3 mdynes Å<sup>-1</sup>, respectively<sup>2,5</sup>. Chlorides of Kr are unlikely to be prepared in view of the weak bond in KrF<sub>2</sub>. Radon chlorides are likely to exist, but there is no definitive evidence for them. (Work with macroscopic quantities of Rn is difficult because of the dangerous radioactivity associated with each of the isotopes.)

Even though the chlorides and bromides of Xe are not formed from the elements, because of the weakness of the bonds and the necessity of providing for halogen-atom attack on the Xe atoms, it is possible to study XeCl<sub>2</sub>, XeCl<sub>4</sub> and XeBr<sub>2</sub> by finding them<sup>6</sup> in the products of the β-decay of their <sup>129</sup>I relatives:  $[ICl_2]^-$ ,  $[ICl_4]^-$ ,  $[IBr_2]^-$ , at liq He T.

There are no fluorides of Kr other than the difluoride. A radon fluoride of low volatility is well established<sup>7a</sup>, and although a volatile fluoride has been claimed<sup>8</sup> the existence has been contested<sup>7b</sup>. The former, although considered to be RnF<sub>2</sub>, may be a monofluoride, RnF, as a consequence of relativistic effects<sup>9</sup> stabilizing the 1+ oxidation state of this highly charged nucleus element. The volatile fluoride has been claimed<sup>8</sup> to yield RnO<sub>3</sub> on hydrolysis and this is used to justify identification of the fluoride as either RnF<sub>4</sub> or RnF<sub>6</sub>.

Xenon is the one noble gas for which several oxidation states are established. Three binary fluorides are known: XeF<sub>2</sub>, XeF<sub>4</sub> and XeF<sub>6</sub>. In spite of much effort, the existence of an octafluoride is not confirmed. The claimed oxy fluorides XeO<sub>3</sub>F<sub>2</sub> and XeO<sub>2</sub>F<sub>4</sub> involve all eight of the valence electrons of Xe in bonding. The compound XeOF<sub>4</sub> is also well characterized, as in XeO<sub>2</sub>F<sub>2</sub>. For oxy fluorides, see §3.9.



Cations have been derived from each of the known fluorides by withdrawing one fluoride ion with a strong fluoride ion acceptor such as Sb pentafluoride. Salts of  $[\text{KrF}]^+{}^{10}$ ,  $[\text{XeF}]^+{}^{11}$ ,  $[\text{XeF}_3]^+{}^{12}$ ,  $[\text{XeF}_5]^+{}^{13}$  each show a G—F bond both shorter and stronger than the bonds in the parent  $\text{GF}_x$  molecule and, in  $[\text{XeF}_3]^+$  and  $[\text{XeF}_5]^+$ , shorter than the other G—F bonds of the cations. This uniquely short bond may be regarded as an electron-pair bond. Thus  $[\text{Kr—F}]^+$  and  $[\text{Xe—F}]^+$  are isoelectronic with  $\text{Br—F}$  and  $\text{I—F}$ , and all can be expressed as classical electron-pair bonds. The addition of two fluorine atoms to the bromine atom of  $\text{Br—F}$  to yield  $\text{BrF}_3$  is closely akin to the analogous derivation of  $[\text{XeF}_3]^+$  from  $[\text{XeF}]^+$ . The  $[\text{XeF}_3]^+$  ion has a geometry like that of  $\text{BrF}_3$ . Similarly,  $[\text{XeF}_5]^+$  is akin to  $\text{IF}_5$ . The addition of two F atoms to the G of  $[\text{G—F}]^+$  is not different from the addition of 2 F atoms to a neutral G atom since the G atom in  $[\text{G—F}]^+$  is (at least formally) an octet species. The bonds that F atoms make with neutral G or with  $[\text{G—F}]^+$  may be represented as single electron bonds. Thus, e.g.,  $[\text{XeF}_5]^+$  may be viewed as having one electron-pair bond, which is the short, strong, axial bond, and four single-electron bonds. The nonbonding valence electron pair of the  $\text{Xe(VI)}$  in this  $\text{C}_4$  symmetry cation is assumed to be occupying a sterically active orbital trans to the short  $\text{Xe—F}$  bond.

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10 MeV protons<sup>4</sup>, or an electric discharge<sup>5</sup> of the gaseous mixture. The irradiation of liq Kr-F<sub>2</sub> mixtures with near-UV light, in a double-vacuum vessel of borosilicate glass with a water-cooled UV lamp mounted internally provides an excellent apparatus<sup>6</sup> that gives multigram quantities of the fluoride. **CAUTION: KrF<sub>2</sub> is thermodynamically unstable and is a more powerful oxidizer than F<sub>2</sub>!**

Calorimetric measurements give<sup>7</sup> a heat of formation:  $\Delta H_{f,298}^\circ(\text{KrF}_2) = 60.2 \text{ kJ mol}^{-1}$ . This signifies a mean bond energy of  $50 \text{ kJ mol}^{-1}$ . This is lower than in F<sub>2</sub> itself and accounts for the power of KrF<sub>2</sub> as an oxidative fluorinator.

Krypton monofluoride is observed in KrF<sub>2</sub> irradiated with  $\gamma$ -rays at low T<sup>8</sup>. The radical, which colors the host crystal violet, decomposes above  $-196^\circ\text{C}$ .

Adducts of KrF<sub>2</sub> are formed with strong electron-pair acceptor acids, e.g., KrF<sub>2</sub>·2 SbF<sub>5</sub><sup>9</sup>. On the basis of its vibrational spectrum, and by analogy with the previously described structure of [XeF][Sb<sub>2</sub>F<sub>11</sub>], it is formulated<sup>10</sup> as [KrF][Sb<sub>2</sub>F<sub>11</sub>]. The [Kr<sub>2</sub>F<sub>3</sub>]<sup>+</sup> salts are also characterized<sup>11,12</sup>, and the cation approximates to two [KrF]<sup>+</sup> sharing a common F<sup>-</sup>.

In contrast with KrF<sub>2</sub>, [KrF]<sup>+</sup> salts with sufficiently strong counterions are stable at RT. From the appearance potential of [KrF]<sup>+</sup>,  $A([\text{KrF}]^+, \text{KrF}_2) = 13.39 \text{ eV}$  ( $= 1289 \text{ kJ mol}^{-1}$ )<sup>13</sup> the bond energy for the cation is ca. 150 kJ. This is about three times the mean bond energy of KrF<sub>2</sub>. The nucleophilicity and oxidizing power of [KrF]<sup>+</sup> are successfully exploited in the synthesis of [BrF<sub>6</sub>]<sup>+</sup><sup>14</sup> and [ReF<sub>6</sub>]<sup>+</sup><sup>15</sup> salts.

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### 2.10.2.2. of Xenon Halides

A study of the Xe-F<sub>2</sub> system provides a basis for maximizing the yield of the binary fluorides XeF<sub>2</sub>, XeF<sub>4</sub> or XeF<sub>6</sub>. The equilibrium constants are given in Table 1. Clearly high Xe and low F<sub>2</sub> partial pressures favor XeF<sub>2</sub> formation, as does high T. Conversely, to maximize the yield of XeF<sub>6</sub>, it is necessary to employ the lowest practicable T, and the partial P of F<sub>2</sub> ought to be high relative to that of Xe. The standard enthalpies and entropies of formation<sup>2</sup> are also included in Table 1. From that information XeF<sub>4</sub>, unlike Xe(IV) oxide or hydroxy species, is stable with respect to disproportionation. The equilibrium constant data show, however, why it is not possible to obtain XeF<sub>4</sub> in high purity by direct interaction of the elements. It can be freed from XeF<sub>2</sub> and XeF<sub>6</sub> by

## 2.10. The Formation of the Halogen-Group 0 Element Bond

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## 2.10.2. Direct Synthesis

## 2.10.2.2. of Xenon Halides

10 MeV protons<sup>4</sup>, or an electric discharge<sup>5</sup> of the gaseous mixture. The irradiation of  $\text{Kr-F}_2$  mixtures with near-UV light, in a double-vacuum vessel of borosilicate glass with a water-cooled UV lamp mounted internally provides an excellent apparatus<sup>6</sup> that gives multigram quantities of the fluoride. **CAUTION:  $\text{KrF}_2$  is thermodynamically unstable and is a more powerful oxidizer than  $\text{F}_2$ !**

Calorimetric measurements give<sup>7</sup> a heat of formation:  $\Delta H_{f,298}^\circ(\text{KrF}_2) = 60.2 \text{ kJ mol}^{-1}$ . This signifies a mean bond energy of  $50 \text{ kJ mol}^{-1}$ . This is lower than in  $\text{F}_2$  itself and accounts for the power of  $\text{KrF}_2$  as an oxidative fluorinator.

Krypton monofluoride is observed in  $\text{KrF}_2$  irradiated with  $\gamma$ -rays at low T<sup>8</sup>. The radical, which colors the host crystal violet, decomposes above  $-196^\circ\text{C}$ .

Adducts of  $\text{KrF}_2$  are formed with strong electron-pair acceptor acids, e.g.,  $\text{KrF}_2 \cdot 2 \text{ SbF}_5$ <sup>9</sup>. On the basis of its vibrational spectrum, and by analogy with the previously described structure of  $[\text{XeF}][\text{Sb}_2\text{F}_{11}]$ , it is formulated<sup>10</sup> as  $[\text{KrF}][\text{Sb}_2\text{F}_{11}]$ . The  $[\text{Kr}_2\text{F}_3]^+$  salts are also characterized<sup>11,12</sup>, and the cation approximates to two  $[\text{KrF}]^+$  sharing a common  $\text{F}^-$ .

In contrast with  $\text{KrF}_2$ ,  $[\text{KrF}]^+$  salts with sufficiently strong counterions are stable at RT. From the appearance potential of  $[\text{KrF}]^+$ ,  $A([\text{KrF}]^+, \text{KrF}_2) = 13.39 \text{ eV}$  ( $= 1289 \text{ kJ mol}^{-1}$ )<sup>13</sup> the bond energy for the cation is ca.  $150 \text{ kJ}$ . This is about three times the mean bond energy of  $\text{KrF}_2$ . The nucleophilicity and oxidizing power of  $[\text{KrF}]^+$  are successfully exploited in the synthesis of  $[\text{BrF}_6]^+{}^{14}$  and  $[\text{ReF}_6]^+{}^{15}$  salts.

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TABLE 1. THERMODYNAMIC PROPERTIES OF THE Xe-F<sub>2</sub> SYSTEM(a) Equilibrium constants<sup>a</sup> for the Xe-F<sub>2</sub> system<sup>1</sup>

T (K)	298.15	523.15	573.15	623.15	673.15	773.15
K <sub>1</sub>	[1.23 × 10 <sup>13</sup> ]	[8.80 × 10 <sup>4</sup> ]	[1.02 × 10 <sup>4</sup> ]	[1670]	[360]	29.8
K <sub>2</sub>	[1.37 × 10 <sup>11</sup> ]	1.43 × 10 <sup>3</sup>	1.55 × 10 <sup>2</sup>	27.2	4.86	0.50
K <sub>3</sub>	[8.2 × 10 <sup>5</sup> ]	0.944	0.211	0.0558	0.0182	0.0033

<sup>a</sup> K<sub>1</sub> = [XeF<sub>2</sub>]/[Xe][F<sub>2</sub>]; K<sub>2</sub> = [XeF<sub>4</sub>]/[XeF<sub>2</sub>][F<sub>2</sub>]; K<sub>3</sub> = [XeF<sub>6</sub>]/[XeF<sub>4</sub>][F<sub>2</sub>]. Values in square brackets are calculated.

(b) Standard enthalpies<sup>2</sup> of formation for XeF<sub>2</sub>, XeF<sub>4</sub> and XeF<sub>6</sub>

	XeF <sub>2</sub> (g)	XeF <sub>4</sub> (g)	XeF <sub>6</sub> (g)
ΔH <sub>f,298.15</sub> <sup>o</sup> (kJ mol <sup>-1</sup> )	107.0 ± 2.6	206.2 ± 0.97	279.0 ± 0.87
ΔS <sub>f,298.15</sub> (J deg <sup>-1</sup> mol <sup>-1</sup> )	112.8 ± 4.6	251.0 ± 0.42	396.2 ± 0.12

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(i) Xenon Difluoride and Other Xenon(II) Fluorospecies<sup>1</sup>. The difluoride, a crystalline solid (mp 129°C) is the easiest Xe fluoride to prepare and is the safest to handle. Although potentially a powerful oxidizer, and an effective fluorinator, it is kinetically inert. Thus it has, in pure H<sub>2</sub>O, in which it is moderately soluble (25 g L<sup>-1</sup> at 0°C), a half-life of ~7 h at 0°C<sup>2</sup>. Unlike XeF<sub>4</sub> and XeF<sub>6</sub>, the hydrolysis of XeF<sub>2</sub> does not produce the detonatable trioxide:



The difluoride dissolves in many normal solvents (e.g., ethylether, acetonitrile) and vibrational spectra show that the XeF<sub>2</sub> molecule is only weakly solvated.

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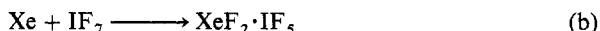
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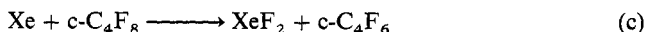
vapor relative to Xe is always low. Circulating the irradiated mixture through a cold trap<sup>3</sup> minimizes contamination by higher fluorides.

For Xe + F<sub>2</sub> reactions carried out in Ni or Monel vessels, kinetic studies show<sup>7</sup> that the reaction is zero order in Xe, that the reaction is primarily heterogeneous and that CoF<sub>3</sub>, NiF<sub>2</sub> and CoF<sub>2</sub> catalyze the reaction. A first-order dependence of the rate of formation of XeF<sub>2</sub> on the F<sub>2</sub> concentration may be due to a slow step involving the dissociation of adsorbed F<sub>2</sub> into adsorbed F atoms. Atomic fluorine (generated in a glow discharge) converts Xe at 77 K to XeF<sub>2</sub> (45% yield in 75 min)<sup>8</sup>. Thus Xe activation is not necessary for XeF<sub>2</sub> formation. This is in accord with all other observations.

Xenon difluoride is also formed by the action of sunlight on Xe-OF<sub>2</sub> mixtures<sup>6</sup> at 25°C, from Xe-O<sub>2</sub>F<sub>2</sub> at -118°C<sup>9</sup>, by γ-irradiation<sup>10</sup> of Xe-F<sub>2</sub> at 4 × 10<sup>6</sup> rad h<sup>-1</sup> at 64°C and from the action of heat<sup>11</sup> on mixtures of Xe with OF<sub>2</sub> (>187°C), CF<sub>3</sub>OF (220–250°C) or FSO<sub>3</sub>F (170–180°C). All are consistent with formation of XeF<sub>2</sub> from Xe and F<sub>2</sub> derived from the other reagent, as is the interaction of Xe with IF<sub>7</sub> at 200°C; here, however, the formation of XeF<sub>2</sub> is also aided by maintaining part of the reaction vessel cool enough for the 1:1 adduct XeF<sub>2</sub>·IF<sub>5</sub> (mp 98°C) to condense:

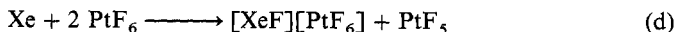


The formation of XeF<sub>2</sub> by passing<sup>13</sup> a high-voltage discharge through Xe-CF<sub>4</sub> mixtures may again represent interaction of Xe with F<sub>2</sub>, but other reaction modes are possible. Thus XeF<sub>2</sub> is reported<sup>14</sup> to be formed via interaction of excited xenon (<sup>3</sup>P<sub>1</sub>) with perfluorocyclobutane:



The high bond polarity of XeF<sub>2</sub> which approximates to <sup>1/2</sup>F—Xe<sup>1+</sup> — F<sup>1/2-</sup> is responsible<sup>15</sup> for the high enthalpy of sublimation of XeF<sub>2</sub> (ΔH<sub>sub</sub><sup>o</sup> = 55.2 kJ mol<sup>-1</sup>)<sup>16</sup> and for the formation of adducts<sup>17–19</sup> with XeF<sub>4</sub>, IF<sub>5</sub>, [XeF<sub>5</sub>]<sup>+</sup>. These represent semiionic interactions. When such interactions are symmetrical about XeF<sub>2</sub> the molecule resembles that in crystalline XeF<sub>2</sub>. Thus in XeF<sub>2</sub>·2 XeF<sub>5</sub>AsF<sub>6</sub>, where XeF<sub>2</sub> is coordinated centrosymmetrically to two [XeF<sub>5</sub>]<sup>+</sup> species the XeF<sub>2</sub> system is linear and symmetrical (Xe—F = 2.01 Å), but in XeF<sub>2</sub>·XeF<sub>5</sub>AsF<sub>6</sub>, where only one [XeF<sub>5</sub>]<sup>+</sup> is coordinated (via a bridging XeF<sub>2</sub> fluorine ligand), the molecule is unsymmetrical (Xe—F<sub>(nonbridging)</sub> = 1.99 Å, Xe—F<sub>(bridging)</sub> = 2.05 Å)<sup>20</sup>. The molecule in the latter situation is in transition towards [F—Xe]<sup>+</sup>...F<sup>-</sup>. Strong fluoride ion acceptors such as SbF<sub>5</sub> and AsF<sub>5</sub> abstract F<sup>-</sup> from XeF<sub>2</sub> to give [XeF]<sup>+</sup> salts<sup>21,22</sup>. The cation shows a shorter, stronger bond (Xe—F = 1.81 Å in [XeF][Sb<sub>2</sub>F<sub>11</sub>]; force constant = 3.7 mdyn Å<sup>-1</sup>) than in XeF<sub>2</sub>. It is representable as a classical electron-pair-bound species. Its stretching frequency (621 cm<sup>-1</sup>) is similar<sup>1</sup> to that of the isoelectronic IF (610 cm<sup>-1</sup>). Because of its charge and high electron affinity, it is more reactive than XeF<sub>2</sub> itself<sup>1</sup> and is exploited<sup>23</sup> in the substitutive fluorination of aromatics.

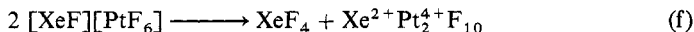
The interaction of Xe with more than 1 mol of PtF<sub>6</sub> yields [XeF][PtF<sub>6</sub>]<sup>24</sup>:



Warming the product formed at RT to ca. 60°C gives the salt [XeF][Pt<sub>2</sub>F<sub>11</sub>]. A mechanism for the formation of [XeF][PtF<sub>6</sub>] supposes that the cation of first formed (1:1) compound, [Xe][PtF<sub>6</sub>], abstracts F<sup>-</sup> from the anion:



and that the XeF radical is oxidized by a second PtF<sub>6</sub> molecule—these processes could be concerted. Displacement with strong fluorobases recovers XeF<sub>2</sub> from these and related salts. Pyrolysis can involve further oxidation of the Xe, e.g.:



The Xe—F radical is sufficiently well bound to favor disproportionation<sup>1</sup>:



rather than F<sub>2</sub> formation:



The radical (which is violet) can be studied<sup>25</sup> in a crystal of XeF<sub>4</sub> γ-irradiated at 77 K. It is an intermediate in reactions of XeF<sub>2</sub> as well as in its synthesis.

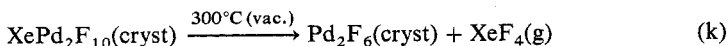
The Xe(II) compounds, AXeF (where A is a highly electronegative ligand)<sup>1</sup>, are derived from XeF<sub>2</sub> and are dealt with elsewhere (see §3.9 and 4.8). The Xe(II)—F bonds in these compounds are intermediate between those in [XeF]<sup>+</sup> and XeF<sub>2</sub>. The compounds are prepared from XeF<sub>2</sub> by ligand exchange, which eliminates one of the F ligands as HF, BF<sub>3</sub> or another thermodynamically favored molecule, e.g.:



Short, terminal Xe—F bonds also occur<sup>26</sup> in the cations [Xe<sub>2</sub>F<sub>3</sub>]<sup>+</sup> and [(XeF)<sub>2</sub>E]<sup>+</sup> (where E is a strong acid anion species, e.g., [SO<sub>3</sub>F]<sup>−</sup>). These cations can be approximately described as [FXe]<sup>+</sup>E<sup>−</sup>[XeF]<sup>+</sup>. They are derived from [XeF]<sup>+</sup> and FXeE.

(ii) Xenon Tetrafluoride. Although XeF<sub>4</sub> is formed by direct interaction of Xe with F<sub>2</sub> (1:5 mol ratio) at 400°C in a Ni reactor<sup>27</sup>, that and related syntheses yield XeF<sub>4</sub> contaminated by the other fluorides. A quantitative conversion is claimed<sup>28</sup> for a F<sub>2</sub>—Xe mixture in mole ratio 2:1 (at an operating pressure of 2–15 mm) in a reaction vessel at −78°C subjected to an electric discharge and is continuously produced. The tetrafluoride is also made using a F<sub>2</sub>:Xe mole ratio of 3:1 and a furnace T of 560°C<sup>29</sup>. Unless flow rate, T and partial pressure are controlled, such continuous production methods give a product of variable composition. Fractionation yields XeF<sub>4</sub> of high purity<sup>30</sup>. The stability of the adduct<sup>17</sup> XeF<sub>2</sub>·XeF<sub>4</sub> means that the synthesis should be carried out to favor XeF<sub>6</sub> rather than XeF<sub>2</sub> as the major contaminant. Purification is best made<sup>31</sup> by exploiting the inferior fluoride ion donor ability of XeF<sub>4</sub> relative to XeF<sub>2</sub> and XeF<sub>6</sub>. Thus the impure XeF<sub>4</sub>, contaminated with XeF<sub>2</sub> or XeF<sub>6</sub> or both, is dissolved in BrF<sub>3</sub> and xs AsF<sub>5</sub> is condensed upon the mixture. The XeF<sub>2</sub> and XeF<sub>6</sub> form salts of low volatility and the solvent and AsF<sub>5</sub> may be removed in vacuum at 0°C, thus leaving a mixture of [Xe<sub>2</sub>F<sub>3</sub>]<sup>+</sup>[AsF<sub>6</sub>]<sup>−</sup>, [XeF<sub>5</sub>]<sup>+</sup>[AsF<sub>6</sub>]<sup>−</sup> and XeF<sub>4</sub>, from which the last can be obtained by vacuum sublimation at 20°C.

Pure tetrafluoride is also formed<sup>24</sup> by the pyrolysis of [XeF]<sup>+</sup> salts of high oxidation state transition-element salts:



The square-planar XeF<sub>4</sub> molecule possesses high bond polarity, which contributes to the formation of the 1:1 adduct with XeF<sub>2</sub><sup>17</sup>. In combination with the fluoroacid



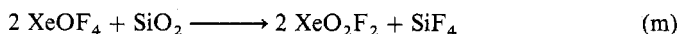
$\text{SbF}_5$ ,  $[\text{XeF}_3]^+[\text{SbF}_6]^-$ <sup>32</sup> and  $[\text{XeF}_3]^+[\text{Sb}_2\text{F}_{11}]^-$ <sup>33</sup> salts are formed. The T-shaped cation shows one short, strong electron-pair bond ( $\text{Xe}-\text{F} = 1.83 \text{ \AA}$ ). The remaining XeF bonds (approximately trans to one another,  $\text{Xe}-\text{F} = 1.89 \text{ \AA}$ ) are more like the bonds in  $\text{XeF}_4$  itself ( $\text{Xe}-\text{F} = 1.91 \text{ \AA}$ ).

(iii) Xenon Hexafluoride and Other Xe(VI) Fluorospecies<sup>1</sup>. High-yield syntheses of the hexafluoride<sup>34</sup> employ xs  $\text{F}_2$  at high pressure at ca.  $300^\circ\text{C}$ . A 95% conversion to  $\text{XeF}_6$  is obtained with  $\text{F}_2:\text{Xe}$  ratios of 20:1 at 50 atm<sup>7</sup>. An electric discharge of a 3:1  $\text{F}_2$ -Xe mixture with the product trapped at  $-78^\circ\text{C}$  also yields<sup>35</sup>  $\text{XeF}_6$ , and  $\text{XeF}_6^-$  is also formed from  $\text{XeF}_4$  by the action of  $\text{O}_2\text{F}_2$  at  $-133$  and  $-78^\circ\text{C}$ . In keeping with its low bond energy,  $\text{KrF}_2$  oxidizes Xe to  $\text{XeF}_6$  at RT or below<sup>36</sup>. The impurities in  $\text{XeF}_6$  prepared from Xe- $\text{F}_2$  mixtures are the tetrafluoride and  $\text{XeOF}_4$ . The latter derives from the facility with which  $\text{XeF}_6$  interacts with oxides. The hexafluoride is purified via its complex with NaF formed at  $50^\circ\text{C}$ . The complex is decomposed at  $125^\circ\text{C}$  to evolve  $\text{XeF}_6$ <sup>34</sup>.

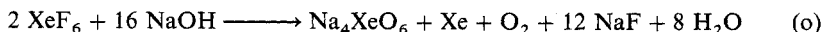
The  $\text{XeF}_6$  product is colorless as a solid (mp  $49.48^\circ\text{C}$ ) but the liquid and vapor are yellow green. It is more volatile than  $\text{XeF}_2$  or  $\text{XeF}_4$ . Of the two crystalline forms, the cubic form contains both tetrameric and hexameric units in the same unit cell. Each oligomer species is an  $\text{F}^-$ -bridged assembly of  $[\text{XeF}_5]^+$  and  $\text{F}^-$  ions. Each structural arrangement is consistent with the location of the nonbonding valence electron pair of Xe(VI) in a spatially directed orbital on the fourfold axis of each  $[\text{XeF}_5]^+$  ion.

In the gas phase,  $\text{XeF}_6$  is a monomer. Vibrational spectroscopy and electron diffraction studies indicate the difference from the  $\text{O}_h$   $\text{TeF}_6$ . Electrostatic-deflection molecular-beam experiments show that the dipole moment (if present) must be less than 0.03 D. The electron diffraction data provide an  $\text{Xe}-\text{F}$  bond distance of  $1.890 \text{ \AA}$ . Thus if the ground-state geometry is  $\text{O}_h$ , there must be low-lying non- $\text{O}_h$  geometries that are populated at ordinary T (see the molecular orbital diagram shown in Figure 1)<sup>37</sup>. Thus the non- $\text{O}_h$  and fluxional behavior of  $\text{XeF}_6$  can be understood in terms of a pseudo-Jahn-Teller effect. This occurs because the  $a_{1g}^*$  orbital (which is fully populated in the ground vibrational state) is accidentally degenerate with the  $t_{1u}^*$  orbitals in certain higher vibrational states. The  $t_{1u}$  symmetry deformational modes have maximum influence in bringing about the pseudo-degeneracy of the  $a_{1g}^*$  and  $t_{1u}^*$  orbitals. The partial occupancy of the latter destroys their degeneracy and further accentuates the departure from  $\text{O}_h$  symmetry.

The mean thermochemical bond energy of  $\text{XeF}_6$  ( $125 \text{ kJ mol}^{-1}$ ) is close to the values for  $\text{XeF}_4$  and  $\text{XeF}_2$  (130 and  $132 \text{ kJ mol}^{-1}$ , respectively—see Table 1, §2.10.2.2 for enthalpies of formation), yet the bond length is shorter than in  $\text{XeF}_4$  or  $\text{XeF}_2$ . The hexafluoride is a more powerful oxidizer and fluorinator than either  $\text{XeF}_2$  or  $\text{XeF}_4$  and has little of the kinetic stability of  $\text{XeF}_2$  and  $\text{XeF}_4$ . Thus, unlike  $\text{XeF}_2$  and  $\text{XeF}_4$ , it is not possible to store  $\text{XeF}_6$  in glass or quartz. There are sequential reactions:



Interaction with  $\text{H}_2\text{O}$  similarly yields  $\text{XeOF}_4$ ,  $\text{XeO}_2\text{F}_2$  and  $\text{XeO}_3$ . Hydrolysis of  $\text{XeF}_6$  in strong base leads to the formation of perxenate, the idealized disproportionation being:



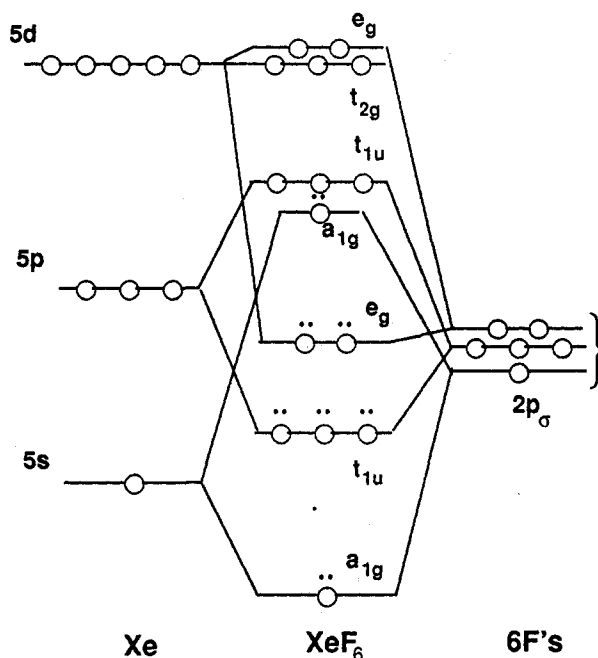


Figure 1. Schematic correlation diagram illustrating MO energy levels for an O<sub>n</sub> molecule.

Hydrolysis in the presence of O<sub>3</sub> generates perxenate more efficiently. The hexafluoride interacts violently with H<sub>2</sub> to yield HF and Xe and with Hg to give Xe and HgF<sub>2</sub>, and both are used in analytical procedures for XeF<sub>6</sub>.

As a fluoride-ion donor XeF<sub>6</sub> with fluoride-ion acceptors form salts<sup>38,39</sup>. Those of formulation [XeF<sub>5</sub>][MF<sub>6</sub>] are typified by the structures of [XeF<sub>5</sub>][AsF<sub>6</sub>] and [XeF<sub>5</sub>][RuF<sub>6</sub>] shown in Figure 2. For M = Au the former structure is adopted, but for M = Pt, Ir, Rh, Tc, Nb, Ta, Sb, the latter is preferred. The 2:1 salts<sup>40</sup> are formulated [Xe<sub>2</sub>F<sub>11</sub>][MF<sub>6</sub>]. The cation is a combination of two [XeF<sub>5</sub>]<sup>+</sup> bridged by an F<sup>-</sup> ligand. The [XeF<sub>5</sub>][M<sub>2</sub>F<sub>11</sub>] salts also exist. Structures have also been characterized for [XeF<sub>5</sub>]<sub>2</sub>[PdF<sub>6</sub>]<sup>41</sup>, [XeF<sub>5</sub>]<sub>2</sub>[NiF<sub>6</sub>] and [Xe<sub>2</sub>F<sub>11</sub>]<sub>2</sub>[NiF<sub>6</sub>]<sup>42</sup>.

Strong fluorobases such as alkali fluorides and nitrosyl fluoride (ONF) form complexes with XeF<sub>6</sub> in which fluoroxenate(VI) anions occur; e.g., (NO)<sub>2</sub>XeF<sub>8</sub> is a salt, [NO<sup>+</sup>]<sub>2</sub>[XeF<sub>8</sub>]<sup>2-</sup><sup>43</sup>, with a Xe atom surrounded by an approximate antiprism of F ligands. The Xe atom is on the pseudo-fourfold axis, but closer to four fluorine atoms than to the other four. This noncentrosymmetry is again indicative of steric activity of the nonbonding Xe(VI) electron pair, although the steric effect is subtle in this case, perhaps as a consequence of the increase in coordination number.

iv. Xenon Oxide Tetrafluoride. This colorless volatile compound may be made<sup>44</sup> by the controlled hydrolysis of XeF<sub>6</sub> using the stoichiometric H<sub>2</sub>O:



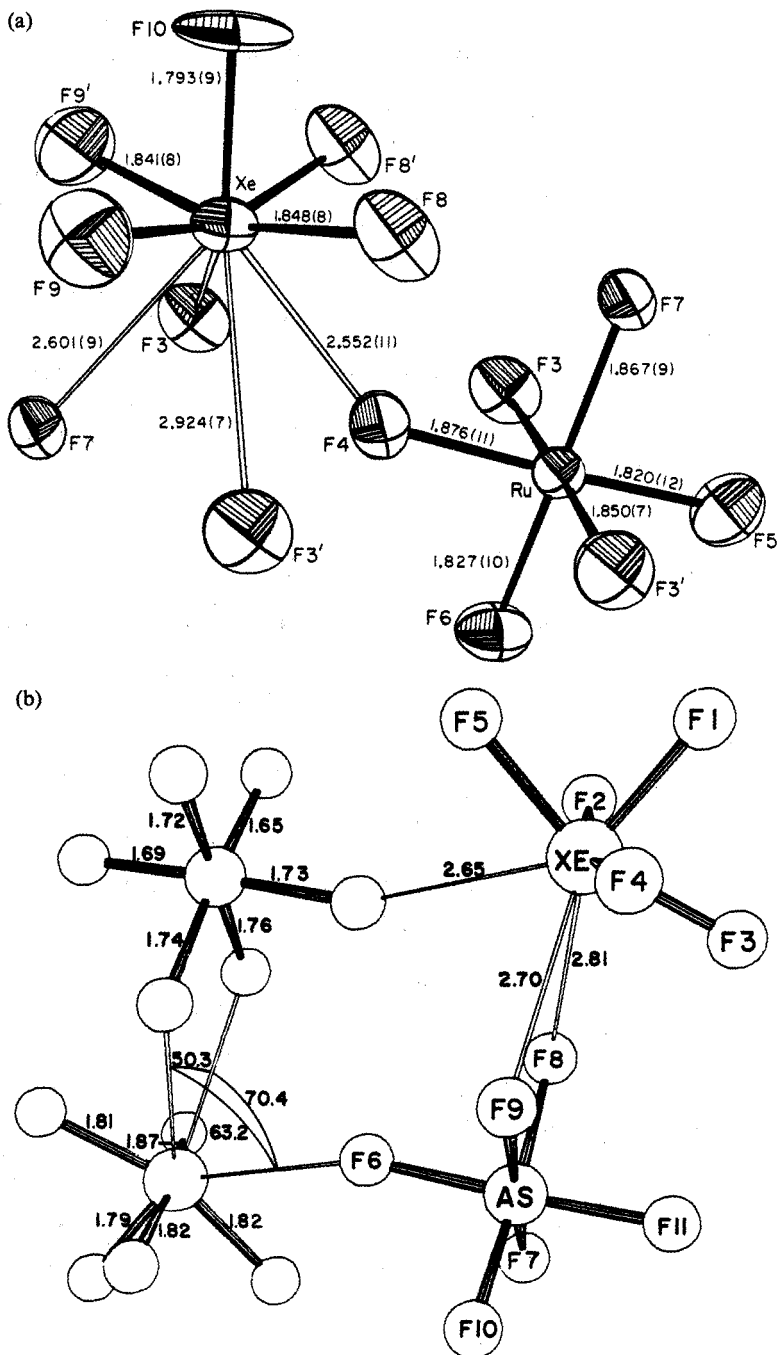


Figure 2. Ion arrangements in the crystal structures of (a)  $[\text{XeF}_5][\text{RuF}_6]$  and (b)  $[\text{XeF}_5][\text{AsF}_6]$ .

It is liquid at RT. The characteristic Xe—O stretching frequency provides for identification (vibrational  $920\text{ cm}^{-1}$ , infrared  $926\text{ cm}^{-1}$ ). Microwave and electron-diffraction studies establish  $C_{4v}$  symmetry, the four F ligands being almost coplanar with the Xe atom (angle O—Xe—F =  $91.8^\circ$ ). The Xe—F bond length ( $1.900\text{ \AA}$ ) is comparable to that in  $\text{XeF}_6$ , whereas the Xe—O bond length ( $1.703\text{ \AA}$ ) is shorter than observed in either  $\text{XeO}_3$  ( $1.76\text{ \AA}$ ) or  $\text{XeO}_4$  ( $1.74\text{ \AA}$ )<sup>1</sup>. ESCA studies show<sup>4,5</sup> that the O ligand withdraws approximately twice the electron density from the Xe atom that each F ligand does. The  $\text{XeOF}_4$  behaves as a fluoride ion donor toward strong  $\text{F}^-$  acceptors such as  $\text{SbF}_5$ , but the weakness of its complex with  $\text{AsF}_5$  and the stability of  $[\text{XeF}_5][\text{AsF}_6]$  provides for the removal of  $\text{XeF}_6$  impurity in  $\text{XeOF}_4$ . The  $[\text{XeOF}_3]^+$  ion is a pseudo-trigonal bipyramid with the oxygen atom equatorial. Good  $\text{F}^-$  donors (although not  $\text{NaF}$ ) form salts with  $\text{XeOF}_4$ , and  $[\text{XeOF}_5]^-$  may occur in such complexes.

v. Xenon Dioxide Difluoride. Hydrolysis of  $\text{XeOF}_4$ <sup>4,6</sup> or interaction of  $\text{XeOF}_4$  with  $\text{XeO}_3$  gives  $\text{XeO}_2\text{F}_2$ . Vibrational spectroscopy indicates  $C_{2v}$  symmetry, the molecule being structurally akin to  $[\text{IO}_2\text{F}_2]^-$ , which is a pseudo-trigonal bipyramid with F ligands axial and O ligands equatorial.

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## 2.10.2. Direct Synthesis

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**2.10.2.2.2. Xenon Chlorides.**

Infrared spectroscopy establishes that the passage of a Xe-Cl<sub>2</sub> mixture (~100:1) through a microwave discharge yields XeCl<sub>2</sub> when the gases are condensed at 20 K<sup>1</sup>, or by photolysis of Cl<sub>2</sub>-Xe mixtures with 4880 Å excitation<sup>2,3</sup>. Higher chlorides are not detected in direct Cl-Xe interactions, although XeCl<sub>4</sub> and other halides are nuclear γ-ray resonance fluorescence detected in studies of <sup>129</sup>I undergoing β decay<sup>4</sup>.

The XeCl<sub>2</sub> is a linear symmetrical molecule<sup>3</sup> characterized by an IR band (ν<sub>3</sub>) at 312 cm<sup>-1</sup> and a Raman band at 254 cm<sup>-1</sup> (ν<sub>1</sub>). The low value of the stretching force constant (f<sub>r</sub> = 1.3 mdyn Å<sup>-1</sup> compared with 2.6 for XeF<sub>2</sub>) indicates that the bonding in XeCl<sub>2</sub> is weak. This is also indicated by the failure to prepare or retain the chloride other than at low T. Thus XeCl<sub>2</sub> ought to be an effective reagent for the syntheses of high oxidation state chlorides. The major practical difficulty is to provide a reaction medium at a T low enough to prevent simple thermal decomposition of the dichloride.

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**2.10.2.3. of Radon Halides**

Fluorine is the only halogen known<sup>1a</sup> to form bonds to Rn. There is a low volatility Rn fluoride<sup>2</sup>, probably RnF<sub>2</sub>. A more volatile fluoride has been claimed<sup>3</sup> but it and the oxide reported to be derived from it have been denied<sup>1b</sup> (see §3.9). On the basis of the hydrolytic behavior the more volatile fluoride could be either RnF<sub>4</sub> or RnF<sub>6</sub>.

## 2.10. The Formation of the Halogen-Group 0 Element Bond

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## 2.10.2. Direct Synthesis

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Fluorine is the only halogen known<sup>1a</sup> to form bonds to Rn. There is a low volatility Rn fluoride<sup>2</sup>, probably RnF<sub>2</sub>. A more volatile fluoride has been claimed<sup>3</sup> but it and the oxide reported to be derived from it have been denied<sup>1b</sup> (see §3.9). On the basis of the hydrolytic behavior the more volatile fluoride could be either RnF<sub>4</sub> or RnF<sub>6</sub>.

## 2.10. The Formation of the Halogen-Group 0 Element Bond

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## 2.10.2. Direct Synthesis

## 2.10.2.3. of Radon Halides

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## 2.10.2.2.2. Xenon Chlorides.

Infrared spectroscopy establishes that the passage of a Xe-Cl<sub>2</sub> mixture (~100:1) through a microwave discharge yields XeCl<sub>2</sub> when the gases are condensed at 20 K<sup>1</sup>, or by photolysis of Cl<sub>2</sub>-Xe mixtures with 4880 Å excitation<sup>2,3</sup>. Higher chlorides are not detected in direct Cl-Xe interactions, although XeCl<sub>4</sub> and other halides are nuclear γ-ray resonance fluorescence detected in studies of <sup>129</sup>I undergoing β decay<sup>4</sup>.

The XeCl<sub>2</sub> is a linear symmetrical molecule<sup>3</sup> characterized by an IR band (ν<sub>3</sub>) at 312 cm<sup>-1</sup> and a Raman band at 254 cm<sup>-1</sup> (ν<sub>1</sub>). The low value of the stretching force constant (f<sub>r</sub> = 1.3 mdyn Å<sup>-1</sup> compared with 2.6 for XeF<sub>2</sub>) indicates that the bonding in XeCl<sub>2</sub> is weak. This is also indicated by the failure to prepare or retain the chloride other than at low T. Thus XeCl<sub>2</sub> ought to be an effective reagent for the syntheses of high oxidation state chlorides. The major practical difficulty is to provide a reaction medium at a T low enough to prevent simple thermal decomposition of the dichloride.

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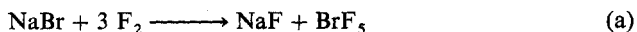
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The low volatility fluoride is prepared<sup>2</sup> by heating the longest-lived isotope,  $^{222}\text{Rn}$ , in  $\text{F}_2$ . Millicurie amounts of Rn react with liq  $\text{F}_2$  at  $-195^\circ\text{C}$ , the activation being provided by the  $\alpha$  radiation<sup>4</sup>. The low-volatility fluoride could be  $\text{RnF}^5$  or  $\text{RnF}_2^{1a}$ . This fluoride is stable to  $\text{H}_2$  at  $200^\circ\text{C}$ , but at  $500^\circ\text{C}$  ( $P_{\text{H}_2}$  ca. 1 atm) reduction is complete in 15 min.

Radon can also be oxidized at  $25^\circ\text{C}$  and lower by the halogen fluorides  $\text{ClF}$ ,  $\text{ClF}_3$ ,  $\text{ClF}_5$ ,  $\text{BrF}_3$ ,  $\text{BrF}_5$  and  $\text{IF}_7$  and by mixed solvent oxidant pairs  $\text{HF}-\text{BrF}_3$ ,  $\text{HF}-\text{BrF}_5$ ,  $\text{IF}_5-\text{BrF}_5$  and  $\text{K}_2\text{NiF}_6$  in  $\text{HF}^{1a}$ . Removal of volatiles leaves an involatile Rn fluoride ( $\text{RnF}_2$ ) or complex fluoride. Electromigration studies of the  $^{222}\text{Rn}$  in those solutions shows it to be cationic, consistent with  $[\text{RnF}]^+$  or  $\text{Rn}^{2+}$  (or even  $\text{Rn}^+$ ) in solution<sup>1a</sup>. With added  $\text{KF}$  or  $\text{CsF}$  there species such as  $[\text{RnF}_3]^-$  or  $[\text{RnF}_4]^{2-}$  form. On the basis of the interaction of  $^{222}\text{Rn}$  with the halogen fluorides, the free energy of formation of the postulated  $\text{RnF}_2$  lies between  $-29$  and  $-51 \text{ kcal mol}^{-1}$ .

Solids containing the oxidizing cations  $[\text{ClF}_2]^+$ ,  $[\text{BrF}_2]^+$ ,  $\text{O}_2^+$ ,  $[\text{N}_2\text{F}]^+$  and  $[\text{IF}_6]^+$  oxidize  $^{222}\text{Rn}$ . By analogy with the behavior of Xe in like reactions,  $[\text{RnF}]^+$  salt formation is postulated<sup>1a</sup>. These salts have been recommended as scrubbers for the removal of Rn from air in, e.g., uranium mines. Hydrolysis of the postulated  $\text{RnF}_2$  or  $[\text{RnF}]^+$  salts yields  $^{222}\text{Rn}$  quantitatively<sup>1a</sup>. Fluorination of a Xe-Rn mixture with 100-fold xs  $\text{F}_2$  (100 atm) at  $300^\circ\text{C}$  forms a nonvolatile Rn fluoride<sup>6</sup> but also a trace of another Rn product, which distills with  $\text{XeF}_6$ . This suggests the existence of a higher Rn fluoride. Given the greater ionicity of  $\text{Rn}-\text{F}$  relative to  $\text{Xe}-\text{F}$  bonds, fluoride ion donors ( $\text{NaF}$ ) in  $\text{BrF}_5$  are used to keep the  $\text{RnF}_2$  from forming cationic ( $[\text{RnF}]^+$ ) complexes, which are resistant to further fluorination<sup>3</sup>. Since  $\text{Ni(IV)}$  salts can act as fluorinating intermediates,  $\text{NiF}_2$  is used as a catalyst. With 400 mg  $\text{NiF}_2$  and 0.5 mL  $\text{BrF}_5$ , microquantities of  $^{222}\text{Rn}$  mixed with Xe and  $\text{F}_2$  in 1:100 mole ratio at  $15-20 \times 10^6$  Pa are heated to  $250^\circ\text{C}$  for 40 h. Volatiles are removed in vacuo at  $-30^\circ\text{C}$ . Alternatively, Xe, Rn and  $\text{F}_2$  in the same quantities as above are condensed upon 300-350 mg  $\text{NaBr}$ , and the mixture is heated to  $250^\circ\text{C}$  for up to 90 h, with fluorine added periodically to ensure complete conversion:



Excess  $\text{F}_2$  and  $\text{BrF}_5$  are removed under vacuum at RT, then at  $80^\circ\text{C}$  for 3 h. Hydrolysis of the residual products indicates formation of an aqueous species, which is reduced by iodide to liberate Rn. Approximately 70% of the dissolved Rn is co-reprecipitated with  $\text{BaXeO}_4$ , suggesting that the original aqueous solution species is  $\text{RnO}_3$ . This is presented as evidence for either  $\text{RbF}_4$  or  $\text{RnF}_6$ . The question of which fluoride yielded the  $\text{RnO}_3$ ,  $\text{RnF}_4$  or  $\text{RnF}_6$ , is not answered, and evidence has been presented<sup>1b</sup> to refute all of these claims for higher oxidation state radon compounds.

(N. BARTLETT)

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## 2.11. The Formation of the High Oxidation State Group-IB, -IIB, and Transition- and Inner-Transition-Metal Fluorides

### 2.11.1. Introduction

This chapter surveys the preparation of transition-metal fluorides in which the transition metals exist in their highest formal oxidation state. The concept of high formal oxidation (or valent) state includes not only the maximum state obtained for a given periodic grouping but unusual high formal oxidation states. Emphasis is given here to the

TABLE 1. BINARY FLUORIDES IN HIGHEST OXIDATION STATE

IIIA	IVA	VA	VIA	VIIA		VIII		IB	IIB
ScF <sub>3</sub>	TiF <sub>4</sub>	VF <sub>5</sub>	CrF <sub>6</sub> <sup>a</sup> CrF <sub>5</sub>	MnF <sub>4</sub>	FeF <sub>3</sub>	CoF <sub>3</sub>	NiF <sub>4</sub> NiF <sub>3</sub>	CuF <sub>2</sub> AgF <sub>3</sub>	ZnF <sub>2</sub>
YF <sub>3</sub>	ZrF <sub>4</sub>	NbF <sub>5</sub>	MoF <sub>6</sub>	TcF <sub>6</sub>	RuF <sub>8</sub> <sup>a</sup> RuF <sub>6</sub>	RhF <sub>6</sub>	PdF <sub>6</sub> <sup>a</sup> PdF <sub>4</sub>	AgF <sub>2</sub> AuF <sub>7</sub> <sup>a</sup>	CdF <sub>2</sub>
LaF <sub>3</sub> <sup>b</sup>	HfF <sub>4</sub>	TaF <sub>5</sub>	WF <sub>6</sub>	ReF <sub>7</sub>	OsF <sub>8</sub> <sup>a</sup> OsF <sub>7</sub> <sup>a</sup> OsF <sub>6</sub>	IrF <sub>6</sub>	PtF <sub>6</sub>	AuF <sub>5</sub>	HgF <sub>2</sub>
AcF <sub>3</sub> <sup>c</sup>									

<sup>a</sup> Only stable at low T.

<sup>b</sup> Lanthanides LaF<sub>3</sub>, CeF<sub>4</sub>, PrF<sub>4</sub>, NdF<sub>3</sub>, PmF<sub>3</sub>, SmF<sub>3</sub>, EuF<sub>3</sub>, GdF<sub>3</sub>, TbF<sub>4</sub>, DyF<sub>3</sub>, HoF<sub>3</sub>, ErF<sub>3</sub>, TmF<sub>3</sub>, YbF<sub>3</sub>, LuF<sub>3</sub>.

<sup>c</sup> Actinides AcF<sub>3</sub>, ThF<sub>4</sub>, PaF<sub>5</sub>, UF<sub>6</sub>, NpF<sub>6</sub>, PuF<sub>6</sub>, AmF<sub>4</sub>, CmF<sub>4</sub>, BkF<sub>4</sub>, CfF<sub>4</sub>, EsF<sub>4</sub>, Fm, Md, No, Lr, Rf, Ha.

TABLE 2. REPRESENTATIVE OXIDE FLUORIDES TRANSITION METALS (FIRST, SECOND, THIRD SERIES)

IIIA	IVA	VA	VIA	VIIA		VIII		IB	IIB
ScOF	TiOF <sub>2</sub>	VOF <sub>3</sub> VO <sub>2</sub> F	CrO <sub>2</sub> F <sub>2</sub> CrOF <sub>4</sub> CrOF <sub>3</sub>	MnO <sub>3</sub> F	FeOF	—	—	—	—
YOF	ZrOF <sub>2</sub>	NbOF <sub>3</sub> NbO <sub>2</sub> F Nb <sub>3</sub> O <sub>7</sub> F	MoO <sub>2</sub> F <sub>2</sub> MoOF <sub>4</sub>	TcO <sub>3</sub> F TcOF <sub>4</sub> Tc <sub>2</sub> O <sub>3</sub> F <sub>4</sub> TcO <sub>2</sub> F <sub>3</sub>	RuOF <sub>4</sub>	—	—	—	—
LaOF <sup>a</sup>	HX <sub>2</sub> OF <sub>6</sub> HX <sub>3</sub> O <sub>2</sub> F <sub>8</sub>	TaOF <sub>3</sub> TaO <sub>2</sub> F Ta <sub>3</sub> O <sub>7</sub> F	WO <sub>2</sub> F <sub>2</sub> WOF <sub>4</sub>	ReOF <sub>5</sub> ReO <sub>3</sub> F ReO <sub>2</sub> F <sub>3</sub> ReOF <sub>4</sub>	OsO <sub>3</sub> F <sub>2</sub> OsOF <sub>5</sub>	—	PtOF <sub>3</sub>	—	—
AcOF <sup>b</sup>									

<sup>a</sup> Lanthanides: MOF (M = La-Lu)

<sup>b</sup> Actinides: AcOF, ThOF<sub>2</sub>, Pa<sub>2</sub>OF<sub>8</sub>, UO<sub>2</sub>F<sub>2</sub>, UOF<sub>4</sub>; NpO<sub>2</sub>F<sub>2</sub>, NpOF<sub>4</sub>; PuO<sub>2</sub>F<sub>2</sub>, PuOF<sub>4</sub>; AmO<sub>2</sub>F<sub>2</sub>.



transition-metal fluorides that (1) contain the transition metal in high formal oxidation states and/or (2) are considered to be exceptionally strong oxidizers. Table 1 lists the transition-metal fluorides in which the metal is in the highest oxidation states. Since  $\text{CrF}_6$ ,  $\text{OsF}_8$ ,  $\text{OsF}_7$ ,  $\text{RuF}_8$ ,  $\text{PdF}_6$  and  $\text{AuF}_7$  are only stable at low T their chemistry is almost nonexistent and as a consequence, their lower binary fluorides are discussed. In Tables 2 and 3, many of the oxyfluorocomplexes (oxide fluoride complexes) and fluorocomplexes are listed; the coverage is not comprehensive or complete but is illustrative of the great many possible derivatives<sup>1-4</sup>.

**CAUTION: Preparative reagents such as  $\text{F}_2$ ,  $\text{ClF}_3$ ,  $\text{IF}_5$ , anhyd HF,  $\text{COF}_2$ , and  $\text{SF}_4$  are commonly used to prepare high oxidation state fluorides and require special care in handling.**

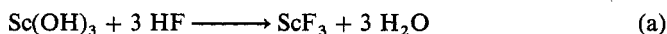
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3. A review concerning preparation of oxide fluorides is J. H. Holloway, D. Laycock, *Advances in Inorganic Chemistry and Radiochemistry*, Vol. 28, H. J. Emeléus, A. G. Sharpe, eds., Academic Press, New York, 1969, pp. 73-79.
4. The author would like to thank Dr. Boris Žemva, Jozsf Stefan Institute, Ljubljara, Yugoslavia for helping to update and review this material.

## 2.11.2. of the First Transition Series (Sc through Zn)

### 2.11.2.1. Synthesis of High Valent Fluorides, Oxide Fluorides and Fluorocomplexes of Sc, Ti, V, Cr, Mn.

The trifluoride of scandium can be prepared<sup>1</sup>:



Other methods include direct reaction of  $\text{Sc}_2\text{O}_3$  with  $[\text{NH}_4][\text{HF}_2]$  or fluorination of the metal<sup>2</sup>.

The oxyfluoride  $\text{ScOF}$  is prepared<sup>3</sup> by partial hydrolysis of  $\text{ScF}_3$  in moist air at elevated T.

Fluorosalt complexes containing  $[\text{ScF}_4]^-$  and  $[\text{ScF}_6]^{3-}$  ions are prepared from melts of  $\text{ScF}_3$  with metal fluorides; for example, melts of  $\text{NaF}$  with  $\text{ScF}_3$  give two compounds<sup>4</sup>:  $3 \text{NaF} \cdot \text{ScF}_3$  and  $\text{NaF} \cdot \text{ScF}_3$ . The adduct  $\text{XeF}_6 \cdot \text{ScF}_3$  is prepared by reacting  $\text{N}_2\text{H}_6 \cdot \text{ScF}_4$  with xs  $\text{XeF}_6$ <sup>5</sup>.

Titanium reacts with  $\text{F}_2$  above  $150^\circ\text{C}$  with conversion to the  $\text{TiF}_4$  being complete at  $200^\circ\text{C}$ ; using  $\text{TiO}_2$  in place of Ti requires higher T ( $350^\circ\text{C}$ ) for complete conversion<sup>6,7</sup>. It is also prepared by reacting HF and  $\text{TiCl}_4$  but extremely pure anhyd HF is required<sup>8</sup>. Other methods include the use of  $\text{ClF}_3$  in a flow system with Ti ( $350^\circ\text{C}$ ) or reacting  $\text{TiO}_2$  with  $\text{SF}_4$  at  $300^\circ\text{C}$  (10 h) in a pressure reactor<sup>9,10</sup>. The following derivatives of  $\text{TiF}_4$  are known<sup>11</sup>:  $\text{TiF}_3\text{Cl}$ ,  $\text{TiF}_2\text{Cl}_2$ ,  $\text{TiF}_3\text{Br}$ ,  $\text{TiF}_3[\text{NO}_3] \cdot \text{N}_2\text{O}_5$  and  $\text{TiO}(\text{OH})\text{F}$ .

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 2.11.2. of the First Transition Series (Sc through Zn)  
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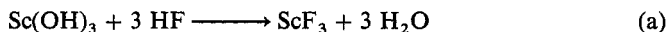
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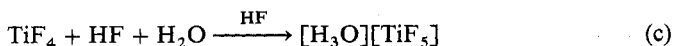
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The oxyfluoride  $\text{TiOF}_2$  is prepared by the following method<sup>12</sup>:

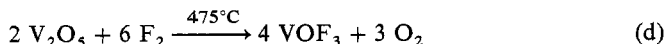


Titanium tetrafluoride forms numerous adducts with a variety of different ligands<sup>13</sup>. Salt-like fluorocomplexes containing  $[\text{TiF}_6]^{2-}$  can be prepared by reacting, in aq HF, the appropriate alkali-metal fluoride and  $\text{TiO}_2$  in correct stoichiometric amounts<sup>14</sup>. In solutions, complex ions  $[\text{TiF}_5 \cdot \text{ROH}]^-$  with  $\text{R} = \text{CH}_3, \text{CH}_3\text{CH}_2, \text{i-C}_3\text{H}_7$  are known<sup>15</sup>. Difluorobis(acetylacetonato)titanium(IV) is prepared by reacting acetylacetone and  $\text{TiF}_4$  in  $\text{CH}_2\text{Cl}_2$  solution<sup>16</sup>. The salt  $[\text{NO}]_2[\text{TiF}_6]$  is prepared by reacting  $\text{BrF}_3$  with Ti metal in the presence of nitrosyl chloride; sublimation of the complex ( $180^\circ\text{C}$ ) in vacuo results in a pure product<sup>17</sup>. The novel dioxygenyl salt<sup>18</sup>,  $[\text{O}_2]_2[\text{Ti}_7\text{F}_{30}]$ , is prepared by reacting  $\text{TiO}_2$  with a mixture of  $\text{F}_2$  and  $\text{O}_2$  ( $300\text{--}450^\circ\text{C}$ ) under higher pressure ( $3.04 \times 10^7 - 3.55 \times 10^8 \text{ N m}^{-2}$  or  $300\text{--}3500 \text{ atm}$ )<sup>18</sup>. The peroxyfluorotitanate salt<sup>19</sup>,  $\text{K}_3[\text{TiO}_2\text{F}_5]$  is prepared by treating  $\text{K}_2[\text{TiF}_6]$  with an excess of 30%  $\text{H}_2\text{O}_2$  in the presence of a slight excess of KOH. A number of xenon fluoride complexes<sup>20</sup> have been prepared ( $3 \text{XeF}_2 \cdot 2 \text{TiF}_4$ ,  $\text{XeF}_2 \cdot \text{TiF}_4$ ,  $\text{XeF}_2 \cdot 2 \text{TiF}_4$ ,  $4 \text{XeF}_6 \cdot \text{TiF}_4$ ,  $\text{XeF}_6 \cdot \text{TiF}_4$ ,  $\text{XeF}_6 \cdot 2 \text{TiF}_4$ ) by reacting  $\text{TiF}_4$  or  $[\text{N}_2\text{H}_6][\text{TiF}_6]$  with  $\text{XeF}_2$  or  $\text{XeF}_6$ . In liq HF, the oxonium complex is formed<sup>21</sup>:

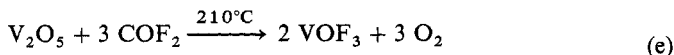


Passing  $\text{F}_2$  over powdered vanadium heated to  $300^\circ\text{C}$  forms  $\text{VF}_5$ <sup>22</sup>. In a static system,  $\text{V}_2\text{O}_5$  is fluorinated to  $\text{VF}_5$  ( $P_{\text{F}_2} = 1.01 \times 10^6\text{--}5.07 \times 10^6 \text{ N m}^{-2}$  or  $10\text{--}50 \text{ atm}$ ,  $200\text{--}475^\circ\text{C}$ ) with fluorine<sup>23</sup>.

The oxyfluoride can be prepared by reacting  $\text{V}_2\text{O}_5$  with  $\text{F}_2$  (at  $475^\circ\text{C}$ )<sup>6</sup>:



or by reacting with  $\text{COF}_2$  at  $210^\circ\text{C}$ <sup>5a</sup>:

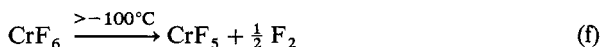


Also known is  $\text{VO}_2\text{F}$  which is prepared by passing a  $\text{F}_2\text{--N}_2$  (1:1) mixture over  $\text{VO}_2\text{Cl}$  ( $75\text{--}80^\circ\text{C}$ )<sup>24</sup>. The following oxyfluorides are prepared from solution or solid-state reaction<sup>25</sup>:  $\text{M}_3[\text{VO}_2\text{F}_4]$  ( $\text{M} = \text{Na}, \text{K}$ ),  $\text{M}_2[\text{VO}_2\text{F}_3]$  ( $\text{M} = \text{K}, \text{Rb}, \text{Cs}$ ),  $\text{M}_3[\text{V}_2\text{O}_4\text{F}_5]$  ( $\text{M} = \text{Rb}, \text{Cs}$ ) and  $\text{M}_2\text{M}'[\text{VO}_2\text{F}_4]$  ( $\text{M} = \text{K}, \text{Rb}, \text{Cs}$ ;  $\text{M}' = \text{Na}, \text{K}, \text{Rb}$ ). The salts,  $[\text{Ph}_4\text{P}][\text{VO}_2\text{F}_2]$  and  $[\text{Ph}_4\text{As}][\text{VO}_2\text{F}_2]$  containing the anion  $[\text{VO}_2\text{F}_2]^-$  (isoelectronic with  $\text{CrO}_2\text{F}_2$ ), are prepared by first reacting a solution of sodium metavanadate(V) with 40% aq HF; addition of the  $[\text{Ph}_4\text{P}]^+$  or  $[\text{Ph}_4\text{As}]^+$  cations results in precipitation of either product<sup>26</sup>. The salt  $\text{CsVOF}_4$  is prepared by reacting  $\text{V}_2\text{O}_5$  with  $\text{CsF}$  in HF ( $-30^\circ\text{C}$ )<sup>27</sup>. The reaction of  $\text{NF}_3$  with  $\text{V}_2\text{O}_5$  ( $400^\circ\text{C}$ ) gives<sup>28</sup> both  $\text{VOF}_3$  and  $[\text{NO}][\text{VOF}_4]$ . The salt  $\text{K}_2[\text{VOF}_5]$  is prepared by cooling a mixture of  $\text{V}_2\text{O}_5$  and  $\text{KF}$  in aq HF; treating  $\text{K}_2[\text{VOF}_5]$  soln with KOH gives  $\text{K}_4[\text{V}_2\text{O}_3\text{F}_8]$  upon evaporation<sup>29</sup>. The reaction of  $\text{Ba}[\text{VO}_2\text{F}_3]$  with KOH in water gives  $\text{Ba}[\text{VO}_3\text{F}]$  as the product<sup>30</sup>. The graphite complex  $\text{C}_{40}\text{VOF}_3$  is prepared<sup>28</sup> from  $\text{VOF}_3$  and pyrographite in HF.

Fluorocomplexes of  $\text{VF}_5$ , such as  $\text{VF}_5 \cdot \text{SbF}_5$ ,  $[\text{NO}_2][\text{VF}_6]$ ,  $[\text{NO}][\text{VF}_6]$ ,  $2 \text{XeOF}_4 \cdot \text{VF}_5$ ,  $2 \text{XeF}_6 \cdot \text{VF}_5$ ,  $\text{XeF}_6 \cdot \text{F}_3$ ,  $\text{XeF}_6 \cdot 2 \text{VF}_5$ ,  $\text{XeF}_2 \cdot \text{VF}_5$  and  $\text{KrF}_2 \cdot \text{VF}_5$  are

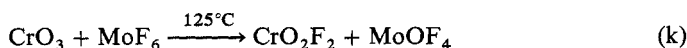
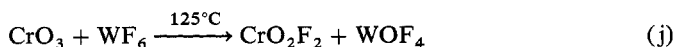
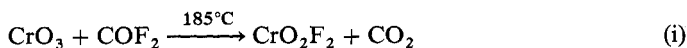
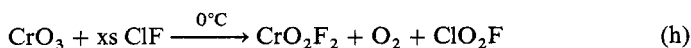
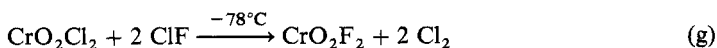
known; in most cases the complexes are prepared by simply adding the reactants together in correct molar proportions<sup>31-38</sup>. The reaction of  $\text{O}_2\text{F}_2$  with  $\text{VF}_5$  gives at RT the unstable  $[\text{O}_2][\text{V}_2\text{F}_{11}]$  compound<sup>39</sup>.

The highest known fluoride of Cr is the unstable  $\text{CrF}_6$ ; it is prepared by reacting Cr with  $\text{F}_2$  ( $2.03 \times 10^7 \text{ N m}^{-2}$  or 200 atm) at  $400^\circ\text{C}$  in a Ni pressure vessel; addition of small amounts of Mn and higher pressure ( $3.55 \times 10^7 \text{ N m}^{-2}$  or 350 atm) increases the yield<sup>40</sup>. It is unstable above  $-100^\circ\text{C}$ , decomposing according to:



Due to the instability of  $\text{CrF}_6$ , the chemistry of high-valent chromium fluoride is the chemistry of  $\text{CrF}_5$ , which is prepared by heating  $\text{CrF}_3$  with  $\text{F}_2$  ( $4.6 \times 10^6 \text{ N m}^{-2}$  or 45 atm at RT) in a Monel pressure vessel for 3 h at  $300^\circ\text{C}$ ; xs  $\text{F}_2$  is vented at  $-78^\circ\text{C}$  and any HF is pumped away (6 h)<sup>41</sup>;  $\text{NiF}_2$  is an effective catalyst in this system<sup>42</sup>.

Three high-valent oxidizing oxyfluorides are known:  $\text{CrO}_2\text{F}_2$ ,  $\text{CrOF}_4$  and  $\text{CrOF}_3$ ;  $\text{CrO}_2\text{F}_2$  is prepared according to<sup>43-44</sup>:



Other reagents such as  $\text{SF}_4$ ,  $\text{CoF}_3$  and  $\text{IF}_5$  can also be used to prepare  $\text{CrO}_2\text{F}_2$ <sup>44</sup>; another route involves reacting nitryl fluoride ( $\text{NO}_2\text{F}$ ) with chromium<sup>45</sup>. Although  $\text{CrOF}_4$  can be prepared by fluorinating heated Cr metal in a flow system<sup>46</sup>, it is reported that fluorination of  $\text{CrO}_3$  ( $220^\circ\text{C}$ , 70 h) in a pressure Monel vessel, with a water-cooled tap, is also an effective method<sup>47</sup>. The reaction of  $\text{CrO}_2\text{F}_2$  with  $\text{KrF}_2$  in HF at RT gives  $\text{CrOF}_4$  in quantitative yield<sup>48,49</sup>. Also,  $\text{CrOF}_4$  can be prepared from  $\text{CrO}_2\text{F}_2$  and xs  $\text{F}_2$  in the presence of CaF at  $200^\circ\text{C}$ <sup>50</sup>. Pure  $\text{CrOF}_3$ <sup>51</sup> can be prepared by fluorinating ( $120^\circ\text{C}$ ) the brick-red solid  $\text{CrOF}_3 \cdot x \text{ClF}$  ( $x = 0.10-0.21$ ), obtained from reacting  $\text{CrO}_3$  with ClF ( $110^\circ\text{C}$ ) or by fluorinating chromyl fluoride with xenon difluoride<sup>52</sup>:

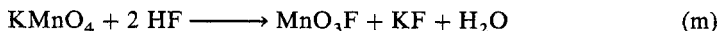


A number of oxyfluorocomplexes of  $\text{CrO}_2\text{F}_2$  and  $\text{CrOF}_3$  are known<sup>33,43,53-55</sup>, e.g.,  $\text{CrO}_2\text{FTaF}_6$ ,  $\text{CrO}_2\text{FSbF}_6$ ,  $\text{CrO}_2\text{FSb}_2\text{F}_{11}$ ;  $\text{M}_2\text{CrOF}_5$  ( $\text{M} = \text{Ag}, \text{K}, \text{Et}_4\text{N}$ ). Salts containing the trioxofluorochromate anions ( $\text{CrO}_3\text{F}^-$ ) are prepared by reacting dichromate salts with 40% HF (aq) or metal carbonates and  $\text{CrO}_3$  with HF ( $\text{M} = \text{NH}_4, \text{Rb}, \text{K}, \text{Cs}$ )<sup>56-57</sup>. The complexes  $\text{KrF}_2 \cdot \text{CrOF}_4$ ,  $[\text{NO}][\text{CrF}_5\text{O}]$  and  $\text{CrOF}_4 \cdot \text{SbF}_5$  are known<sup>48,49</sup>.

Fluorocomplexes such as  $\text{Cs}[\text{CrF}_6]$  and  $[\text{NO}][\text{CrF}_6]$  have been prepared<sup>58</sup>. The strongly oxidizing and stable salt  $[\text{NF}_4][\text{CrF}_6]$  is known; in this report, attempts at preparing  $\text{CrF}_6$  as described previously were not successful<sup>59</sup>.

Crystalline  $\text{MnF}_4$  is prepared by heating  $\text{MnF}_2$  with  $\text{F}_2$  ( $\approx 3 \times 10^8 \text{ N m}^{-2}$  or  $\approx 3000 \text{ atm}$ ) and in the presence of small amounts of  $\text{BrF}_3$  and  $\text{O}_2$  for 5–6 d at  $\approx 400^\circ\text{C}$ ; after heating, the autoclave is slowly cooled to RT ( $10^\circ\text{C}$  per day). This method<sup>60</sup> produces dark blue needles of  $\text{MnF}_4$ . Also,  $\text{MnF}_4$  is quantitatively prepared by reacting Mn powder with  $\text{F}_2$  in a fluidized bed at very high temperatures<sup>61</sup>. Pure  $\text{MnF}_4$  is also prepared from  $\text{MnF}_2$  and  $\text{KrF}_2$  in HF at RT<sup>62</sup>.

Permanganyl fluoride,  $\text{MnO}_3\text{F}$ , is unstable above  $0^\circ\text{C}$  but can be prepared<sup>63</sup> by reacting  $\text{KMnO}_4$  with either  $\text{HSO}_3\text{F}$  or HF;



In addition to using  $\text{HSO}_3\text{F}$  or HF,  $\text{IF}_5$  may be used<sup>64</sup>; interestingly,  $\text{MnO}_3\text{F}$  is stable in  $\text{IF}_5$  solution under reflux. In all preparations the  $\text{MnO}_3\text{F}$  needs to be further purified by vacuum distillation; if HF is present then a second treatment is needed using either xs  $\text{KMnO}_4$  or KF, which reacts with the HF to form  $\text{MnO}_3\text{F}$  or  $\text{KHF}_2$ , respectively<sup>63</sup>.

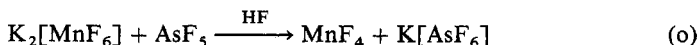
Fluorosalts of Mn(IV) are known<sup>65</sup>;  $\text{K}_2\text{MnF}_6$  is prepared:

1. by reduction of  $\text{KMnO}_4$  with diethyl ether or  $\text{H}_2\text{O}$  in aq HF
2. by electrolytic oxidation of  $\text{MnF}_2$  in a solution of  $\text{KHF}_2$  in aq HF

For example, a  $\text{MnF}_2$  solution in aq HF is electrolyzed (2–3 V with current of 0.75 A) until a clear red-brown color is obtained, at which time solid  $\text{K}[\text{HF}_2]$  or a saturated soln of  $\text{K}[\text{HF}_2]$  in 40% aq HF is added; this solution is further electrolyzed with the formation of the yellow crystalline  $\text{K}_2[\text{MnF}_6]$ . After the reaction solution is decanted the product is washed with a small amount of 40% aq HF and then with alcohol and ether<sup>66</sup>. The  $[\text{NH}_4]_2\text{MnF}_6$  salt is prepared analogously except that the initial washing with 40% aq HF is omitted<sup>66</sup>.

3. by treating an equimolar mixture of  $\text{KMnO}_4$  and KCl with bromine trifluoride<sup>34</sup>.

A general method for preparing not only  $\text{K}_2[\text{MnF}_6]$  but other alkali metals and alkaline-earth metal salts involves fluorinating appropriate mixtures of manganese and alkali-metal salts at high T<sup>67,68</sup>. Moreover,  $\text{K}_2[\text{MnF}_6]$ ,  $\text{Rb}_2[\text{MnF}_6]$  and  $\text{Cs}_2[\text{MnF}_6]$ , prepared by fluorinating  $\text{MMn}[\text{SO}_4]_2$  salts ( $\text{M} = \text{K, Rb, Cs}$ ) at  $350^\circ\text{C}$ , are air-stable solids; in earlier reports, apparently impurities have been responsible for the decomposition of these compounds in air<sup>69,70</sup>. It should be noted that dissolution of  $\text{K}_2\text{MnF}_6$  in HF solutions containing  $\text{AsF}_5$  gives<sup>71</sup>:



The pentafluoromanganates(IV) salts<sup>67</sup>,  $\text{MMnF}_5$  ( $\text{M} = \text{K, Rb, Cs}$ ) are formed by fluorinating  $\text{M}[\text{MnF}_3]$  salts at  $450\text{--}500^\circ\text{C}$ .

The interesting dioxygenyl salt  $[\text{O}_2][\text{Mn}_2\text{F}_9]$  is prepared by reacting  $\text{MnO}_2$  or  $\text{MnF}_x$  ( $x = 2, 3, 4$ ) with a mixture of  $\text{F}_2$  and  $\text{O}_2$  ( $P_{\text{F}_2/\text{O}_2} \approx 3 \times 10^7$  to  $3.6 \times 10^8 \text{ N m}^{-2}$  or

$\approx 300\text{--}3500$  atm) at  $350\text{--}500^\circ\text{C}$  <sup>73</sup>. Also, a second dioxygenyl salt,  $[\text{O}_2][\text{MnF}_5]$ , is known <sup>74,75</sup>. The reaction of  $\text{MnF}_2$  with xs  $\text{XeF}_2$  ( $120^\circ\text{C}$ ) or xs  $\text{XeF}_6$  ( $60^\circ\text{C}$ ) gives  $n \text{XeF}_2 \cdot \text{MnF}_4$  ( $n = 1, 0.5$ ) and  $n \text{XeF}_6 \cdot \text{MnF}_4$  ( $n = 4, 2, 1, 0.5$ ), respectively <sup>76</sup>. The complex  $[\text{NF}_4]_2[\text{MnF}_6]$  has been reported <sup>77,78</sup>.

(J.M. CANICH, G.L. GARD)

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### 2.11.2.2. Synthesis of High-Valent Fluorides, Oxide Fluorides and Fluorocomplexes of Fe, Co, Ni.

The preparation of  $\text{FeF}_3$  is achieved by reacting  $\text{FeCl}_3$  with  $\text{F}_2$ ,  $\text{BrF}_3$ ,  $\text{ClF}_3$  or  $\text{HF}^{1-3}$ ; e.g.,  $\text{FeCl}_3$  in a Ni boat is gradually heated to  $300^\circ\text{C}$  in a stream of  $\text{ClF}_3$  and is removed, ground and then reheated to  $550^\circ\text{C}$  (1 h) in  $\text{ClF}_3$ . This process is repeated until no  $\text{FeCl}_3$  is left. Fluorination<sup>4</sup> of  $\text{FeF}_2$  with  $\text{F}_2$  under pressure ( $3.6 \times 10^6 \text{ N m}^{-2}$  or 35 atm at  $20^\circ\text{C}$ ) at  $300^\circ\text{C}$  gives  $\text{FeF}_3$ . Interestingly,  $\text{FeS}_2$  reacts with  $\text{SF}_4$  ( $350^\circ\text{C}$ ) under pressure to form  $\text{FeF}_3$  and  $\text{S}_8$ ; the  $\text{S}_8$  is extracted with  $\text{CS}_2$ <sup>5</sup>. A trihydrate of iron(III) fluoride is known<sup>6</sup>.

The oxyfluoride ( $\text{FeOF}$ ) is prepared by heating a mixture of  $\text{FeF}_3$  and  $\text{Fe}_2\text{O}_3$  at  $800\text{--}900^\circ\text{C}$  in  $\text{O}_2$ <sup>7</sup>.

Fluorocomplexes containing  $[\text{FeF}_6]^{3-}$ ,  $[\text{FeF}_5]^{2-}$  and  $[\text{FeF}_4]^-$  may be prepared from melts or from aq  $\text{HF}$  soln<sup>8</sup>. The ammonium salt complex  $[\text{NH}_4]_3[\text{FeF}_6]$  is prepared by reacting  $\text{FeBr}_3$  with  $[\text{NH}_4]\text{F}$  in  $\text{MeOH}$ , whereas  $[\text{NH}_4][\text{FeF}_4]$  is prepared

## 2.11. Formation of Group-IB, -IIB, and Transition-Metal Fluorides

## 2.11.2. of the First Transition Series (Sc through Zn)

## 2.11.2.2. Synthesis of Fluorocomplexes of Fe, Co, Ni.

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by heating a mixture (3:1 mole ratio) of  $[\text{NH}_4]\text{F}$  and  $\text{FeF}_3$  in a Ni boat to  $180^\circ\text{C}$  in a stream of extra-dry  $\text{N}_2$  and with a second boat containing  $[\text{NH}_4]\text{F}$  upstream from the sample. The sample is heated for several days to constant weight<sup>9</sup>.

The reaction of  $[\text{N}_2\text{H}_6][\text{FeF}_5]$  with xs  $\text{XeF}_6$  at RT gives  $\text{XeF}_6 \cdot \text{FeF}_3$ <sup>4</sup>.

Strongly oxidizing  $\text{CoF}_3$  is prepared in 90–95% yields by passing  $\text{F}_2$  (g) over  $\text{CoCl}_2$  or  $\text{Co}_2\text{O}_3$  (heated from RT to  $300^\circ\text{C}$ )<sup>10</sup> or by treating  $\text{CoCl}_2$  with  $\text{ClF}_3$  in a flow system at  $250^\circ\text{C}$ <sup>11</sup>. Also  $\text{XeF}_2$  fluorinates  $\text{CoF}_2$ ,  $\text{CoCl}_2$  or Co to  $\text{CoF}_3$ <sup>12</sup>.

A blue hydrate,  $\text{CoF}_3 \cdot 3.5 \text{H}_2\text{O}$ , is obtained by the electrolytic oxidation of  $\text{CoF}_2$  in hydrofluoric acid; once dry this solid can be stored almost indefinitely in a desiccator without decomposition<sup>13</sup>. Also, the compound  $\text{CoF}_3 \cdot 3 \text{H}_2\text{O}$  has been reported<sup>14</sup>.

Fluorosalts  $\text{M}_3[\text{CoF}_6]$  and  $\text{M}[\text{CoF}_4]$  containing Co(III) are known:  $\text{M}_3[\text{CoF}_6]$  salts are prepared by the fluorination of a 3:1 mixture of  $\text{MCl}:\text{CoCl}_2$  at  $400^\circ\text{C}$  or, preferably,  $\text{M}_3[\text{Co}(\text{CN})_6]$  with  $\text{M} = \text{Li}, \text{Na}, \text{K}$  at  $300\text{--}350^\circ\text{C}$  (5–7 h)<sup>15</sup>;  $\text{Ba}_3[\text{CoF}_6]_2$  is also prepared in a similar manner but an attempt at preparing  $\text{La}[\text{CoF}_6]$  via fluorinating  $\text{La}[\text{Co}(\text{CN})_6]$  has been unsuccessful<sup>15</sup>. The  $\text{M}[\text{CoF}_4]$  salts are synthesized by fluorinating  $\text{M}[\text{CoF}_3]$  ( $\text{M} = \text{Na}, \text{K}$ ) or  $\text{M}[\text{CoCl}_3]$  ( $\text{M} = \text{Li}, \text{Rb}, \text{Cs}$ ) between  $250^\circ\text{C}$  and  $500^\circ\text{C}$ <sup>16</sup>; also, these salts can be prepared by fluorinating mixtures of  $\text{MCl}$  ( $\text{M} = \text{Li}, \text{Na}$ ) or  $\text{M}_2\text{CO}_3$  ( $\text{M} = \text{K}, \text{Rb}, \text{Cs}$ ) with  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  at  $400\text{--}430^\circ\text{C}$  for 7–8 h<sup>17</sup>.

In addition to Co(III) fluorocomplexes, higher oxidation state Co(IV) salts are known and are prepared by fluorinating Co(II) salts such as  $\text{Cs}_2[\text{CoCl}_4]$  or  $\text{Cs}_2\text{Co}[\text{SO}_4]_2$  at ( $300^\circ\text{C}$ ) to  $\text{Cs}_2[\text{CoF}_6]$ ;  $\text{Rb}_2[\text{CoF}_6]$  has also been made<sup>18,19</sup>.

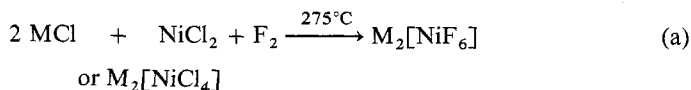
The interesting complex,  $[\text{Coen}_2\text{F}_2][\text{HF}_2]$  is obtained by air oxidation of a  $\text{CoF}_2$  soln in aq en followed by addition of aq HF and subsequent evaporation to dryness<sup>20</sup>. Another complex,  $[\text{Co}(\text{NH}_3)_6][\text{CoF}_6] \cdot 0.5 \text{H}_2\text{O}$ , is formed by gently heating  $[\text{Co}(\text{NH}_3)_6]\text{F}_3$ <sup>21</sup>. The complex  $\text{XeF}_6 \cdot \text{CoF}_3$  is prepared from  $\text{CoF}_2$  and xs  $\text{XeF}_6$  ( $60^\circ\text{C}$ , 5 d); in place of  $\text{CoF}_2$ ,  $[\text{N}_2\text{H}_5][\text{CoF}_3]$  can be used (RT, 1 d)<sup>4</sup>.

The highest binary fluoride of nickel is  $\text{NiF}_4$ . It is prepared<sup>22</sup> by bubbling gaseous  $\text{AsF}_5$  into a  $[\text{XeF}_5]_2[\text{NiF}_6]$  soln in anhyd HF.

The next highest fluoride is  $\text{NiF}_3$ , prepared by reacting  $\text{K}_2[\text{NiF}_6]$  with  $\text{AsF}_5$  in HF ( $-80^\circ\text{C}$ ); this reaction is carried<sup>23</sup> out at  $20^\circ\text{C}$  when  $\text{BF}_3$  is used instead of  $\text{AsF}_5$ .

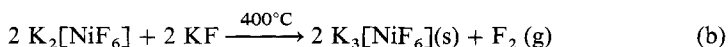
The Ni(III) fluoride salts,  $\text{M}_3[\text{NiF}_6]$  ( $\text{M} = \text{K}, \text{Na}$ ) are prepared by fluorinating 3:1 mixtures of alkali-metal chlorides and  $\text{NiCl}_2$  or  $\text{NiSO}_4$  ( $300\text{--}400^\circ\text{C}$ );  $\text{Ba}[\text{NiF}_5]$  is prepared by fluorinating  $\text{Ba}[\text{Ni}(\text{CN})_4]$  at  $300^\circ\text{C}$ . A brown modification of  $\text{Ba}[\text{NiF}_5]$  results upon further reaction at  $500^\circ\text{C}$ <sup>24</sup>.

The salts of  $\text{M}_2[\text{NiF}_6]$  ( $\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ) are known and prepared by<sup>25</sup>:



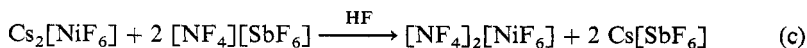
or by fluorination of  $\text{M}_2[\text{Ni}(\text{CN})_4]$  with  $\text{M} = \text{K}, \text{Rb}$  in a flow system at  $425^\circ\text{C}$  followed by a static  $\text{F}_2$  treatment ( $3 \times 10^5 \text{ N m}^{-2}$  or 3 atm,  $425^\circ\text{C}$ , 24 h) and then refluorination (static) after remixing<sup>26</sup>. The high-pressure fluorination of  $\text{Na}_2[\text{Ni}(\text{CN})_4] \cdot 3 \text{H}_2\text{O}$  at  $3 \times 10^7 \text{ N m}^{-2}$  pressure ( $300^\circ\text{C}$ , 18 h) gives pure  $\text{Na}_2[\text{NiF}_6]$ ; with  $\text{Ba}[\text{Ni}(\text{CN})_4] \cdot 4 \text{H}_2\text{O}$ ,  $\text{Ba}[\text{NiF}_6]$  is formed ( $300^\circ\text{C}$ ,  $5 \times 10^9 \text{ N m}^{-2}$ )<sup>27,28</sup>.

In the presence of KF the potassium salt  $\text{K}_2\text{NiF}_6$  decomposes:

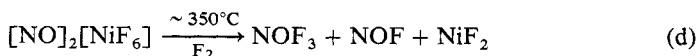


This decomposition reaction, assumed to proceed as written, can be used to generate fluorine with a purity  $>99.7\%$ <sup>29</sup>. Additional salts such as  $\text{Sr}[\text{NiF}_6]$ ,  $\text{Ba}[\text{NiF}_6]$ ,  $\text{CsRb}[\text{NiF}_6]$  and  $\text{RbK}[\text{NiF}_6]$  can be prepared by high-pressure fluorination reactions<sup>30</sup>.

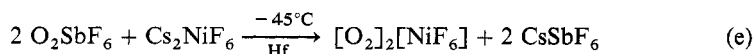
The highly unusual and stable  $[\text{NF}_4]_2\text{NiF}_6$  is prepared by<sup>31</sup>:



The  $\text{Cs}[\text{SbF}_6]$  is removed by filtration at  $-78^\circ\text{C}$ . Novel  $[\text{NO}]_2[\text{NiF}_6]$  is prepared by treating  $\text{NiF}_2$  with a mixture of  $\text{F}_2$  ( $4.1 \times 10^5 \text{ N m}^{-2}$  or 4.1 atm) and xs  $\text{NOF}$  ( $\approx 3.4 \times 10^5 \text{ N m}^{-2}$  or 3.4 atm) in a Ni reactor ( $200^\circ\text{C}$ ); pyrolysis of this salt in  $\text{F}_2$  ( $4.8 \times 10^5 \text{ N m}^{-2}$  or 4.8 atm) at  $\sim 350^\circ\text{C}$  results in the following decomposition<sup>32</sup>:



The complexes  $[\text{XeF}_5]_2[\text{NiF}_6]$  and  $[\text{Xe}_2\text{F}_{11}]_2[\text{NiF}_6]$  are prepared<sup>33</sup> from  $\text{NiF}_2$ ,  $\text{KrF}_2$  and  $\text{XeF}_6$ . The complex  $[\text{O}_2]_2[\text{NiF}_6]$  is prepared<sup>34</sup>:



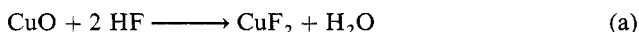
(J.M. CANICH, G.L. GARD)

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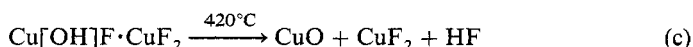
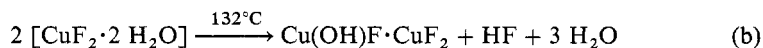
### 2.11.2.3. Synthesis of High-Valent Fluorides, Oxide Fluorides and Fluorocomplexes of Cu and Zn.

Fluorination of Cu and CuBr<sub>2</sub>, CuCl<sub>2</sub> and CuSO<sub>4</sub> is effective in preparing CuF<sub>2</sub><sup>1</sup>. The reaction of CuS with SF<sub>4</sub> (190°C) in an autoclave is useful<sup>2</sup> as is the reaction of CuO with HF:



The product is dehydrated at 400°C in a completely dry HF stream<sup>3</sup>.

The hydrate of CuF<sub>2</sub>, CuF<sub>2</sub>·2 H<sub>2</sub>O, is prepared by adding Cu(OH)<sub>2</sub>·CuCO<sub>3</sub> to a twofold excess of 40% aq HF. The precipitated hydrate is filtered, washed with EtOH and air dried. The hydrate is unstable, with decomposition proceeding according to<sup>4</sup>:



The basic fluoride Cu[OH]F is prepared by boiling an aqueous solution of the dihydrate; the filtered product is washed with alcohol and ether and air dried.

Salts containing [CuF<sub>6</sub>]<sup>4-</sup>, [CuF<sub>4</sub>]<sup>2-</sup> and [CuF<sub>3</sub>]<sup>-</sup> are prepared by fusing stoichiometric amounts of CuF<sub>2</sub> and metal fluoride<sup>5</sup>; the complexes CuF<sub>2</sub>(CH<sub>3</sub>CN)<sub>4</sub>·4 IF<sub>5</sub>, Cu[SbF<sub>6</sub>]<sub>2</sub> and Cu[AsF<sub>6</sub>]<sub>2</sub> are known<sup>6-8</sup>.

The complex K<sub>3</sub>[CuF<sub>6</sub>] is prepared by fluorinating a 3:1 mixture of KCl and CuCl<sub>2</sub> (250°C) in a flow system<sup>9</sup>; the Na complex Na<sub>3</sub>[CuF<sub>6</sub>] is prepared under pressure at 450°C<sup>10</sup>.

There are only a few copper(IV) fluorosalts; Cs<sub>2</sub>[CuF<sub>6</sub>] is prepared by high-pressure fluorination (Monel autoclave; 3 d, 410°C, 3.55 × 10<sup>7</sup> N m<sup>-2</sup> or 350 atm) of prefluorinated mixtures of Cs[CuCl<sub>3</sub>] and CsCl (15 h, 370°C, F<sub>2</sub> stream)<sup>11</sup>.

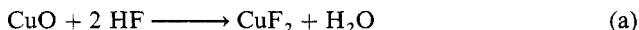
Zinc fluoride is prepared by dissolving ZnCO<sub>3</sub> in hot conc aq HF, evaporating the solution to dryness and then drying the product at 800°C<sup>12</sup>. It is also obtained by fluorinating Zn, ZnO, ZnBr<sub>2</sub> or ZnS. With Zn dust at 250°C only 50% conversion is obtained; multiple fluorination at 550°C with ZnO resulted in a 93% conversion; ZnBr<sub>2</sub> (500°C) produces pure ZnF<sub>2</sub> (repeated fluorinations) with less than 0.1% bromide; ZnS

2.11. Formation of Group-IB, -IIB, and Transition-Metal Fluorides 279  
 2.11.2. of the First Transition Series (Sc through Zn)  
 2.11.2.3. Synthesis of Fluorocomplexes of Cu and Zn.

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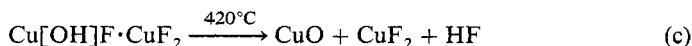
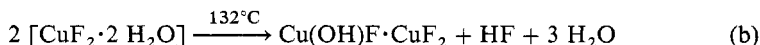
**2.11.2.3. Synthesis of High-Valent Fluorides, Oxide Fluorides and Fluorocomplexes of Cu and Zn.**

Fluorination of Cu and CuBr<sub>2</sub>, CuCl<sub>2</sub> and CuSO<sub>4</sub> is effective in preparing CuF<sub>2</sub><sup>1</sup>. The reaction of CuS with SF<sub>4</sub> (190°C) in an autoclave is useful<sup>2</sup> as is the reaction of CuO with HF:



The product is dehydrated at 400°C in a completely dry HF stream<sup>3</sup>.

The hydrate of CuF<sub>2</sub>, CuF<sub>2</sub>·2 H<sub>2</sub>O, is prepared by adding Cu(OH)<sub>2</sub>·CuCO<sub>3</sub> to a twofold excess of 40% aq HF. The precipitated hydrate is filtered, washed with EtOH and air dried. The hydrate is unstable, with decomposition proceeding according to<sup>4</sup>:



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Salts containing [CuF<sub>6</sub>]<sup>4-</sup>, [CuF<sub>4</sub>]<sup>2-</sup> and [CuF<sub>3</sub>]<sup>-</sup> are prepared by fusing stoichiometric amounts of CuF<sub>2</sub> and metal fluoride<sup>5</sup>; the complexes CuF<sub>2</sub>(CH<sub>3</sub>CN)<sub>4</sub>·4 IF<sub>5</sub>, Cu[SbF<sub>6</sub>]<sub>2</sub> and Cu[AsF<sub>6</sub>]<sub>2</sub> are known<sup>6-8</sup>.

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reacts vigorously with  $F_2$  even at RT—refluorination at  $500^\circ\text{C}$ , after grinding, gives  $ZnF_2$  free of sulfur<sup>13</sup>. The treatment of  $ZnS$  with  $SF_4$  ( $60^\circ\text{C}$ ) under pressure forms  $ZnF_2$ <sup>14</sup>.

Zinc fluoride forms a tetrahydrate,  $ZnF_2 \cdot 4 H_2O$ , via reaction of  $ZnO$  with aq  $HF$ <sup>15</sup>. Slow dehydration of the hydrate in a stream of  $HF$  also gives anhyd  $ZnF_2$ <sup>15</sup>.

Phase studies obtained from melts of  $ZnF_2$  and metal fluorides show the existence of salt complexes containing  $[ZnF_3]^-$  and  $[ZnF_4]^{2-}$  ions; however, a phase study of  $AgF$  and  $ZnF_2$  showed the existence of only one compound,  $Ag[ZnF_3]$ <sup>15-17</sup>.

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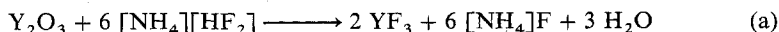
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5. R. Colton, J. H. Canterford, eds., *Halides of the Transition Elements. Halides of the First Row Transition Metals*, John Wiley and Sons, London, 1969, p. 526-529, and references contained therein.
6. J. A. Berry, D. W. A. Sharp, J. M. Winfield, *Inorg. Nucl. Chem. Lett.*, **12**, 869 (1976).
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17. W. L. W. Ludekens, A. J. E. Welch, *Acta Crystallogr.*, **5**, 841 (1952).

## 2.11.3. of the Second Transition Series (Y through Ag)

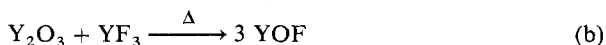
### 2.11.3.1. Pre-Platinum Metals: Synthesis of High-Valent Fluorides, Oxide Fluorides and Fluorocomplexes of Y, Zr, Nb, Mo, Tc.

Some useful methods for preparing  $YF_3$  include (1) passing a dry  $H_2$ - $HF$  mixture over  $Y_2O_3$  ( $100^\circ\text{C}$ ) contained in a Pt crucible for 2 h or (2) adding aq  $HF$  to a heated solution prepared by dissolving  $Y_2O_3$  in  $HCl$ , neutralizing with  $[NH_4]OH$  and reacidifying with aq  $HCl$ . The precipitate is dried in air at  $100$ – $150^\circ\text{C}$  and then dried in vacuo at  $1000$ – $1400^\circ\text{C}$  (1 h)<sup>1</sup>.

With heating  $[NH_4][HF_2]$  reacts directly with  $Y_2O_3$ <sup>2</sup>:



The oxyfluoride YOF is prepared by heating  $Y_2O_3$ - $YF_3$  mixtures in correct molar ratios (1:1)<sup>3</sup>:



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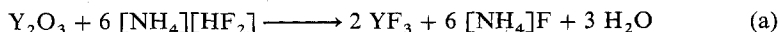
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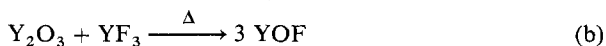
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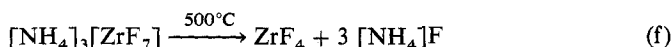
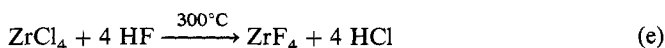
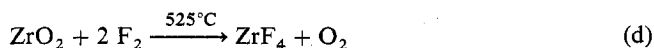




Stable trivalent complexes containing  $[\text{YF}_4]^-$  and  $[\text{YF}_6]^{3-}$  are prepared from melts of metal fluorides with  $\text{YF}_3$ ; from  $\text{NaF}$  and  $\text{YF}_3$  melts two compounds,  $\text{NaF} \cdot \text{YF}_3$  and the complex  $5 \text{ NaF} \cdot 9 \text{ YF}_3$ , are formed<sup>2,4</sup>;  $[\text{XeF}_5][\text{YF}_6]$  is also known<sup>5</sup>.

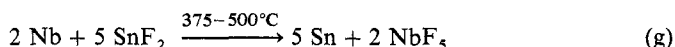
Fluorine reacts with Zr metal above  $190^\circ\text{C}$  but fluoride coating of the metal prevents complete conversion to  $\text{ZrF}_4$ ; a maximum yield of 90% is obtained at  $420^\circ\text{C}$ ; Zirconium(IV) oxide is converted to  $\text{ZrF}_4$  at  $400^\circ\text{C}$  (80% yield) and at  $525^\circ\text{C}$  is complete<sup>6</sup>.

Other methods include: (1) halogen exchange with  $\text{ZrCl}_4$  and  $\text{HF}$  ( $300^\circ\text{C}$ )<sup>7,8</sup>; and (2) thermal decomposition of  $[\text{NH}_4]_3[\text{ZrF}_7]$ .



Derivatives of  $\text{ZrF}_4$ , from hydrates ( $\text{ZrF}_4 \cdot 3 \text{ H}_2\text{O}$  and  $\text{ZrF}_4 \cdot \text{H}_2\text{O}$ ), to oxide fluorides ( $\text{Zr}_3\text{O}_2\text{F}_8$ ,  $\text{ZrOF}_2 \cdot 2 \text{ H}_2\text{O}$ ), to fluorocomplexes can be prepared<sup>7-10</sup>. One general method to prepare fluorocomplexes involves melting alkali-metal fluorides with  $\text{ZrF}_4$ ; e.g., in a phase equilibria study of  $\text{CsF}$  with  $\text{ZrF}_4$ , three intermediate compounds were isolated and identified:  $\text{Cs}_3[\text{ZrF}_7]$ ,  $\text{Cs}_2[\text{ZrF}_6]$ ,  $\text{Cs}[\text{ZrF}_5]$ <sup>10</sup>. Another general method for preparing  $[\text{ZrF}_6]^{2-}$  complexes is by the evaporating saturated 40% aq  $\text{HF}$  soln containing stoichiometric amounts of  $\text{ZrO}_2$  and the appropriate alkali-metal fluoride<sup>11,12</sup>;  $\text{XeF}_6 \cdot \text{ZrF}_4$  is also known<sup>13</sup>.

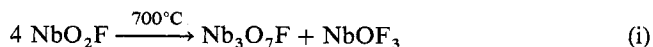
The pentafluoride of niobium is prepared either by using  $\text{HF}$  with the pentachloride or by fluorinating the metal in a Ni reactor ( $300^\circ\text{C}$ )<sup>14,15</sup>. The yield of  $\text{NbF}_5$  is sensitive to oxygen in the fluorine stream, which causes the formation of an oxyfluoride<sup>16</sup>. Also  $\text{NbF}_5$  is prepared from  $\text{HF}$  with powdered Nb in a Ni reactor at  $250^\circ\text{C}$ ; progress of the reaction is followed by measuring the volume of  $\text{H}_2$  evolved<sup>17</sup>. The reaction:



is convenient since it involves the use of easy to handle chemicals<sup>18</sup>. Another convenient preparation uses<sup>19</sup>  $\text{COF}_2$ :



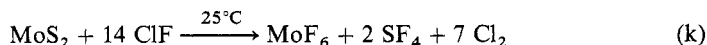
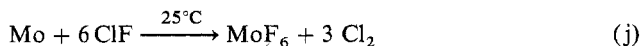
An oxide fluoride ( $\text{NbO}_2\text{F}$ ) is formed by dissolving  $\text{Nb}_2\text{O}_5$  in 48% aq  $\text{HF}$ <sup>20</sup>. It decomposes as follows<sup>21</sup>:



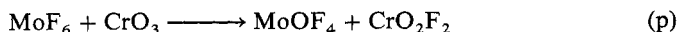
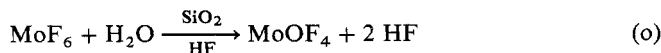
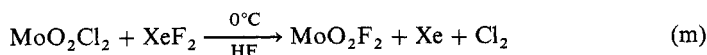
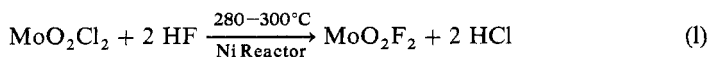
Additional ternary oxyfluorides are known<sup>20</sup>. The oxysalts  $\text{K}_3[\text{NbOF}_6]$  and  $[\text{NH}_4]_3[\text{NbOF}_6]$  are prepared by brominating Nb in  $\text{MeOH}$  followed by the addition of  $\text{KF}$  or  $[\text{NH}_4]\text{F}$  in  $\text{MeOH}$ <sup>22</sup>. Complexes such as  $\text{K}_2[\text{NbOF}_5]$ ,  $\text{K}_2[\text{NbO}_3\text{F}]$ ,  $\text{K}[\text{Nb}_2\text{O}_5\text{F}]$  and  $\text{M}_3[\text{NbOF}_6]$  ( $\text{M} = \text{K}, \text{NH}_4$ ) are also known<sup>23</sup>, as well as  $\text{K}_2[\text{NbO}_2\text{F}_5] \cdot \text{H}_2\text{O}$ , a peroxyfluorocomplex<sup>24</sup>.

Numerous complexes of NbF<sub>5</sub> with NH<sub>3</sub>, py, SO<sub>3</sub>, Et<sub>2</sub>O, EtCN, (CH<sub>3</sub>)<sub>2</sub>SO, XeF<sub>2</sub>, XeF<sub>6</sub> and BrF<sub>3</sub> exist<sup>25-27</sup>. In addition, other complexes with ClOF<sub>3</sub> and KrF<sub>2</sub>, among others, can be prepared<sup>28,29</sup>; with tetra-n-butylammonium (TBA) fluoroborate and NbF<sub>5</sub>, fluorocomplexes such as [TBA][NbF<sub>6</sub>] and [TBA][Nb<sub>2</sub>F<sub>11</sub>] can be prepared and characterized in solution<sup>30</sup>; other complex systems such as [NbF<sub>8</sub>]<sup>3-</sup> and [NbF<sub>7</sub>]<sup>2-</sup> are known<sup>31</sup>. The reaction of NbF<sub>5</sub> with SeF<sub>4</sub> at RT produces an adduct SeF<sub>4</sub>·2 NbF<sub>5</sub>, formulated as the ionic complex [SeF<sub>3</sub>][Nb<sub>2</sub>F<sub>11</sub>], with substantial interaction between ions through fluorine bridging<sup>32</sup>. However, with SbF<sub>5</sub> a 1:1 adduct is formed; in this case, the structure has an endless chain arrangement with a major contribution from the ionic system [NbF<sub>4</sub>][SbF<sub>6</sub>]<sup>33</sup>. The salts O<sub>2</sub>[NbF<sub>6</sub>] and O<sub>2</sub>[Nb<sub>2</sub>F<sub>11</sub>] are prepared by reacting powdered Nb at 330°C with 5 × 10<sup>5</sup> N m<sup>-2</sup> or 5 atm of a (10:3) F<sub>2</sub>-O<sub>2</sub> mixture in a Monel reactor with a water-cooled top; this method fails to prepare the individual O<sub>2</sub>[NbF<sub>6</sub>] and O<sub>2</sub>[Nb<sub>2</sub>F<sub>11</sub>] salts in pure form<sup>34</sup>. The oxonium salt [H<sub>3</sub>O][NbF<sub>6</sub>] is prepared by reacting H<sub>2</sub>O and NbF<sub>5</sub> in aq HF<sup>35</sup>.

Molybdenum hexafluoride is prepared by direct fluorination of the powdered metal in a Cu vessel. It is purified by trap to trap vacuum distillation and stored over dried NaF<sup>36</sup>. The reaction of MoO<sub>3</sub> with SF<sub>4</sub> in a bomb (350°C) is an alternate useful method<sup>37</sup>. The more reactive interhalogens (ClF<sub>3</sub>, BrF<sub>3</sub>, IF<sub>5</sub>) form MoF<sub>6</sub> from MoO<sub>3</sub><sup>38</sup>. Also, a convenient and easy preparation involves reacting Mo or MoS<sub>2</sub> with ClF at 25°C<sup>39</sup>:



High yields of MoF<sub>6</sub> can be achieved by the electrical explosion of the metal in SF<sub>6</sub><sup>40</sup>. The oxyfluorides MoO<sub>2</sub>F<sub>2</sub> and MoOF<sub>4</sub> are prepared by<sup>19,36,41-45</sup>:



Reaction of MoO<sub>2</sub>F<sub>2</sub> with equimol XeF<sub>2</sub> in HF gives MoOF<sub>4</sub><sup>41</sup>. High yields of MoOF<sub>4</sub> (M = Mo, W) are obtained<sup>42</sup> by reacting MF<sub>6</sub> with SiO<sub>2</sub> at 120°C. The reaction of NF<sub>3</sub> with MoO<sub>3</sub> (430°C, 10 h) gives NO[MoO<sub>2</sub>F<sub>3</sub>], which can also be prepared by reacting NOF and MoF<sub>4</sub><sup>46,47</sup>. Additional complexes such as NO[Mo<sub>2</sub>O<sub>2</sub>F<sub>9</sub>], ClOF<sub>2</sub>[MoOF<sub>5</sub>],

$[\text{NO}]_2[\text{MoOF}_6]$ ,  $\text{XeF}_2 \cdot n \text{ MoOF}_4$  ( $n = 1, 2$ ),  $\text{KrF}_2 \cdot n \text{ MoOF}_4$  ( $n = 1, 3$ ), among others, are known<sup>47-49</sup>. The thio- and selenofluorides of Mo(VI) are prepared according to<sup>50</sup>:



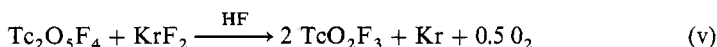
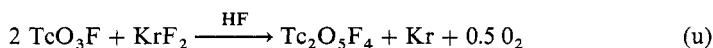
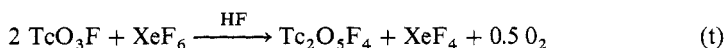
where  $\text{X} = \text{S, Se}$ . The peroxyfluorosalts  $\text{K}_2[\text{MoO}_5\text{F}_2] \cdot \text{H}_2\text{O}$  and  $\text{K}_2[\text{MoO}_3\text{F}_4] \cdot \text{H}_2\text{O}$  are known<sup>51</sup>. Additional oxyfluoro salts containing groups such as  $[\text{MoO}_2\text{F}_3]^-$ ,  $[\text{Mo}_2\text{O}_2\text{F}_9]^-$ ,  $[\text{MoO}_2\text{F}_4]^{2-}$  and  $[\text{Mo}_4\text{O}_{13}\text{F}]^{3-}$  groups have also been reported<sup>52-54</sup>.

Numerous fluorocomplexes are known; for example,  $\text{NOF}$  and  $\text{NO}_2\text{F}$  react with  $\text{MoF}_6$  to give  $\text{NO}[\text{MoF}_7]$  and  $\text{NO}_2[\text{MoF}_7]$ , respectively<sup>55</sup>. While  $\text{MO}$  and  $\text{MF}$  in  $\text{BrF}_3$  gives the  $\text{M}_2[\text{MoF}_8]$  complexes ( $\text{M} = \text{K, Rb, Cs}$ )<sup>56</sup>, the compound  $\text{K}_2[\text{MoF}_8]$  can be prepared by reacting  $\text{KF}$  with  $\text{MoF}_6$  in liq  $\text{SO}_2$ <sup>57</sup>. The reaction of sodium or potassium molybdates with  $\text{ClF}$  at  $300^\circ\text{C}$  gives the expected  $2 \text{ MF} \cdot \text{MoF}_6$  ( $\text{M} = \text{Na, K}$ ) complexes<sup>39</sup>. Trifluoroethoxymolybdenum(VI) fluorides are prepared by reacting  $\text{CF}_3\text{CH}_2\text{OSi}(\text{CH}_3)_3$  with  $\text{MoF}_6$  in  $\text{CHFC}_2$  solution<sup>58</sup>; with  $\text{B}(\text{OTeF}_5)_3$ , compounds of the types  $[\text{MoF}_{12}(\text{OTeF}_5)_{6-n}]$  form<sup>59</sup>.

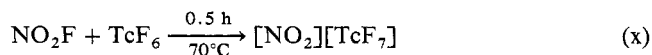
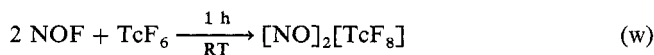
The adduct  $\text{MoOF}_4 \cdot \text{SbF}_5$  is prepared by reacting  $\text{MoOF}_4$  with xs  $\text{SbF}_5$ <sup>60</sup>.

Fluorination of Tc in a Ni reactor ( $400^\circ\text{C}$ ) gives  $\text{TcF}_6$ ; this reaction can be carried out in a flow system ( $350^\circ\text{C}$ )<sup>61-62</sup>.

Pertechnyl fluoride ( $\text{TcO}_3\text{F}$ ), or technetium trioxide fluoride, is prepared by passing  $\text{F}_2$  gas over  $\text{TcO}_2$  heated to  $150^\circ\text{C}$ <sup>63</sup>. The  $[\text{NH}_4][\text{TcO}_4]$  complex dissolves slightly in  $\text{HF}$  to give  $\text{TcO}_3\text{F}$  in solution<sup>64</sup>. The blue oxide tetrafluoride,  $\text{TcOF}_4$ , is formed as a minor product by fluorinating Tc metal in a flow system<sup>62</sup>. In  $\text{HF}$  soln, the two oxyfluorides,  $\text{Tc}_2\text{O}_5\text{F}_4$  and  $\text{TcO}_2\text{F}_3$ , are prepared and tentatively identified; with  $\text{TcO}_3\text{F}$  and  $\text{XeF}_6$  or xs  $\text{KrF}_2$  the following equations are proposed<sup>65</sup>:



The fluorocomplexes  $[\text{NO}]_2[\text{TcF}_8]$  and  $[\text{NO}_2][\text{TcF}_7]$  are prepared in an Ni or chlorofluorocarbon vessel<sup>66</sup>:



(J.M. CANICH, G.L. GARD)

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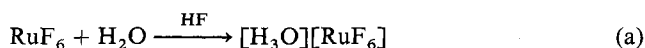
### 2.11.3.2. Platinum Metals: Synthesis of High-Valent Fluorides, Oxide Fluorides and Fluorocomplexes of Ru, Rh and Pd.

Heating Ru metal in a quartz reactor with  $F_2$  produces  $RuF_6$  which is quickly cooled with the cold finger; the product is purified by fractional distillation<sup>1</sup>. Even though  $RuF_6$  is unstable it can be stored for weeks at RT in a Ni vessel with only slight decomposition to  $RuF_5$  and  $F_2$ <sup>1</sup>. There is a report for preparing  $RuF_8$  by fluorinating Ru or  $RuO_2$ ; the compound is handled at very low temperatures ( $-100^\circ C$ )<sup>2</sup>.

The compound  $RuF_5$  is extremely reactive; it is prepared by fluorinating the metal ( $\sim 300^\circ C$ ) in a flow system<sup>3</sup>. Fluorocomplex salts containing  $[RuF_6]^-$  are prepared by fluorinating ( $350^\circ C$ ) the mixture MCl and  $RuCl_3$  ( $M = K, Rb, Cs$ ) in a flow system or by the reaction of Ru metal with KBr, CsCl, or AgBr in  $BrF_5$  solvent<sup>4</sup>. The adducts,  $RuF_5 \cdot SF_4$ ,  $XeF_2 \cdot RuF_5$ ,  $XeF_2 \cdot 2 RuF_5$ ,  $2 XeF_2 \cdot RuF_5$ ,  $2 XeF_6 \cdot RuF_5$  and  $XeF_6 \cdot RuF_5$  are known<sup>5-7</sup>.

Impure  $RuOF_4$  results when Ru metal reacts with a mixture of  $BrF_3$  and  $Br_2$  at  $20^\circ C$ . The removal of volatile unused reactants leaves behind the colorless  $RuOF_4$  contaminated with a small amount of green material; complete separation of  $RuOF_4$  from the green impurity was not achieved<sup>3</sup>.

The hexafluoride of ruthenium reacts not only with dried glass<sup>1</sup> but also with NO or NOF to give  $[NO][RuF_6]$  as the product<sup>8</sup>. With  $O_2$ , the dioxygenyl complex,  $O_2[RuF_6]$ , is prepared by heating ( $300^\circ C$ , 14 h) the mixture,  $F_2-O_2-Ru$  (molar ratio 8:2:1) in a Monel reactor with a water-cooled top<sup>9</sup>. The oxonium salt is prepared as follows<sup>10</sup>:



Rhodium hexafluoride is prepared by burning the metal in  $F_2$  and quickly cooling the product on a surface cooled with liq  $N_2$ . It is a reactive material and dissociates to  $F_2$  and  $RhF_5$  at RT<sup>11</sup>;  $RhF_6$  reacts with Xe or  $O_2$ , giving  $XeRhF_6$  and  $O_2[RhF_6]$ , respectively<sup>9,12</sup>.

2.11. Formation of Group-IB, -IIB, and Transition-Metal Fluorides 285  
 2.11.3. of the Second Transition Series (Y through Ag)  
 2.11.3.2. Platinum Metals: Fluorocomplexes of Ru, Rh and Pd.

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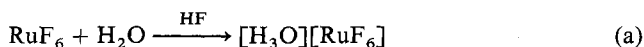
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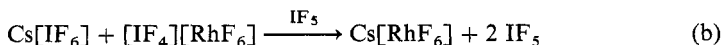
The hexafluoride of ruthenium reacts not only with dried glass<sup>1</sup> but also with  $NO$  or  $NOF$  to give  $[NO][RuF_6]$  as the product<sup>8</sup>. With  $O_2$ , the dioxygenyl complex,  $O_2[RuF_6]$ , is prepared by heating ( $300^\circ C$ , 14 h) the mixture,  $F_2-O_2-Ru$  (molar ratio 8:2:1) in a Monel reactor with a water-cooled top<sup>9</sup>. The oxonium salt is prepared as follows<sup>10</sup>:



Rhodium hexafluoride is prepared by burning the metal in  $F_2$  and quickly cooling the product on a surface cooled with liq  $N_2$ . It is a reactive material and dissociates to  $F_2$  and  $RhF_5$  at RT<sup>11</sup>;  $RhF_6$  reacts with  $Xe$  or  $O_2$ , giving  $XeRhF_6$  and  $O_2[RhF_6]$ , respectively<sup>9,12</sup>.

The pentafluoride  $\text{RhF}_5$  is an extremely powerful oxidizing and fluorinating agent; it is prepared by reacting  $\text{F}_2$  ( $9.1 \times 10^6 \text{ N m}^{-2}$  or 90 psi) with  $\text{RhF}_3$  ( $400^\circ\text{C}$ )<sup>13</sup>.

The salt  $\text{Cs}[\text{RhF}_6]$  is prepared by reacting  $\text{CsF}$  with  $\text{RhF}_5$  in  $\text{IF}_5$  according to<sup>13</sup>:



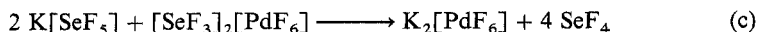
Also, by reacting  $\text{M}_2[\text{CO}_3]$  ( $\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ) with  $\text{RhCl}_3$  under high  $\text{F}_2$  pressure (4–7 d) and at  $T$   $400\text{--}500^\circ\text{C}$ ,  $\text{M}[\text{RhF}_6]$  complexes can be prepared<sup>14</sup>. The complexes  $2 \text{XeF}_2 \cdot \text{RhF}_5$ ,  $\text{XeF}_2 \cdot \text{RhF}_5$  and  $\text{XeF}_2 \cdot 2 \text{RhF}_5$  are prepared<sup>7</sup>.

The highest fluoride of palladium,  $\text{PdF}_6$ , is formed by fluorinating palladium with fluorine atoms<sup>15</sup>; it decomposes at an appreciable rate at  $0^\circ\text{C}$ .

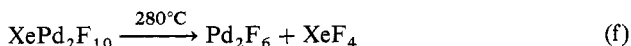
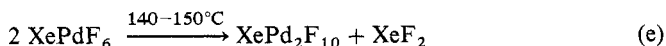
The dioxygenyl complex,  $\text{O}_2[\text{PdF}_6]$ , is prepared by the oxyfluorination of Pd powder ( $320^\circ\text{C}$ ,  $4.13 \times 10^8 \text{ N m}^{-2}$  or  $\sim 4100 \text{ atm}$ )<sup>16</sup>.

Fluorination<sup>17</sup> of “ $\text{PdF}_3$ ” ( $\text{Pd}_2\text{F}_6$ ), which is  $\text{Pd}^{2+}[\text{PdF}_6]^{2-}$ , under  $7 \times 10^5 \text{ N m}^{-2}$  or  $\sim 7 \text{ atm}$   $\text{F}_2$  ( $300^\circ\text{C}$ ) produces  $\text{PdF}_4$ , which is also prepared by the fluorination ( $\text{F}_2$ ,  $5.37 \times 10^6 \text{ N m}^{-2}$  or 780 psi at  $\sim 20^\circ\text{C}$ ) of  $\text{Pd}[\text{GeF}_6]$  at  $280^\circ\text{C}$  ( $\sim 58 \text{ h}$ ); the latter method<sup>18</sup> gives material with little or no  $\text{Pd}_2\text{F}_6$ .

The fluorocomplexes containing Pd(IV) can be prepared either by dissolution in  $\text{BrF}_3$  or by fluorinating ( $200\text{--}300^\circ\text{C}$ ) the hexachloropalladates(IV) of K, Rb, Cs;<sup>19,20</sup> mixing  $\text{KSeF}_5$  with  $(\text{SeF}_3)_2\text{PdF}_6$  in refluxing  $\text{SeF}_4$ , gives<sup>21</sup>:



The reaction of  $\text{Pd}_2\text{F}_6$  with  $\text{XeF}_2$  ( $140\text{--}150^\circ\text{C}$ ) gives  $\text{XePd}_2\text{F}_{10}$ ; which is unstable at  $280^\circ\text{C}$ <sup>18</sup>:



It is worth noting that the net effect of summing Eqs. (d)–(f) provides for the conversion of  $\text{XeF}_2$  to  $\text{XeF}_4$ . The complexes  $4 \text{XeF}_6 \cdot \text{PdF}_4$  and  $2 \text{XeF}_6 \cdot \text{PdF}_4$  are known<sup>22</sup>.

(J.M. CANICH, G.L. GARD)

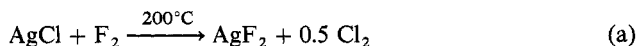
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### 2.11.3.3. Post-Platinum Metals: Synthesis of High-Valent Fluorides, Oxide Fluorides and Fluorocomplexes of Ag and Cd.

The highest fluoride known,  $\text{AgF}_3$ , can be prepared<sup>1</sup> by adding  $\text{AsF}_5$  to a  $\text{XeF}_5\text{AgF}_4$  soln in HF at 20°C; another route using  $\text{KRF}_2$  has been reported<sup>2</sup>.

Silver difluoride is obtained by fluorinating the metal<sup>3</sup> or  $\text{AgCl}$  as the starting reagent<sup>4</sup>:



Treating  $\text{AgCl}$  with  $\text{ClF}_3$  (250°C) is also a useful method<sup>3</sup>. It is possible<sup>6</sup> to oxidize  $\text{AgF}$  in HF with  $\text{F}_2$ . Ternary fluorides of divalent silver— $\text{Ag}[\text{MF}_6]_2$ , with  $\text{M} = \text{Nb}, \text{Ta}$ ;  $\text{Ag}_3\text{M}_2\text{F}_{14}$ , with  $\text{M} = \text{Zr}, \text{Hf}$ —and a new complex fluoride,  $\text{NaAgZr}_2\text{F}_{11}$ , are known<sup>7-9</sup>.

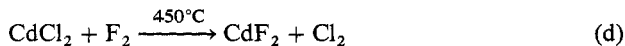
Fluorocomplexes of  $\text{Ag(III)}$ ,  $\text{M}[\text{AgF}_4]$  ( $\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ), are prepared by direct fluorination of equimol  $\text{AgNO}_3$ -alkali-metal chloride mixtures at 200–400°C<sup>10,11</sup>.

The complex  $\text{Cs}_2[\text{AgF}_6]$  is prepared at high  $\text{F}_2$  pressure<sup>12</sup>:



The complex  $\text{Cs}_2\text{Ga}_{0.5}\text{Ag}_{0.5}\text{F}_6$  is also known<sup>12</sup>;  $[\text{XeF}_5][\text{AgF}_4]$  is prepared<sup>13</sup> by treating  $\text{AgF}_2$  with xs  $\text{KrF}_2$  and  $\text{XeF}_6$  at RT in HF.

Cadmium(II) fluoride is obtained by the fluorination of cadmium or cadmium salts<sup>14</sup>:



High yields of  $\text{CdF}_2$  are obtained with  $\text{CdCl}_2$  or  $\text{CdS}$ .

Fluorocomplexes of cadmium such as  $\text{K}[\text{CdF}_3]$  are prepared by either precipitation or fusion of alkali-metal fluoride with  $\text{CdF}_2$  in the correct molar ratio<sup>15</sup>.

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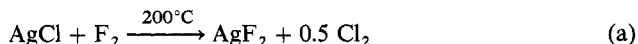
2.11. Formation of Group-IB, -IIB, and Transition-Metal Fluorides 287  
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 2.11.3.3. Post-Platinum Metals: Fluorocomplexes of Ag and Cd.

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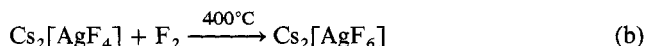
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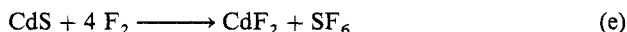
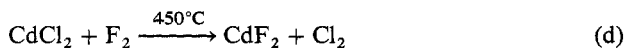
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Fluorocomplexes of cadmium such as  $\text{K}[\text{CdF}_3]$  are prepared by either precipitation or fusion of alkali-metal fluoride with  $\text{CdF}_2$  in the correct molar ratio<sup>15</sup>.

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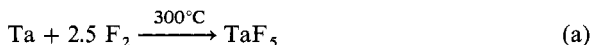
## 2.11.4. of the Third Transition Series (Hf through Hg)

### 2.11.4.1. Pre-Platinum Metals: Synthesis of High-Valent Fluorides, Oxide Fluorides and Fluorocomplexes of Hf, Ta, W, Re.

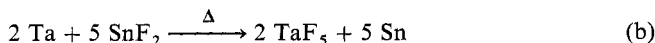
The most interesting  $\text{HfF}_4$  has been synthesized by (1) fluorination of the metal<sup>1</sup>, (2) fluorination of  $\text{HfC}$  (300°C) or  $\text{HfB}_2$  (350–550°C)<sup>2</sup> (3) and reaction of HF with Hf (225°C)<sup>3</sup>. The oxyfluoride  $\text{Hf}_2\text{OF}_6$  is prepared by heating  $\text{HfF}_4 \cdot 3 \text{H}_2\text{O}$  to 200°C in vacuo; further heating (350°C) of  $\text{Hf}_2\text{OF}_6$  gives<sup>4</sup>  $\text{Hf}_3\text{O}_2\text{F}_8$ .

Fluorocomplexes containing  $[\text{HfF}_7]^{3-}$  and  $[\text{HfF}_6]^{2-}$  can be prepared by reacting  $\text{HfF}_4$  with MF in aq HF<sup>5</sup>. The pentafluorohafnates are prepared by reacting MF and  $\text{HfF}_4$  as a melt<sup>5</sup>. The complex  $\text{XeF}_6 \cdot \text{HfF}_4$  has been prepared<sup>6</sup>.

A good method for preparing  $\text{TaF}_5$  is by direct fluorination of the metal, which is then purified by sublimation<sup>7</sup>:



Another method uses HF (250°C)<sup>8</sup>. Although interhalogens such as  $\text{ClF}_3$  and  $\text{BrF}_3$  can be used, it is difficult to obtain a pure product<sup>9</sup>. Pure product can be prepared by reacting  $\text{SnF}_2$  with Ta according to<sup>10</sup>:



Anhydrous  $\text{TaF}_5$  is also prepared by treating a HF soln of  $\text{Ta}_2\text{O}_5$  with a dehydrating agent<sup>11</sup> or by reacting  $\text{Ta}_2\text{O}_5$  with  $\text{COF}_2$  at 210°C<sup>12</sup>.

The oxyfluoride  $\text{TaOF}_3$  is formed by reacting  $\text{TaF}_5$  with silica at elevated temperatures<sup>13</sup>. Dissolution of Ta in 48% aq HF gives  $\text{TaO}_2\text{F}$ <sup>13</sup>. Decomposition of  $\text{TaO}_2\text{F}$  (850°C)<sup>14</sup> gives  $\text{Ta}_3\text{O}_7\text{F}$  and  $\text{TaF}_5$ . The oxysalt  $\text{K}_3[\text{TaOF}_6]$  or  $[\text{NH}_4]_3[\text{TaOF}_6]$  is prepared by brominating the metal in MeOH followed by the addition of KF or  $\text{NH}_4\text{F}$  in MeOH<sup>15</sup>; complexes containing  $[\text{TaOF}_5]^{2-}$  are also known, as well as the peroxyfluorocomplex  $\text{K}_2[\text{TaO}_2\text{F}_5]$ <sup>15,16</sup>.

## 2.11. Formation of Group-IB, -IIB, and Transition-Metal Fluorides

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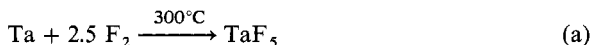
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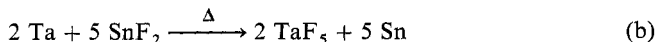
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A good method for preparing  $\text{TaF}_5$  is by direct fluorination of the metal, which is then purified by sublimation<sup>7</sup>:



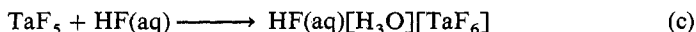
Another method uses HF (250°C)<sup>8</sup>. Although interhalogens such as  $\text{ClF}_3$  and  $\text{BrF}_3$  can be used, it is difficult to obtain a pure product<sup>9</sup>. Pure product can be prepared by reacting  $\text{SnF}_2$  with Ta according to<sup>10</sup>:



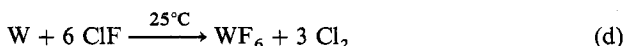
Anhydrous  $\text{TaF}_5$  is also prepared by treating a HF soln of  $\text{Ta}_2\text{O}_5$  with a dehydrating agent<sup>11</sup> or by reacting  $\text{Ta}_2\text{O}_5$  with  $\text{COF}_2$  at 210°C<sup>12</sup>.

The oxyfluoride  $\text{TaOF}_3$  is formed by reacting  $\text{TaF}_5$  with silica at elevated temperatures<sup>13</sup>. Dissolution of Ta in 48% aq HF gives  $\text{TaO}_2\text{F}$ <sup>13</sup>. Decomposition of  $\text{TaO}_2\text{F}$  (850°C)<sup>14</sup> gives  $\text{Ta}_3\text{O}_7\text{F}$  and  $\text{TaF}_5$ . The oxysalt  $\text{K}_3[\text{TaOF}_6]$  or  $[\text{NH}_4]_3[\text{TaOF}_6]$  is prepared by brominating the metal in MeOH followed by the addition of KF or  $\text{NH}_4\text{F}$  in MeOH<sup>15</sup>; complexes containing  $[\text{TaOF}_5]^{2-}$  are also known, as well as the peroxyfluorocomplex  $\text{K}_2[\text{TaO}_2\text{F}_5]$ <sup>15,16</sup>.

Numerous complexes of  $\text{TaF}_5$  with  $\text{py}$ ,  $\text{SO}_3$ ,  $\text{Et}_2\text{O}$ ,  $\text{Me}_2\text{SO}$ ,  $\text{EtCN}$ ,  $\text{XeF}_2$ ,  $\text{XeF}_6$  and  $\text{I}_2$  exist<sup>6,18</sup>. In addition, other complexes with  $\text{ClOF}_3$ ,  $\text{CrO}_2\text{F}_2$  and  $\text{KrF}_2$ , among others, can be prepared<sup>6,19-21</sup>. Fluorocomplexes of  $[\text{TaF}_6]^-$  and  $[\text{Ta}_2\text{F}_{11}]^-$  can be prepared and studied in  $\text{CH}_2\text{Cl}_2$ <sup>22</sup>. Interesting complexes such as  $[\text{PH}_4][\text{TaF}_6]$  and mixtures of  $[\text{H}_3\text{S}][\text{TaF}_6]$ - $[\text{H}_3\text{S}][\text{Ta}_2\text{F}_{11}]$  and  $[\text{AsH}_4][\text{TaF}_6]$ - $[\text{AsH}_4][\text{Ta}_2\text{F}_{11}]$  are prepared by reacting  $\text{PH}_3$ ,  $\text{H}_2\text{S}$  and  $\text{AsH}_3$  respectively<sup>23</sup>, with  $\text{TaF}_5$  in  $\text{HF}$ . Complexes<sup>24</sup> containing  $[\text{TaF}_8]^{3-}$  and  $[\text{TaF}_7]^{2-}$  are prepared by fusing appropriate amounts of alkali-metal fluoride and  $\text{TaF}_5$ . The dioxygenyl salt  $\text{O}_2[\text{Ta}_2\text{F}_{11}]$  is prepared by reacting powdered Ta at  $375^\circ\text{C}$  with  $5 \times 10^5 \text{ N m}^{-2}$  or 5 atm of a 9:3  $\text{F}_2$ - $\text{O}_2$  mixture in a Monel reactor with a water-cooled top<sup>25</sup>. The oxonium salt  $[\text{H}_3\text{O}][\text{TaF}_6]$  is prepared by<sup>26</sup>:

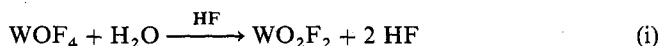
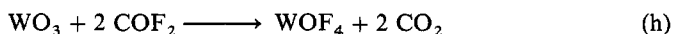
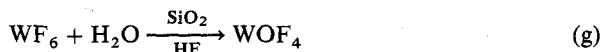
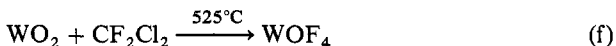
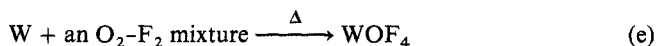


The highest binary fluoride of tungsten ( $\text{WF}_6$ ) is prepared by treating pure W with  $\text{F}_2$  in a tube ( $350$ – $400^\circ\text{C}$ ); the product is purified by distillation and stored over  $\text{KF}$ <sup>27</sup>. The reaction of W with  $\text{Cl}_2$  and  $\text{HF}$  in a Monel cylinder ( $200^\circ\text{C}$ ) is a useful way of preparing  $\text{WF}_6$  in high yields<sup>26</sup>. Sulfur tetrafluoride reacts with  $\text{WO}_3$  ( $350^\circ\text{C}$ ) in a bomb giving  $\text{WF}_6$  in high yields<sup>27</sup>. A convenient method involves the reaction<sup>28</sup>:

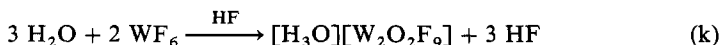
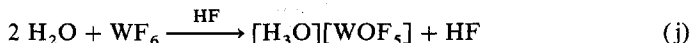


The  $\text{Cl}_2$  is easily removed at  $-78^\circ\text{C}$ . Other methods include reacting  $\text{WO}_3$  with  $\text{ClF}_3$ ,  $\text{ClF}$ ,  $\text{BrF}_3$  and  $\text{IF}_5$ , or reacting  $\text{WBr}_2$  with  $\text{HF}$  in a flow system ( $550^\circ\text{C}$ ), or by the electrical explosion of W in  $\text{SF}_6$  or  $\text{CF}_4$ <sup>29-31</sup>. Reacting  $\text{TiCl}_4$  with xs  $\text{WF}_6$  ( $5^\circ\text{C}$ ) forms  $\text{WF}_5\text{Cl}$ <sup>32</sup>.

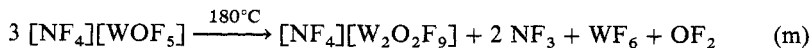
The oxyfluorides  $\text{WOF}_4$  and  $\text{WO}_2\text{F}_2$  are prepared by<sup>12,35-38</sup>:



The reaction<sup>39</sup> of  $\text{NF}_3$  with  $\text{WO}_3$  gives  $[\text{NO}][\text{WOF}_5]$ , while the reaction<sup>40</sup> of  $\text{KF}$ ,  $\text{WO}_3$  and  $\text{SeF}_4$  gives  $\text{K}[\text{WOF}_5]$ ;  $\text{Cs}[\text{WOF}_5]$  is prepared<sup>41</sup> by reacting  $\text{W}(\text{CO})_6$  and moist  $\text{CsI}$  in  $\text{IF}_5$ . Adducts such as  $[\text{NO}]_2\text{WOF}_6$ ,  $\text{XeF}_2 \cdot \text{WOF}_4$ ,  $\text{XeF}_2 \cdot 2 \text{WOF}_4$ ,  $\text{KrF}_2 \cdot \text{WOF}_4$ , among others, are known<sup>19,42,43</sup>. Additional salts containing  $[\text{WO}_2\text{F}_3]^-$ ,  $[\text{WO}_2\text{F}_4]^{2-}$ ,  $[\text{WO}_3\text{F}]^-$ ,  $[\text{W}_2\text{O}_2\text{F}_9]^-$  and  $[\text{WOF}_5]^-$  have been reported as well as the peroxyfluorocomplexes  $\text{K}_2[\text{WO}_3\text{F}_4]$ <sup>44-46,17</sup>. The oxonium salts  $[\text{H}_3\text{O}][\text{WOF}_5]$  and  $[\text{H}_3\text{O}][\text{W}_2\text{O}_2\text{F}_9]$  are prepared by<sup>47</sup>:



The following perfluoroammonium fluorotungstate salts are prepared accordingly<sup>47</sup>:



The adduct  $\text{WOF}_4 \cdot \text{SbF}_5$  is prepared<sup>48</sup> from  $\text{WOF}_4$  and xs of  $\text{SbF}_5$ .

Numerous fluorocomplexes of  $\text{WF}_6$  are known; e.g.,  $\text{NOF}$  and  $\text{NO}_2\text{F}$  react with  $\text{WF}_6$  to give  $[\text{NO}][\text{WF}_7]$ ,  $[\text{NO}]_2[\text{WF}_8]$  and  $[\text{NO}_2][\text{WF}_7]$ , respectively<sup>49</sup>, while  $\text{KI}$  and  $\text{W}(\text{CO})_6$  in  $\text{IF}_5$  give  $\text{K}_2[\text{WF}_8]$  as the product<sup>41</sup>. The reaction<sup>30</sup> of  $\text{Na}_2[\text{WO}_4]$  with  $\text{ClF}$  at  $300^\circ\text{C}$  (2 h) gives  $\text{Na}_2[\text{WF}_8]$ ; this compound can also be prepared by heating a mixture of  $\text{WO}_3$ ,  $\text{NaF}$  and  $\text{SF}_4$  in a pressure vessel<sup>29</sup>.

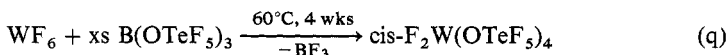
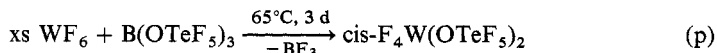
The reaction of xs  $\text{WF}_6$  with  $(\text{CH}_3)_3\text{SiN}_3$  gives<sup>50</sup>:



The alkoxyl fluorocomplexes  $(\text{RO})_n\text{WF}_{6-n}$  have been reported, as well as n-alkylimido fluorotungstates<sup>51,52</sup>. Thio and seleno derivatives of  $\text{WF}_6$  are prepared as follows<sup>53,54</sup>:



where  $\text{X} = \text{S}, \text{Se}$ . With  $\text{B}(\text{OTeF}_5)_3$ , the compounds  $\text{cis-F}_4\text{W}(\text{OTeF}_5)_2$  and  $\text{cis-F}_2\text{W}(\text{OTeF}_5)_4$  are prepared<sup>55</sup>:



The highest fluoride of rhenium,  $\text{ReF}_7$ , is obtained by fluorinating  $\text{Re}$  at  $400^\circ\text{C}$  under pressure; reaction of  $\text{ReF}_7$  with  $\text{Re}$  metal gives<sup>56,57</sup> pure  $\text{ReF}_6$ . It is also possible to prepare  $\text{ReF}_7$  in a fluidized-bed process at high  $T$  with  $\text{F}_2$ <sup>58</sup>.

The complexes  $\text{ReF}_6\text{SbF}_6$  and  $\text{ReF}_6\text{Sb}_2\text{F}_{11}$  are formed from  $\text{ReF}_7$  and  $\text{SbF}_5$  in a fluorine atmosphere<sup>59</sup>.

Perrhenyl fluoride ( $\text{ReO}_3\text{F}$ ) or rhenium trioxide fluoride is prepared<sup>60</sup> by reacting  $\text{ReO}_3\text{Cl}$  with  $\text{HF}$ . It is also prepared in good yield by reacting  $\text{KReO}_4$  with  $\text{IF}_5$  and is purified by vacuum sublimation at  $140^\circ\text{C}$ <sup>61</sup>. More recently, a method involving heating  $\text{ReF}_7$  with  $\text{Re}_2\text{O}_7$  ( $150^\circ\text{C}$ , 20 h) in a Monel reactor, followed by sublimation in a quartz tube ( $65^\circ\text{C}$ ), is used<sup>62</sup>.

The high-valent oxide fluoride  $\text{ReOF}_5$  is obtained from the fluorination (flow system) of  $\text{KReO}_4$  or  $\text{ReO}_2$ ; also produced is  $\text{ReO}_2\text{F}_3$ , which is easily recovered by sublimation<sup>63</sup>. Static fluorination<sup>64,65</sup> of  $\text{ReO}_2$  gives better yields of  $\text{ReOF}_5$ . Other methods include the static fluorination of  $\text{ReOF}_4$  ( $300^\circ\text{C}$ ) in 50% xs  $\text{F}_2$  or fluorination of  $\text{ReO}_3$  at  $200^\circ\text{C}$  (17 h)<sup>62</sup>.

The oxyfluoride  $\text{ReOF}_4$  is conveniently prepared by the slow hydrolysis of  $\text{ReF}_6$  with quartz wool in  $\text{HF}$  (2–4 h)<sup>37</sup>. Another good route<sup>62</sup> is by the oxyfluorination of  $\text{Re}$ .

In addition to preparing  $\text{ReO}_2\text{F}_3$  from  $\text{ReO}_2$  or  $\text{KReO}_4$ , fluorination of  $\text{ReO}_3$  or  $\text{Re}_2\text{O}_7$  is used<sup>62</sup>.

The oxyfluoro complexes  $M\text{ReO}_2\text{F}_4$  ( $M = \text{Rb}, \text{Cs}, \text{Ag}$ ) are prepared<sup>66</sup> by dissolving  $M\text{ReO}_4$  in  $\text{BrF}_3$ . Partial hydrolysis of salts containing  $[\text{ReF}_8]^{3-}$  produce salts containing the  $[\text{ReOF}_5]^{3-}$  ions<sup>67</sup>. The adduct<sup>48</sup>,  $\text{ReOF}_4 \cdot \text{SbF}_5$  is prepared from the reaction of  $x$   $\text{SbF}_5$  with  $\text{ReOF}_4$ .

Fluoro complexes of  $\text{ReF}_6$  are known; for example<sup>48</sup>,  $\text{NOF}$  reacts with  $\text{ReF}_6$  in a chlorofluorocarbon vessel (RT, 1 h) to give  $[\text{NO}]_2[\text{ReF}_8]$ . Additional complexes containing  $[\text{ReF}_8]^{2-}$  and  $[\text{ReF}_7]^-$  ions are known<sup>68</sup>.

The unique complexes<sup>69</sup>,  $\text{ReF}_5(\text{NCl})$  and  $\text{ReF}_5(\text{NF})$ , which contain Re in the 7+ state, are prepared from  $\text{ReF}_6$  and  $(\text{CH}_3)_3\text{SiN}_3$  followed by treatment with  $\text{ClF}_3$ . **CAUTION: The initial reaction between  $\text{ReF}_6$  and  $(\text{CH}_3)_3\text{SiN}_3$  in  $\text{CClF}_2\text{CCl}_2\text{F}$  is violent and detonation is possible even if maximum control is exercised by repeated cooling with liquid nitrogen.**

(J.M. CANICH, G.L. GARD)

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### 2.11.4.2. Platinum Metals: Synthesis of High-Valent Fluorides, Oxide Fluorides and Fluorocomplexes of Os, Ir, Pt.

The highest stable fluoride in this group is  $\text{OsF}_7$  (only limited evidence exists for the unstable  $\text{OsF}_8$ ) and it is prepared from Os at high pressures of fluorine ( $3.55 \times 10^7$  to  $4.05 \times 10^7 \text{ N m}^{-2}$  or 350–400 atm) at 500–600°C in a Ni bomb<sup>1</sup>; it decomposes above –100°C into  $\text{OsF}_6$  and  $\text{F}_2$ . Due to the instability of  $\text{OsF}_7$ , the chemistry of  $\text{OsF}_6$  is covered here. The hexafluoride of osmium is prepared by passing  $\text{F}_2$  (g) at a pressure of 250 mm over osmium metal heated in a borosilicate glass furnace tube; the material was purified by trap-to-trap distillation under high-vacuum conditions<sup>2</sup>.

## 2.11. Formation of Group-IB, -IIB, and Transition-Metal Fluorides

## 2.11.4. of the Third Transition Series (Hf through Hg)

## 2.11.4.2. Platinum Metals: Fluorocomplexes of Os, Ir, Pt.

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### 2.11.4.2. Platinum Metals: Synthesis of High-Valent Fluorides, Oxide Fluorides and Fluorocomplexes of Os, Ir, Pt.

The highest stable fluoride in this group is OsF<sub>7</sub> (only limited evidence exists for the unstable OsF<sub>8</sub>) and it is prepared from Os at high pressures of fluorine ( $3.55 \times 10^7$  to  $4.05 \times 10^7$  N m<sup>-2</sup> or 350–400 atm) at 500–600°C in a Ni bomb<sup>1</sup>; it decomposes above –100°C into OsF<sub>6</sub> and F<sub>2</sub>. Due to the instability of OsF<sub>7</sub>, the chemistry of OsF<sub>6</sub> is covered here. The hexafluoride of osmium is prepared by passing F<sub>2</sub> (g) at a pressure of 250 mm over osmium metal heated in a borosilicate glass furnace tube; the material was purified by trap-to-trap distillation under high-vacuum conditions<sup>2</sup>.



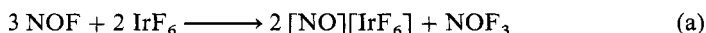
The interesting  $\text{OsO}_3\text{F}_2$  [Os(VIII)] is prepared<sup>3</sup> by either the reaction of  $\text{OsO}_4$  with  $\text{BrF}_3$  ( $\sim 50^\circ\text{C}$ ) or by heating Os with a 2:1 mixture of  $\text{O}_2$  and  $\text{F}_2$ . Also, it is possible to fluorinate  $\text{OsO}_4$  (2:1) at  $300^\circ\text{C}$  ( $\sim 50\text{ h}$ )<sup>4</sup>. In the (VII) state, the oxyfluoride of osmium  $\text{OsOF}_5$  is prepared by the fluorination of  $\text{OsO}_2$  [Os(VII)] ( $250^\circ\text{C}$ ) or by passing an  $\text{O}_2$ - $\text{F}_2$  mixture (1:2) over Os ( $250^\circ\text{C}$ ); the product is purified by trap-to-trap transfer<sup>5</sup>. Static oxyfluorination of osmium<sup>6</sup> is also a good method for preparing  $\text{OsOF}_5$ . The reaction<sup>4</sup> of an equimol  $\text{OsO}_4$  and  $\text{OsF}_6$  mixture ( $150^\circ\text{C}$ , 17 h) in a Monel reactor produces  $\text{OsO}_2\text{F}_3$ .

The salts  $\text{M}[\text{OsO}_3\text{F}_3]$ , with  $\text{M}$  = alkali metal or  $\text{Ag}^+$ , are prepared by reacting  $\text{OsO}_4$  with  $\text{MBr}$  ( $\text{M}$  = alkali metal) in  $\text{BrF}_3$ ; for the silver salt,  $\text{AgIO}_3$  is used<sup>3</sup>. More recently,  $\text{M}[\text{OsO}_3\text{F}_3]$  salts ( $\text{M}$  = Cs, Rb, K) have been prepared by reacting  $\text{OsO}_3\text{F}_2$  directly with the appropriate alkali-metal fluoride; also the salts  $\text{M}_2[\text{OsO}_4\text{F}_2]$  ( $\text{M}$  = Cs, Rb) are produced by reacting  $\text{OsO}_4$  with  $\text{MF}$  in an aqueous solution<sup>7</sup>.

The fluorosalt  $[\text{NO}]_2[\text{OsF}_8]$  is prepared by reacting  $\text{NOF}$  with  $\text{OsF}_6$  (in a chlorofluorocarbon reactor)<sup>8,9</sup>; above  $-30^\circ\text{C}$  it loses  $\text{NOF}$  and forms  $[\text{NO}][\text{OsF}_7]$ . The interesting complex  $\text{Br}_2\text{OsF}_6$  is formed from  $\text{Br}_2$  and  $\text{OsF}_6$ , while the complex  $[\text{N}_2\text{H}_6][\text{OsF}_6]_2$  is prepared from  $\text{OsF}_6$  and  $\text{N}_2\text{H}_6\text{F}_2$  in  $\text{HF}$ <sup>10,11</sup>.

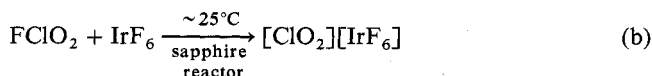
Iridium hexafluoride is prepared<sup>12</sup> by passing fluorine over Ir metal heated to  $300$ – $400^\circ\text{C}$ .

$\text{IrF}_6$  is an extremely reactive compound; for example, with  $\text{NO}$  a mixture of  $[\text{NO}][\text{IrF}_6]$  and  $[\text{NO}]_2[\text{IrF}_6]$  forms<sup>9,12</sup>; with  $\text{NOF}$  the following reaction occurs:



A little  $\text{F}_2$  is also present<sup>13</sup>.

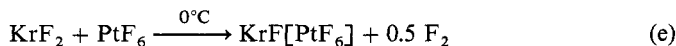
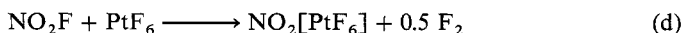
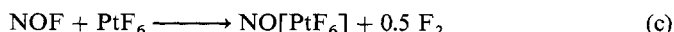
Apparently because of its extreme reactivity, no oxyfluorides or fluorocomplexes of Ir in 6+ state are known. Fluorocomplexes of  $\text{Ir}^{5+}$  are known and are prepared<sup>14</sup> by reaction of alkali-metal bromides with  $\text{IrBr}_3$  in  $\text{BrF}_3$ . The pentafluoride of iridium is prepared by reacting a stoichiometric mixture of the elements at  $350$ – $380^\circ\text{C}$  in a Monel reactor<sup>15</sup>. The complex  $[\text{ClO}_2][\text{IrF}_6]$  is prepared as follows<sup>16</sup>:



In liq  $\text{BrF}_5$ ,  $\text{XeF}_2$  and  $\text{XeF}_6$  react with  $\text{IrF}_5$  in the appropriate molar ratios to give  $\text{Xe}_2\text{F}_3\text{IrF}_6$ ,  $\text{XeFIrF}_6$ ,  $\text{XeFIr}_2\text{F}_{11}$  and  $\text{Xe}_2\text{F}_{11}\text{IrF}_6$  or  $\text{XeF}_5\text{IrF}_6$ , respectively<sup>17</sup>.

The reactive  $\text{PtF}_6$  is prepared by igniting a Pt wire in  $\text{F}_2$  with an electric current and purified by vacuum distillation<sup>18</sup>. Also, reaction of Pt sponge with  $\text{F}_2$  ( $1.5 \times 10^6 \text{ N m}^{-2}$  or 15 atm at  $22^\circ\text{C}$ ) at  $200^\circ\text{C}$  gives good yields of  $\text{PtF}_6$ <sup>19</sup>.

Platinum hexafluoride is one of the most powerful oxidizing agents; it reacts with  $\text{O}_2$  and  $\text{Xe}$  to give  $\text{O}_2[\text{PtF}_6]$  and  $\text{Xe}(\text{PtF}_6)_{n=1,2}$ , respectively<sup>20,21</sup>. It is so reactive that molecular fluorine is liberated in the following reactions at low  $T$ <sup>16,22–24</sup>:

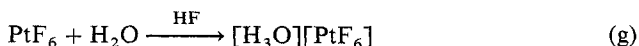


Attempts to prepare  $[\text{PtF}_7]^-$  complexes have failed even in the presence of  $\text{xs F}_2$ .

The next lower fluoride,  $\text{PtF}_5$  is prepared by reacting  $\text{F}_2$  with  $\text{PtCl}_2$  ( $\sim 350^\circ\text{C}$ )<sup>25</sup>. The oxyfluoride,  $\text{PtOF}_3$ , is formed by fluorinating  $\text{PtO}_2$  ( $200^\circ\text{C}$ )<sup>25</sup>.

The complex  $\text{XeF}_5\text{PtF}_6$  is prepared by reacting Xe with  $\text{PtF}_5$  in the presence of  $\text{F}_2$  at  $5.5 \times 10^5 \text{ N m}^{-2}$  or 80 psi ( $200^\circ\text{C}$ )<sup>26</sup>; with  $\text{IF}_5$  the complex  $\text{PtF}_5 \cdot \text{IF}_5$  is formed<sup>25</sup>. Other known xenon fluoride complexes are<sup>27</sup>  $2 \text{XeF}_2 \cdot \text{PtF}_5$ ,  $\text{XeF}_2 \cdot \text{PtF}_5$ ,  $\text{XeF}_2 \cdot 2 \text{PtF}_5$ ,  $2 \text{XeF}_6 \cdot \text{PtF}_5$  and  $\text{XeF}_6 \cdot \text{PtF}_5$ . The salt  $\text{K}[\text{PtF}_6]$  is prepared<sup>25</sup> by reacting  $\text{KF}$  with  $\text{O}_2[\text{PtF}_6]$  in  $\text{IF}_5$ , while  $\text{Rb}[\text{PtF}_6]$  and  $\text{Cs}[\text{PtF}_6]$  are prepared<sup>21</sup> by first mixing  $\text{PtF}_6$ , Xe and  $\text{MF}$  ( $\text{RbF}$  or  $\text{CsF}$ ) in a silica vessel at RT and then adding  $\text{IF}_5$ .

Additional complexes of  $\text{PtF}_6$  include<sup>16,25,28,29</sup>:  $\text{ClF}_2\text{PtF}_6$ ,  $\text{ClF}_4\text{PtF}_6$ ,  $\text{ClF}_6\text{PtF}_6$  and  $\text{ClO}_2\text{F}_2\text{PtF}_6$ . The oxonium salt  $\text{H}_3\text{OPtF}_6$  is prepared by<sup>30</sup>:



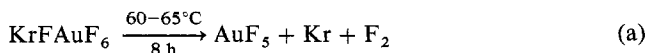
With xs  $\text{H}_2\text{O}$   $[\text{H}_3\text{O}]_2[\text{PtF}_6]$  is formed.

(J.M. CANICH, G.L. GARD)

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### 2.11.4.3. Post-Platinum Metals: Synthesis of High-Valent Fluorides, Oxide Fluorides and Fluorocomplexes of Au and Hg.

The highest fluoride of gold is  $\text{AuF}_7$ , prepared<sup>1</sup> by reacting  $\text{AuF}_5$  with atomic F. The next highest fluoride of gold,  $\text{AuF}_5$ , is prepared by the pyrolysis reaction<sup>2,3</sup>:



294 2.11. Formation of Group-IB, -IIB, and Transition-Metal Fluorides  
 2.11.4. of the Third Transition Series (Hf through Hg)  
 2.11.4.3. Post-Platinum Metals: Fluorocomplexes of Au and Hg.

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The complex  $\text{XeF}_5\text{PtF}_6$  is prepared by reacting Xe with  $\text{PtF}_5$  in the presence of  $\text{F}_2$  at  $5.5 \times 10^5 \text{ N m}^{-2}$  or 80 psi ( $200^\circ\text{C}$ )<sup>26</sup>; with  $\text{IF}_5$  the complex  $\text{PtF}_5 \cdot \text{IF}_5$  is formed<sup>25</sup>. Other known xenon fluoride complexes are<sup>27</sup>  $2 \text{XeF}_6 \cdot \text{PtF}_5$ ,  $\text{XeF}_2 \cdot \text{PtF}_5$ ,  $\text{XeF}_2 \cdot 2 \text{PtF}_5$ ,  $2 \text{XeF}_6 \cdot \text{PtF}_5$  and  $\text{XeF}_6 \cdot \text{PtF}_5$ . The salt  $\text{K}[\text{PtF}_6]$  is prepared<sup>25</sup> by reacting  $\text{KF}$  with  $\text{O}_2[\text{PtF}_6]$  in  $\text{IF}_5$ , while  $\text{Rb}[\text{PtF}_6]$  and  $\text{Cs}[\text{PtF}_6]$  are prepared<sup>21</sup> by first mixing  $\text{PtF}_6$ , Xe and  $\text{MF}$  ( $\text{RbF}$  or  $\text{CsF}$ ) in a silica vessel at RT and then adding  $\text{IF}_5$ .

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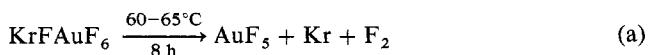
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(J.M. CANICH, G.L. GARD)

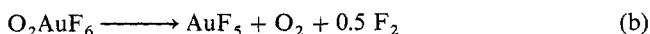
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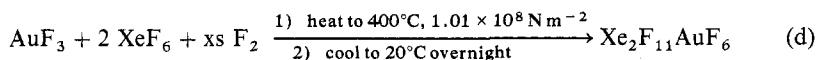


It is also prepared by decomposing  $\text{O}_2[\text{AuF}_6]$  at 160–200°C in a fused silica sublimation apparatus with a cold finger<sup>4</sup>;



Another reactive fluoride of gold is  $\text{AuF}_3$ ; it is prepared by direct fluorination of  $\text{AuCl}_3 \cdot x \text{H}_2\text{O}$  at 200°C<sup>4</sup>.

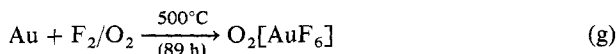
Salts of Au(V) are prepared as follows<sup>2,6–8</sup>



where  $\text{M} = \text{K}, \text{Cs}, \text{NO}$ ;

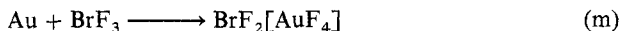
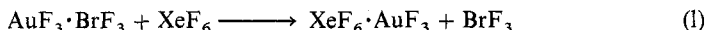
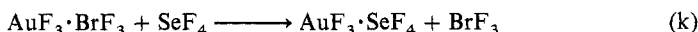
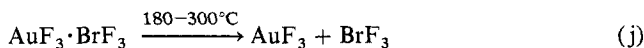


where  $\text{M} = \text{K}, \text{Cs}, \text{NO}$ ;



If the  $\text{Xe}_2\text{F}_{11}[\text{AuF}_6]$  salt is heated to 110°C under vacuum, the new salt,  $\text{XeF}_5[\text{AuF}_6]$ , is obtained<sup>7</sup>. The krypton complex  $\text{KrF} \cdot \text{AuF}_6$  reacts with  $\text{XeF}_2$  and  $\text{NOF}$ , giving  $\text{Xe}_2\text{F}_3[\text{AuF}_6]$  and  $\text{NO}[\text{AuF}_6]$ , respectively; also reported are  $\text{NaF} \cdot \text{AuF}_5$  and  $\text{BrF}_7 \cdot \text{AuF}_5$  complexes<sup>3</sup>.

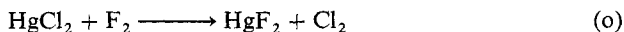
Salts or adducts of Au(III) are prepared by<sup>9–12</sup>:



The salts  $\text{M}[\text{AuF}_4]$  ( $\text{M} = \text{K}-\text{Cs}$ ) and  $\text{FCu}[\text{AuF}_4]$  are known<sup>13,14</sup>.

The series  $\text{M}[\text{AuF}_4]_2$ , with  $\text{M} = \text{Mg}, \text{Ni}, \text{Zn}, \text{Ba}, \text{Cd}, \text{Hg}, \text{Pd}$ , is also reported<sup>15</sup>.

Mercury(II) fluoride is prepared by reacting Hg or its salts with  $\text{F}_2$  in a flow system or under mild pressure<sup>16,17</sup>.



A convenient method involves heating  $\text{HgO}$  with  $\text{SF}_4$  (150°C, 10 h) in a pressure vessel<sup>18</sup>.

The dihydrate,  $\text{HgF}_2 \cdot 2 \text{H}_2\text{O}$  is obtained<sup>19</sup> by treating  $\text{HgO}$  several times with 50% aq HF.

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2.11.5. of the Lanthanides and Actinides  
2.11.5.1. Synthesis of Lanthanide Fluorides and Fluorocomplexes (La–Lu).

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The pyridinium salt,  $[\text{C}_5\text{H}_6\text{N}]_2[\text{HgF}_4]$ , is prepared<sup>20</sup> from  $\text{HgO}$ , py and HF in MeOH. The novel mercury(II) hydroxide fluoride is prepared<sup>21</sup> from an  $\text{HgO}$  soln in aq HF.

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Additional interesting methods include: (1) the thermal decomposition of rare-earth trifluoromethylsulfonates  $\text{M}[\text{CF}_3\text{SO}_3]_3$ , with  $\text{M} = \text{La, Pr, Gd, Eu}$  and  $\text{Y}$ <sup>3</sup>; (2) exchange reaction in  $\text{KNO}_3$  melts with rare-earth nitrates  $\text{M}(\text{NO}_3)_3$ , with  $\text{M} = \text{La, Pr, Nd, Er}$  and

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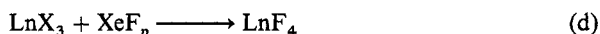
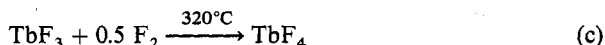
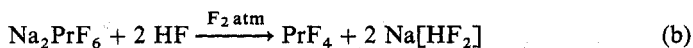
KF in a correct stoichiometric ratio<sup>4</sup>; (3) high T reaction<sup>5</sup> between  $M_2O_3$  ( $M = La, Pr, Nd, Tb$ ) and  $SF_6$ .

Oxyfluorides (MOF) for many of the lanthanides have been prepared by partial hydrolysis of the trifluorides in moist air or ammonia vapor at 800°C<sup>6</sup>.

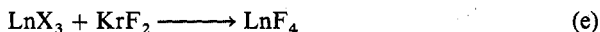
Numerous salt complexes containing  $[MF_4]^-$ ,  $[MF_6]^{3-}$  are known and have been prepared by melting together stoichiometric amounts of component fluorides or have been identified by phase studies<sup>7</sup>.

The complexes  $4 XeF_6 \cdot MF_4$  and  $XeF_6 \cdot MF_4$  ( $M = Ce, Pr, Nd$ ),  $XeF_6 \cdot 4 PrF_4$  and  $3 XeF_6 \cdot MF_3$  ( $M = Dy, Ho$ ) are also prepared<sup>8</sup>.

The tetrafluorides of Ce, Pr and Tb can be prepared according to the following methods<sup>9-12</sup>:



where  $n = 2, 4, 6$ ;



where  $Ln = Ce, Pr, Tb$ ;  $X = Cl, F$ . The reaction of  $ClF_3$  with  $CeO_2$  or  $CeF_3$  (400–450°C), and with  $Tb_4O_7$  or  $TbF_3$  (300–350°C), and with  $Pr_6O_{11}$  and  $NaCl$  (400–500°C) followed by HF treatment produces the respective tetrafluorides<sup>13</sup>. Also,  $CeF_4$  is prepared by the fluorination of  $CeO_2$  (350–500°C)<sup>14</sup>.

Many alkali-metal compounds containing Ce(IV), Pr(IV) and Tb(IV) are prepared by fluorination of stoichiometric mixtures of  $MCl$  ( $M = \text{alkali metals}$ ) with  $CeO_2$ ,  $Pr_6O_4$  or  $Tb_4O_7$ , or with  $MCl_3$  ( $M = Ce, Pr, Tb$ ) at 200–500°C<sup>15-19</sup>. The oxidizing alkaline-earth fluorocomplexes  $BaPrF_6$  and  $SrPrF_6$  have been prepared<sup>20</sup>; in order to prepare  $Ba[PrF_6]$ ,  $Ba[PrCl_5]$  is first prefluorinated with  $F_2$  (400°C, 12 h) and then treated with  $F_2$  under pressure ( $P_{F_2} = 3.04 \times 10^7 \text{ N m}^{-2}$  or 300 atm, 500°C, 24 h), while for  $Sr[PrF_6]$  an intimate mixture of  $SrF_2$  and  $PrF_3$  is first heated (1000°C, 7 d, in vacuo), ground and then treated with  $F_2$  ( $P_{F_2} = 3.04 \times 10^7 \text{ N m}^{-2}$  or 300 atm, 500°C, 24 h).

Although  $MF_4$  for  $M = Nd$  and  $Dy$  are unknown, salts containing tetravalent lanthanides are known;  $XeF_n$  ( $n = 2, 4, 6$ ) or  $KrF_2$  with  $Cs_3[LnF_6]$  or  $Cs_3[LnCl_6]$  ( $Ln = Ce, Pr, Nd, Tb, Dy, Tm$ ) produces the corresponding salt,  $Cs_3[LnF_7]$  in high purity<sup>12</sup>.

(J.M. CANICH, G.L. GARD)

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### 2.11.5.2. Synthesis of the High-Valent Actinide Fluorides, Oxide Fluorides and Fluorocomplexes (Ac-Ha).

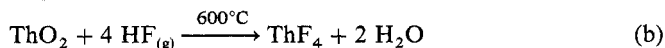
The highest reported binary fluoride of Ac is  $\text{AcF}_3$ . It is prepared by treating  $\text{Ac}(\text{OH})_3$  (s) with HF (g) at  $700^\circ\text{C}$  in a Pt hydrofluorination apparatus<sup>1</sup>. The same product was obtained by adding aq HF to a solution of Ac and drying the precipitate at  $70^\circ\text{C}$ <sup>2</sup>.

Actinium oxide fluoride is prepared by the partial hydrolysis of the trifluoride in the presence of  $\text{NH}_3$  (g) at  $900\text{--}1000^\circ\text{C}$ <sup>3</sup>:



It was possible to monitor the progress of this reaction by observing the formation of  $[\text{NH}_4]\text{F}$  during hydrolysis.

Thorium forms a tetrafluoride either by reaction of the elements at  $500^\circ\text{C}$  or by<sup>4</sup>:



$\text{ThF}_4$  can be precipitated from an aqueous solution and dehydrated with heat in an HF atmosphere<sup>4</sup>.

Thorium oxide difluoride,  $\text{ThOF}_2$ , is formed when  $\text{ThF}_4$  and  $\text{ThO}_2$  react at  $900^\circ\text{C}$  in an inert atmosphere<sup>5</sup>.

Numerous salt complexes containing fluorocomplex ions such as  $[\text{ThF}_5]^-$ ,  $[\text{ThF}_6]^{2-}$ ,  $[\text{ThF}_7]^{3-}$  and  $[\text{ThF}_8]^{4-}$  are known<sup>6</sup>.

The pentafluoride of protactinium can be prepared<sup>7</sup> by slowly passing  $\text{F}_2$  over  $\text{PaF}_4$  at  $700^\circ\text{C}$  or by fluorination<sup>8</sup> of Pa,  $\text{PaC}$  or  $\text{PaCl}_5$ . The interesting oxide fluoride<sup>7</sup>  $\text{Pa}_2\text{OF}_8$  can be formed by heating  $\text{Pa}_2\text{O}_5$  with  $\text{F}_2$  or with an equimolar mixture of HF (g) and  $\text{O}_2$ . Thermal decomposition of the hydrate<sup>7</sup>  $\text{PaF}_5 \cdot 2 \text{H}_2\text{O}$  at  $160^\circ\text{C}$  also produces  $\text{Pa}_2\text{OF}_8$ .



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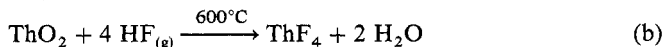
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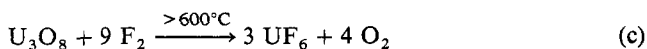
Thorium oxide difluoride,  $\text{ThOF}_2$ , is formed when  $\text{ThF}_4$  and  $\text{ThO}_2$  react at  $900^\circ\text{C}$  in an inert atmosphere<sup>5</sup>.

Numerous salt complexes containing fluorocomplex ions such as  $[\text{ThF}_5]^-$ ,  $[\text{ThF}_6]^{2-}$ ,  $[\text{ThF}_7]^{3-}$  and  $[\text{ThF}_8]^{4-}$  are known<sup>6</sup>.

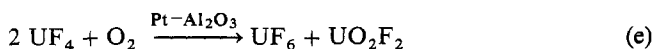
The pentafluoride of protactinium can be prepared<sup>7</sup> by slowly passing  $\text{F}_2$  over  $\text{PaF}_4$  at  $700^\circ\text{C}$  or by fluorination<sup>8</sup> of Pa, PaC or  $\text{PaCl}_5$ . The interesting oxide fluoride<sup>7</sup>  $\text{Pa}_2\text{OF}_8$  can be formed by heating  $\text{Pa}_2\text{O}_5$  with  $\text{F}_2$  or with an equimolar mixture of HF (g) and  $\text{O}_2$ . Thermal decomposition of the hydrate<sup>7</sup>  $\text{PaF}_5 \cdot 2 \text{H}_2\text{O}$  at  $160^\circ\text{C}$  also produces  $\text{Pa}_2\text{OF}_8$ .

It is possible to prepare the complex fluorides  $M[\text{PaF}_6]$ ,  $M_2[\text{PaF}_7]$  and  $M_3[\text{PaF}_8]$  ( $M$  = alkali-metal cation) from an aq HF soln containing MF and protactinium(V)<sup>9</sup>. Anhydrous preparations can be made by grinding weighed amounts of alkali-metal fluorides with  $\text{PaF}_4$  (in 1:1, 2:1, 3:1 stoichiometric ratios) in an inert atmosphere and then fluorinating the mixture in a sapphire dish (400°C)<sup>9</sup>.

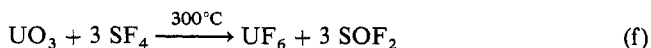
The volatile  $\text{UF}_6$ , first prepared<sup>10</sup> by Ruff and Heinzelmann via the reaction of U with  $\text{F}_2$  can also be prepared from uranium oxides with  $\text{F}_2$  or halogen fluorides<sup>11,12</sup>:



In place of uranium or uranium oxides, uranium tetrafluoride can be used<sup>13-15</sup>:

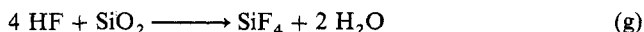


The rate of oxidation of  $\text{UF}_4$  by  $\text{O}_2$  is enhanced by the addition of a platinum catalyst on alumina<sup>15</sup>. Another preparation of  $\text{UF}_6$  involves treating  $\text{UO}_3$ ,  $\text{U}_3\text{O}_8$  or  $\text{UO}_2\text{F}_2$  with  $\text{SF}_4$  at 300-400°C in a Ni reactor<sup>16</sup>:



Also treatment of U,  $\text{UO}_3$ ,  $\text{U}_3\text{O}_8$ ,  $\text{UO}_2\text{F}_2$  or  $\text{UF}_4$  with  $\text{XeF}_2$  (57-150°C) gives  $\text{UF}_6$  in quantitative yields<sup>17</sup>. A photochemical reaction of  $\text{UF}_4$  with  $\text{F}_2$  gives<sup>18,19</sup>  $\text{UF}_6$ .

The oxide,  $\text{UO}_2\text{F}_2$ ,<sup>20,21</sup> can be obtained by treating  $\text{UO}_3$  with HF or  $\text{F}_2$ . The synthesis of  $\text{UOF}_4$  is accomplished from the combination of xs  $\text{UF}_6$  and quartz wool ( $\text{SiO}_2$ ) in HF; the slow reaction is<sup>22</sup>:

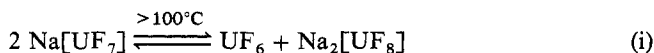


and provides for a one-step, controlled, partial hydrolysis of the starting hexafluoride:



Numerous uranyl complexes are known as well as  $M[\text{UO}_3\text{F}]$  ( $M$  = Na, K) salts<sup>23</sup>. The complexes  $\text{K}_3[\text{UO}_2\text{F}_5]$  and  $[\text{NH}_4]_3[\text{UO}_2\text{F}_5]$  are prepared<sup>24</sup> by bromination of uranium in MeOH followed by addition of KF or  $\text{NH}_4\text{F}$ . The complexes  $[\text{NF}_4][\text{UOF}_5]$ ,  $\text{UF}_4\text{O} \cdot \text{X SbF}_5$  ( $x = 1-3$ ) and  $\text{UF}_2\text{O}_2 \cdot 4 \text{SbF}_5$  are known<sup>25-27</sup>.

Various complexes, e.g.,  $M[\text{UF}_7]$ ,  $M_2[\text{UF}_8]$  ( $M$  = Na, K, NO,  $\text{NO}_2$ ),  $\text{XeF}_2 \cdot \text{UF}_6$ ,  $2 \text{XeF}_6 \cdot \text{UF}_5$ ,  $\text{XeF}_6 \cdot \text{UF}_5$ , have been reported<sup>28,29</sup>. The alkali-metal heptafluorouranates decompose on heating in vacuo:



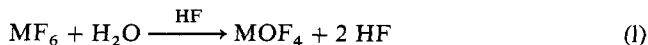
The methoxyfluorouranium(VI) complexes,  $\text{U}(\text{OCH}_3)_n\text{F}_{6-n}$  ( $n = 1-5$ ) can be prepared as follows<sup>30</sup>:



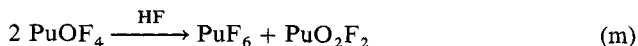
The high-valent fluoride of plutonium,  $\text{PuF}_6$ , is prepared by fluorinating a mixture of lower fluorides of plutonium (predominantly  $\text{PuF}_3$ ) at 500–550°C (1 h) in a stainless steel reactor equipped with an external cooling trough (–78°C); the  $\text{PuF}_6$  is condensed as formed in the cooled (–78°C) region of the reactor<sup>31</sup>. High yields of  $\text{PuF}_6$  are obtained by treating  $\text{PuF}_4$  with  $\text{O}_2\text{F}_2$  at RT for only a few minutes<sup>32</sup> ( $\text{KrF}_2$  has also been used); other Pu compounds (oxides, oxyfluorides) are also converted to  $\text{PuF}_6$ . Irradiation of a mixture of solid  $\text{PuF}_4$  with  $\text{F}_2$  at RT gives  $\text{PuF}_6$  as a product<sup>33</sup>.

The hexafluoride of Np is prepared by reacting  $\text{F}_2$  with a lower fluoride of Np<sup>13</sup>. It has been shown that  $\text{KrF}_2$  converts  $\text{NpOF}_4$  in HF to  $\text{NpF}_6$ <sup>34</sup>.

The oxyfluorides  $\text{NpO}_2\text{F}_2$  and  $\text{PuO}_2\text{F}_2$  have also been prepared and characterized<sup>35</sup>;  $\text{NpO}_2\text{F}_2$  can be obtained by heating  $\text{NpO}_3$  with gaseous HF or  $\text{F}_2$ ;  $\text{PuO}_2\text{F}_2$  is formed by treating with HF, the precipitate obtained by adding MeOH and gaseous HF to an Pu(VI) aq soln. The oxide tetrafluorides can be prepared by the controlled hydrolysis of the hexafluoride; for example<sup>34,36</sup>



where M = Pu, Np. The plutonium oxyfluoride rearranges in HF:



The oxyfluorides salts  $\text{Cs}[\text{NpO}_2\text{F}_3]$ ,  $\text{Cs}_3[\text{NpO}_2\text{F}_5]$  and  $[\text{C}_9\text{H}_7\text{NH}][\text{PuO}_2\text{F}_3] \cdot 3 \text{H}_2\text{O}$  are known<sup>23</sup>. Attempts to prepare a Np(VI) salt with CsF and  $\text{NpF}_6$  lead only to  $\text{Cs}[\text{NpF}_6]$ <sup>34</sup>. **CAUTION: Great care must be exercised in handling the actinium hexafluorides ( $\text{UF}_6$ ,  $\text{NpF}_6$ ,  $\text{PuF}_6$ ): (1) they must be handled in thoroughly dry borosilicate glass or quartz containers; (2)  $\text{NpF}_6$  and  $\text{PuF}_6$  undergo photodecomposition; (3) solid  $\text{PuF}_6$  undergoes extensive decay via  $\alpha$ -emission and should be stored in the gaseous state; (4) plutonium is extremely toxic and must be handled with extreme care<sup>37</sup>.**

The highest valent binary americium, californium, berkelium and curium fluorides known are the respective tetrafluorides. For Am, Cm and Cf, the tetrafluorides are prepared by fluorinating, with heat, their respective trifluorides<sup>38–40</sup>. For example, treatment of  $\text{CfF}_3$  (or  $\text{Cf}_2\text{O}_3$ ,  $\text{CfCl}_3$ ) with  $\text{F}_2$  ( $3 \times 10^5 \text{ N m}^{-2}$  or 3 atm, 400–450°C) gives  $\text{CfF}_4$ . In order to prepare  $\text{BkF}_4$ , it is necessary to fluorinate a ion-exchange bead containing berkelium in a sapphire crucible (400°C with  $\text{F}_2$  pressure up to  $2 \times 10^5 \text{ N m}^{-2}$  or 2 atm for 16 h)<sup>41</sup>.

The oxyfluoride  $\text{AmO}_2\text{F}_2$  and salts such as  $\text{KAmF}_5$ ,  $\text{RbAmO}_2\text{F}_2$ ,  $\text{Rb}_2\text{AmF}_6$  are known<sup>35,38,42</sup>. Americyl fluoride was obtained by evaporating an americium(VI) solution in HF (g) followed by treatment with HF. The rubidium salts were obtained by treating  $\text{RbAmO}_2\text{CO}_3$  with xs  $\text{RbF}$ ; at first  $\text{RbAmO}_2\text{F}_2$  is formed but then is slowly (overnight) converted to  $\text{Rb}_2\text{AmF}_6$ .

Einsteinium trifluoride and tetrafluoride are known<sup>43,44</sup>.

(J.M. CANICH, G.L. GARD)

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# **3. Formation of Bonds to Group-VIB (O, S, Se, Te, Po) Elements (Part 1)**

## 3.1. Introduction

Formation of bonds between the group-VIB elements and hydrogen is described in Volume 1, §1.4. Bonds to halogens are described in Volume 3, §2.3. This volume describes formation of group-VIB element bonds to group-IA, -IIA, -IIIB, -IVB, -VB and -VIB elements. Volume 6 completes the description of the formation of group-VIB bonds.

## 3.2. Formation of Group-VIB

### (O, S, Se, Te, Po)–Group-VIB

### (O, S, Se, Te, Po) Element Bond

#### 3.2.1. Introduction

In this chapter are found the reactions used to prepare bonds between chalcogens.

#### 3.2.2. Formation of the Oxygen–Oxygen Bond

Numerous compounds contain oxygen–oxygen bonds<sup>1–5</sup>, which range in formal bond orders from unity to 2.5 (Table 1)<sup>4</sup>. Covalent peroxides with an O—O bond order of 1 and structure ROOR are most common; H<sub>2</sub>O<sub>2</sub> is the most notable of these. Related to these are the polyoxides, chains of divalent oxygen atoms terminated by an atom or group<sup>3,4</sup>.

Most compounds containing oxygen–oxygen bonds are prepared<sup>1–5</sup> from species already containing such linkages, such as H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub>, ROOH, but here only reactions in which O—O bonds are formed from species not previously containing such

TABLE 1. OXYGEN–OXYGEN BONDS

Species <sup>a</sup>	Name	Bond order	Refs.
[O <sub>2</sub> ] <sup>+</sup>	Oxygenyl	2.5	4
O <sub>2</sub>	Dioxygen	2.0	4
[O <sub>2</sub> ] <sup>–</sup>	Superoxide	1.5	4
[O <sub>2</sub> ] <sup>2–</sup>	Peroxide (ionic)	1	4
ROOR	Peroxide (covalent)	1	1–4
ROOOR	Trioxide	1	3, 4
ROOOOR	Tetraoxide	1	3, 4
O <sub>3</sub>	Ozone	1.5	4
[O <sub>3</sub> ] <sup>–</sup>	Ozonide	1.25	4

<sup>a</sup> R = organic group, perfluoro moiety, H, or F.

## 3.2.2. Formation of the Oxygen–Oxygen Bond

## 3.2.2.1. by Reactions Involving Free Radicals

## 3.2.2.1.2. in the Formation of Compounds with —OR Groups.

linkages are described. **It is important to note that owing to the instability of the O—O single bond, many covalent peroxides and polyoxides are unstable and unpredictably explosive<sup>1–5</sup>.**

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## 3.2.2.1. by Reactions Involving Free Radicals

## 3.2.2.1.1. In the Formation of Compounds with —OH Groups.

Hydroperoxides<sup>1–9</sup>, ROOH, with an alkyl, aryl, acyl or organometallic<sup>5</sup> group, are prepared either from the insertion of O<sub>2</sub> into the corresponding hydride, RH, or by the reaction of the parent H<sub>2</sub>O<sub>2</sub> with RX, X being a halogen, a sulfate or a similar group<sup>2–5</sup>. No important preparative routes actually involve O—O bond formation. **The low molecular weight hydroperoxides are particularly explosive<sup>3,5</sup>.**

Hydrogen tri- and tetroxides, studied spectroscopically at low temperatures, are produced by electrical discharges of H<sub>2</sub>O or H<sub>2</sub>O–H<sub>2</sub>O<sub>2</sub> mixtures, by electron beams on H<sub>2</sub>O and O<sub>2</sub> or by the reaction of atomic hydrogen and liquid ozone. Alkyl hydrotrioxides are short-lived intermediates in the low-temperature ozonation of some saturated organic compounds<sup>6</sup>.

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## 3.2.2.1.2. In the Formation of Compounds with —OR Groups.

The covalent peroxides ROOR', in which R and R' can be alkyl, aryl, acyl or organometallic moieties<sup>1–5</sup>, are, like their hydroperoxide counterparts, generally



- 4            3.2.2. Formation of the Oxygen–Oxygen Bond  
              3.2.2.1. by Reactions Involving Free Radicals  
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3. D. Swern, *Organic Peroxides*, 3 vols., Wiley-Interscience, New York, 1970–1972.
4. E. A. V. Ebsworth, J. A. Connor, J. J. Turner, in *Comprehensive Inorganic Chemistry*, Vol. 2, A. J. Trotman-Dickenson, ed., Pergamon Press, Oxford, 1973, p. 685.
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### 3.2.2.1. by Reactions Involving Free Radicals

#### 3.2.2.1.1. In the Formation of Compounds with —OH Groups.

Hydroperoxides<sup>1-9</sup>, ROOH, with an alkyl, aryl, acyl or organometallic<sup>5</sup> group, are prepared either from the insertion of O<sub>2</sub> into the corresponding hydride, RH, or by the reaction of the parent H<sub>2</sub>O<sub>2</sub> with RX, X being a halogen, a sulfate or a similar group<sup>2-5</sup>. No important preparative routes actually involve O—O bond formation. **The low molecular weight hydroperoxides are particularly explosive<sup>3,5</sup>.**

Hydrogen tri- and tetroxides, studied spectroscopically at low temperatures, are produced by electrical discharges of H<sub>2</sub>O or H<sub>2</sub>O–H<sub>2</sub>O<sub>2</sub> mixtures, by electron beams on H<sub>2</sub>O and O<sub>2</sub> or by the reaction of atomic hydrogen and liquid ozone. Alkyl hydrotrioxides are short-lived intermediates in the low-temperature ozonation of some saturated organic compounds<sup>6</sup>.

(L. B. PETER)

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4. G. Sosnovsky, J. H. Brown, *Chem. Rev.*, **66**, 529 (1966). Organometallic peroxides.
5. R. A. Seldon, in *The Chemistry of the Peroxides*, S. Patai, ed., Wiley-Interscience, New York, 1983, p. 161.
6. B. Plesnicar, in *The Chemistry of the Peroxides*, S. Patai, ed., Wiley-Interscience, New York, 1983, p. 483.

#### 3.2.2.1.2. In the Formation of Compounds with —OR Groups.

The covalent peroxides ROOR', in which R and R' can be alkyl, aryl, acyl or organometallic moieties<sup>1-5</sup>, are, like their hydroperoxide counterparts, generally

formed from reagents already containing O—O bonds<sup>1–6</sup>, most often O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, or ROOH.

Unlike their sulfur analog, most alcohols, alkoxides, phenols and phenoxides cannot be oxidized to their corresponding peroxides. An important exception is the dehydrooxidation<sup>7</sup> of certain phenols with [Fe(CN)<sub>6</sub>]<sup>3–</sup>. The phenolic moieties can stabilize intermediate RO· free radicals to allow coupling. Some phenols can be oxidized to stable free radicals<sup>8,9</sup>, which dimerize only slowly in the solid phase, e.g., in the oxidation of substituted phenanthrolenes.

Catenation in oxygen with more than two atoms is rare, but t-butyl trioxide<sup>10</sup>, t-BuOOOBu-t, and tetraoxide<sup>11</sup>, t-BuOOOOBu-t are synthesized at low T. The trioxide is produced by low-T oxidation of t-BuOOH in CH<sub>2</sub>Cl<sub>2</sub> by lead tetraacetate<sup>10</sup>. The tetraoxide comes from the dimerization at –110°C of t-BuOO· radicals generated from the photolysis of di-t-butyl peroxy carbonate<sup>10</sup>, and the photolysis of a 1:2 CFCl<sub>3</sub>–CF<sub>2</sub>Cl<sub>2</sub> solution of t-Bu<sub>2</sub>N<sub>2</sub> and O<sub>2</sub> also at low T<sup>12</sup>.

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### 3.2.2.1.3. in the Formation of Compounds with —OR<sub>F</sub> Groups.

The perfluoroalkyl peroxides, which are analogous to the organic dialkyl peroxides, are structurally similar to the hydrocarbon peroxide counterparts, but they are prepared differently<sup>1–5</sup>.

The simplest member of this group is the bis(trifluoromethyl)peroxide<sup>1</sup> CF<sub>3</sub>OOCF<sub>3</sub>, prepared by the reaction of CF<sub>3</sub>OF and COF<sub>2</sub> at 290°C in a nickel vessel. Several other methods<sup>1</sup> are listed in Table 1. Methods 1, 2, and 4 are useful for producing large quantities of the compound, whereas method 6 is for relatively small amounts. Additional procedures of varying efficiency are known<sup>1</sup>. **Fluorination, especially oxyfluorination reactions, can proceed explosively. Adequate shields and safety equipment should be employed. Additionally, both reactants and products should not come in contact with standard vacuum line materials such as mercury, hydrocarbon grease or other reducing substances<sup>1,5</sup>.**

### 3.2.2. Formation of the Oxygen–Oxygen Bond

5

#### 3.2.2.1. by Reactions Involving Free Radicals

##### 3.2.2.1.3. in the Formation of Compounds with —OR<sub>F</sub> Groups.

formed from reagents already containing O—O bonds<sup>1–6</sup>, most often O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, or ROOH.

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##### 3.2.2.1.3. in the Formation of Compounds with —OR<sub>F</sub> Groups.

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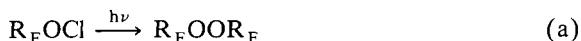
The simplest member of this group is the bis(trifluoromethyl)peroxide<sup>1</sup> CF<sub>3</sub>OOCF<sub>3</sub>, prepared by the reaction of CF<sub>3</sub>OF and COF<sub>2</sub> at 290°C in a nickel vessel. Several other methods<sup>1</sup> are listed in Table 1. Methods 1, 2, and 4 are useful for producing large quantities of the compound, whereas method 6 is for relatively small amounts. Additional procedures of varying efficiency are known<sup>1</sup>. **Fluorination, especially oxyfluorination reactions, can proceed explosively. Adequate shields and safety equipment should be employed. Additionally, both reactants and products should not come in contact with standard vacuum line materials such as mercury, hydrocarbon grease or other reducing substances<sup>1,5</sup>.**

3.2.2. Formation of the Oxygen–Oxygen Bond  
 3.2.2.1. by Reactions Involving Free Radicals  
 3.2.2.1.3. in the Formation of Compounds with —OR<sub>F</sub> Groups.

TABLE 1. PREPARATION OF CF<sub>3</sub>OOCF<sub>3</sub>

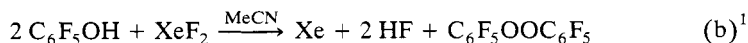
No.	Reagents	Conditions	Yield (%)	Refs.
1	CO + F <sub>2</sub>	180°C, AgF <sub>2</sub> -coated Cu	60	1
2	COF <sub>2</sub> + CF <sub>3</sub> OF	265°C, Ni-lined autoclave	93	1
3	F <sub>2</sub> + Metal oxalates	80–90°C, flow reaction		1
4	ClF <sub>3</sub> + COF <sub>2</sub>	250°C, group-1A fluorides	92	1
5	CF <sub>3</sub> OF + Xe →	XeF <sub>2</sub> + CF <sub>3</sub> OOCF <sub>3</sub>		1
6	CF <sub>3</sub> OCl	RT photolysis	90	1–6

In addition to CF<sub>3</sub>OOCF<sub>3</sub>, several other symmetrical fluorinated alkyl or aryl peroxides are found in low yields as side products in the preparations of other fluoroxy compounds, but a useful general method is that similar to 6 in Table 1, i.e., the photolysis followed by dimerization of the perfluoroalkyl hypochlorite<sup>6,7</sup>:

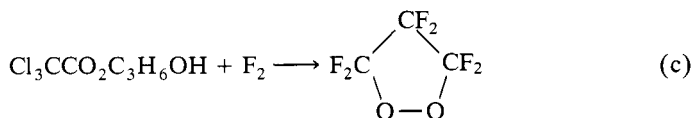


Temperature and lamp power used depend on the species involved, but this method is not universally applicable. Symmetrical fluorinated peroxides can also be prepared in ≤ 80% yields by dehydrooxidation of fluoroalkyl alcohols, R<sub>F</sub>OH, by ClF<sub>3</sub>. These reactions proceed at RT for totally fluorinated alkyl groups, but reactions involving partially hydrogenated alkyl group must be carried out at low T<sup>1</sup>.

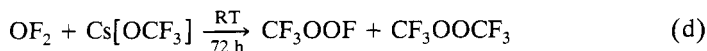
Bis(pentafluorophenyl)peroxide is prepared<sup>8</sup> by the oxidation of the corresponding phenol with XeF<sub>2</sub>:



There are no general methods for synthesizing unsymmetrical peroxides, R<sub>F</sub>OOR<sub>F</sub>, but ethylmethylperoxide, CF<sub>3</sub>OOC<sub>2</sub>F<sub>5</sub>, is a side product of the fluorination of trifluoroacetate salts. The compound CF<sub>3</sub>OOC(CF<sub>3</sub>)<sub>3</sub> is a side product (8%) of the reaction of OF<sub>2</sub> and Na[OC(CF<sub>3</sub>)<sub>3</sub>] in a bomb reactor. Five-membered ring, cyclic perfluoroalkyl peroxides are also prepared in < 5% yield by the fluorination of Cu(II) or Ni(II) hexafluoroacetylacetonates of 1-hydroxy-3-trichloroacetoxypropane:



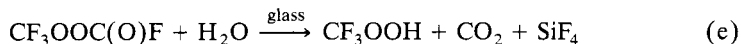
Of the unsymmetrical fluorinated alkyl peroxides, the R<sub>F</sub>OOF, only CF<sub>3</sub>OOF is synthesized by methods appropriate for discussion here. This methyl compound is prepared as a side product (along with C<sub>2</sub>F<sub>5</sub>OOF) in the fluorination of sodium trifluoroacetate<sup>1</sup>, but in much better yield by<sup>1,7</sup>:



The OF<sub>2</sub>/CsOCF<sub>3</sub> ratio should be about 4:1, and the products are separated by

fractional condensation. This general method is not worthwhile in preparing higher  $R_F\text{OOF}$  compounds<sup>1</sup>.

Related to  $\text{CF}_3\text{OOF}$  is the hydroperoxide  $\text{CF}_3\text{OOH}$ . It is prepared in 80% yield by the hydrolysis of fluoroformyl(trifluoromethyl)peroxide,  $\text{CF}_3\text{OOC}(\text{O})\text{F}$ , or  $(\text{CF}_3\text{OO})_2\text{CO}$ , bis(trifluoromethylperoxy)carbonate<sup>1</sup>:



Liquid-phase reactions using xs  $\text{H}_2\text{O}$  afford better yields and easier separation. The product can be used as a reagent in the production of  $\text{CF}_3\text{OOF}$  and  $\text{CF}_3\text{OOCl}$ , the chlorine analog<sup>1</sup>.

Just as the perfluoroalkyl peroxides are in general more stable than the corresponding hydrocarbon peroxides, a like situation exists for the trioxides. In §3.2.2.1.3 the low-T preparations of some unstable dialkyl polyoxides are described. A few perfluorotrioxides are remarkably stable at RT and above<sup>1,5</sup>. The fluorination of metal trifluoroacetates produces low yields of  $\text{CF}_3\text{OOOCF}_3$ ,  $\text{CF}_3\text{OOOC}_2\text{F}_5$  and  $\text{C}_2\text{F}_5\text{OOOC}_2\text{F}_5$ , the last only in trace amounts<sup>1</sup>;  $\text{CF}_3\text{OOOC}_2\text{F}_5$  and  $\text{C}_2\text{F}_5\text{OOOC}_2\text{F}_5$  are also isolated from the reaction of  $\text{OF}_2$  with  $\text{CsOC}_2\text{F}_5$ , and  $\text{CF}_3\text{OOOCF}_3$  is prepared in  $\leq 90\%$  yields by the RT reaction of  $\text{OF}_2$  and  $\text{COF}_2$  over a  $\text{CsF}$  catalyst<sup>1,10</sup>. Other less efficient, but useful, methods of preparing the bis(perfluoromethyl) compound include photolyzing a mixture of  $(\text{CF}_3)_2\text{CO}$ ,  $\text{F}_2$  and  $\text{O}_2$ , which produces this trioxide in 60% yield<sup>1</sup>.

The perfluoroalkyl tetraoxide,  $\text{CF}_3\text{OOOOCF}_3$ <sup>1,5</sup>, may be prepared by the low-T oxidation of  $\text{CF}_3\text{OOH}$  with  $\text{XeF}_2$ :



(L. B. PETER)

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#### 3.2.2.1.4. in the Formation of Compounds with —OF Groups.

The formation of the symmetric di- and polyoxygen fluorides, compounds consisting of divalent oxygen chains terminated at both ends by fluorine, is described here<sup>1–3</sup>. Similar compounds with one end terminated by other groups are covered in §3.2.2.1.3 and 3.2.2.1.6.

### 3.2.2. Formation of the Oxygen–Oxygen Bond

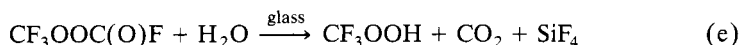
7

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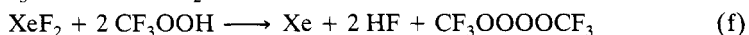
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The formation of the symmetric di- and polyoxygen fluorides, compounds consisting of divalent oxygen chains terminated at both ends by fluorine, is described here<sup>1–3</sup>. Similar compounds with one end terminated by other groups are covered in §3.2.2.1.3 and 3.2.2.1.6.

Dioxygen difluoride, O<sub>2</sub>F<sub>2</sub>, the simplest and most intensively studied member of this family, is commonly prepared by passing an electrical discharge through a low-pressure gaseous 1:1 mixture of O<sub>2</sub> and F<sub>2</sub> at low T<sup>1-3</sup>, e.g., with a total gas pressure of 90 N m<sup>-2</sup> (12 torr), temperature of 90 K, power 25–30 mA at 2.1–2.4 kV. The yield depends on reaction ratio, pressure, temperature and electrical power. Other preparative methods include<sup>1-4</sup> low-T photolysis of either liquid or gaseous mixtures of O<sub>2</sub> and F<sub>2</sub>, photolysis of a 2:1 mixture of O<sub>3</sub> and F<sub>2</sub> at –150°C and electrical discharge of an OF<sub>2</sub>–O<sub>2</sub> gaseous mixture. The conditions of the last reaction are an OF<sub>2</sub>/O<sub>2</sub> ratio of 2:1, pressure of 130–1300 Pa (1 to 10 torr), temperature of –183°C and discharge power of 44–65 W. The procedure that reportedly produces the purest O<sub>2</sub>F<sub>2</sub> sample involves irradiating liquid mixtures of O<sub>2</sub> and F<sub>2</sub> with a 3 MeV Bremsstrahlung for 1–4 h at –196 K. **Dioxygen difluoride and other O—F compounds are strong oxidizing and fluorinating agents. They react explosively even under cryogenic conditions! Inadvertent contact with organic material and other reducing substances must be scrupulously avoided, and reactions should be done under low-temperature conditions!**

Although perfluorinated alkyls are stable at RT, no procedure exists for the corresponding fluoride, O<sub>3</sub>F<sub>2</sub>. Earlier reports of its synthesis have since been disproved<sup>1-3</sup>. The compound O<sub>4</sub>F<sub>2</sub>, however, exists at low T<sup>1-3</sup>. It is prepared similarly to O<sub>2</sub>F<sub>2</sub>; i.e., an electrical discharge of 4.6 mA and 0.8–1.5 kV is passed through a 2:1 O<sub>2</sub>–F<sub>2</sub> gaseous mixture at 35–115 N m<sup>-2</sup> (5–15 torr) and 60–70 K. The discharge conditions are milder than those used in the preparation of O<sub>2</sub>F<sub>2</sub>. Discharge of OF<sub>2</sub>–O<sub>2</sub> mixtures and radiolysis of O<sub>2</sub>–F<sub>2</sub> mixtures also lead to O<sub>4</sub>F<sub>2</sub> formation. When higher O<sub>2</sub>/F<sub>2</sub> ratios are used, total gas pressure is lower and electrical discharge conditions are milder. O<sub>5</sub>F<sub>2</sub> and O<sub>6</sub>F<sub>2</sub> are formed<sup>2,3</sup>, but conclusive characterization has not been accomplished.

(L. B. PETER)

1. I. J. Solomon, *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed., Vol. 10, Wiley-Interscience, New York, 1980, p. 773.
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### 3.2.2.1.5. in the Formation of Compounds with —OSO<sub>2</sub>F Groups.

An intensely studied inorganic compound containing an O—O bond is S<sub>2</sub>O<sub>6</sub>F<sub>2</sub> (or FSO<sub>2</sub>OOSO<sub>2</sub>F), bis(fluorosulfonyl)peroxide (or peroxodisulfonyl difluoride), which consists of two ·OSO<sub>2</sub>F groups connected by an O—O single bond. It is prepared in ≥ 90% yield in large quantities by a flow reaction of F<sub>2</sub> and SO<sub>3</sub> at 160°C in the presence of an AgF<sub>2</sub> catalyst. **Small amounts of explosive FSO<sub>3</sub>F are also formed, so caution is advised. The peroxide itself is a powerful oxidizing agent and caution should be exercised to prevent its exposure to organic materials or other reducing agents<sup>1</sup>.** Good yields of S<sub>2</sub>O<sub>6</sub>F<sub>2</sub> can also be produced by the static reaction of SO<sub>3</sub> and F<sub>2</sub> at 170°C, S<sub>2</sub>O<sub>5</sub>F<sub>2</sub> being the primary side product. It is also a product in the fluorination of metal fluorosulfates, the reaction of the xenon fluorides, XeF<sub>n</sub>, n = 2, 4, 6, with HSO<sub>3</sub>F or SO<sub>3</sub>, and other reactions involving sulfur–oxygen–fluorine



## 3.2.2. Formation of the Oxygen–Oxygen Bond

## 3.2.2.1. by Reactions Involving Free Radicals

3.2.2.1.5. in the Formation of Compounds with —OSO<sub>2</sub>F Groups.

Dioxygen difluoride, O<sub>2</sub>F<sub>2</sub>, the simplest and most intensively studied member of this family, is commonly prepared by passing an electrical discharge through a low-pressure gaseous 1:1 mixture of O<sub>2</sub> and F<sub>2</sub> at low T<sup>1–3</sup>, e.g., with a total gas pressure of 90 N m<sup>–2</sup> (12 torr), temperature of 90 K, power 25–30 mA at 2.1–2.4 kV. The yield depends on reaction ratio, pressure, temperature and electrical power. Other preparative methods include<sup>1–4</sup> low-T photolysis of either liquid or gaseous mixtures of O<sub>2</sub> and F<sub>2</sub>, photolysis of a 2:1 mixture of O<sub>3</sub> and F<sub>2</sub> at –150°C and electrical discharge of an OF<sub>2</sub>–O<sub>2</sub> gaseous mixture. The conditions of the last reaction are an OF<sub>2</sub>/O<sub>2</sub> ratio of 2:1, pressure of 130–1300 Pa (1 to 10 torr), temperature of –183°C and discharge power of 44–65 W. The procedure that reportedly produces the purest O<sub>2</sub>F<sub>2</sub> sample involves irradiating liquid mixtures of O<sub>2</sub> and F<sub>2</sub> with a 3 MeV Bremsstrahlung for 1–4 h at –196 K. **Dioxygen difluoride and other O–F compounds are strong oxidizing and fluorinating agents. They react explosively even under cryogenic conditions! Inadvertent contact with organic material and other reducing substances must be scrupulously avoided, and reactions should be done under low-temperature conditions!**

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compounds<sup>1</sup>. It can also be produced electrochemically from solutions of  $\text{HSO}_3\text{F}$  and  $\text{KSO}_3\text{F}$  at 193 K.

Peroxo derivatives of  $\text{S}_2\text{O}_6\text{F}_2$ , e.g., the stable, simple fluoro derivative  $\text{FSO}_2\text{OOF}$ , can be prepared by the near-UV photolysis of a mixture of  $\text{OF}_2$  and  $\text{SO}_3$ . A 6 : 1 molar xs of  $\text{OF}_2$  and radiation of wavelengths higher than 365 nm are needed for good yields. Higher energy radiation leads to other products<sup>1</sup>.

Analogous perfluoroalkyl compounds, e.g., the simplest,  $\text{FSO}_2\text{OOCF}_3$ , can be prepared by reacting  $\text{CF}_3\text{OF}$  with  $\text{SO}_3$  at 245–260°C, reacting  $\text{S}_2\text{O}_6\text{F}_2$  with  $\text{CF}_3\text{OF}$ , and reacting  $\text{S}_2\text{O}_6\text{F}_2$  with  $\text{COF}_2$  in the presence of dry powdered KF. The latter two reactions proceed smoothly at RT. Reactions analogous to the latter two are also used to prepare higher perfluoroalkyl derivatives<sup>2</sup>.

Much of the rich reaction chemistry of  $\text{S}_2\text{O}_6\text{F}_2$  proceeds by mechanisms dominated by  $\cdot\text{OSO}_2\text{F}$  radical formation, e.g., in the photolytic reaction used in the formation<sup>1</sup> of the peroxo derivative  $\text{FSO}_2\text{OOSF}_5$ . When equimolar amounts of  $\text{SF}_5\text{OOSF}_5$  and  $\text{S}_2\text{O}_6\text{F}_2$  are photoreacted, nearly identical amounts of  $\text{FSO}_2\text{OOSO}_2\text{F}$ ,  $\text{SF}_5\text{OOSF}_5$  and  $\text{FSO}_2\text{OOSF}_5$  result. The mixed peroxide is prepared in low yield by the reaction of  $\text{SF}_5\text{OF}$  and  $\text{SO}_3$  at 210°C and in 40% yield in the RT reaction of  $\text{S}_2\text{O}_6\text{F}_2$  and  $\text{SOF}_4$  in the presence of dry, finely divided KF.

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3. S. Singh, R. D. Verma, *Indian J. Chem., A*, 25, 51 (1986).

### 3.2.2.1.6. In the Formation of Compounds with $\text{OEF}_5$ Groups (E = S, Se or Te).

The parent of many substances containing an O—O bond is  $\text{SF}_5\text{OOSF}_5$ . This stable symmetrical molecule is synthesized by several procedures<sup>1</sup>, generally with low to moderate yields and with several other sulfur–oxygen–fluorine compounds produced simultaneously. One of the higher yield static methods reacts  $\text{SF}_5\text{OF}$  with  $\text{SOF}_2$  in a copper vessel under high pressure and 168°C. After 12 h the peroxide is recovered in 33% yield. This compound is also obtained by reacting  $\text{SF}_5\text{OF}$  with  $\text{SOF}_4$ , reacting  $\text{SF}_5\text{OF}$  with  $\text{SF}_4$ , the photolysis of  $\text{SF}_5\text{OF}$ , and the photolysis of  $\text{SF}_5\text{ClO}_2$  mixtures. The highest yields are obtained (> 70%) when the  $\text{S}_2\text{O}_2\text{F}_{10}$  is continuously removed to prevent secondary reactions. The best conditions are a circulation system in which a 3 : 1  $\text{SF}_5\text{Cl}-\text{O}_2$  mixture is photolyzed over a period of 40 h, and the peroxide is trapped at –80°C.

Peroxo derivatives of this compound include<sup>1</sup>  $\text{SF}_5\text{OOF}$ ,  $\text{SF}_5\text{OOCF}_3$  and  $\text{SF}_5\text{OOH}$ .

The unstable  $\text{SF}_5\text{OOF}$  is a product of the low-T reaction of  $\text{SF}_4$  and  $\text{O}_2\text{F}_2$ , but it is not well characterized. The more stable  $\text{SF}_5\text{OOCF}_3$  can be prepared by photolysis of a 1 : 1 molar mixture of the parent  $\text{SF}_5\text{OOSF}_5$  and  $\text{CF}_3\text{OOCF}_3$ . This radical coupling system also leads to substantial amounts of the reformed parents<sup>1</sup>. Other lower yield methods are also known<sup>1</sup>.

The hydroperoxide  $\text{SF}_5\text{OOH}$  is prepared by a method analogous to that for  $\text{CF}_3\text{OOH}$ . It is prepared<sup>2</sup> from the hydrolysis of  $\text{SF}_5\text{OOC(O)F}$  at 0°C. When just stoichiometric amounts of water are used, the yield is nearly quantitative. This stable

### 3.2.2. Formation of the Oxygen–Oxygen Bond

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#### 3.2.2.1. by Reactions Involving Free Radicals

##### 3.2.2.1.6. in the Formation of Compounds with OEF<sub>5</sub> Groups

compounds<sup>1</sup>. It can also be produced electrochemically from solutions of HSO<sub>3</sub>F and KSO<sub>3</sub>F at 193 K.

Peroxo derivatives of S<sub>2</sub>O<sub>6</sub>F<sub>2</sub>, e.g., the stable, simple fluoro derivative FSO<sub>2</sub>OOF, can be prepared by the near-UV photolysis of a mixture of OF<sub>2</sub> and SO<sub>3</sub>. A 6:1 molar xs of OF<sub>2</sub> and radiation of wavelengths higher than 365 nm are needed for good yields. Higher energy radiation leads to other products<sup>1</sup>.

Analogous perfluoroalkyl compounds, e.g., the simplest, FSO<sub>2</sub>OOCF<sub>3</sub>, can be prepared by reacting CF<sub>3</sub>OF with SO<sub>3</sub> at 245–260°C, reacting S<sub>2</sub>O<sub>6</sub>F<sub>2</sub> with CF<sub>3</sub>OF, and reacting S<sub>2</sub>O<sub>6</sub>F<sub>2</sub> with COF<sub>2</sub> in the presence of dry powdered KF. The latter two reactions proceed smoothly at RT. Reactions analogous to the latter two are also used to prepare higher perfluoroalkyl derivatives<sup>2</sup>.

Much of the rich reaction chemistry of S<sub>2</sub>O<sub>6</sub>F<sub>2</sub> proceeds by mechanisms dominated by ·OSO<sub>2</sub>F radical formation, e.g., in the photolytic reaction used in the formation<sup>1</sup> of the peroxo derivative FSO<sub>2</sub>OOSF<sub>5</sub>. When equimolar amounts of SF<sub>5</sub>OOSF<sub>5</sub> and S<sub>2</sub>O<sub>6</sub>F<sub>2</sub> are photoreacted, nearly identical amounts of FSO<sub>2</sub>OOSO<sub>2</sub>F, SF<sub>5</sub>OOSF<sub>5</sub> and FSO<sub>2</sub>OOSF<sub>5</sub> result. The mixed peroxide is prepared in low yield by the reaction of SF<sub>5</sub>OF and SO<sub>3</sub> at 210°C and in 40% yield in the RT reaction of S<sub>2</sub>O<sub>6</sub>F<sub>2</sub> and SOF<sub>4</sub> in the presence of dry, finely divided KF.

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##### 3.2.2.1.6. In the Formation of Compounds with OEF<sub>5</sub> Groups (E = S, Se or Te).

The parent of many substances containing an O—O bond is SF<sub>5</sub>OOSF<sub>5</sub>. This stable symmetrical molecule is synthesized by several procedures<sup>1</sup>, generally with low to moderate yields and with several other sulfur–oxygen–fluorine compounds produced simultaneously. One of the higher yield static methods reacts SF<sub>5</sub>OF with SOF<sub>2</sub> in a copper vessel under high pressure and 168°C. After 12 h the peroxide is recovered in 33% yield. This compound is also obtained by reacting SF<sub>5</sub>OF with SOF<sub>4</sub>, reacting SF<sub>5</sub>OF with SF<sub>4</sub>, the photolysis of SF<sub>5</sub>OF, and the photolysis of SF<sub>5</sub>ClO<sub>2</sub> mixtures. The highest yields are obtained (> 70%) when the S<sub>2</sub>O<sub>2</sub>F<sub>10</sub> is continuously removed to prevent secondary reactions. The best conditions are a circulation system in which a 3:1 SF<sub>5</sub>Cl–O<sub>2</sub> mixture is photolyzed over a period of 40 h, and the peroxide is trapped at –80°C.

Peroxo derivatives of this compound include<sup>1</sup> SF<sub>5</sub>OOF, SF<sub>5</sub>OOCF<sub>3</sub> and SF<sub>5</sub>OOH.

The unstable SF<sub>5</sub>OOF is a product of the low-T reaction of SF<sub>4</sub> and O<sub>2</sub>F<sub>2</sub>, but it is not well characterized. The more stable SF<sub>5</sub>OOCF<sub>3</sub> can be prepared by photolysis of a 1:1 molar mixture of the parent SF<sub>5</sub>OOSF<sub>5</sub> and CF<sub>3</sub>OOCF<sub>3</sub>. This radical coupling system also leads to substantial amounts of the reformed parents<sup>1</sup>. Other lower yield methods are also known<sup>1</sup>.

The hydroperoxide SF<sub>5</sub>OOH is prepared by a method analogous to that for CF<sub>3</sub>OOH. It is prepared<sup>2</sup> from the hydrolysis of SF<sub>5</sub>OOC(O)F at 0°C. When just stoichiometric amounts of water are used, the yield is nearly quantitative. This stable

substance may be useful in the formation of higher polyoxides, which are currently unknown; e.g., the corresponding tetraoxide might be produced in a low-T reaction:



Selenium and Te analogs of  $S_2O_2F_{10}$  are known; e.g.,  $SeF_5OOSeF_5$  is prepared by a flow reaction between  $SeO_2$  and  $F_2$  (diluted by  $N_2$ ) at  $110^\circ C$  catalyzed by silver-plated copper<sup>1</sup>, the fluorination of  $Hg(OFSeF_5)_2$  with a yield<sup>3</sup> of 47% or the photolysis of  $Xe(OFSeF_5)_2$ . The last method yields nearly quantitative amounts of the peroxide, but the starting material is exotic. The somewhat less stable  $TeF_5OOTeF_5$  can also be prepared quantitatively from the photolytic decomposition of  $Xe(OTeF_5)_2$  or higher coordinated xenon compounds of the same ligand<sup>5</sup>. The trioxide  $SF_5OOOSF_5$  is a product<sup>7</sup> of the low-T reaction of  $SF_4$ ,  $F_2$  and  $O_2$ .

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### 3.2.2.2. by Oxidation of $O^{2-}$

Compared to the number of compounds prepared under the conditions described in §3.2.2.1, oxygen–oxygen bond formation under the conditions discussed in the following sections is relatively unfruitful. Nevertheless, some important chemical species are prepared routinely by these methods.

(L. B. PETER)

#### 3.2.2.2.1. In Solution.

Oxide or, more accurately, species containing oxygen in the 2 – oxidation state can be oxidized in solution by chemically reacting the substance with a strong chemical oxidizing agent, such as  $F_2$ , or by an electrolytic process, examples of which follow.

In aqueous solution,  $F_2$  is the strongest chemical oxidizing agent known. The following is a summary of substances oxidized by  $F_2$  in aqueous solution and the oxygen–oxygen products<sup>1</sup>:

(i) Pure  $H_2O$  produces  $H_2O_2$ ,  $O_2$  and  $O_3$ ; (ii) cold  $HNO_3$  produces  $N_2O_6$ , which decomposes yielding  $H_2O_2$ ; (iii)  $[SO_4]^{2-}$  or  $[HSO_4]^-$  produces  $[S_2O_8]^{2-}$ ; (iv)  $B(OH)_3$  produces perborate; (v)  $[CO_3]^{2-}$  produces percarbonate and (vi) cold  $H_3PO_4$  or  $[HPO_4]^{2-}$  produces  $H_4P_2O_8$  or its anions. Besides  $H_2O_2$ ,  $O_2$  and  $O_3$ , only alkali-metal salts of  $[S_2O_8]^{2-}$  and  $[P_2O_8]^{4-}$  of the above products are isolated.

Because of the toxicity and corrosive behavior of fluorine compounds, aqueous oxidation by  $F_2$  is often replaced by electrolysis. Large quantities of ammonium and potassium salts of the peroxyanion  $[S_2O_8]^{2-}$  are prepared routinely by electrolyzing

3.2.2. Formation of the Oxygen–Oxygen Bond  
 3.2.2.2. by Oxidation of  $O^{2-}$   
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substance may be useful in the formation of higher polyoxides, which are currently unknown; e.g., the corresponding tetraoxide might be produced in a low-T reaction:



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Oxide or, more accurately, species containing oxygen in the 2 – oxidation state can be oxidized in solution by chemically reacting the substance with a strong chemical oxidizing agent, such as  $F_2$ , or by an electrolytic process, examples of which follow.

In aqueous solution,  $F_2$  is the strongest chemical oxidizing agent known. The following is a summary of substances oxidized by  $F_2$  in aqueous solution and the oxygen–oxygen products<sup>1</sup>:

(i) Pure  $H_2O$  produces  $H_2O_2$ ,  $O_2$  and  $O_3$ ; (ii) cold  $HNO_3$  produces  $N_2O_6$ , which decomposes yielding  $H_2O_2$ ; (iii)  $[SO_4]^{2-}$  or  $[HSO_4]^-$  produces  $[S_2O_8]^{2-}$ ; (iv)  $B(OH)_3$  produces perborate; (v)  $[CO_3]^{2-}$  produces percarbonate and (vi) cold  $H_3PO_4$  or  $[HPO_4]^{2-}$  produces  $H_4P_2C_8$  or its anions. Besides  $H_2O_2$ ,  $O_2$  and  $O_3$ , only alkali-metal salts of  $[S_2O_8]^{2-}$  and  $[P_2O_8]^{4-}$  of the above products are isolated.

Because of the toxicity and corrosive behavior of fluorine compounds, aqueous oxidation by  $F_2$  is often replaced by electrolysis. Large quantities of ammonium and potassium salts of the peroxyanion  $[S_2O_8]^{2-}$  are prepared routinely by electrolyzing

the corresponding sulfate solutions using Pt electrodes<sup>2</sup>. Ozone and  $O_2$  are generated as side products. Hydrogen peroxide is also obtained by electrolyzing aq  $H_2SO_4$  using high current densities<sup>3</sup>. The potassium salt of peroxydiphosphate can be made in 80% yield by electrolyzing alkaline phosphate solutions to which  $K_2CrO_4$  has been added<sup>4</sup>.

Electrolysis is also performed in nonaqueous ionizing solvents; e.g., the molecular peroxocompound  $FSO_2OOSO_2F$  can be obtained by electrolyzing solutions of  $[SO_3F]^-$  in  $HSO_3F$ <sup>5,6</sup>. Conditions vary considerably depending on the solvent, solute and desired product.

(L. B. PETER)

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6. S. Singh, R. D. Verma, *Indian J. Chem.*, **A**, **25**, 51 (1986).

### 3.2.2.2.2. in Heterogeneous Reactions.

Oxidation of  $O^{2-}$  by heterogeneous reactions to form substances containing an oxygen–oxygen bond is not frequently observed. In the area of transition-metal chemistry,  $O_2$  is frequently captured in heterogeneous reactions to produce complexes containing O—O bonds, but no new O—O linkages are formed. However,  $O^{2-}$  oxidation coupling does occur in the following examples.

Depending on conditions,  $O_2$  combines with alkali and alkaline-earth metals to form either oxides, peroxides, superoxides or mixtures of two of these<sup>1–4</sup>. Heterogeneous reactions between gaseous  $O_2$  and solid oxides or hydroxides of these metals form the corresponding peroxides;  $Na_2O$ ,  $SrO$  and  $BaO$  undergo this reaction most readily, with  $BaO_2$  formation being the most important<sup>3,4</sup>. Barium oxide converts smoothly, although slowly, to the peroxide in air, and despite the slowness,  $BaO$  is sometimes used as an oxygen scavenger.

Ozone also can act as a  $O^{2-}$  oxidizer in heterogeneous reactions, e.g., in the reaction of  $O_3$  with solid hydroxides to form the ozonides:



Production of  $O_2$  from formal  $O^{2-}$ -containing substances by thermal reactions is common on a laboratory scale, e.g., the  $HgO$  decomposition to the elements, and the thermal decomposition of  $KClO_3$  in the presence of  $MnO_2$  as a catalyst.

Finally, molecular  $O_2$  itself can be produced in laboratory-scale amounts by the thermal decomposition of  $HgO$  or  $KClO_3$  in the presence of  $MnO_2$ . The  $O_2$  can be converted partially to  $O_3$  by exposing it to intense UV radiation or passing a silent electric discharge through it<sup>5</sup>.

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1. E. A. V. Ebsworth, J. A. Connor, J. J. Turner, in *Comprehensive Inorganic Chemistry*, Vol. 2, A. J. Trotman-Dickenson, ed., Pergamon Press, Oxford, 1973, p. 685.

3.2.2. Formation of the Oxygen–Oxygen Bond  
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11

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12      3.2. Formation of Group-VIB–Group-VIB Element Bond  
          3.2.3. Formation of the Oxygen Bond with Other Group-VIB Elements  
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### 3.2.3. Formation of the Oxygen Bond with Other Group-VIB Elements

There are two types of bonding between oxygen and the other group-VIB elements: one involves dicoordinated oxygen forming single bonds, but a terminal oxygen bond with an order  $> 1$  is more common.

(L. B. PETER)

#### 3.2.3.1. from the Elements.

Elemental sulfur burns with a blue flame to yield  $\text{SO}_2$  and  $\text{SO}_3$ , the latter of which occurs in various physical forms. Under most conditions  $\text{SO}_2$  production is overwhelmingly favored<sup>1</sup>. Nearly pure  $\text{SO}_2$  can be made by sealing stoichiometric amounts of sulfur and  $\text{O}_2$  into a borosilicate glass vessel and heating to  $> 250^\circ\text{C}$  for several hours. **Care must be taken that the  $\text{O}_2$  and/or  $\text{SO}_2$  gas pressures are not so high as to explode the vessel at the higher temperatures.** This slow method is particularly useful in preparing isotopically labeled<sup>2</sup>  $\text{SO}_2$ .

Sulfur trioxide can be obtained by direct reaction between the elements, but the conditions must be carefully controlled to obtain even modest yields, and larger amounts of  $\text{SO}_2$  are simultaneously produced<sup>1</sup>. The most effective process for  $\text{SO}_3$  from the elements is a smooth flow reaction involving sulfur vapor and  $\text{O}_2$ , using  $\text{N}_2$  as a carrier gas. Dry  $\text{HCl}$  is added to stabilize the  $\text{SO}_3$ , which forms in yields  $> 40\%$ ,  $\text{SO}_2$  being the other product. In the gas phase  $\text{SO}_3$  is trigonal planar, but it trimerizes in an electron-pair donor–acceptor acid–base manner to  $\text{S}_3\text{O}_9$  if condensed<sup>1,3</sup> at temperatures  $< -80^\circ\text{C}$ . Liquid  $\text{SO}_3$  is unstable and it, as well as the trimer, readily polymerizes to either of two distinctly different modifications, especially if trace amounts of water are present<sup>1,3</sup>. Most methods of producing  $\text{SO}_3$  start with  $\text{SO}_2$  rather than elemental sulfur and various catalysts, such as metal oxides, have been used<sup>1</sup> (see §3.2.3.2).

The Se, Te and Po dioxides can be obtained by burning the elements in air<sup>4</sup>. For more controlled oxidation, the elements can be sealed with a small excess of  $\text{O}_2$  and heated above their mp for several hours. Like the analogous reaction with sulfur, this latter method is particularly useful when isotopically pure products are desired.

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- 12     3.2. Formation of Group-VIB–Group-VIB Element Bond  
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### 3.2.3.2. Sulfur Oxides

The following sulfur oxides are known: SO, SO<sub>2</sub>, SO<sub>3</sub>, SO<sub>4</sub>, S<sub>2</sub>O, S<sub>2</sub>O<sub>2</sub>, S<sub>3</sub>O<sub>9</sub>, S<sub>5</sub>O, S<sub>6</sub>O, S<sub>7</sub>O, S<sub>8</sub>O, S<sub>9</sub>O, S<sub>10</sub>O, S<sub>6</sub>O<sub>2</sub>, S<sub>7</sub>O<sub>2</sub>, S<sub>12</sub>O<sub>2</sub>, polymeric forms of SO<sub>3</sub>, and several other nondistinct (S<sub>x</sub>O, S<sub>x</sub>O<sub>2</sub>; x = 5–10) polymeric forms<sup>1,2</sup>. The binary oxides SO, SO<sub>4</sub>, S<sub>2</sub>O<sub>2</sub>, S<sub>5</sub>O exist as short-lived intermediates, low-T matrix species or only in mixtures and are not discussed here.

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#### 3.2.3.2.1. Sulfur Dioxide

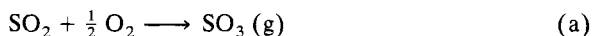
Sulfur dioxide is the most easily obtainable sulfur oxide<sup>1</sup>. Thousands of tons annually are produced by design or by accident by industry<sup>2</sup>. It is the primary combustion product of both organic and inorganic sulfur-containing compounds as well as in the combustion of elemental sulfur itself. The most convenient method of preparation is combining the elements as described in §3.2.3.1.

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#### 3.2.3.2.2. Sulfur Trioxides

Small amounts of SO<sub>3</sub> are normally produced along with SO<sub>2</sub> during the combustion of sulfur, and the SO<sub>3</sub> yield can be increased to ≤ 40%<sup>1</sup> (see §3.2.3.1.2). Usually, however, SO<sub>3</sub> is obtained by the O<sub>2</sub> oxidation of SO<sub>2</sub><sup>1,2</sup>:



a reaction that is thermodynamically favored, but slow even at 1000°C, and requires a catalyst such as the metal oxides, V<sub>2</sub>O<sub>5</sub>, Fe<sub>2</sub>O<sub>3</sub>, etc. Commercially the reaction is crucial in the production of H<sub>2</sub>SO<sub>4</sub> where NO is used as a homogeneous catalyst<sup>4,5</sup>. Laboratory amounts of SO<sub>3</sub> can be obtained by thermal decomposition of anhyd Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> or from fuming sulfuric acid. Preparation of SO<sub>3</sub> trimer and polymers is discussed in §3.2.3.1.

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3.2.3. Formation of the Oxygen Bond with Other Group-VIB Elements 13  
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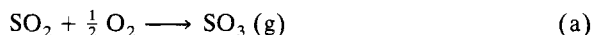
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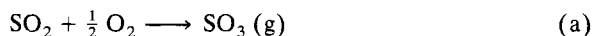
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a reaction that is thermodynamically favored, but slow even at 1000°C, and requires a catalyst such as the metal oxides, V<sub>2</sub>O<sub>5</sub>, Fe<sub>2</sub>O<sub>3</sub>, etc. Commercially the reaction is crucial in the production of H<sub>2</sub>SO<sub>4</sub> where NO is used as a homogeneous catalyst<sup>4,5</sup>. Laboratory amounts of SO<sub>3</sub> can be obtained by thermal decomposition of anhyd Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> or from fuming sulfuric acid. Preparation of SO<sub>3</sub> trimer and polymers is discussed in §3.2.3.1.

(L. B. PETER)

1. "Schwefel Oxide," *Gmelins Handbuch der Anorganischen Chemie*, Erzsbd. 3, Springer Verlag, Berlin, 1980.
2. M. Schmidt, W. Siebert, in *Comprehensive Inorganic Chemistry*, Vol. 2, A. F. Trotman-Dickenson, ed., Pergamon Press, Oxford, 1973, pp. 795–933.

**3.2.3. Formation of the Oxygen Bond with Other Group-VIB Elements 13**

**3.2.3.2. Sulfur Oxides**

**3.2.3.2.2. Sulfur Trioxides**

4. K. W. Bagnall, in *Comprehensive Inorganic Chemistry*, Vol. 2, A. F. Trotman-Dickenson, ed., Pergamon Press, Oxford, 1973, p. 935.

**3.2.3.2. Sulfur Oxides**

The following sulfur oxides are known: SO, SO<sub>2</sub>, SO<sub>3</sub>, SO<sub>4</sub>, S<sub>2</sub>O, S<sub>2</sub>O<sub>2</sub>, S<sub>3</sub>O<sub>9</sub>, S<sub>5</sub>O, S<sub>6</sub>O, S<sub>7</sub>O, S<sub>8</sub>O, S<sub>9</sub>O, S<sub>10</sub>O, S<sub>6</sub>O<sub>2</sub>, S<sub>7</sub>O<sub>2</sub>, S<sub>12</sub>O<sub>2</sub>, polymeric forms of SO<sub>3</sub>, and several other nondistinct (S<sub>x</sub>O, S<sub>x</sub>O<sub>2</sub>; x = 5–10) polymeric forms<sup>1,2</sup>. The binary oxides SO, SO<sub>4</sub>, S<sub>2</sub>O<sub>2</sub>, S<sub>5</sub>O exist as short-lived intermediates, low-T matrix species or only in mixtures and are not discussed here.

(L. B. PETER)

1. "Schwefel Oxide," *Gmelins Handbuch der Anorganischen Chemie*, Erzsbd. 3, Springer Verlag, Berlin, 1980.
2. R. Steudel, *Phosphorus Sulfur*, 23, 33 (1985).

**3.2.3.2.1. Sulfur Dioxide**

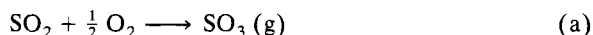
Sulfur dioxide is the most easily obtainable sulfur oxide<sup>1</sup>. Thousands of tons annually are produced by design or by accident by industry<sup>2</sup>. It is the primary combustion product of both organic and inorganic sulfur-containing compounds as well as in the combustion of elemental sulfur itself. The most convenient method of preparation is combining the elements as described in §3.2.3.1.

(L. B. PETER)

1. "Schwefel Oxide," *Gmelins Handbuch der Anorganischen Chemie*, Erzsbd. 3, Springer Verlag, Berlin, 1980.
2. B. Meyer, *Sulfur, Energy and Environment*, Elsevier, Amsterdam, 1977.

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Small amounts of SO<sub>3</sub> are normally produced along with SO<sub>2</sub> during the combustion of sulfur, and the SO<sub>3</sub> yield can be increased to ≤ 40%<sup>1</sup> (see §3.2.3.1.2). Usually, however, SO<sub>3</sub> is obtained by the O<sub>2</sub> oxidation of SO<sub>2</sub><sup>1,2</sup>:



a reaction that is thermodynamically favored, but slow even at 1000°C, and requires a catalyst such as the metal oxides, V<sub>2</sub>O<sub>5</sub>, Fe<sub>2</sub>O<sub>3</sub>, etc. Commercially the reaction is crucial in the production of H<sub>2</sub>SO<sub>4</sub> where NO is used as a homogeneous catalyst<sup>4,5</sup>. Laboratory amounts of SO<sub>3</sub> can be obtained by thermal decomposition of anhyd Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> or from fuming sulfuric acid. Preparation of SO<sub>3</sub> trimer and polymers is discussed in §3.2.3.1.

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14      3.2.3. Formation of the Oxygen Bond with Other Group-VIB Elements  
           3.2.3.2. Sulfur Oxides  
           3.2.3.2.4. Cyclopolsulfur Oxides

3. "Schwefel," *Gmelin Handbuch der Anorganischen Chemie*, Teil A, Verlag Chemie, Weinheim, 1953.
4. B. Meyer, *Sulfur, Energy and Environment*, Elsevier, Amsterdam, 1977.
5. U. H. F. Sander, H. Fischer, U. Rothe, R. Cola, in *Sulphur, Sulphur Dioxide, and Sulphuric Acid*, A. I. More, ed., British Sulphur Corporation, London, 1984.

**3.2.3.2.3. Disulfur Monoxide**

The unstable triatomic gas,  $S_2O$ , can be kept for several days if it is prepared and stored at low pressures<sup>1</sup>, i.e., < 130 Pa (1 torr). Several preparative reactions are known<sup>1,2</sup> including the reaction of  $SOCl_2$  with metal sulfides, the reaction of  $H_2S$  and  $SOCl_2$  at 200–360°C and the reaction of either  $S_2Cl_2$  or elemental sulfur with metal oxides at 100–400°C, conditions depending on the identity of the reactants. The low-pressure reaction of  $SOCl_2$  vapor with  $Ag_2S$  at 160°C is the most successful<sup>1</sup>. It is found among the decomposition products of some of the cyclopolsulfur oxides<sup>1</sup>, but these decompositions are not recommended as preparative routes to  $S_2O$ .

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**3.2.3.2.4. Cyclopolsulfur Oxides**

Monomeric  $SO_2$  and  $SO_3$  have been known since antiquity, and the polymeric oxides and  $S_2O$  are decades old. However, a whole new class of sulfur oxides has been discovered, the cyclopolsulfur oxides<sup>1–3</sup>,  $S_xO_y$  ( $x = 6–12$ ,  $y = 1$  or 2), consisting of divalent rings with one or two oxygens. They are analogous to cyclic organic sulfoxides or disulfoxides; e.g.,  $S_8O$  is prepared in low yield by the reaction of  $SOCl_2$  with a mixture of  $H_2S_x$  compounds, called crude sulfanes<sup>1</sup>. This oxide can be obtained in

**TABLE 1. PREPARATIVE CONDITIONS FOR CYCLOPOLYSULFUR OXIDES<sup>3</sup>**

Compound	$S_x/CF_3CO_3H$ ratio	Solvent	T (K)	Yield (%)
$\alpha$ - $S_6O$	1 : 1.2	$CH_2Cl_2$	253	5
$\beta$ - $S_6O$	1 : 2.2	$CH_2Cl_2$	263	1.5
$S_7O$	1 : 1.5	$CH_2Cl_2$	253	45
$S_8O$	1 : 1.5	$CH_2Cl_2$	263	20
$S_9O$	1 : 2	$CS_2$	243	10
$S_{10}O$	1 : 3	$CS_2$	243	14
$S_6O$		$CH_2Cl_2$		
$S_7O_2$	$S_8$ 1 : 5	$CH_2Cl_2$	263	11
$S_{12}O_2$ <sup>a</sup>		$CS_2$	223	

<sup>a</sup> Adduct with 2  $SbCl_5$ , not prepared directly from  $CF_3CO_3H$ .

14      3.2.3. Formation of the Oxygen Bond with Other Group-VIB Elements  
           3.2.3.2. Sulfur Oxides  
           3.2.3.2.4. Cyclopolsulfur Oxides

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$S_{12}O_2^a$		$CS_2$	223	

<sup>a</sup> Adduct with 2  $SbCl_5$ , not prepared directly from  $CF_3CO_3H$ .

14     3.2.3. Formation of the Oxygen Bond with Other Group-VIB Elements  
        3.2.3.2. Sulfur Oxides  
        3.2.3.2.4. Cyclopolsulfur Oxides

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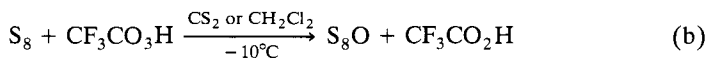
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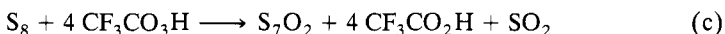
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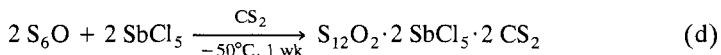
better yield by the oxidation in  $\text{CS}_2$  or  $\text{CH}_2\text{Cl}_2$  solns of the stable  $\text{S}_8$  with  $\text{CF}_3\text{CO}_3\text{H}$ , peroxytrifluoroacetic acid<sup>3</sup>:



This method has been used<sup>1-6</sup> to prepare  $\text{S}_6\text{O}$  (two modifications),  $\text{S}_7\text{O}$ ,  $\text{S}_8\text{O}$ ,  $\text{S}_9\text{O}$  and  $\text{S}_{10}\text{O}$ ; the conditions for these syntheses are summarized in Table 1. With excess peroxyacid, the disulfoxides can be isolated; e.g.,  $\text{S}_7\text{O}_2$  can be prepared<sup>7</sup> from  $\text{S}_8$  by:



The hexasulfur dioxide is also known<sup>6</sup>. The largest cyclosulfur oxide,  $\text{S}_{12}\text{O}_2$  is prepared stabilized as a  $\text{SbCl}$  adduct by the slow dimerization of  $\text{S}_6\text{O}$  in the presence of  $\text{SbCl}_5$  in  $\text{CS}_2$  solution<sup>8</sup>:



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1. "Schwefel Oxide," *Gmelins Handbuch der Anorganischen Chemie*, Erzsbd. 3, Springer Verlag, Berlin, 1980.
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3. R. Steudel, *Phosphorus Sulphur*, 23, 33 (1985).
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5. R. Steudel, *Comments Inorg. Chem.*, 1, 313 (1982).

### 3.2.3.3. Sulfur Oxyacids

Sulfur forms more oxyacids than most other elements. Sulfuric acid,  $\text{H}_2\text{SO}_4$ , is produced in greater amounts industrially than any other substance. Most sulfur-oxygen bond formation occurs in aqueous solution. In some cases sulfur-sulfur bond formation is of equal or greater importance than  $\text{S}-\text{O}$  formation, but these procedures are discussed here for continuity. The formation of peroxydisulfuric acid is discussed in §3.2.2.2.

(L. B. PETER)

#### 3.2.3.3.1. Sulfurous Acid Systems

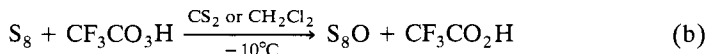
When  $\text{SO}_2$  is dissolved in water it produces a weak acidic solution often referred to as sulfurous acid,  $\text{H}_2\text{SO}_3$  being the hypothetical formula. These solutions are mostly just dissolved  $\text{SO}_2$  with tiny amounts of hydrolysis products, and no  $\text{H}_2\text{SO}_3$  has been detected. However, three series of salts<sup>1-3</sup>, which are nominally neutralization products of sulfurous acid, can be prepared by reacting  $\text{SO}_2$  with aqueous hydroxides or carbonates. These are ionic compounds of sulfite  $[\text{SO}_3]^{2-}$ , hydrogen sulfite  $[\text{HSO}_3]^-$  and disulfite  $[\text{S}_2\text{O}_5]^{2-}$ . Nearly quantitative yields of the simple or hydrated sulfites are produced when the cations are divalent or the base is in excess. These sulfites are easily precipitated from solution. Compounds of  $[\text{HSO}_3]^{2-}$  or  $[\text{S}_2\text{O}_5]^{2-}$  and univalent cations can be obtained at pH 2-7, the identity of the sulfoxo

### 3.2.3. Formation of the Oxygen Bond with Other Group-VIB Elements 15

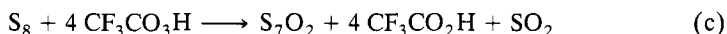
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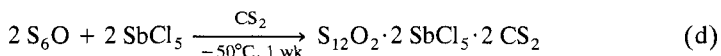
better yield by the oxidation in CS<sub>2</sub> or CH<sub>2</sub>Cl<sub>2</sub> solns of the stable S<sub>8</sub> with CF<sub>3</sub>CO<sub>3</sub>H, peroxytrifluoroacetic acid<sup>3</sup>:



This method has been used<sup>1-6</sup> to prepare S<sub>6</sub>O (two modifications), S<sub>7</sub>O, S<sub>8</sub>O, S<sub>9</sub>O and S<sub>10</sub>O; the conditions for these syntheses are summarized in Table 1. With excess peroxyacid, the disulfoxides can be isolated; e.g., S<sub>7</sub>O<sub>2</sub> can be prepared<sup>7</sup> from S<sub>8</sub> by:



The hexasulfur dioxide is also known<sup>6</sup>. The largest cyclosulfur oxide, S<sub>12</sub>O<sub>2</sub> is prepared stabilized as a SbCl<sub>5</sub> adduct by the slow dimerization of S<sub>6</sub>O in the presence of SbCl<sub>5</sub> in CS<sub>2</sub> solution<sup>8</sup>:



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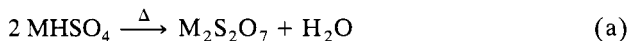
anion being dependent on the identity of the cation<sup>1,2</sup>. Among the alkali metals, Na<sup>+</sup> and K<sup>+</sup> crystallize with [S<sub>2</sub>O<sub>5</sub>]<sup>2-</sup>, and Rb and Cs<sup>+</sup> produce [HSO<sub>3</sub>]<sup>-</sup> compounds. The Rb and Cs hydrogen sulfites can be converted to the disulfites by gentle heating in vacuum<sup>1,2</sup>. Sulfites and unstable disulfites, e.g., Li<sub>2</sub>S<sub>2</sub>O<sub>5</sub> and Tl<sub>2</sub>S<sub>2</sub>O<sub>5</sub>, are prepared by direct reaction of the oxides or hydroxides with xs liq SO<sub>2</sub> and a trace of water<sup>1,2,4</sup>.

(L. B. PETER)

1. L. B. Peter, Ph.D. dissertation, University of Washington, 1979; University Microforms Int., No. 8013581, *Diss. Abstr., Int. B.*, 40, 5664 (1980); *Chem. Abstr.*, 93, 84,158 (1980).
2. B. Meyer, L. Peter, C. Shasky-Rosenlund, *Spectrochim. Acta*, 35A, 345 (1979).
3. M. Schmidt, W. Siebert, in *Comprehensive Inorganic Chemistry*, Vol. 2, A. F. Trotman-Dickenson, ed., Pergamon Press, Oxford, 1973, p. 795.
4. L. Peter, B. Meyer, *Inorg. Chem.*, 24, 3071 (1985).

### 3.2.3.3.2. Sulfuric Acid Systems

Sulfuric acid is formed by the vigorous reaction of SO<sub>3</sub> and water<sup>1-4</sup>. It is the parent of two series of salts, the sulfates with [SO<sub>4</sub>]<sup>2-</sup> and the hydrogen sulfates, which can be prepared by neutralizing the acid with an oxide, hydroxide or carbonate of the desired cations<sup>3,4</sup>. The [HSO<sub>4</sub>]<sup>-</sup> compounds can only be crystallized with univalent cations, but these substances can be thermally dehydrated to compounds with [S<sub>2</sub>O<sub>7</sub>]<sup>2-</sup>, pyrosulfate:



When xs SO<sub>3</sub> is dissolved in pure H<sub>2</sub>SO<sub>4</sub>, an oily liquid, commonly called oleum, is produced. Polysulfate species such as [S<sub>3</sub>O<sub>10</sub>]<sup>2-</sup> and [S<sub>4</sub>O<sub>13</sub>]<sup>3-</sup> exist in these solutions, and some have been isolated<sup>5</sup>.

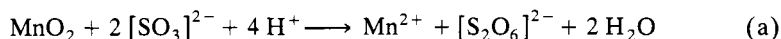
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16     3.2.3. Formation of the Oxygen Bond with Other Group-VIB Elements  
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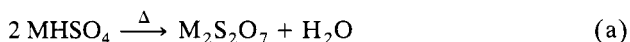
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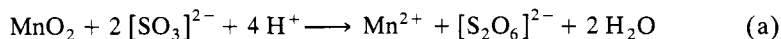
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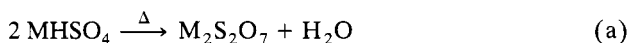
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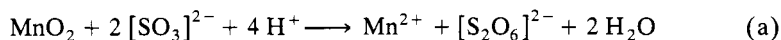
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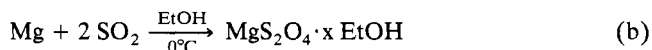
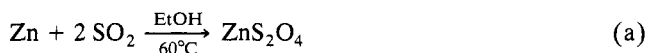
The dithionate ion is often isolated initially in the form of its barium salt,  $\text{BaS}_2\text{O}_6 \cdot 2 \text{H}_2\text{O}$ , as it is the only appreciably water-soluble oxysulfur compound, therefore facilitating separation from oxidation side products. The unstable free acid is produced by adding stoichiometric amounts of  $\text{H}_2\text{SO}_4$  to aqueous solutions of the barium compound<sup>1,2</sup>. It decomposes by disproportionation to  $\text{H}_2\text{SO}_4$  and sulfur dioxide.

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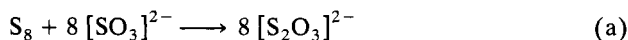
Other methods are the electrolytic reduction of  $\text{SO}_2$  in DMF, DMSO or other nonaqueous solvents<sup>5</sup> and the heterogeneous reaction of  $\text{SO}_2$  with saline hydrides yielding the dithionite and  $\text{H}_2$  as the only products<sup>1</sup>. Dithionites are oxidized by air to sulfates and sulfites and decompose in the absence of air to sulfites and thiosulfates.

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#### 3.2.3.3.5. Thiosulfuric Acid<sup>1,2</sup>

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### 3.2.3. Formation of the Oxygen Bond with Other Group-VIB Elements 17

#### 3.2.3.3. Sulfur Oxyacids

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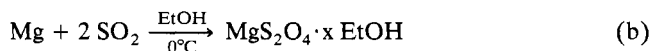
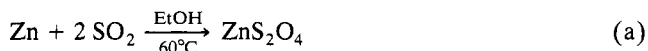
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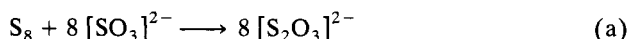
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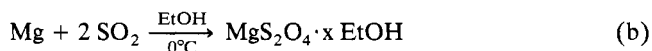
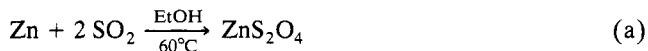
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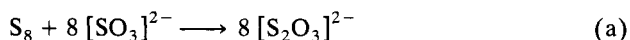
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18      3.2.3. Formation of the Oxygen Bond with Other Group-VIB Elements  
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           3.2.3.3.6. Sulfane Mono- and Disulfonic Acids

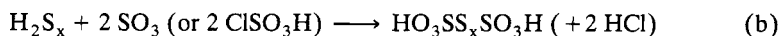
anhydrous ether at 195 K by the reaction of  $\text{H}_2\text{S}$  and  $\text{ClSO}_3\text{H}$ , and it is the first of a series of sulfane monosulfonic acids,  $\text{HS}_x\text{SO}_3\text{H}$ .

(L. B. PETER)

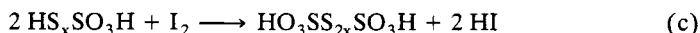
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**3.2.3.3.6. Sulfane Mono- and Disulfonic Acids**

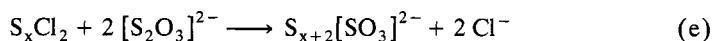
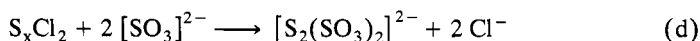
The free sulfane mono- and disulfonic ( $\text{HO}_3\text{SS}_x\text{SO}_3\text{H}$ ) acids are unstable under most conditions but can be synthesized at low temperatures<sup>1,2</sup>. Both the mono- and diacids can be prepared in dry ether at 195 K by the kinetically controlled reactions of the sulfanes and  $\text{SO}_3$  or chlorosulfonic acid:



In addition, larger diacids can be prepared by  $\text{I}_2$  oxidation of the monoacids to dimers:



The sulfane disulfonic acids are usually found as active metal salts of the conjugate anions and are referred to as polythionates<sup>1-3</sup>. The anions exist together in aqueous solution as being among the decomposition products of the reaction of  $\text{H}_2\text{S}$  and aq  $\text{SO}_2$ , and in the acidification of  $[\text{S}_2\text{O}_3]^{2-}$  solutions. Compounds of  $[\text{S}_x(\text{SO}_3)_2]^{2-}$ ,  $x = 1-4$ , can be prepared individually. Methods of preparation unique to each anion are known, but a general method is the shaking together of solutions of dichlorosulfanes in inert solvents with aqueous sulfite or thiosulfate solutions<sup>3</sup>:



High-pressure liquid chromatography studies indicate<sup>4,5</sup> that a mixture in solution of higher order sulfane disulfonates (with up to 22 S atoms) by an extension of Eq. (e).

(L. B. PETER)

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## Author Index

The entries of this index were derived directly by computer program from the lists of references. The accuracy of the references was the sole responsibility of the authors. No editorial check, except for format and journal-title abbreviation, was applied. Consequently, errors occurring in authors' names in the references will recur in this index.

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| Goetze, U.         | 2.8.5            | 2.6.15           |
| 2.6.11.1           | 2.8.6.1          | 2.6.16           |
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| 2.8.4.1            | 2.6.15           | 2.8.23.2         |
| Goldfield, S. A.   | Granier, W.      | Gregory, N. W.   |
| 2.8.10             | 2.11.2.1         | 2.8.2            |
| Goldschmidt, H.    | Grannec, J.      | 2.8.7.1          |
| 2.8.14.4           | 2.6.6.3          | 2.8.8.1          |
| Goldwhite, H.      | 2.6.14.2         | 2.8.11.1         |
| 2.7.1              | 2.8.2            | 2.8.11.2         |
| 2.7.5              | 2.11.2.1         | 2.9.2.3          |
| Golovanov, B. V.   | 2.11.2.2         | 2.9.2.4          |
| 2.9.12.7           | 2.11.2.3         | 2.9.3.2          |
| 2.11.3.1           | 2.11.3.3         | 2.9.4.1          |
| Goltyere, A.       | Grant, L. R.     | 2.9.4.2          |
| 2.8.11.1           | 2.7.4            | Grey, I. E.      |
| Goltzene, A.       | 2.7.9            | 2.9.10           |
| 2.8.11.2           | Graulier, M.     | Griffith, W. P.  |
| Golubera, E. I.    | 2.8.18           | 2.9.2            |
| 2.8.23.5           | Gray, H. B.      | 2.9.13           |
| Gomm, P. S.        | 2.8.4.1          | 2.9.13.1.1       |
| 2.8.4.1            | 2.9.15.1.1       | 2.9.13.1.2       |
| Goncharov, A. I.   | Gray, J. L.      | 2.9.13.2         |
| 2.7.4              | 2.6.15           | 2.9.13.3.1       |
| Gonzalez, V. R.    | 2.6.16           | 2.9.15.1         |
| 2.8.17.3           | Graybill, B. M.  | 2.11.2.1         |
| Good, B. W.        | 2.6.4.1          | 2.11.3.1         |
| 2.8.12             | Grays, J.        | 2.11.4.1         |
| Good, M. L.        | 2.8.10           | Griffiths, J. E. |
| 2.9.10             | Green, J. H. S.  | 2.8.2            |
| Goodenough, R. D.  | 2.6.12.2         | 2.11.2.1         |
| 2.7.5              | 2.6.16           | 2.11.3.1         |
| Goodgame, D. M. L. | Green, M. L. H.  | 2.11.3.2         |
| 2.9.10             | 2.6.10.2         | 2.11.4.1         |

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| 2.11.4.3            | Günther, I.         | 2.8.2           |
| Griffitts, F. A.    | 2.6.3.3             | 2.8.7.1         |
| 2.9.12.1            | Gupta, O. D.        | 2.8.8.1         |
| Grim, S. O.         | 2.11.2.1            | 2.8.8.2         |
| 2.6.11.1            | 2.11.3.1            | 2.8.9           |
| Grimes, R. N.       | 2.11.4.1            | 2.8.10          |
| 2.6.4.1             | 2.11.5.2            | 2.8.15.1        |
| 2.6.5.1             | Gurd, T. H.         | 2.8.16.1        |
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| 2.6.11.2            | Gurev, N. I.        | 2.9.3.4         |
| Grishkin, Y. A.     | 2.6.13.3            | 2.9.4.1         |
| 2.6.4.2             | Gurskii, M. E.      | 2.9.12.1        |
| Griswold, E.        | 2.8.23.2            | 2.11.2.1        |
| 2.6.14.1            | Gusev, B. A.        | 2.11.2.2        |
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| 2.7.1               | Gut, R.             | 2.11.3.1        |
| Groeneveld, W. L.   | 2.11.2.1            | 2.11.3.3        |
| 2.8.9               | 2.11.4.1            | 2.11.4.1        |
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| 2.7.4               | 2.9.2.2             | Haeseler, H.    |
| 2.7.5               | Guthe, A.           | 2.6.8.1         |
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| 2.9.12.2            | Gütlich, P.         | Hagemann, F.    |
| 2.11.2.1            | 2.8.4.1             | 2.11.5.2        |
| 2.11.4.1            | Gutman, V.          | Hagen, H.       |
| 2.10.2.1            | 2.8.11.1            | 2.9.2.3         |
| 2.10.2.2.1          | 2.8.14.4            | 2.9.11.2        |
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| 2.8.8.1             | 2.9.2.1             | 2.6.6.3         |
| 2.8.10              | 2.9.2.2             | 2.6.7.1         |
| Grossmann, H.       | 2.9.2.3             | 2.6.14.2        |
| 2.8.22              | 2.9.3.2             | 2.8.2           |
| Gruder, H. J.       | 2.9.3.4             | 2.11.2.2        |
| 2.6.16              | 2.9.10              | 2.11.2.3        |
| Grünauer, H.        | 2.11.4.1            | 2.11.3.3        |
| 2.8.14.5            | Guy, J. J.          | Hagg, G.        |
| Gruner, E.          | 2.8.4.1             | 2.8.19          |
| 2.8.8.2             | Gverdtsiteli, M. G. | Hair, M. L.     |
| Guen, L.            | 2.8.23.2            | 2.9.12.3        |
| 2.8.12              |                     | 2.11.4.1        |
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| 2.8.10              | Habeeb, J. J.       | 2.8.22          |
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| Guggenberger, L. J. | 2.8.4.2             | 2.8.22          |
| 2.6.4.1             | 2.8.7.1             | Hale, P. K.     |
| Guggenheim, H. J.   | 2.8.10              | 2.8.10          |
| 2.9.3.2             | 2.8.11.1            | Hall, D.        |
| Guichard, F.        | 2.8.23.1            | 2.8.4.1         |
| 2.8.23.5            | 2.9.3.7             | Hall, J. L.     |
| Guidoboni, R.       | 2.9.10.4            | 2.6.2           |
| 2.9.4.2             | Hachmeister, K.     | Hall, J. W.     |
| Gunn, S. R.         | 2.8.22              | 2.8.10          |
| 2.10.1              | Hadenfeldt, C.      | Hallack, R. B.  |
| 2.10.2.1            | 2.7.3.2.1           | 2.6.2           |
| Günter, K.          | Haendler, H. M.     | Halpern, J.     |
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| 2.6.11.1           | 2.9.10.3         | Helling, C.           |
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| 2.8.14.2           | 2.8.18           | Helmolz, L.           |
| Hammer, R. R.      | 2.8.22           | 2.9.10                |
| 2.8.2              | Hartl, H.        | Helvenstan, E. P.     |
| 2.8.7.1            | 2.8.12           | 2.9.7                 |
| 2.8.8.1            | Hartman, H.      |                       |
| 2.8.11.1           | 2.8.23.5         | Helvenston, E. P.     |
| 2.8.11.2           | Hartman, J. S.   | 2.8.8.3               |
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| 2.8.5              | Haskew, C. A.    | Helwig, H.            |
| Hancock, K. G.     | 2.6.3.1          | 2.9.2.3               |
| 2.6.13.3           | Hatfield, W. E.  | Hemmings, R. T.       |
| Handy, L. B.       | 2.8.10           | 2.6.7.3               |
| 2.11.3.1           | Hathaway, B. J.  | Hempel, C. W.         |
| 2.11.4.1           | 2.8.10           | 2.8.21.2              |
| Handy, L. L.       | Hausen, H. D.    | Hencher, J. L.        |
| 2.9.2.4            | 2.6.10.3         | 2.6.13.1              |
| 2.9.3.2            | 2.6.16           | 2.6.14.1              |
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| 2.8.12             | Hayden, J. H.    | Henry, O.             |
| Hansen, J. J.      | 2.9.10.5         | 2.8.21.3              |
| 2.8.10             | Hayter, R. G.    | Hensgen, C.           |
| Hanzel, D.         | 2.6.7            | 2.8.17.1              |
| 2.11.2.2           | Heaton, B. J.    | Henze, G.             |
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| 2.8.14.3           | Hebert, G. M.    | 2.8.14.4              |
| Hardt, H. D.       | 2.11.3.1         | 2.8.15.3              |
| 2.8.8.3            | Hecht, H.        | Hepner, L. G.         |
| 2.8.11.2           | 2.8.9            | 2.8.3.1.1             |
| 2.8.12             | 2.9.4.5          | Hepworth, M. A.       |
| 2.8.17.3           | 2.9.12.5         | 2.9.2.1               |
| Hargreaves, G. B.  | Heckmann, I.     | 2.9.3.4               |
| 2.9.2.1            | 2.9.13.1.1       | 2.9.11.2              |
| 2.9.6              | Hedburg, K.      | 2.9.12.3              |
| 2.9.10             | 2.11.2.1         | 2.9.13.1.1            |
| 2.9.11.1           | Hedin, R.        | 2.11.4.2              |
| 2.9.11.2           | 2.9.4.6          | Herdtschew, E.        |
| 2.9.12.1           | Heinicke, K.     | 2.8.10                |
| 2.9.13.3.1         | 2.9.15.2         | Herlinger, A. W.      |
| 2.11.3.1           | Heintz, E. A.    | 2.8.22                |
| 2.11.4.1           | 2.9.10.2         | Hermanek, S.          |
| Harnischmacher, W. | Heinzlemann, A.  | 2.6.7.2               |
| 2.8.2              | 2.11.5.2         | 2.6.7.3               |
| 2.9.10.5           | Heisig, G. B.    | Hermann, G.           |
| 2.11.2.3           | 2.9.4.6          | 2.8.22                |
| Harris, C. M.      | Helgesson, G.    | Hermannsdörfer, K.-H. |
| 2.8.4.1            | 2.8.12           | 2.6.11.1              |
| 2.8.6.1            | Hellberg, K. H.  | 2.6.11.2              |
| 2.8.12             | 2.9.2.1          | Herold, A.            |
| Harris, J.         | 2.9.11.1         | 2.11.2.1              |
| 2.6.8.1            | 2.11.2.1         | Hertwig, K. A.        |
| Harrison, B. A.    | 2.11.4.1         | 2.6.8.2               |
| 2.8.6.2            | 2.11.4.2         | Hetfrich, G. F.       |
| Harrison, H.       | Heller, W.       | 2.9.10.4              |
| 2.8.13             | 2.9.11.2         |                       |

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| 2.11.2.1          | 2.11.4.3        | Howe, D. V.        | 2.6.4.1    |
| Hettich, A.       | 2.11.5.2        | Howe, J. L.        | 2.9.13.1.2 |
| 2.8.13            | 2.10.2.1        | Howell, J. A. S.   | 2.9.13.1.1 |
| Hewitt, A. J.     | 2.10.2.2.1      |                    | 2.11.2.1   |
| 2.9.15.1.1        | Holmberg, B.    | Hsieh, A. T. T.    | 2.6.13.1   |
| Hewkin, D.        | 2.8.11.1        |                    | 2.6.13.2   |
| 2.9.13.1.2        | Holt, E. M.     |                    | 2.6.13.3   |
| Hieber, W.        | 2.8.12          |                    | 2.6.16     |
| 2.9.6             | Holt, M. L.     | Huang, J.          | 2.11.2.1   |
| 2.9.15.1.1        | 2.9.2.2         | Hubbard, W. N.     | 2.6.8.1    |
| 2.9.15.1.3        | Homann, R.      |                    | 2.9.2.1    |
| 2.9.15.2          | 2.8.4.1         |                    | 2.10.1     |
| Hileman, J. C.    | 2.8.22          |                    | 2.11.4.1   |
| 2.9.15.1.1        | 2.11.3.3        |                    | 2.10.2.2   |
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| 2.6.12.2          | 2.9.2.4         | Hudson, H. R.      | 2.6.8.2    |
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| 2.8.12            | 2.8.14.1        | Huggins, D. K.     | 2.9.15.1.1 |
| Hindermann, D. K. | 2.8.14.2        | Hugill, D.         | 2.9.2.1    |
| 2.8.13            | 2.8.17.1        |                    | 2.9.10     |
| Hindman, J. C.    | 2.8.19          |                    | 2.11.3.1   |
| 2.10.2.1          | Hoodless, R. A. | Huglen, R.         | 2.6.16     |
| Hitchcock, P. B.  | 2.9.2.2         | Hulett, G. A.      | 2.8.14.5   |
| 2.8.6.1           | 2.9.2.3         | Hunseler, F.       | 2.8.22     |
| Hobson, R. J.     | 2.9.4.5         | Huntington, O. W.  | 2.8.17.1   |
| 2.9.14.4          | Hooper, E. W.   |                    | 2.8.19     |
| Hodges, J. R.     | 2.9.2.2         | Huppmann, V. P.    | 2.11.4.1   |
| 2.8.14.1          | Hope, E. G.     | Hurd, L. C.        | 2.9.2.2    |
| Hodgson, D. J.    | 2.9.4.1         | Hush, N. S.        | 2.8.10     |
| 2.8.10            | 2.9.12.1        | Huss, E.           | 2.8.2      |
| Hodosan, I.       | 2.9.12.3        |                    | 2.11.2.3   |
| 2.7.5             | Hoppe, R.       | Hussain, M. S.     | 2.8.4.1    |
| Hoffman, J. W.    | 2.6.16          | Hussey, C. L.      | 2.6.6.3    |
| 2.8.19            | 2.8.2           | Huston, J. L.      | 2.10.2.2.1 |
| Hoffmann, G. G.   | 2.8.4.1         | Hutchinson, W. E.  | 2.6.7.2    |
| 2.6.7.1           | 2.8.10          |                    |            |
| 2.6.7.2           | 2.8.12          |                    |            |
| 2.6.7.3           | 2.8.22          |                    |            |
| Hofmeister, P.    | 2.9.10.5        |                    |            |
| 2.8.23.2          | 2.11.2.1        |                    |            |
| Hogarth, J. W.    | 2.11.2.2        |                    |            |
| 2.9.10.2          | 2.11.2.3        |                    |            |
| Hohmann, F.       | 2.11.3.2        |                    |            |
| 2.9.15.1.2        | 2.11.3.3        |                    |            |
| Holländer, F. J.  | 2.11.4.3        |                    |            |
| 2.10.2.2.1        | 2.11.5.1        |                    |            |
| Höllerer, G.      | 2.10.2.2.1      |                    |            |
| 2.6.11.1          | Horak, M.       |                    |            |
| 2.6.11.2          | 2.6.16          |                    |            |
| Holloway, J. H.   | Horner, S. M.   |                    |            |
| 2.6.6.3           | 2.6.6.3         |                    |            |
| 2.9.2.1           | 2.9.10          |                    |            |
| 2.9.4.6           | 2.9.13.3.1      |                    |            |
| 2.9.10            | Horner, W. W.   |                    |            |
| 2.9.14.4          | 2.9.10          |                    |            |
| 2.9.15.1.1        | Hoskins, K.     |                    |            |
| 2.11.3.1          | 2.8.6.1         |                    |            |
| 2.11.3.2          | House, H. O.    |                    |            |
| 2.11.4.1          | 2.8.23.2        |                    |            |

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| Hüttel, R.          | 2.9.4.6           | 2.6.5.2           |
| 2.8.5               |                   | 2.6.10.1          |
| Hüttig, G. F.       |                   | 2.6.10.3          |
| 2.7.2               | <b>J</b>          | 2.6.15            |
| Huttlinger, A.      | Jache, A. W.      | Jelus, B. L.      |
| 2.9.2.2             | 2.8.8.1           | 2.6.10.1          |
| Huy, T. B.          | 2.8.8.3           | Jenker, H.        |
| 2.8.2               | 2.11.3.1          | 2.6.10.3          |
| 2.11.3.3            | 2.11.3.3          | Jenkins, C. R.    |
| Hyatt, D. E.        | 2.11.4.1          | 2.9.15.1.2        |
| 2.6.4.1             | Jack, K. H.       | Jenkins, L. S.    |
| 2.6.4.2             | 2.8.3.1.3         | 2.9.14.4          |
| Hyde, K. R.         | 2.8.3.1.5         | Jenkins, W. A.    |
| 2.7.5               | 2.9.2.1           | 2.9.12.6          |
| 2.7.6               | 2.9.3.2           | Jenne, H.         |
| 2.7.7               | 2.11.4.3          | 2.6.12.3          |
| 2.9.2.2             | Jacob, E.         | Jesih, A.         |
| Hyman, H. H.        | 2.11.4.1          | 2.11.2.1          |
| 2.11.4.2            | Jacob, P.         | 2.11.2.2          |
|                     | 2.6.12.2          | 2.11.3.3          |
|                     | Jacobs, J. J.     | 2.10.2.2.1        |
|                     | 2.7.9             | Jha, N. K.        |
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| 2.9.12.7            | Jacobson, G. B.   | 2.11.4.1          |
| 2.11.3.1            | 2.6.4.2           | 2.11.4.2          |
| Il'yasov, I. I.     | 2.6.5.3           | Jimenez, R.       |
| 2.8.22              | Jacobson, R. A.   | 2.8.5             |
| Il'yukevich, L. A.  | 2.8.10            | Jocobi, K. R.     |
| 2.8.10              | Jacox, M. E.      | 2.8.23.2          |
| Imhof, V.           | 2.9.2.2           | Johannesen, R. B. |
| 2.6.9.3             | Jagner, S.        | 2.9.12.5          |
| Immerwahr, C.       | 2.8.12            | Johansson, L.     |
| 2.8.22              | James, B. D.      | 2.8.12            |
| Ingold, C. K.       | 2.6.6.3           | Johnson, B. F. G. |
| 2.8.23.2            | James, R. G.      | 2.9.10.3          |
| Insley, H.          | 2.9.13.1.2        | 2.9.15.1.1        |
| 2.9.10              | 2.9.13.2          | 2.9.15.1.3        |
| 2.11.3.1            | Jander, F.        | 2.9.15.2          |
| Iorns, T. V.        | 2.8.22            | Johnson, B. M.    |
| 2.6.11.1            | Jander, G.        | 2.11.2.1          |
| Ip, D. P.           | 2.8.3.1.4         | Johnson, C. E.    |
| 2.7.4               | 2.8.14.1          | 2.11.5.2          |
| Ippolitiv, E. G.    | 2.9.4.5           | Johnson, F. A.    |
| 2.9.3.4             | 2.9.12.5          | 2.6.12.3          |
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| 2.10.2.2.1          | 2.8.22            | Johnson, G. K.    |
| Isakhanyan, A. L.   | Janov, J.         | 2.10.1            |
| 2.8.23.3            | 2.11.5.2          | 2.10.2.2          |
| Isbell, H. S.       | Janssen, E. M. W. | Johnson, G. L.    |
| 2.8.5               | 2.8.2             | 2.6.17            |
| Ishikawa, T.        | 2.8.3.1.1         | 2.8.4.1           |
| 2.9.5               | 2.8.11.2          | 2.8.24            |
| Issleib, K.         | Jardine, F. H.    | 2.9.11.1          |
| 2.8.23.2            | 2.8.2             | 2.9.16            |
| Itoh, K.            | Jarvis, J. A. J.  | Johnson, R. E.    |
| 2.8.6.2             | 2.8.6.2           | 2.7.2             |
| Ivashentsev, Ya. I. | Jeffery, E. A.    | 2.7.8             |
| 2.6.6.3             | 2.6.3.2           | Johnson, R. L.    |
| 2.8.15.3            | 2.6.5.1           | 2.11.3.1          |
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| Yeh, S. M.<br>2.10.2.1          | Zakharëv, Yu. V.<br>2.11.5.1           | Zimmer, H. S.<br>2.8.23.3                 |
| Yeoh, T.-K.<br>2.8.10           | Zakharkin, L. I.<br>2.6.4.1<br>2.6.5.1 | Zirin, M. H.<br>2.8.14.1<br>2.10.2.3      |
| Yoke, J. T.<br>2.8.12           | Zalivina, E. N.<br>2.8.8.1             | Zizlsperger, H.<br>2.9.15.1.2             |
| Yoshida, H.<br>2.10.1           | Zalka, L.<br>2.9.12.6                  | Zolkins, A.<br>2.11.3.2                   |
| Yoshizawa, S.<br>2.9.5          | Zalkin, A.<br>2.8.2                    | Zol'nikova, G. P.<br>2.9.15.1.3           |
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| 2.6.3.1                         | 2.10.1                                 | Zshby, E. C.<br>2.7.3.2.1                 |
| 2.7.3.1                         | 2.10.2.1                               | Zürrer, T.<br>2.7.6                       |
| 2.8.11.1                        | 2.10.2.2.1                             | Zylka, L.<br>2.9.11.3                     |
| 2.8.14.1                        | 2.11.3.1                               | 2.9.11.4                                  |
| 2.8.14.2                        | Zara, T. V.<br>2.8.23.2                | Zyryanov, M. N.<br>2.8.3.1.1              |
| 2.8.19                          | Zeller, K. P.<br>2.8.23<br>2.8.23.2    |   |
| Youinou, M.-T.<br>2.9.13.3.1    | Žemva, B.<br>2.9.2.1                   |   |
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| Young, D. C.<br>2.6.4.1         |  |   |

## Compound Index

This index lists individual, fully specified compositions of matter that are mentioned in the text. It is an index of empirical formulas, ordered according to the following system: the elements within a given formula occur in alphabetical sequence except for C, or C and H if present, which always come first. The formulas are ordered alphanumerically without exception.

The index is augmented by successively permuted versions of all empirical formulas. As an example,  $C_3H_3AlO_9$  will appear as such and, at the appropriate positions in the alphanumeric sequence, as  $H_3AlO_9 \cdot C_3$ ,  $AlO_9 \cdot C_3H_3$  and  $O_9 \cdot C_3H_3Al$ . The asterisk identifies a permuted formula and allows the original formula to be reconstructed by shifting to the front the elements that follow the asterisk.

Whenever an empirical formula does not show how the elements are combined in groups, it is followed by a linearized structural formula, which reveals the connectivity of the compound(s) underlying the empirical formula and serves to distinguish substances which are identical in composition but differ in the arrangement of elements.

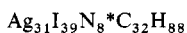
The nonpermuted empirical formulas are followed by keywords. They describe the context in which the compounds represented by the empirical formulas are discussed. Section numbers direct the reader to relevant positions in the book.

**Ac**  
Ac  
Reaction with HF: 2.11.5.2  
**AcFO**  
AcOF  
Formation: 2.11.5.2  
**AcF<sub>3</sub>**  
AcF<sub>3</sub>  
Formation: 2.11.5.2

Partial hydrolysis in aq NH<sub>3</sub>: 2.11.5.2  
**AcH<sub>3</sub>O<sub>3</sub>**  
Ac(OH)<sub>3</sub>  
Reaction with HF: 2.11.5.2  
**Ag**  
Ag  
Fluorination: 2.11.3.3  
Reacts with At: 2.8.4.1

- AgAt**  
**AgAt**  
 Formation: 2.8.4.1
- AgAtO<sub>3</sub>**  
**Ag[AtO<sub>3</sub>]**  
 Formation: 2.8.4.1
- AgAuCl<sub>6</sub>Cs<sub>2</sub>**  
**Cs<sub>2</sub>[AgAuCl<sub>6</sub>]**  
 Structure: 2.8.4.1
- AgAuF<sub>4</sub>**  
**Ag[AuF<sub>4</sub>]**  
 Formation: 2.8.4.1
- AgAu<sub>3</sub>I<sub>8</sub>Rb<sub>2</sub>**  
**Rb<sub>2</sub>[AgAu<sub>3</sub>I<sub>8</sub>]**  
 Formation: 2.8.4.1
- AgBaF<sub>4</sub>**  
**Ba[AgF<sub>4</sub>]**  
 Formation: 2.8.10
- AgBaF<sub>5</sub>**  
**Ba[AgF<sub>5</sub>]**  
 Formation: 2.8.4.1
- AgBa<sub>2</sub>F<sub>6</sub>**  
**Ba<sub>2</sub>[AgF<sub>6</sub>]**  
 Formation: 2.8.10
- AgBr**  
**AgBr**  
 Formation: 2.8.2, 2.9.8.  
 Precipitation from Ag<sup>+</sup> solutions:  
 2.8.11.1  
 Reaction with Ga: 2.6.3.3
- AgBr<sub>2</sub>N\*C<sub>4</sub>H<sub>12</sub>**  
**AgBr<sub>2</sub>P\*C<sub>24</sub>H<sub>20</sub>**  
**AgBr<sub>4</sub>P<sub>3</sub>\*C<sub>57</sub>H<sub>54</sub>**
- AgCaF<sub>4</sub>**  
**Ca[AgF<sub>4</sub>]**  
 Formation: 2.8.10
- AgCdF<sub>4</sub>**  
**Cd[AgF<sub>4</sub>]**  
 Formation: 2.8.10
- AgCl**  
**AgCl**  
 Fluorination: 2.11.3.3  
 Formation: 2.8.2, 2.9.8  
 Precipitation from Ag<sup>+</sup> solutions:  
 2.8.11.1  
 Reactions with F<sub>2</sub> and ClF<sub>3</sub>: 2.8.8.1  
 Reaction with Ag<sub>2</sub>Te: 2.9.14.2  
 Reaction with Al: 2.6.3.3  
 Reaction with ClF<sub>3</sub>: 2.11.3.3
- AgCl<sub>2</sub>Cs**  
**Cs[AgCl<sub>2</sub>]**  
 Formation: 2.8.12
- AgCl<sub>2</sub>N\*C<sub>4</sub>H<sub>12</sub>**  
**AgCl<sub>3</sub>Cu**  
**Ag[CuCl<sub>3</sub>]**  
 Formation: 2.8.10
- AgCsF<sub>3</sub>**  
**Cs[AgF<sub>3</sub>]**  
 Formation: 2.8.10
- AgCsF<sub>4</sub>**  
**Cs[AgF<sub>4</sub>]**  
 Formation: 2.8.4.1
- AgCs<sub>2</sub>F<sub>4</sub>**  
**Cs<sub>2</sub>[AgF<sub>4</sub>]**  
 Fluorination: 2.11.3.3  
 Formation: 2.8.10
- AgCs<sub>2</sub>F<sub>6</sub>**  
**Cs<sub>2</sub>[AgF<sub>6</sub>]**  
 Formation: 2.8.2, 2.11.3.3
- AgCs<sub>2</sub>F<sub>6</sub>K**  
**Cs<sub>2</sub>K[AgF<sub>6</sub>]**  
 Thermal decomposition: 2.8.4.1
- AgCs<sub>2</sub>I<sub>3</sub>**  
**Cs<sub>2</sub>[AgI<sub>3</sub>]**  
 Formation: 2.8.12
- AgF**  
**AgF**  
 Fluorinating agent: 2.6.12.3  
 Formation: 2.8.2, 2.9.8.  
 Formation from Ag<sub>2</sub>O or Ag<sub>2</sub>CO<sub>3</sub>:  
 2.8.11.1  
 Formation from the metal: 2.8.11.1  
 Reactions with F<sub>2</sub> and ClF<sub>3</sub>: 2.8.8.1  
 Reaction with B: 2.6.3.3  
 Reaction with F<sub>2</sub>-HF: 2.11.3.3  
 Reaction with Hg<sub>2</sub>Cl<sub>2</sub>: 2.8.21.1  
 Reduction of AgF<sub>2</sub>: 2.8.11.1
- AgF<sub>2</sub>**  
**AgF<sub>2</sub>**  
 Formation: 2.8.2, 2.8.7.1, 2.8.8.1, 2.8.8.2,  
 2.11.3.3  
 Oxidation of H<sub>2</sub>O: 2.8.7.3
- AgF<sub>3</sub>**  
**AgF<sub>3</sub>**  
 Formation: 2.8.2, 2.8.3.1.2
- AgF<sub>3</sub>K**  
**K[AgF<sub>3</sub>]**  
 Formation: 2.8.10
- AgF<sub>3</sub>NO**  
**[NO][AgF<sub>3</sub>]**  
 Formation: 2.8.10
- AgF<sub>3</sub>Rb**  
**Rb[AgF<sub>3</sub>]**  
 Formation: 2.8.10

- AgF<sub>3</sub>Zn**  
 Ag[ZnF<sub>3</sub>]  
 Formation: 2.11.2.3  
**AgF<sub>4</sub>Hg**  
 Hg[AgF<sub>4</sub>]  
 Formation: 2.8.10  
**AgF<sub>4</sub>K**  
 K[AgF<sub>4</sub>]  
 Formation: 2.8.4.1, 2.9.10.5  
**AgF<sub>4</sub>K<sub>2</sub>**  
 K<sub>2</sub>[AgF<sub>4</sub>]  
 Formation: 2.8.10  
**AgF<sub>4</sub>Na**  
 Na[AgF<sub>4</sub>]  
 Formation: 2.8.4.1  
**AgF<sub>4</sub>O<sub>2</sub>**  
 [O<sub>2</sub>][AgF<sub>4</sub>]  
 Decomposition: 2.8.3.1.2  
 Formation: 2.8.4.1  
**AgF<sub>4</sub>Rb**  
 Rb[AgF<sub>4</sub>]  
 Formation: 2.8.4.1  
**AgF<sub>4</sub>Rb<sub>2</sub>**  
 Rb<sub>2</sub>[AgF<sub>4</sub>]  
 Formation: 2.8.10  
**AgF<sub>4</sub>Sr**  
 Sr[AgF<sub>4</sub>]  
 Formation: 2.8.10  
**AgI**  
 AgI  
 Coprecipitates At: 2.8.4.1  
 Formation: 2.8.2  
 Precipitation from Ag<sup>+</sup> solutions:  
 2.8.11.1  
 Reaction with Ag<sub>2</sub>S: 2.9.14.2  
**AgI<sub>2</sub>N\*C<sub>4</sub>H<sub>12</sub>**  
**AgI<sub>3</sub>K<sub>2</sub>**  
 K<sub>2</sub>[AgI<sub>3</sub>]  
 Formation: 2.8.12  
 Structure: 2.8.12  
**AgI<sub>3</sub>P<sub>2</sub>\*C<sub>38</sub>H<sub>36</sub>**  
**AgN\*C**  
**AgNO\*C**  
**AgNO<sub>3</sub>**  
 AgNO<sub>3</sub>  
 Fluorination: 2.11.3.3  
 Reaction with F<sub>2</sub>: 2.8.8.2  
**Ag<sub>2</sub>As<sub>3</sub>Cl<sub>5</sub>\*C<sub>72</sub>H<sub>60</sub>**  
**Ag<sub>2</sub>Au<sub>3</sub>Cl<sub>17</sub>H<sub>24</sub>N<sub>6</sub>**  
 [NH<sub>4</sub>]<sub>6</sub>[Ag<sub>2</sub>Au<sub>3</sub>Cl<sub>17</sub>]  
 Structure: 2.8.4.2  
**Ag<sub>2</sub>Br<sub>2</sub>CuI<sub>2</sub>N<sub>4</sub>\*C<sub>4</sub>H<sub>16</sub>**  
**Ag<sub>2</sub>Br<sub>3</sub>N\*C<sub>8</sub>H<sub>20</sub>**  
**Ag<sub>2</sub>Br<sub>4</sub>N<sub>4</sub>Ni\*C<sub>4</sub>H<sub>16</sub>**  
**Ag<sub>2</sub>Br<sub>4</sub>P<sub>2</sub>\*C<sub>48</sub>H<sub>40</sub>**  
**Ag<sub>2</sub>Cl<sub>3</sub>N\*C<sub>8</sub>H<sub>20</sub>**  
**Ag<sub>2</sub>Cl<sub>4</sub>P<sub>2</sub>\*C<sub>48</sub>H<sub>40</sub>**  
**Ag<sub>2</sub>CsI<sub>3</sub>**  
 Cs[Ag<sub>2</sub>I<sub>3</sub>]  
 Structure: 2.8.12  
**Ag<sub>2</sub>F**  
 Ag<sub>2</sub>F  
 By cathodic reduction of AgF solution:  
 2.8.13  
 Decomposition: 2.8.13  
 Formation: 2.8.2  
 From reaction of AgF with Ag: 2.8.13  
 Structure: 2.8.13  
**Ag<sub>2</sub>FH<sub>2</sub>IO**  
 Ag<sub>2</sub>IF·H<sub>2</sub>O  
 Formation: 2.8.11.1  
**Ag<sub>2</sub>H<sub>16</sub>I<sub>4</sub>O<sub>8</sub>Sr**  
 [Sr(H<sub>2</sub>O)<sub>8</sub>][AgI<sub>2</sub>]<sub>2</sub>  
 Formation: 2.8.12  
 Structure: 2.8.12  
**Ag<sub>2</sub>HgI<sub>4</sub>**  
 Ag<sub>2</sub>[HgI<sub>4</sub>]  
 Formation: 2.8.22  
 Reaction with Mo(CO)<sub>6</sub>, W(CO)<sub>6</sub>:  
 2.9.15.1.1  
**Ag<sub>2</sub>I<sub>3</sub>N\*C<sub>4</sub>H<sub>10</sub>**  
**Ag<sub>2</sub>I<sub>3</sub>N\*C<sub>4</sub>H<sub>12</sub>**  
**Ag<sub>2</sub>O**  
 Ag<sub>2</sub>O  
 Reactions with X<sub>2</sub>: 2.8.11.1  
 Reactions with hydrohalic acids: 2.8.11.1  
 Reaction with F<sub>2</sub>: 2.8.8.2  
**Ag<sub>2</sub>S**  
 Ag<sub>2</sub>S  
 Reaction with AgX: 2.9.14.2  
**Ag<sub>2</sub>Te**  
 Ag<sub>2</sub>Te  
 Reaction with AgX: 2.9.14.2  
**Ag<sub>3</sub>I<sub>4</sub>N\*C<sub>16</sub>H<sub>36</sub>**  
**Ag<sub>4</sub>I<sub>5</sub>Rb**  
 Rb[Ag<sub>4</sub>I<sub>5</sub>]  
 Formation: 2.8.12  
 Structure: 2.8.12  
**Ag<sub>7</sub>F<sub>2</sub>HO<sub>8</sub>**  
 [Ag<sub>7</sub>O<sub>8</sub>][HF<sub>2</sub>]  
 Electrolytic formation from AgF solution:  
 2.8.13  
 Structure: 2.8.13  
**Ag<sub>7</sub>F<sub>5</sub>H<sub>5</sub>I<sub>2</sub>O<sub>2.5</sub>**  
 Ag<sub>7</sub>I<sub>2</sub>F<sub>5</sub>·2.5 H<sub>2</sub>O  
 Formation: 2.8.11.1



Al

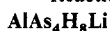
Al

Reaction with  $\text{HgX}_2$ ,  $\text{PbX}_2$ ,  $\text{Cu}_2\text{X}_2$ ,

AgX: 2.6.3.3

Reaction with RX: 2.6.3.2

Reaction with HX: 2.6.3.1

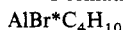
Reaction with  $\text{X}_2$ : 2.6.2.1Li[Al(AsH<sub>2</sub>)<sub>4</sub>]Reaction with  $\text{R}_3\text{SiX}$ ,  $\text{R}_3\text{GeX}$ : 2.6.9.3Reaction with  $\text{R}_3\text{SnBr}$ : 2.6.9.3Al(BH<sub>4</sub>)<sub>3</sub>

Formation: 2.6.5.3



AlBr

Formation: 2.6.14.1

AlH<sub>2</sub>Br

Formation: 2.6.5.3



AlSBr

Formation: 2.6.7.3



AlSeBr

Formation: 2.6.7.3



AlTeBr

Formation: 2.6.7.3

AlHBr<sub>2</sub>

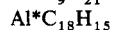
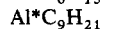
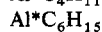
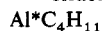
Formation: 2.6.5.3

AlBr<sub>3</sub>

Formation: 2.6.2.1, 2.6.6.2, 2.6.7.3

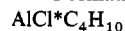
Reaction with AlH<sub>3</sub>: 2.6.5.3Reaction with Al<sub>2</sub>Y<sub>3</sub>: 2.6.7.3Reaction with BF<sub>3</sub>: 2.6.12.2

Reaction with MO: 2.9.4.8

Reaction with NH<sub>4</sub>F: 2.6.12.3

AlCl

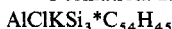
Formation: 2.6.14.1

AlH<sub>2</sub>Cl

Formation: 2.6.5.3

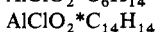
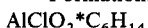
Li[AlH<sub>3</sub>Cl]

Formation: 2.6.5.3



AlOCl

Formation: 2.6.7.1



AlSCl

Formation: 2.6.7.3, 2.6.16

Reaction with  $\text{X}_2$ : 2.6.7.1

AlSeCl

Formation: 2.6.7.3



AlTeCl

Formation: 2.6.16

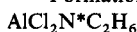


AlTeCl

Formation: 2.6.7.3

AlHCl<sub>2</sub>

Formation: 2.6.5.3

AlCl<sub>3</sub>

Catalyst in acylation: 2.8.23.4

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Halogenation reagent: 2.9.12.5

Metathesis: 2.6.12.1

Reaction with AlH<sub>3</sub>: 2.6.5.3Reaction with Al<sub>2</sub>Y<sub>3</sub>: 2.6.7.3Reaction with BX<sub>3</sub>: 2.6.12.2Reaction with BF<sub>3</sub>: 2.6.12.2

Reaction with CdS: 2.8.16.2

Reaction with HgS: 2.8.16.2

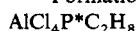
Reaction with OPX<sub>3</sub>: 2.6.12.2

Reaction with MO: 2.9.4.8

Reaction with ZnS: 2.8.16.2

[NO][AlCl<sub>4</sub>]

Formation: 2.6.3.3

Cl<sub>3</sub>Al · S<sub>2</sub>Cl<sub>2</sub>

Formation: 2.6.6.2

[SCl<sub>3</sub>][AlCl<sub>4</sub>]

Formation: 2.6.6.4

**AlCl<sub>8</sub>P**[PCl<sub>4</sub>][AlCl<sub>4</sub>]

Formation: 2.6.6.4

**AlF**

AlF

Formation: 2.6.14.1

AlF·C<sub>4</sub>H<sub>10</sub>**AlF<sub>3</sub>**AlF<sub>3</sub>

Fluorinating agent: 2.6.12.3

Formation: 2.6.12.3

**AlHI<sub>2</sub>**AlHI<sub>2</sub>

Formation: 2.6.5.3

**AlH<sub>2</sub>I**AlH<sub>2</sub>I

Formation: 2.6.5.3

**AlH<sub>3</sub>**AlH<sub>3</sub>Reaction with BX<sub>3</sub>: 2.6.5.3Reaction with PX<sub>3</sub>: 2.6.5.3Reaction with AlX<sub>3</sub>: 2.6.5.3**AlH<sub>4</sub>Li**Li[AlH<sub>4</sub>]Reaction with RPH<sub>2</sub>: 2.6.9.3Reaction with X<sub>2</sub>: 2.6.5.1Reaction with CCl<sub>4</sub>: 2.6.5.3

Thermal stability: 2.6.5.1

**AlH<sub>6</sub>LiN<sub>4</sub>**Li[Al(NH<sub>2</sub>)<sub>4</sub>]

Reaction with RX: 2.6.9.3

**AlH<sub>6</sub>LiP<sub>4</sub>**Li[Al(PH<sub>2</sub>)<sub>4</sub>]

Reaction with RX: 2.6.9.3

Reaction with H<sub>3</sub>SiX, H<sub>3</sub>GeX: 2.6.9.3**AlI**

AlI

Formation: 2.6.14.1

AlI·C<sub>4</sub>H<sub>10</sub>**AlIS**

AlSI

Formation: 2.6.7.3

**AlISe**

AlSeI

Formation: 2.6.7.3

**AlITe**

AlTeI

Formation: 2.6.7.3

AlI<sub>2</sub>·C<sub>2</sub>H<sub>5</sub>**AlI<sub>3</sub>**AlI<sub>3</sub>

Formation: 2.6.2.1

Reaction with Al<sub>2</sub>Y<sub>3</sub>: 2.6.7.3

Reaction with Cd: 2.8.14.5

Reaction with Cr<sub>2</sub>S<sub>3</sub>: 2.9.5

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Reaction with AlH<sub>3</sub>: 2.6.5.3Reaction with CX<sub>4</sub>: 2.6.12.2

Reaction with Zn: 2.8.14.5

**AlI<sub>6</sub>P**[PI<sub>4</sub>][AlI<sub>4</sub>]

Formation: 2.6.16

AlLiN<sub>4</sub>·C<sub>8</sub>H<sub>24</sub>AlLiP<sub>3</sub>·C<sub>3</sub>H<sub>13</sub>AlLiS<sub>4</sub>·C<sub>4</sub>H<sub>12</sub>AlLiSe<sub>4</sub>·C<sub>24</sub>H<sub>20</sub>AlLiTe<sub>4</sub>·C<sub>4</sub>H<sub>12</sub>**AlN**

AlN

Reaction with X<sub>2</sub>: 2.6.8.1

Reaction with HX: 2.6.8.2

AlP·C<sub>4</sub>H<sub>12</sub>AlP<sub>6</sub>Si<sub>3</sub>·C<sub>24</sub>H<sub>63</sub>AlP<sub>9</sub>·C<sub>21</sub>H<sub>54</sub>AlSe<sub>3</sub>·C<sub>18</sub>H<sub>15</sub>Al<sub>2</sub>I<sub>3</sub>·C<sub>6</sub>H<sub>15</sub>**Al<sub>2</sub>I<sub>7</sub>Li**Li[Al<sub>2</sub>I<sub>7</sub>]

Formation: 2.6.5.1

**Al<sub>2</sub>Mg**MgAl<sub>2</sub>

Reaction with RX: 2.6.3.2

**Al<sub>2</sub>O<sub>3</sub>**Al<sub>2</sub>O<sub>3</sub>Catalyst for the reaction of UF<sub>4</sub> with O<sub>2</sub>: 2.11.5.2Reaction with MF<sub>3</sub>: 2.6.6.4Reaction with PCl<sub>5</sub>: 2.6.6.4Reaction with S<sub>2</sub>Cl<sub>2</sub>-Cl<sub>2</sub>: 2.6.6.2Reaction with C-X<sub>2</sub>: 2.6.6.2Reaction with F<sub>2</sub>, Cl<sub>2</sub>: 2.6.6.1Reaction with CCl<sub>4</sub>: 2.6.6.4

Reaction with ag HX: 2.6.6.3

**Al<sub>2</sub>S<sub>3</sub>**Al<sub>2</sub>S<sub>3</sub>Formation from ZnS and AlCl<sub>3</sub>: 2.8.16.2Reaction with AlX<sub>3</sub>: 2.6.7.3Reaction with Se<sub>2</sub>Cl<sub>2</sub>: 2.6.7.3

Reaction with HX: 2.6.7.2

**Al<sub>2</sub>Se<sub>3</sub>**Al<sub>2</sub>Se<sub>3</sub>Reaction with Se<sub>2</sub>Cl<sub>2</sub>: 2.6.7.3Reaction with AlX<sub>3</sub>: 2.6.7.3

- Al<sub>2</sub>Te<sub>3</sub>**  
 Al<sub>2</sub>Te<sub>3</sub>  
 Reaction with AlX<sub>3</sub>: 2.6.7.3
- Al<sub>4</sub>Cl<sub>30</sub>O<sub>6</sub>P<sub>6</sub>**  
 [Al(OPCl<sub>3</sub>)<sub>6</sub>][AlCl<sub>4</sub>]<sub>3</sub>  
 Formation: 2.6.12.2
- AmF<sub>2</sub>O<sub>2</sub>**  
 AmO<sub>2</sub>F<sub>2</sub>  
 Formation: 2.11.5.2
- AmF<sub>2</sub>O<sub>2</sub>Rb**  
 Rb[AmO<sub>2</sub>F<sub>2</sub>]  
 Formation: 2.11.5.2
- AmF<sub>4</sub>**  
 AmF<sub>4</sub>  
 Fluorination: 2.11.5.2  
 Formation: 2.11.5.2
- AmF<sub>6</sub>Rb<sub>2</sub>**  
 Rb<sub>2</sub>[AmF<sub>6</sub>]  
 Formation: 2.11.5.2
- AmO<sub>3</sub>Rb\*Cl**  
 AsAuBr<sub>2</sub>\*C<sub>26</sub>H<sub>26</sub>  
 AsAuBr<sub>2</sub>F<sub>5</sub>\*C<sub>24</sub>H<sub>15</sub>  
 AsAuBr<sub>2</sub>NO\*C<sub>19</sub>H<sub>15</sub>  
 AsAuBr<sub>2</sub>N<sub>2</sub>O<sub>2</sub>\*C<sub>26</sub>H<sub>20</sub>  
 AsAuBr<sub>3</sub>\*C<sub>18</sub>H<sub>15</sub>  
 AsAuCl<sub>2</sub>\*C<sub>26</sub>H<sub>26</sub>  
 AsAuCl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>\*C<sub>26</sub>H<sub>20</sub>  
 AsAuCl<sub>4</sub>\*C<sub>24</sub>H<sub>20</sub>  
 AsAuCl<sub>5</sub>\*C<sub>24</sub>H<sub>15</sub>  
 AsAuCl<sub>7</sub>\*C<sub>24</sub>H<sub>15</sub>  
 AsAuF<sub>5</sub>\*C<sub>24</sub>H<sub>15</sub>  
 AsAuI\*C<sub>18</sub>H<sub>15</sub>  
 AsAuI<sub>2</sub>\*C<sub>26</sub>H<sub>26</sub>  
 AsAuI<sub>3</sub>\*C<sub>18</sub>H<sub>15</sub>  
 AsAuNO\*C<sub>19</sub>H<sub>15</sub>  
 AsAuN<sub>2</sub>O<sub>2</sub>\*C<sub>26</sub>H<sub>20</sub>  
 AsBN<sub>2</sub>\*C<sub>6</sub>H<sub>18</sub>  
 AsB<sub>10</sub>Cl<sub>2</sub>\*C<sub>2</sub>H<sub>11</sub>  
 AsBr<sub>2</sub>\*C<sub>3</sub>H<sub>9</sub>  
 AsBr<sub>2</sub>In\*C<sub>6</sub>H<sub>18</sub>
- AsBr<sub>3</sub>**  
 AsBr<sub>3</sub>  
 Reaction with Au<sub>2</sub>O<sub>3</sub>: 2.8.3.1.4  
 Reaction with R<sub>2</sub>NBX—NR'BX<sub>2</sub>:  
 2.6.8.3
- AsCl<sub>3</sub>**  
 AsCl<sub>3</sub>  
 Reaction with Au: 2.8.3.1.2  
 Reaction with R<sub>2</sub>NBXNR'BX<sub>2</sub>: 2.6.8.3
- AsCu<sub>3</sub>I<sub>4</sub>\*C<sub>19</sub>H<sub>18</sub>**  
**AsF<sub>2</sub>O<sub>2</sub>V\*C<sub>24</sub>H<sub>20</sub>**  
**AsF<sub>3</sub>**  
 AsF<sub>3</sub>  
 Reaction with BX<sub>3</sub>: 2.6.12.2
- AsF<sub>5</sub>**  
 AsF<sub>5</sub>  
 Reaction with Zn: 2.8.14.4
- AsF<sub>6</sub>H<sub>4</sub>Ta**  
 [AsH<sub>4</sub>][TaF<sub>6</sub>]  
 Formation: 2.11.4.1
- AsF<sub>11</sub>H<sub>4</sub>Ta<sub>2</sub>**  
 [AsH<sub>4</sub>][Ta<sub>2</sub>F<sub>11</sub>]  
 Formation: 2.11.4.1
- AsF<sub>11</sub>Xe**  
 [XeF<sub>5</sub>][AsF<sub>6</sub>]  
 Formation: 2.10.2.2.1
- AsGe\*CH<sub>7</sub>**  
**AsGe\*C<sub>3</sub>H<sub>11</sub>**  
**AsGeH<sub>5</sub>**  
 H<sub>3</sub>GeAsH<sub>2</sub>  
 Formation: 2.6.9.3
- AsGe<sub>2</sub>H<sub>7</sub>**  
 Ge<sub>2</sub>H<sub>5</sub>AsH<sub>2</sub>  
 Formation: 2.6.9.3
- AsH<sub>5</sub>Si**  
 H<sub>3</sub>SiAsH<sub>2</sub>  
 Formation: 2.6.9.3
- AsH<sub>7</sub>Si<sub>2</sub>**  
 (H<sub>3</sub>Si)<sub>2</sub>AsH  
 Formation: 2.6.9.3
- Si<sub>2</sub>H<sub>5</sub>AsH<sub>2</sub>**  
 Formation: 2.6.9.3
- AsI<sub>3</sub>**  
 AsI<sub>3</sub>  
 Formation: 2.6.12.2
- AsSi\*CH<sub>7</sub>**  
**AsSi\*C<sub>3</sub>H<sub>11</sub>**  
**AsSn\*C<sub>3</sub>H<sub>11</sub>**  
**As<sub>2</sub>AuI<sub>3</sub>\*C<sub>10</sub>H<sub>16</sub>**  
**As<sub>2</sub>Cl<sub>8</sub>Re<sub>2</sub>\*C<sub>48</sub>H<sub>40</sub>**  
**As<sub>2</sub>O<sub>3</sub>**  
 As<sub>2</sub>O<sub>3</sub>  
 Reaction with TiCl<sub>4</sub>, VOCl<sub>3</sub>: 2.9.12.7
- As<sub>3</sub>Cl<sub>5</sub>\*C<sub>72</sub>H<sub>60</sub>Ag<sub>2</sub>**  
**As<sub>4</sub>AuI\*C<sub>10</sub>H<sub>16</sub>**  
**As<sub>4</sub>Au<sub>2</sub>I<sub>2</sub>\*C<sub>20</sub>H<sub>32</sub>**  
**As<sub>4</sub>H<sub>8</sub>Li\*Al**  
**At\*Ag**  
**AtCsI<sub>3</sub>**  
 Cs[IAtl]  
 Coprecipitates with CsI<sub>3</sub>: 2.7.9
- AtIPd**  
 PdAtI  
 Formation: 2.9.11.1
- AtI<sub>2</sub>Tl**  
 Tl[IAtl]  
 Formation: 2.6.14.2



**AtK****KAt**

Formation of alkali and alkaline earth salts: 2.7.9

**AtO<sub>3</sub>\*Ag****At(Tl)****TlAt**

Formation: 2.6.14.2

**Au****Au**

Adsorbs At: 2.8.4.1

Reaction with KrF<sub>2</sub>: 2.11.4.3

Reaction with Se-X<sub>2</sub>, Te-X<sub>2</sub>: 2.9.14.1.2

Reaction with F<sub>2</sub>-O<sub>2</sub>: 2.11.4.3

Reaction with BrF<sub>3</sub>: 2.11.4.3

**AuBr****AuBr**

Formation: 2.8.2, 2.8.11.2

**AuBrClN<sub>3</sub>\*C<sub>6</sub>H<sub>12</sub>****AuBrCl<sub>2</sub>P\*C<sub>6</sub>H<sub>15</sub>****AuBrCl<sub>2</sub>P\*C<sub>18</sub>H<sub>15</sub>****AuBrF<sub>5</sub>N\*C<sub>22</sub>H<sub>36</sub>****AuBrF<sub>6</sub>****AuF<sub>3</sub>·BrF<sub>3</sub>**

Formation: 2.11.4.3

Reaction with SeF<sub>4</sub>: 2.11.4.3

Thermal decomposition: 2.11.4.3

**[BrF<sub>2</sub>][AuF<sub>4</sub>]**

Formation: 2.11.4.3

Formation and thermal decomposition:

2.8.3.1.2, 2.8.3.1.5

Reaction with NOCl: 2.11.4.3

**AuBrF<sub>15</sub>N\*C<sub>34</sub>H<sub>36</sub>****AuBrFeP\*C<sub>22</sub>H<sub>19</sub>****AuBrKN<sub>3</sub>\*C<sub>3</sub>****AuBrP\*C<sub>3</sub>H<sub>9</sub>****AuBrP\*C<sub>6</sub>H<sub>15</sub>****AuBrP\*C<sub>8</sub>H<sub>11</sub>****AuBrP\*C<sub>18</sub>H<sub>15</sub>****AuBrP\*C<sub>20</sub>H<sub>17</sub>****AuBrP\*C<sub>21</sub>H<sub>19</sub>****AuBrS****AuSBr**

Formation: 2.9.14.1.2

**AuBrS\*C<sub>14</sub>H<sub>14</sub>****AuBrTe<sub>2</sub>****AuTe<sub>2</sub>Br**

Formation: 2.9.14.1.2

**AuBr<sub>2</sub>\*C<sub>26</sub>H<sub>26</sub>As****AuBr<sub>2</sub>ClP\*C<sub>6</sub>H<sub>15</sub>****AuBr<sub>2</sub>ClP\*C<sub>18</sub>H<sub>15</sub>****AuBr<sub>2</sub>F<sub>5</sub>\*C<sub>24</sub>H<sub>15</sub>As****AuBr<sub>2</sub>F<sub>5</sub>P\*C<sub>24</sub>H<sub>15</sub>****AuBr<sub>2</sub>F<sub>5</sub>S\*C<sub>10</sub>H<sub>8</sub>****AuBr<sub>2</sub>F<sub>10</sub>N\*C<sub>28</sub>H<sub>36</sub>****AuBr<sub>2</sub>KN<sub>2</sub>\*C<sub>2</sub>****AuBr<sub>2</sub>N\*C<sub>8</sub>H<sub>20</sub>****AuBr<sub>2</sub>N\*C<sub>16</sub>H<sub>36</sub>****AuBr<sub>2</sub>NO\*C<sub>19</sub>H<sub>15</sub>As****AuBr<sub>2</sub>NOP\*C<sub>19</sub>H<sub>15</sub>****AuBr<sub>2</sub>NS<sub>2</sub>\*C<sub>5</sub>H<sub>10</sub>****AuBr<sub>2</sub>NS<sub>2</sub>\*C<sub>9</sub>H<sub>18</sub>****AuBr<sub>2</sub>N<sub>2</sub>O<sub>2</sub>\*C<sub>26</sub>H<sub>20</sub>As****AuBr<sub>3</sub>****AuBr<sub>3</sub>**

Formation: 2.8.2, 2.8.3.1.1, 2.8.3.1.4

Reaction with (CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>MgCl: 2.8.5

Reaction with HBr: 2.8.4.1

Reaction with dialkyl gold bromides:

2.8.5

**AuBr<sub>3</sub>\*C<sub>18</sub>H<sub>15</sub>As****AuBr<sub>3</sub>F<sub>5</sub>N\*C<sub>22</sub>H<sub>36</sub>****AuBr<sub>3</sub>FeP\*C<sub>22</sub>H<sub>19</sub>****AuBr<sub>3</sub>P\*C<sub>3</sub>H<sub>9</sub>****AuBr<sub>3</sub>P\*C<sub>6</sub>H<sub>15</sub>****AuBr<sub>3</sub>P\*C<sub>18</sub>H<sub>15</sub>****AuBr<sub>3</sub>P\*C<sub>20</sub>H<sub>17</sub>****AuBr<sub>3</sub>P\*C<sub>21</sub>H<sub>19</sub>****AuBr<sub>3</sub>S\*C<sub>2</sub>H<sub>6</sub>****AuBr<sub>3</sub>S\*C<sub>14</sub>H<sub>14</sub>****AuBr<sub>4</sub>H<sub>9</sub>O<sub>4</sub>****H[AuBr<sub>4</sub>]·4 H<sub>2</sub>O**

Formation: 2.8.4.1

**AuBr<sub>4</sub>K****K[AuBr<sub>4</sub>]**

Formation: 2.8.4.1

**AuBr<sub>4</sub>N\*C<sub>8</sub>H<sub>20</sub>****AuBr<sub>4</sub>O<sub>4</sub>\*H<sub>9</sub>****AuBr<sub>4</sub>Rb****Rb[AuBr<sub>4</sub>]**

Thermal decomposition: 2.8.4.1

**Au\*C<sub>3</sub>H<sub>9</sub>****AuCl****AuCl**

Formation: 2.8.2

Formation by chlorination of Au:

2.8.11.1

Formation from AuCl<sub>3</sub>: 2.8.11.2

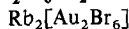
Reaction with F<sub>2</sub>: 2.8.3.1.3

**AuClF<sub>10</sub>N\*C<sub>17</sub>H<sub>5</sub>****AuClI<sub>2</sub>P\*C<sub>6</sub>H<sub>15</sub>****AuClKN<sub>3</sub>\*C<sub>3</sub>****AuClO****AuOCl**

Formation: 2.8.3.1.4

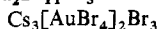
- AuClO<sup>\*</sup>C**  
**AuClP<sup>\*</sup>C<sub>6</sub>H<sub>15</sub>**  
**AuClP<sup>\*</sup>C<sub>8</sub>H<sub>11</sub>**  
**AuClP<sup>\*</sup>C<sub>18</sub>H<sub>15</sub>**  
**AuClSe**  
   AuSeCl  
     Formation: 2.9.14.1.2  
**AuClTe<sub>2</sub>**  
   AuTe<sub>2</sub>Cl  
     Formation: 2.9.14.1.2  
**AuCl<sub>2</sub><sup>\*</sup>C<sub>26</sub>H<sub>26</sub>As**  
**AuCl<sub>2</sub>Cs<sup>\*</sup>C<sub>2</sub>H<sub>6</sub>**  
**AuCl<sub>2</sub>F<sub>5</sub>S<sup>\*</sup>C<sub>10</sub>H<sub>8</sub>**  
**AuCl<sub>2</sub>F<sub>10</sub>N<sup>\*</sup>C<sub>28</sub>H<sub>36</sub>**  
**AuCl<sub>2</sub>KN<sub>2</sub><sup>\*</sup>C<sub>2</sub>**  
**AuCl<sub>2</sub>KN<sub>2</sub>O<sup>\*</sup>C<sub>2</sub>H<sub>2</sub>**  
**AuCl<sub>2</sub>N<sup>\*</sup>C<sub>8</sub>H<sub>20</sub>**  
**AuCl<sub>2</sub>N<sup>\*</sup>C<sub>16</sub>H<sub>36</sub>**  
**AuCl<sub>2</sub>N<sub>2</sub>O<sub>2</sub><sup>\*</sup>C<sub>26</sub>H<sub>20</sub>As**  
**AuCl<sub>2</sub>N<sub>3</sub>O<sub>4</sub><sup>\*</sup>C<sub>16</sub>H<sub>20</sub>**  
**AuCl<sub>2</sub>N<sub>3</sub>O<sub>4</sub><sup>\*</sup>C<sub>18</sub>H<sub>24</sub>**  
**AuCl<sub>3</sub>**  
   AuCl<sub>3</sub>  
     Fluorination: 2.11.4.3  
     Formation: 2.8.2, 2.8.3.1.1, 2.8.3.1.2  
     Reaction with Au(CO)Cl: 2.8.8.1  
     Reaction with PCl<sub>5</sub>: 2.8.4.1  
     Reaction with F<sub>2</sub>: 2.8.3.1.5  
     Reaction with BrF<sub>3</sub>: 2.8.3.1.5  
     Reaction with KI: 2.8.3.1.5  
     Reaction with HCl: 2.8.4.1  
     Reaction with arenes: 2.8.5  
     Reaction with but-2-yne: 2.8.5  
**AuCl<sub>3</sub>H<sub>3</sub>N**  
   AuCl<sub>3</sub>·NH<sub>3</sub>  
     Formation: 2.8.4.1  
**AuCl<sub>3</sub>N<sup>\*</sup>C<sub>5</sub>H<sub>5</sub>**  
**AuCl<sub>3</sub>N<sup>\*</sup>C<sub>7</sub>H<sub>5</sub>**  
**AuCl<sub>3</sub>P<sup>\*</sup>C<sub>6</sub>H<sub>15</sub>**  
**AuCl<sub>3</sub>P<sup>\*</sup>C<sub>18</sub>H<sub>15</sub>**  
**AuCl<sub>4</sub><sup>\*</sup>C<sub>24</sub>H<sub>20</sub>As**  
**AuCl<sub>4</sub>Cs**  
   Cs[AuCl<sub>4</sub>]  
     Formation: 2.8.4.1  
**AuCl<sub>4</sub>H<sub>4</sub>KO<sub>2</sub>**  
   K[AuCl<sub>4</sub>]·2 H<sub>2</sub>O  
     Formation: 2.8.4.1  
**AuCl<sub>4</sub>H<sub>4</sub>N**  
   [NH<sub>4</sub>][AuCl<sub>4</sub>]  
     Thermal decomposition: 2.8.4.1  
**AuCl<sub>4</sub>H<sub>4</sub>NaO<sub>2</sub>**  
   Na[AuCl<sub>4</sub>]·2 H<sub>2</sub>O  
     Formation: 2.8.4.1  
**AuCl<sub>4</sub>H<sub>9</sub>O<sub>4</sub>**  
   H[AuCl<sub>4</sub>]·4 H<sub>2</sub>O  
     Formation: 2.8.4.1  
     Reaction with SOCl<sub>2</sub>: 2.8.3.1.2  
     Reaction with N, N-dimethylacetamide: 2.8.4.1  
     Reaction with KI or [NH<sub>4</sub>]I: 2.8.4.1  
     Thermal decomposition: 2.8.3.1.1  
**AuCl<sub>4</sub>K**  
   K[AuCl<sub>4</sub>]  
     Reaction with (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>AsCl: 2.8.4.1  
     Thermal decomposition: 2.8.4.1  
**AuCl<sub>4</sub>N<sup>\*</sup>C<sub>5</sub>H<sub>6</sub>**  
**AuCl<sub>4</sub>N<sup>\*</sup>C<sub>8</sub>H<sub>20</sub>**  
**AuCl<sub>4</sub>N<sub>2</sub>O<sub>2</sub><sup>\*</sup>C<sub>8</sub>H<sub>19</sub>**  
**AuCl<sub>4</sub>Na**  
   Na[AuCl<sub>4</sub>]  
     Reaction with CsCl: 2.8.4.1  
**AuCl<sub>5</sub><sup>\*</sup>C<sub>24</sub>H<sub>15</sub>As**  
**AuCl<sub>6</sub>Cs<sub>2</sub><sup>\*</sup>Ag**  
**AuCl<sub>7</sub><sup>\*</sup>C<sub>24</sub>H<sub>15</sub>As**  
**AuCl<sub>7</sub>S**  
   [SCl<sub>3</sub>][AuCl<sub>4</sub>]  
     Formation: 2.8.4.1  
**AuCl<sub>7</sub>Se**  
   [SeCl<sub>3</sub>][AuCl<sub>4</sub>]  
     Formation: 2.8.4.1  
**AuCl<sub>7</sub>Te**  
   [TeCl<sub>3</sub>][AuCl<sub>4</sub>]  
     Formation: 2.8.4.1  
**AuCl<sub>8</sub>P**  
   [PCl<sub>4</sub>][AuCl<sub>4</sub>]  
     Formation: 2.8.4.1  
**AuCsF<sub>4</sub>**  
   Cs[AuF<sub>4</sub>]  
     Fluorination: 2.11.4.3  
**AuCsF<sub>6</sub>**  
   Cs[AuF<sub>6</sub>]  
     Formation: 2.8.2, 2.11.4.3  
**AuF**  
   AuF  
     Non-existence: 2.8.2  
**AuF<sub>3</sub>**  
   AuF<sub>3</sub>  
     Formation: 2.8.2, 2.8.3.1.1, 2.8.3.1.2,  
       2.8.3.1.3, 2.8.3.1.5, 2.11.4.3  
     Reaction with XeF-F<sub>2</sub>: 2.11.4.3  
**AuF<sub>4</sub><sup>\*</sup>Ag**  
**AuF<sub>4</sub>K**  
   K[AuF<sub>4</sub>]  
     Fluorination: 2.11.4.3  
**AuF<sub>4</sub>NO**  
   [NO][AuF<sub>4</sub>]  
     Fluorination: 2.11.4.3

- Formation: 2.8.4.1, 2.11.4.3
- AuF<sub>4</sub>NO<sub>2</sub>**  
 [NO]<sub>2</sub>[AuF<sub>4</sub>]  
 Formation: 2.8.4.1
- AuF<sub>5</sub>**  
 AuF<sub>5</sub>  
 Formation: 2.11.4.3  
 Formation from AuF<sub>6</sub><sup>-</sup>: 2.8.2
- AuF<sub>5</sub>\*C<sub>24</sub>H<sub>15</sub>As  
 AuF<sub>5</sub>P\*C<sub>24</sub>H<sub>15</sub>  
 AuF<sub>5</sub>S\*C<sub>10</sub>H<sub>8</sub>
- AuF<sub>6</sub>K**  
 K[AuF<sub>6</sub>]  
 Formation: 2.11.4.3
- AuF<sub>6</sub>NO**  
 [NO][AuF<sub>6</sub>]  
 Formation: 2.11.4.3
- AuF<sub>6</sub>No**  
 [NO][AuF<sub>6</sub>]  
 Formation: 2.11.4.3
- AuF<sub>6</sub>O<sub>2</sub>**  
 [O<sub>2</sub>][AuF<sub>6</sub>]  
 Formation: 2.8.2, 2.11.4.3  
 Reaction with IF<sub>5</sub>: 2.11.4.3  
 Thermal decomposition: 2.8.2, 2.11.4.3
- AuF<sub>7</sub>Kr**  
 [KrF][AuF<sub>6</sub>]  
 Formation: 2.8.2, 2.11.4.3  
 Pyrolysis: 2.11.4.3  
 Reaction with XeF<sub>2</sub>: 2.11.4.3  
 Reaction with ONF: 2.11.4.3  
 Thermal decomposition: 2.8.2
- AuF<sub>7</sub>Se**  
 AuF<sub>3</sub>\*SeF<sub>4</sub>  
 Formation: 2.11.4.3
- AuF<sub>9</sub>Xe<sub>2</sub>**  
 [Xe<sub>2</sub>F<sub>3</sub>][AuF<sub>6</sub>]  
 Formation: 2.11.4.3
- AuF<sub>11</sub>Xe**  
 [XeF<sub>5</sub>][AuF<sub>6</sub>]  
 Formation: 2.11.4.3
- AuF<sub>12</sub>I**  
 [IF<sub>6</sub>][AuF<sub>6</sub>]  
 Formation: 2.11.4.3
- AuF<sub>17</sub>Xe<sub>2</sub>**  
 [Xe<sub>2</sub>F<sub>11</sub>][AuF<sub>6</sub>]  
 Formation: 2.8.2, 2.11.4.3  
 Heating: 2.11.4.3  
 Reaction with CsF, KF, or NOF: 2.11.4.3
- AuI**  
 AuI  
 Formation: 2.8.2
- Formation from Au: 2.8.11.1  
 Formation from H[AuCl<sub>4</sub>]: 2.8.11.2  
 Reaction with F<sub>2</sub>: 2.8.3.1.3
- AuI\*C<sub>10</sub>H<sub>16</sub>As<sub>4</sub>  
 AuI\*C<sub>18</sub>H<sub>15</sub>As  
 AuIP\*C<sub>6</sub>H<sub>15</sub>
- AuITe**  
 AuTeI  
 Formation: 2.9.14.1.2
- AuITe<sub>2</sub>**  
 AuTe<sub>2</sub>I  
 Formation: 2.9.14.1.2
- AuI<sub>2</sub>\*C<sub>26</sub>H<sub>26</sub>As  
 AuI<sub>2</sub>KN<sub>2</sub>\*C<sub>2</sub>  
 AuI<sub>2</sub>N\*C<sub>8</sub>H<sub>20</sub>  
 AuI<sub>2</sub>N\*C<sub>16</sub>H<sub>36</sub>
- AuI<sub>3</sub>**  
 AuI<sub>3</sub>  
 Non-existence: 2.8.2  
 Non-formation: 2.8.3.1.5
- AuI<sub>3</sub>\*C<sub>10</sub>H<sub>16</sub>As<sub>2</sub>  
 AuI<sub>3</sub>\*C<sub>18</sub>H<sub>15</sub>As  
 AuI<sub>3</sub>N\*C<sub>22</sub>H<sub>41</sub>  
 AuI<sub>3</sub>P\*C<sub>6</sub>H<sub>15</sub>  
 AuI<sub>4</sub>N\*C<sub>8</sub>H<sub>20</sub>  
 AuKN<sub>2</sub>\*C<sub>2</sub>  
 AuKN<sub>4</sub>\*C<sub>4</sub>  
 AuN\*C  
 AuNO\*C<sub>19</sub>H<sub>15</sub>As  
 AuNOP\*C<sub>19</sub>H<sub>15</sub>  
 AuNS<sub>2</sub>\*C<sub>5</sub>H<sub>10</sub>  
 AuNS<sub>2</sub>\*C<sub>6</sub>H<sub>18</sub>  
 AuN<sub>2</sub>O<sub>2</sub>\*C<sub>26</sub>H<sub>20</sub>As  
 AuN<sub>3</sub>S<sub>2</sub>Se<sub>2</sub>\*C<sub>7</sub>H<sub>10</sub>  
 AuN<sub>3</sub>S<sub>4</sub>\*C<sub>7</sub>H<sub>10</sub>  
 AuO<sub>2</sub>\*C<sub>7</sub>H<sub>13</sub>  
 AuP\*C<sub>24</sub>H<sub>20</sub>
- Au<sub>2</sub>BaCl<sub>8</sub>**  
 Ba[AuCl<sub>4</sub>]<sub>2</sub>  
 Reaction with F<sub>2</sub>: 2.8.4.1
- Au<sub>2</sub>BaF<sub>8</sub>**  
 Ba[AuF<sub>4</sub>]<sub>2</sub>  
 Formation: 2.8.4.1
- Au<sub>2</sub>Br<sub>2</sub>\*C<sub>4</sub>H<sub>12</sub>  
 Au<sub>2</sub>Br<sub>2</sub>\*C<sub>8</sub>H<sub>20</sub>  
 Au<sub>2</sub>Br<sub>2</sub>\*C<sub>10</sub>H<sub>20</sub>  
 Au<sub>2</sub>Br<sub>2</sub>\*C<sub>12</sub>H<sub>28</sub>  
 Au<sub>2</sub>Br<sub>2</sub>\*C<sub>20</sub>H<sub>44</sub>  
 Au<sub>2</sub>Br<sub>2</sub>F<sub>20</sub>\*C<sub>24</sub>  
 Au<sub>2</sub>Br<sub>2</sub>N<sub>2</sub>S<sub>4</sub>\*C<sub>10</sub>H<sub>20</sub>  
 Au<sub>2</sub>Br<sub>4</sub>\*C<sub>2</sub>H<sub>6</sub>  
 Au<sub>2</sub>Br<sub>4</sub>Cl<sub>2</sub>P<sub>2</sub>\*C<sub>25</sub>H<sub>22</sub>

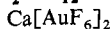
**Au<sub>2</sub>Br<sub>6</sub>Rb<sub>2</sub>**

Formation and thermal decomposition:

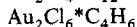
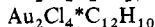
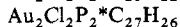
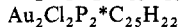
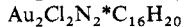
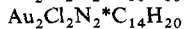
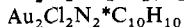
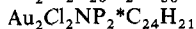
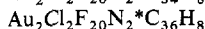
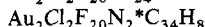
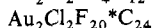
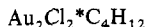
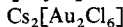
2.8.4.1

**Au<sub>2</sub>Br<sub>11</sub>Cs<sub>3</sub>**

Formation and decomposition: 2.8.4.1

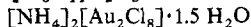
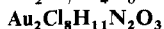
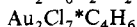
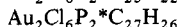
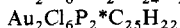
**Au<sub>2</sub>CaF<sub>12</sub>**

Formation: 2.8.2

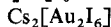
**Au<sub>2</sub>Cl<sub>6</sub>Cs<sub>2</sub>**

Effect of pressure: 2.8.4.1

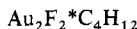
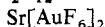
Formation: 2.8.4.1



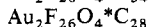
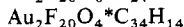
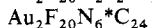
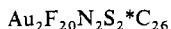
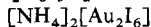
Formation: 2.8.4.1

**Au<sub>2</sub>Cs<sub>2</sub>I<sub>6</sub>**

Formation: 2.8.4.1

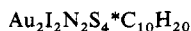
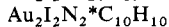
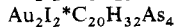
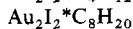
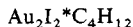
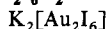
**Au<sub>2</sub>F<sub>12</sub>Sr**

Formation: 2.8.2

**Au<sub>2</sub>H<sub>8</sub>I<sub>6</sub>N<sub>2</sub>**

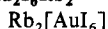
Formation: 2.8.4.1

Thermal decomposition: 2.8.4.1

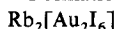
**Au<sub>2</sub>I<sub>6</sub>K<sub>2</sub>**

Formation: 2.8.4.1

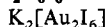
Structure: 2.8.4.1

**Au<sub>2</sub>I<sub>6</sub>Rb<sub>2</sub>**

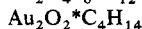
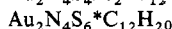
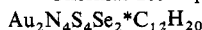
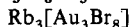
Formation: 2.8.4.1



Thermal decomposition: 2.8.4.1

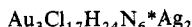
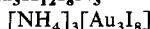
**Au<sub>2</sub>K<sub>6</sub>I<sub>6</sub>**

Thermal decomposition: 2.8.4.1

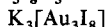
**Au<sub>2</sub>O<sub>3</sub>**Reaction with AsBr<sub>3</sub>: 2.8.3.1.4**Au<sub>3</sub>Br<sub>6</sub>Rb<sub>3</sub>**

Formation and thermal decomposition:

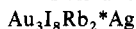
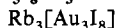
2.8.4.1

**Au<sub>3</sub>H<sub>12</sub>I<sub>8</sub>N<sub>3</sub>**

Formation: 2.8.4.1

**Au<sub>3</sub>I<sub>8</sub>K<sub>3</sub>**

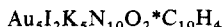
Formation: 2.8.4.1

**Au<sub>3</sub>I<sub>8</sub>Rb<sub>3</sub>**

Formation: 2.8.4.1

**Au<sub>4</sub>Cl<sub>8</sub>**

Formation: 2.8.8.1

**B****B**

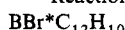
Reaction with AgX, CuX: 2.6.3.3

Reaction with PCl<sub>3</sub>: 2.6.3.3

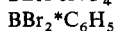
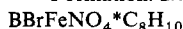
Reaction with RX: 2.6.3.2

Reaction with GeCl<sub>4</sub>: 2.6.3.3Reaction with C<sub>6</sub>H<sub>6</sub>-Br<sub>2</sub>: 2.6.16

Reaction with HX: 2.6.3.1

**BBrCl<sub>2</sub>**

Formation: 2.6.15



**BBr<sub>2</sub>Cl**

Formation: 2.6.15

**BBr<sub>3</sub>**

Formation: 2.6.3.1, 2.6.3.2, 2.6.5.1, 2.6.6.2, 2.6.7.1, 2.6.10.1, 2.6.12.2, 2.6.13.1

Halogenation agent: 2.9.12.5

Metathesis: 2.6.12.1

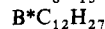
Reaction with BX<sub>3</sub>, R<sub>3</sub>B: 2.6.15Reaction with [B(SH)S]<sub>3</sub>: 2.6.7.3Reaction with B<sub>6</sub>H<sub>10</sub>, B<sub>2</sub>H<sub>6</sub>: 2.6.5.3Reaction with CdCl<sub>2</sub>: 2.8.18

Reaction with HgO: 2.8.20.1, 2.8.15.3

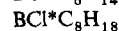
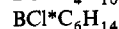
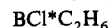
Reaction with MX: 2.7.9

Reaction with (RSB)<sub>2</sub>S<sub>3</sub>: 2.6.7.3Reaction with (R<sub>2</sub>N)<sub>3</sub>B, (R<sub>2</sub>N)<sub>3</sub>Al:

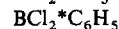
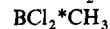
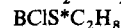
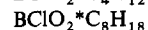
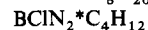
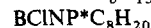
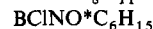
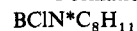
2.6.8.3

Reaction with M<sub>2</sub>O<sub>3</sub>: 2.6.6.4Reaction with AlX<sub>3</sub>, SnX<sub>4</sub>, TiX<sub>4</sub>, CoX<sub>2</sub>,CuX<sub>2</sub>: 2.6.12.2**BCl**

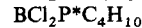
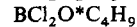
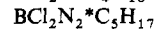
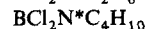
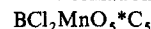
Formation: 2.6.14.1



Formation: 2.6.16



Formation: 2.6.16

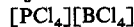
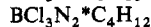
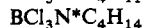
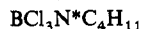
**BCl<sub>3</sub>**

Formation: 2.6.3.1, 2.6.3.3, 2.6.5.1, 2.6.6.2, 2.6.6.4, 2.6.7.2, 2.6.13.1, 2.6.13.2

Metathesis: 2.6.12.1

Reaction with AlH<sub>3</sub>: 2.6.5.3Reaction with BX<sub>3</sub>, R<sub>3</sub>B: 2.6.15Reaction with (R<sub>2</sub>N)<sub>3</sub>B: 2.6.8.3Reaction with (R<sub>2</sub>N)<sub>3</sub>B, (R<sub>2</sub>N)<sub>3</sub>Al: 2.6.8.3Reaction with [B(SH)S]<sub>3</sub>: 2.6.7.3Reaction with M<sub>2</sub>O<sub>3</sub>: 2.6.6.4Reaction with R<sub>2</sub>Hg: 2.6.15Reaction with (ROBO)<sub>3</sub>: 2.6.6.4Reaction with R<sub>3</sub>B: 2.6.16Reaction with (R<sub>2</sub>NBNH)<sub>3</sub>: 2.6.8.3

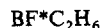
Reaction with ZnO: 2.8.15.3

Reaction with C<sub>6</sub>F<sub>6</sub>: 2.6.16Reaction with CaF<sub>2</sub>: 2.6.12.2Reaction with C<sub>6</sub>H<sub>6</sub>: 2.6.16

Formation: 2.6.9.1

**BF**

Formation: 2.6.8.1, 2.6.14.1



Formation: 2.6.8.1



Fluorinating agent: 2.6.12.3, 2.9.13

Formation: 2.6.6.3, 2.6.8.1, 2.6.12.3

Metathesis: 2.6.12.1

Reaction with LiAl[N(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>: 2.6.8.3Reaction with AlX<sub>3</sub>: 2.6.12.2Reaction with BX<sub>3</sub>, R<sub>3</sub>B: 2.6.15Reaction with (R<sub>2</sub>N)<sub>3</sub>B, (R<sub>2</sub>N)<sub>3</sub>Al: 2.6.8.3Reaction with ClF<sub>3</sub>: 2.6.15

Reaction with KX: 2.6.12.2



Formation: 2.6.8.2

Reaction with AlX<sub>3</sub>: 2.6.12.2

**BF<sub>4</sub>NO**[NO][BF<sub>4</sub>]

Formation: 2.6.16

BF<sub>4</sub>N<sub>3</sub>S\*C<sub>6</sub>H<sub>18</sub>BF<sub>9</sub>S<sub>3</sub>\*C<sub>3</sub>BFe<sub>2</sub>NO<sub>6</sub>S<sub>2</sub>\*C<sub>8</sub>H<sub>6</sub>**BH<sub>4</sub>K**K[BH<sub>4</sub>]Reaction with X<sub>2</sub>: 2.6.5.1**BH<sub>4</sub>Li**Li[BH<sub>4</sub>]Reaction with X<sub>2</sub>: 2.6.5.1

Thermal stability: 2.6.5.1

BIN<sub>2</sub>\*C<sub>4</sub>H<sub>12</sub>BIN<sub>2</sub>P\*C<sub>9</sub>H<sub>25</sub>BI<sub>2</sub>N\*C<sub>4</sub>H<sub>10</sub>**BI<sub>3</sub>**BI<sub>3</sub>

Formation: 2.6.3.1, 2.6.5.1

Reaction with B<sub>2</sub>Cl<sub>4</sub>: 2.6.12.2Reaction with B<sub>6</sub>H<sub>10</sub>, B<sub>2</sub>H<sub>6</sub>: 2.6.5.3Reaction with M<sub>2</sub>O<sub>3</sub>: 2.6.6.4BLiSi<sub>4</sub>\*C<sub>12</sub>H<sub>36</sub>BMnN<sub>2</sub>O<sub>5</sub>\*C<sub>9</sub>H<sub>12</sub>BMnO<sub>4</sub>P\*C<sub>34</sub>H<sub>25</sub>BMoO<sub>3</sub>\*C<sub>20</sub>H<sub>15</sub>**BN**

BN

Reaction with X<sub>2</sub>: 2.6.8.1

Reaction with HF: 2.6.8.2

BNP<sub>2</sub>\*C<sub>12</sub>H<sub>30</sub>BN<sub>2</sub>\*C<sub>6</sub>H<sub>18</sub>AsBN<sub>2</sub>P\*C<sub>8</sub>H<sub>22</sub>BN<sub>2</sub>Si\*C<sub>7</sub>H<sub>21</sub>BN<sub>2</sub>Sn\*C<sub>10</sub>H<sub>27</sub>BN<sub>2</sub>Tl\*C<sub>6</sub>H<sub>18</sub>BN<sub>3</sub>\*C<sub>6</sub>H<sub>18</sub>BN<sub>3</sub>\*C<sub>12</sub>H<sub>30</sub>**BO**

BO

Reaction with SF<sub>4</sub>: 2.6.6.4BO<sub>3</sub>\*C<sub>3</sub>H<sub>9</sub>BO<sub>3</sub>\*C<sub>12</sub>H<sub>27</sub>**BP**

BP

Reaction with X<sub>2</sub>: 2.6.9.1BS\*C<sub>2</sub>H<sub>9</sub>BS\*C<sub>3</sub>H<sub>9</sub>BSe<sub>3</sub>\*C<sub>18</sub>H<sub>15</sub>**B<sub>2</sub>BrH<sub>5</sub>**B<sub>2</sub>H<sub>5</sub>Br

Formation: 2.6.5.2, 2.6.5.3

**B<sub>2</sub>Br<sub>4</sub>**B<sub>2</sub>Br<sub>4</sub>

Formation: 2.6.14.1

B<sub>2</sub>Br<sub>4</sub>S<sub>2</sub>\*C<sub>2</sub>H<sub>6</sub>**B<sub>2</sub>Cl<sub>4</sub>**B<sub>2</sub>Cl<sub>4</sub>

Formation: 2.6.14.1

Reaction with BX<sub>3</sub>: 2.6.12.2Reaction with SbF<sub>3</sub>, TiF<sub>4</sub>: 2.6.14.1Reaction with X<sub>2</sub>: 2.6.13.1B<sub>2</sub>Cl<sub>4</sub>S<sub>2</sub>\*C<sub>2</sub>H<sub>6</sub>B<sub>2</sub>FFeIO<sub>3</sub>S\*C<sub>9</sub>H<sub>10</sub>**B<sub>2</sub>F<sub>2</sub>S<sub>3</sub>**(FB)<sub>2</sub>S<sub>3</sub>

Formation: 2.6.7.3

**B<sub>2</sub>F<sub>4</sub>**B<sub>2</sub>F<sub>4</sub>

Formation: 2.6.6.4, 2.6.14.1

B<sub>2</sub>FeI<sub>2</sub>O<sub>3</sub>S\*C<sub>9</sub>H<sub>10</sub>**B<sub>2</sub>H<sub>5</sub>I**B<sub>2</sub>H<sub>5</sub>I

Formation: 2.6.5.3

**B<sub>2</sub>H<sub>6</sub>**B<sub>2</sub>H<sub>6</sub>

Formation: 2.6.5.1

Reaction with X<sub>2</sub>: 2.6.5.1

Reaction with HX: 2.6.5.2

**B<sub>2</sub>Hf**HfB<sub>2</sub>

Fluorination: 2.11.4.1

**B<sub>2</sub>I<sub>4</sub>**B<sub>2</sub>I<sub>4</sub>

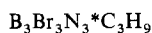
Formation: 2.6.12.2, 2.6.14.1

B<sub>2</sub>N<sub>2</sub>\*C<sub>16</sub>H<sub>22</sub>**B<sub>2</sub>O<sub>3</sub>**B<sub>2</sub>O<sub>3</sub>Reaction with SF<sub>4</sub>: 2.6.6.4Reaction with PX<sub>5</sub>: 2.6.6.4Reaction with BrF<sub>3</sub>: 2.6.6.4Reaction with CCl<sub>4</sub>: 2.6.6.4B<sub>2</sub>O<sub>4</sub>\*C<sub>4</sub>H<sub>12</sub>B<sub>2</sub>O<sub>4</sub>\*C<sub>8</sub>H<sub>20</sub>**B<sub>2</sub>S<sub>3</sub>**B<sub>2</sub>S<sub>3</sub>Reaction with VCl<sub>5</sub>, NbCl<sub>5</sub>, ReF<sub>6</sub>, WF<sub>6</sub>:  
2.9.14.4Reaction with WCl<sub>6</sub>, NbCl<sub>5</sub>, MoCl<sub>5</sub>:  
2.6.7.3Reaction with X<sub>2</sub>: 2.6.7.1

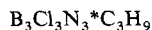
Reaction with HX: 2.6.7.2

B<sub>2</sub>S<sub>5</sub>\*C<sub>4</sub>H<sub>10</sub>**B<sub>2</sub>Se<sub>3</sub>**B<sub>2</sub>Se<sub>3</sub>

Reaction with HX: 2.6.7.2



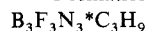
Formation: 2.6.7.3



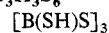
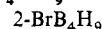
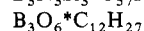
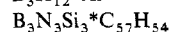
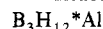
Formation: 2.6.6.4



Formation: 2.6.7.3



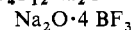
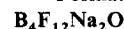
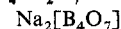
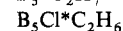
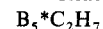
Formation: 2.6.14.1

Reaction with  $\text{BX}_3$ : 2.6.7.3

Formation: 2.6.5.1



Formation: 2.6.14.1

Reaction with  $\text{H}_2\text{SO}_4$ : 2.6.6.3Reaction with  $\text{HX}$ : 2.6.5.2Reaction with  $\text{HF}$ : 2.6.6.4Reaction with  $\text{HX}$ : 2.6.6.3

Formation: 2.6.5.3



Formation: 2.6.5.3

Reaction with  $\text{BX}_3$ : 2.6.5.3

Formation: 2.6.14.1



Formation: 2.6.12.2, 2.6.14.1



Formation: 2.6.14.1



Formation: 2.6.14.1



Formation: 2.6.14.1



Formation: 2.6.12.2, 2.6.14.1



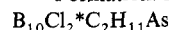
Formation: 2.6.14.1



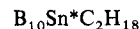
Formation: 2.6.14.1



Formation: 2.6.14.1



Formation: 2.6.14.1

Reaction with  $\text{X}_2$ : 2.6.5.1

Formation: 2.6.14.1



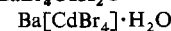
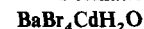
Formation: 2.6.14.1



Formation: 2.6.14.1

Reaction with  $\text{X}_2$ : 2.7.2Reaction with  $\text{HX}$ : 2.7.3.1

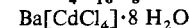
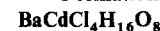
Formation: 2.7.2



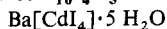
Formation: 2.8.22



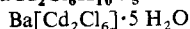
Formation: 2.8.22



Formation: 2.8.22

**BaCdH<sub>10</sub>I<sub>4</sub>O<sub>5</sub>**

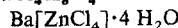
Formation: 2.8.22

**BaCd<sub>2</sub>Cl<sub>6</sub>H<sub>10</sub>O<sub>5</sub>**

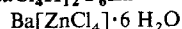
Formation: 2.8.22

**BaCl<sub>2</sub>**

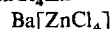
Formation: 2.7.2

**BaCl<sub>4</sub>H<sub>8</sub>O<sub>4</sub>Zn**

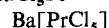
Formation: 2.8.22

**BaCl<sub>4</sub>H<sub>12</sub>O<sub>6</sub>Zn**

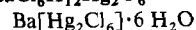
Formation: 2.8.22

**BaCl<sub>4</sub>Zn**

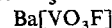
Formation: 2.8.22

**BaCl<sub>5</sub>Pr**

Fluorination: 2.11.5.1

**BaCl<sub>6</sub>H<sub>12</sub>Hg<sub>2</sub>O<sub>6</sub>**

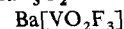
Formation: 2.8.22

**BaCl<sub>8</sub>\*Au<sub>2</sub>****BaFO<sub>3</sub>V**

Formation: 2.11.2.1

**BaF<sub>2</sub>**

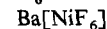
Formation: 2.7.2, 2.7.5

**BaF<sub>3</sub>O<sub>2</sub>V**

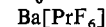
Reaction with KOH: 2.11.2.1

**BaF<sub>4</sub>\*Ag****BaF<sub>5</sub>\*Ag****BaF<sub>5</sub>Ni**

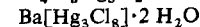
Formation: 2.11.2.2

**BaF<sub>6</sub>Ni**

Formation: 2.11.2.2

**BaF<sub>6</sub>Pr**

Formation: 2.11.5.1

**BaF<sub>8</sub>\*Au<sub>2</sub>****BaH<sub>2</sub>**Reaction with [NH<sub>4</sub>]X: 2.7.9**BaH<sub>4</sub>Cl<sub>8</sub>Hg<sub>3</sub>O<sub>2</sub>**

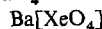
Formation: 2.8.22

**BaI<sub>2</sub>**

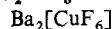
Formation: 2.7.2

Reaction with Zn[SO<sub>4</sub>]: 2.8.17.2**BaN<sub>4</sub>Ni\*C<sub>4</sub>****BaN<sub>4</sub>NiO<sub>4</sub>\*C<sub>4</sub>H<sub>8</sub>****BaO**

Reaction with HX: 2.7.5

**BaO<sub>4</sub>S**Formation from BaI<sub>2</sub> and Zn[SO<sub>4</sub>]:  
2.8.17.2**BaO<sub>4</sub>Xe**

Formation: 2.10.2.2.2

**Ba<sub>2</sub>CuF<sub>6</sub>**

Formation: 2.8.10

**Ba<sub>2</sub>F<sub>6</sub>\*Ag****Be**

Safety: 2.7.1

**BeBr<sub>2</sub>**

Formation: 2.7.2, 2.7.6, 2.7.8

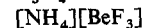
Formation R<sub>2</sub>Be: 2.7.3.2.2**Be\*C<sub>4</sub>H<sub>10</sub>****Be\*C<sub>10</sub>H<sub>22</sub>****BeCl\*CH<sub>3</sub>****BeCl<sub>2</sub>**

Formation: 2.7.2, 2.7.3.1, 2.7.6

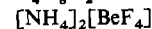
Safety: 2.7.1

**BeF<sub>2</sub>**

Formation: 2.7.5

**BeF<sub>3</sub>H<sub>4</sub>N**

Formation: 2.7.5

**BeF<sub>4</sub>H<sub>8</sub>N<sub>2</sub>**

Formation: 2.7.5

**BeH<sub>2</sub>O<sub>2</sub>**

Reaction with HX: 2.7.5

**BeI<sub>2</sub>**

Formation: 2.7.2, 2.7.3.1, 2.7.8

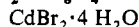
Reaction with SiO<sub>2</sub>: 2.7.2**BeO**Reaction with X<sub>2</sub>: 2.7.6



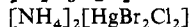
- Reaction with  $X_2-C$ : 2.7.6  
 Reaction with  $HX$ : 2.7.5  
**Be<sub>2</sub>\*C**  
**Be<sub>2</sub>F<sub>5</sub>H<sub>8</sub>N<sub>2</sub>**  
 [NH<sub>4</sub>]<sub>2</sub>[Be<sub>2</sub>F<sub>5</sub>]  
 Formation: 2.7.5  
**BiF<sub>3</sub>**  
 BiF<sub>3</sub>  
 Reaction with Cr: 2.9.3.6  
**Bi<sub>2</sub>O<sub>3</sub>**  
 Bi<sub>2</sub>O<sub>3</sub>  
 Reaction with TiCl<sub>4</sub>, VOCl<sub>3</sub>: 2.9.12.7  
**Bk**  
 Bk  
 Fluorination: 2.11.5.2  
**BkF<sub>4</sub>**  
 BkF<sub>4</sub>  
 Formation: 2.11.5.2  
**Br\*Ag**  
**Br\*Al**  
**Br\*Au**  
**Br\*C<sub>4</sub>H<sub>10</sub>Al**  
**Br\*C<sub>6</sub>H<sub>5</sub>**  
**Br\*C<sub>12</sub>H<sub>10</sub>B**  
**BrCdCl<sub>2</sub>N\*C<sub>12</sub>H<sub>28</sub>**  
**BrCdHO**  
 CdOHBr  
 Formation of: 2.8.14.1  
**BrCdI<sub>2</sub>N\*C<sub>12</sub>H<sub>28</sub>**  
**BrCeS**  
 CeSBr  
 Formation: 2.9.14.1.1  
**BrClCu**  
 CuBrCl  
 Formation: 2.8.8.1  
**BrClF<sub>2</sub>\*C**  
**BrClHg**  
 HgClBr  
 Formation from Hg<sub>2</sub>Cl<sub>2</sub> and Br<sub>2</sub>:  
 2.8.20.1  
**BrClN<sub>3</sub>\*C<sub>6</sub>H<sub>12</sub>Au**  
**BrCl<sub>2</sub>\*B**  
**BrCl<sub>2</sub>H<sub>4</sub>HgN**  
 [NH<sub>4</sub>][HgBrCl<sub>2</sub>]  
 Formation: 2.8.22  
**BrCl<sub>2</sub>Hg\*C<sub>7</sub>H<sub>5</sub>**  
**BrCl<sub>2</sub>P\*C<sub>6</sub>H<sub>15</sub>Au**  
**BrCl<sub>2</sub>P\*C<sub>18</sub>H<sub>15</sub>Au**  
**BrCl<sub>3</sub>CuN<sub>2</sub>\*C<sub>2</sub>H<sub>12</sub>**  
**BrCl<sub>4</sub>MoO**  
 [MoOBrCl<sub>4</sub>]<sup>2-</sup>  
 Formation: 2.9.13.4  
**BrCrS**  
 CrSBr  
 Formation: 2.9.14.2  
**BrCs**  
 CsBr  
 Formation: 2.7.3.1  
**BrCu**  
 CuBr  
 Electrochemical formation: 2.8.11.1  
 Formation: 2.8.2, 2.8.7.3, 2.9.8.  
 Formation from Cu[OAc]<sub>2</sub>: 2.8.11.2  
 Formation from CuBr<sub>2</sub>: 2.8.11.2  
 Formation from the metal: 2.8.11.1  
 Reaction with Cd: 2.8.14.5  
 Reaction with HgBr<sub>2</sub>: 2.8.21.2  
 Reaction with X<sub>2</sub>: 2.8.8.1  
 Reaction with Zn: 2.8.14.5  
 Reaction with elemental Te, Se: 2.9.14.3  
**BrCuIN\*C<sub>5</sub>H<sub>6</sub>**  
**BrCuSe<sub>3</sub>**  
 CuSe<sub>3</sub>Br  
 Formation: 2.9.14.3  
**BrDyS**  
 DySBr  
 Formation: 2.9.14.1.1  
**BrErS**  
 ErSBr  
 Formation: 2.9.14.1.1  
**BrFHg**  
 HgBrF  
 Formation from Hg<sub>2</sub>F<sub>2</sub> and Br<sub>2</sub>:  
 2.8.20.1  
**BrF<sub>3</sub>**  
 BrF<sub>3</sub>  
 Fluorinating agent: 2.6.12.3  
 Reaction with Au: 2.8.3.1.2  
 Reaction with M<sub>2</sub>O<sub>3</sub>: 2.6.6.4  
 Reaction with WO<sub>3</sub>, MoO<sub>3</sub>: 2.9.4.4  
 Reaction with transition-metals: 2.9.3.4  
**BrF<sub>5</sub>**  
 BrF<sub>5</sub>  
 Formation: 2.10.2.2.2  
**BrF<sub>5</sub>N\*C<sub>22</sub>H<sub>36</sub>Au**  
**BrF<sub>6</sub>\*Au**  
**BrF<sub>10</sub>Ru**  
 RuF<sub>5</sub>\*BrF<sub>5</sub>  
 Formation: 2.9.12.3  
**BrF<sub>10</sub>Tl\*C<sub>12</sub>**  
**BrF<sub>15</sub>N\*C<sub>34</sub>H<sub>36</sub>Au**  
**BrFeNO<sub>4</sub>\*C<sub>8</sub>H<sub>10</sub>B**  
**BrFeP\*C<sub>22</sub>H<sub>19</sub>Au**  
**BrGdS**  
 GdSBr  
 Formation: 2.9.14.1.1

- BrGe\*CH<sub>5</sub>**  
**BrGe\*C<sub>6</sub>H<sub>15</sub>**  
**BrGeH<sub>3</sub>**  
   H<sub>3</sub>GeBr  
     Reaction with Li[Al(AsH<sub>2</sub>)<sub>4</sub>]: 2.6.9.3  
     Reaction with Li[Al(PH<sub>2</sub>)<sub>4</sub>]: 2.6.9.3  
**BrGe<sub>2</sub>H<sub>5</sub>**  
   Ge<sub>2</sub>H<sub>5</sub>Br  
     Reaction with Li[Al(AsH<sub>2</sub>)<sub>4</sub>]: 2.6.9.3  
**BrH**  
   HBr  
     Metathesis: 2.6.12.1  
     Reaction with Group IIIB–Group IVB bonds: 2.6.11.2  
     Reaction with B, Al, Ga, In Tl: 2.6.3.1  
     Reaction with [B<sub>3</sub>H<sub>3</sub>]<sup>−</sup>: 2.6.4.2  
     Reaction with CdCO<sub>3</sub>: 2.8.17.1  
     Reaction with H<sub>3</sub>Ga·NR<sub>3</sub>: 2.6.5.2  
     Reaction with Hg: 2.8.14.2, 2.8.14.3  
     Reaction with HgO: 2.8.15.2  
     Reaction with MO, MOH, MCO<sub>3</sub>: 2.7.5  
     Reaction with M<sub>2</sub>O<sub>3</sub>: 2.6.6.3  
     Reaction with R<sub>3</sub>B ... R<sub>3</sub>Tl: 2.6.10.2  
     Reaction with Zn: 2.8.14.1  
     Reaction with ZnO: 2.8.15.2  
     Reaction with group-IA and group-IIA metals: 2.7.3.1  
     Reaction with transition-metal oxides: 2.9.4.3  
     Reaction with transition-metals: 2.9.3.2, 2.9.14.1.1  
     Use as reducing agent: 2.9.13.2  
**BrHHgl<sub>2</sub>**  
   HHgBrI<sub>2</sub>  
     Formation: 2.8.22  
**BrHO**  
   HOBr  
     Formation from Hg[NO<sub>3</sub>]<sub>2</sub> and Br<sub>2</sub>: 2.8.17.3  
**BrH<sub>2</sub>\*Al**  
**BrH<sub>3</sub>Si**  
   H<sub>3</sub>SiBr  
     Reaction with Li[Al(AsH<sub>2</sub>)<sub>4</sub>]: 2.6.9.3  
     Reaction with Li[Al(PH<sub>2</sub>)<sub>4</sub>]: 2.6.9.3  
     Reaction with LiAl[N(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>: 2.6.8.3  
**BrH<sub>4</sub>N**  
   NH<sub>4</sub>Br  
     Reaction with Mg: 2.7.3.2.1  
**BrH<sub>5</sub>\*B<sub>2</sub>**  
**BrH<sub>5</sub>Si<sub>2</sub>**  
   Si<sub>2</sub>H<sub>5</sub>Br  
     Reaction with Li[Al(AsH<sub>2</sub>)<sub>4</sub>]: 2.6.9.3  
**BrH<sub>9</sub>\*B<sub>4</sub>**  
**BrH<sub>9</sub>\*B<sub>6</sub>**  
**BrHg\*C<sub>6</sub>H<sub>5</sub>**  
**BrHgl**  
   HglBr  
     Formation from Hg<sub>2</sub>Br<sub>2</sub> and I<sub>2</sub>: 2.8.20.1  
**BrHgIN\*CH<sub>6</sub>**  
**BrHoS**  
   HoSBr  
     Formation: 2.9.14.1.1  
**BrI**  
   IBr  
     Formation from HgBr<sub>2</sub> and ICl: 2.8.18  
     Reaction with Hg: 2.8.14.4  
**BrIn**  
   InBr  
     Formation: 2.6.14.1  
**BrInMn<sub>2</sub>O<sub>10</sub>\*C<sub>10</sub>**  
**BrK**  
   KBr  
     Reaction with Hg[NO<sub>3</sub>]<sub>2</sub>: 2.8.17.2  
     Reaction with Hg<sub>2</sub>[NO<sub>3</sub>]<sub>2</sub>: 2.8.21.1  
     Reaction with Hg<sub>2</sub>Cl<sub>2</sub>: 2.8.21.1  
**BrKN<sub>3</sub>\*C<sub>3</sub>Au**  
**BrLaS**  
   LaSBr  
     Formation: 2.9.14.1.1  
**BrLuS**  
   LuSBr  
     Formation: 2.9.14.1.1  
**BrMg\*C<sub>4</sub>H<sub>3</sub>**  
**BrMnO<sub>5</sub>\*C<sub>5</sub>**  
**BrMoS**  
   MoSBr  
     Formation: 2.9.14.1.2  
**BrNO**  
   ONBr  
     Reaction with Mo(CO)<sub>6</sub>, W(CO)<sub>6</sub>: 2.9.15.1.2  
**BrNa**  
   NaBr  
     Reaction with HgSO<sub>4</sub>: 2.8.17.2  
**BrNdS**  
   NdSBr  
     Formation: 2.9.14.1.1  
**BrO\*C<sub>2</sub>H<sub>3</sub>**  
**BrO<sub>5</sub>Re\*C<sub>5</sub>**  
**BrO<sub>5</sub>Tc\*C<sub>5</sub>**  
**BrP\*C<sub>3</sub>H<sub>9</sub>Au**  
**BrP\*C<sub>6</sub>H<sub>15</sub>Au**  
**BrP\*C<sub>8</sub>H<sub>11</sub>Au**  
**BrP\*C<sub>18</sub>H<sub>15</sub>Au**

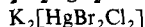
- BrP\*** $C_{20}H_{17}Au$   
**BrP\*** $C_{21}H_{19}Au$   
**BrPrS**  
     **PrSBr**  
         Formation: 2.9.14.1.1  
**BrS\*Al**  
**BrS\*Au**  
**BrS\*** $C_{14}H_{14}Au$   
**BrSSm**  
     **SmSBr**  
         Formation: 2.9.14.1.1  
**BrSTb**  
     **TbSBr**  
         Formation: 2.9.14.1.1  
**BrSY**  
     **YSBr**  
         Formation: 2.9.14.1.1  
**BrSYb**  
     **YbSBr**  
         Formation: 2.9.14.1.1  
**BrSe\*Al**  
**BrSi\*CH<sub>5</sub>**  
**BrSi\*** $C_{18}H_{15}$   
**BrSi<sub>3</sub>Sn\*** $C_{12}H_{33}$   
**BrSn\*** $C_3H_9$   
**BrSn\*** $C_6H_{15}$   
**BrTe\*Al**  
**BrTe<sub>2</sub>\*Au**  
**BrTl**  
     **TlBr**  
         Formation: 2.6.13.3  
**BrTl\*** $C_2H_6$   
**BrTl\*** $C_4H_{10}$   
**Br<sub>2</sub>**  
     **Br<sub>2</sub>**  
         Formation from  $Hg_2Br_2$  and  $I_2$ : 2.8.20.1  
         Reaction with Al, Ga, In, Tl: 2.6.2.1  
         Reaction with  $(HBNR)_3$ : 2.6.5.1  
         Reaction with  $B_2X_4$ : 2.6.13.1  
         Reaction with  $B_{10}H_{14}$ : 2.6.5.1  
         Reaction with  $[B_{12}H_{12}]^{2-}$ : 2.6.4.1  
         Reaction with Cd: 2.8.14.1  
         Reaction with  $\eta^5$ -CpMoNO(CO)<sub>2</sub>:  
             2.9.15.1.2  
         Reaction with  $Fe(CO)_5$ ,  $Ru(CO)_5$ :  
             2.9.15.1.1  
         Reaction with Group IIIB–Group IVB  
         bonds: 2.6.11.1  
         Reaction with  $Hg[NO_3]_2$ : 2.8.17.3  
         Reaction with  $HgCl_2$ : 2.8.18  
         Reaction with Hg: 2.8.14.1  
         Reaction with  $HgO$ : 2.8.15.1  
         Reaction with  $HgS$ : 2.8.16.1  
         Reaction with  $Hg_2F_2$ : 2.8.20.1  
         Reaction with  $Hg_2Cl_2$ : 2.8.20.1  
         Reaction with  $Mn_2(CO)_{10}$ ,  $Tc_2(CO)_{10}$ :  
             2.9.15.1.1  
         Reaction with  $MoTe_2$ ,  $ReSe_2$ ,  $Re_2Te_5$ :  
             2.9.14.2  
         Reaction with  $M[BH_4]$ : 2.6.5.1  
         Reaction with MOH: 2.7.4  
         Reaction with  $M(CO)_6$ : 2.9.6  
         Reaction with MO: 2.7.6  
         Reaction with  $M_2S_3$ : 2.6.7.1  
         Reaction with  $M_2O_3$ : 2.6.6.2  
         Reaction with  $R_2BSH$ : 2.6.7.1  
         Reaction with  $R_3B \dots R_3Tl$ : 2.6.10.1  
         Reaction with  $U_3O_2S_4$ : 2.9.5  
         Reaction with Zn: 2.8.14.1  
         Reaction with group-IA and -IIA me-  
         tals: 2.7.2  
         Reaction with transition-metal oxides:  
             2.9.4.1  
         Reaction with transition-metals: 2.9.2.3  
**Br<sub>2</sub>\*Ba**  
**Br<sub>2</sub>\*Be**  
**Br<sub>2</sub>\*C**  
**Br<sub>2</sub>\*C<sub>3</sub>H<sub>9</sub>As**  
**Br<sub>2</sub>\*C<sub>4</sub>H<sub>12</sub>Au<sub>2</sub>**  
**Br<sub>2</sub>\*C<sub>6</sub>H<sub>5</sub>B**  
**Br<sub>2</sub>\*C<sub>8</sub>H<sub>20</sub>Au<sub>2</sub>**  
**Br<sub>2</sub>\*C<sub>10</sub>H<sub>20</sub>Au<sub>2</sub>**  
**Br<sub>2</sub>\*C<sub>12</sub>H<sub>28</sub>Au<sub>2</sub>**  
**Br<sub>2</sub>\*C<sub>20</sub>H<sub>44</sub>Au<sub>2</sub>**  
**Br<sub>2</sub>\*C<sub>26</sub>H<sub>26</sub>AsAu**  
**Br<sub>2</sub>Ca**  
     **CaBr<sub>2</sub>**  
         Formation: 2.7.2  
**Br<sub>2</sub>Cd**  
     **CdBr<sub>2</sub>**  
         Anhydrous: 2.8.19  
         Formation From Cd and CuBr: 2.8.14.5  
         Formation from  $Cd[OAc]_2$  and  $AcBr$ :  
             2.8.17.3  
         Formation from  $CdCO_3$  and  $HBr$ :  
             2.8.17.1  
         Formation from Cd and  $Br_2$ : 2.8.14.1  
         Formation from  $CdO$  and  $CF_2BrCl$ :  
             2.8.15.3  
         Formation from  $CdCl_2$  and  $BBr_3$ : 2.8.18  
         Reaction with  $(CH_3)_2Cd$ : 2.8.23.2  
**Br<sub>2</sub>CdClN\*** $C_{12}H_{28}$   
**Br<sub>2</sub>CdH<sub>2</sub>O**  
     **CdBr<sub>2</sub>·H<sub>2</sub>O**  
         Stability: 2.8.19

**Br<sub>2</sub>CdH<sub>8</sub>O<sub>4</sub>**

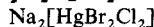
Stability: 2.8.19

**Br<sub>2</sub>CdIN·C<sub>12</sub>H<sub>28</sub>****Br<sub>2</sub>Cl\*B****Br<sub>2</sub>ClHg·C<sub>7</sub>H<sub>5</sub>****Br<sub>2</sub>ClP·C<sub>6</sub>H<sub>15</sub>Au****Br<sub>2</sub>ClP·C<sub>18</sub>H<sub>15</sub>Au****Br<sub>2</sub>Cl<sub>2</sub>H<sub>8</sub>HgN<sub>2</sub>**

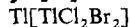
Formation: 2.8.22

**Br<sub>2</sub>Cl<sub>2</sub>HgK<sub>2</sub>**

Formation: 2.8.22

**Br<sub>2</sub>Cl<sub>2</sub>HgNa<sub>2</sub>**

Formation: 2.8.22

**Br<sub>2</sub>Cl<sub>2</sub>Tl<sub>2</sub>**

Formation: 2.6.16

**Br<sub>2</sub>Cl<sub>3</sub>Cs<sub>3</sub>Hg**

Formation: 2.8.22

**Br<sub>2</sub>Co**

Electrochemical formation: 2.9.3.7

Formation: 2.9.3.2, 2.9.7, 2.9.9.1

**Br<sub>2</sub>Cr**

Formation: 2.9.3.2, 2.9.7

**Br<sub>2</sub>CrO<sub>2</sub>**

Formation: 2.9.12.2

**Br<sub>2</sub>Cu**

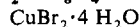
Fluorination: 2.11.2.3

Formation: 2.8.2, 2.8.7.1, 2.8.8.1, 2.8.8.2,

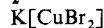
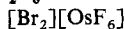
2.8.8.3, 2.8.9, 2.9.7

Formation from HgBr<sub>2</sub> and CuBr:

2.8.21.2

Reactions with F<sub>2</sub> and ClF<sub>3</sub>: 2.8.8.1**Br<sub>2</sub>CuH<sub>8</sub>O<sub>4</sub>**

Formation: 2.8.8.3

**Br<sub>2</sub>CuI<sub>2</sub>N<sub>4</sub>·C<sub>4</sub>H<sub>16</sub>Ag<sub>2</sub>****Br<sub>2</sub>CuK**Formation from Cu<sup>2+</sup>: 2.8.12**Br<sub>2</sub>CuN·C<sub>16</sub>H<sub>36</sub>****Br<sub>2</sub>CuP·C<sub>20</sub>H<sub>20</sub>****Br<sub>2</sub>CuP·C<sub>21</sub>H<sub>22</sub>****Br<sub>2</sub>CuP·C<sub>22</sub>H<sub>24</sub>****Br<sub>2</sub>CuP·C<sub>24</sub>H<sub>20</sub>****Br<sub>2</sub>F<sub>5</sub>·C<sub>24</sub>H<sub>15</sub>AsAu****Br<sub>2</sub>F<sub>5</sub>P·C<sub>24</sub>H<sub>15</sub>Au****Br<sub>2</sub>F<sub>5</sub>S·C<sub>10</sub>H<sub>8</sub>Au****Br<sub>2</sub>F<sub>6</sub>Os**

Formation: 2.11.4.2

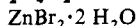
**Br<sub>2</sub>F<sub>10</sub>N·C<sub>28</sub>H<sub>36</sub>Au****Br<sub>2</sub>F<sub>20</sub>·C<sub>24</sub>Au<sub>2</sub>****Br<sub>2</sub>Fe**

Electrochemical formation: 2.9.3.7

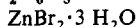
Formation: 2.9.2.3, 2.9.3.2, 2.9.3.8, 2.9.4.2

**Br<sub>2</sub>FeO<sub>4</sub>·C<sub>4</sub>****Br<sub>2</sub>Ga<sub>2</sub>**

Reaction with RX: 2.6.13.3

**Br<sub>2</sub>H\*Al****Br<sub>2</sub>H<sub>4</sub>O<sub>2</sub>Zn**

Stability: 2.8.19

**Br<sub>2</sub>H<sub>6</sub>O<sub>3</sub>Zn**

Stability: 2.8.19

**Br<sub>2</sub>Hg**Formation from Hg[NO<sub>3</sub>]<sub>2</sub> and KBr:

2.8.17.2

Formation from Hg[NO<sub>3</sub>]<sub>2</sub> and Br<sub>2</sub>:

2.8.17.3

Formation from HgCl<sub>2</sub> and Br<sub>2</sub>: 2.8.18Formation from Hg and PBr<sub>3</sub>: 2.8.14.4Formation from Hg and OSBr<sub>2</sub>: 2.8.14.4

Formation from Hg and IBr: 2.8.14.4

Formation from Hg and HBr: 2.8.14.2

Formation from Hg and Br<sub>2</sub>: 2.8.14.1,

2.8.14.3

Formation from HgO and BBr<sub>3</sub>:

2.8.15.3, 2.8.20.1

Formation from HgO and HBr: 2.8.15.2

Formation from HgO and Br<sub>2</sub>: 2.8.15.1Formation from HgS and Br<sub>2</sub>: 2.8.16.1Formation from Hg<sub>2</sub>F<sub>2</sub> and Br<sub>2</sub>:

2.8.20.1

Formation from Hg<sub>2</sub>Br<sub>2</sub>: 2.8.20.2Formation from Hg<sub>2</sub>Br<sub>2</sub> and SO<sub>3</sub>:

2.8.20.1

Formation from Hg<sub>2</sub>Cl<sub>2</sub> and Br<sub>2</sub>:

2.8.20.1

Formation from Hg[SO<sub>4</sub>] and NaBr:

2.8.17.2

Reaction with CuBr: 2.8.21.2

- Reaction with Hg: 2.8.21.2  
 Reaction with  $\text{LiC}_6\text{H}_4\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ :  
 2.8.23.2  
 Reaction with  $\text{R}_2\text{NBX}-\text{NR}'\text{BX}_2$ :  
 2.6.8.3  
 Reaction with ICl: 2.8.18  
 Reaction with  $\text{H}_2$ : 2.8.21.2  
 Reaction with  $\text{H}_2\text{S}$ : 2.8.21.2  
 **$\text{Br}_2\text{HgIN}^*\text{CH}_6$**   
 **$\text{Br}_2\text{HgI}_2\text{N}_2^*\text{C}_2\text{H}_{12}$**   
 **$\text{Br}_2\text{HgI}_2\text{Rb}_2$**   
 $\text{Rb}_2[\text{HgBr}_2\text{I}_2]$   
 Formation: 2.8.22  
 **$\text{Br}_2\text{HgO}_6$**   
 $\text{Hg}[\text{BrO}_3]_2$   
 Formation from  $\text{HgO}$  and  $\text{Br}_2$ : 2.8.15.1  
 **$\text{Br}_2\text{Hg}_2$**   
 $\text{Hg}_2\text{Br}_2$   
 Disproportionation: 2.8.20.2  
 Formation from  $\text{HgBr}_2$  and  $\text{CuBr}$ :  
 2.8.21.2  
 Formation from  $\text{HgBr}_2$  and  $\text{Hg}$ : 2.8.21.2  
 Formation from  $\text{HgBr}_2$  and  $\text{H}_2$ : 2.8.21.2  
 Formation from  $\text{HgBr}_2$  and  $\text{H}_2\text{S}$ :  
 2.8.21.2  
 Formation from  $\text{Hg}_2[\text{NO}_3]_2$  and  $\text{KBr}$ :  
 2.8.21.1  
 Formation from  $\text{Hg}_2\text{Cl}_2$  and  $\text{KBr}$ :  
 2.8.21.1  
 Formation from  $\text{Hg}$  and  $\text{CBr}_4$ : 2.8.21.3  
 Reaction with  $\text{SO}_3$ : 2.8.20.1  
 Reaction with  $\text{KI}$ : 2.8.21.1  
 Reaction with  $\text{I}_2$ : 2.8.20.1  
 **$\text{Br}_2\text{In}^*\text{C}_6\text{H}_{18}\text{As}$**   
 **$\text{Br}_2\text{InMnO}_5^*\text{C}_5$**   
 **$\text{Br}_2\text{Ir}$**   
 $\text{IrBr}_2$   
 Formation: 2.9.4.2  
 **$\text{Br}_2\text{KN}_2^*\text{C}_2\text{Au}$**   
 **$\text{Br}_2\text{Mg}$**   
 $\text{MgBr}_2$   
 Formation: 2.7.2, 2.7.3.1, 2.7.3.2.1  
 **$\text{Br}_2\text{Mn}$**   
 $\text{MnBr}_2$   
 Electrochemical formation: 2.9.3.7  
 Formation: 2.9.7  
 **$\text{Br}_2\text{Mo}$**   
 $\text{MoBr}_2$   
 Formation: 2.9.2.3  
 **$\text{Br}_2\text{MoO}_2$**   
 $\text{MoO}_2\text{Br}_2$   
 Formation: 2.9.11.2, 2.9.12.5  
 **$\text{Br}_2\text{MoO}_4^*\text{C}_4$**   
 **$\text{Br}_2\text{MoS}_2$**   
 $\text{MoS}_2\text{Br}_2$   
 Formation: 2.9.14.1.2  
 **$\text{Br}_2\text{N}^*\text{C}_4\text{H}_{12}\text{Ag}$**   
 **$\text{Br}_2\text{N}^*\text{C}_6\text{H}_{20}\text{Au}$**   
 **$\text{Br}_2\text{N}^*\text{C}_{16}\text{H}_{36}\text{Au}$**   
 **$\text{Br}_2\text{NO}^*\text{C}_{19}\text{H}_{15}\text{AsAu}$**   
 **$\text{Br}_2\text{NOP}^*\text{C}_{19}\text{H}_{15}\text{Au}$**   
 **$\text{Br}_2\text{NS}_2^*\text{C}_5\text{H}_{10}\text{Au}$**   
 **$\text{Br}_2\text{NS}_2^*\text{C}_9\text{H}_{18}\text{Au}$**   
 **$\text{Br}_2\text{N}_2\text{O}_2^*\text{C}_{26}\text{H}_{20}\text{AsAu}$**   
 **$\text{Br}_2\text{N}_2\text{O}_2\text{W}$**   
 $\text{W}(\text{NO})_2\text{Br}_2$   
 Formation: 2.9.15.1.2  
 **$\text{Br}_2\text{N}_2\text{S}_4^*\text{C}_{10}\text{H}_{20}\text{Au}_2$**   
 **$\text{Br}_2\text{NbS}_2$**   
 $\text{NbS}_2\text{Br}_2$   
 Formation: 2.9.14.1.2  
 **$\text{Br}_2\text{NbSe}_2$**   
 $\text{NbSe}_2\text{Br}_2$   
 Formation: 2.9.14.1.2  
 **$\text{Br}_2\text{Ni}$**   
 $\text{NiBr}_2$   
 Electrochemical formation: 2.9.3.7  
 Formation: 2.9.2.3, 2.9.3.2, 2.9.7, 2.9.9.1  
 **$\text{Br}_2\text{OS}$**   
 $\text{OSBr}_2$   
 Reaction with  $\text{Hg}$  metal: 2.8.14.4  
 Reaction with  $\text{MO}$ : 2.7.7  
 **$\text{Br}_2\text{OV}$**   
 $\text{VOBr}_2$   
 Formation: 2.9.12.5  
 **$\text{Br}_2\text{OW}$**   
 $\text{WOBr}_2$   
 Formation: 2.9.11.3  
 **$\text{Br}_2\text{O}_2\text{Ti}^*\text{C}_2\text{H}_3$**   
 **$\text{Br}_2\text{O}_2\text{W}$**   
 $\text{WO}_2\text{Br}_2$   
 Formation: 2.9.11.2, 2.9.11.3, 2.9.12.4  
 **$\text{Br}_2\text{O}_4\text{Ru}^*\text{C}_4$**   
 **$\text{Br}_2\text{O}_4\text{W}^*\text{C}_4$**   
 **$\text{Br}_2\text{O}_6\text{Sr}$**   
 $\text{Sr}[\text{BrO}_3]_2$   
 Formation: 2.7.4  
 **$\text{Br}_2\text{O}_8\text{Tc}_2^*\text{C}_8$**   
 **$\text{Br}_2\text{P}^*\text{C}_{24}\text{H}_{20}\text{Ag}$**   
 **$\text{Br}_2\text{Pb}$**   
 $\text{PbBr}_2$   
 Reaction with  $\text{Ga}$ : 2.6.3.3  
 **$\text{Br}_2\text{Pt}$**   
 $\text{PtBr}_2$   
 Formation: 2.9.2.3

- Br<sub>2</sub>Ra**  
RaBr<sub>2</sub>  
Formation: 2.7.2
- Br<sub>2</sub>ReS**  
ReSBr<sub>2</sub>  
Formation: 2.9.14.3
- Br<sub>2</sub>ReSe**  
ReSeBr<sub>2</sub>  
Formation: 2.9.14.3
- Br<sub>2</sub>S<sub>2</sub>**  
S<sub>2</sub>Br<sub>2</sub>  
Reaction with MoS<sub>3</sub>: 2.9.14.2  
Reaction with MO: 2.7.7  
Reaction with transition-metals:  
2.9.14.1.2
- Br<sub>2</sub>Sr**  
SrBr<sub>2</sub>  
Formation: 2.7.2, 2.7.4
- Br<sub>2</sub>V**  
VBr<sub>2</sub>  
Electrochemical formation: 2.9.3.7
- Br<sub>2</sub>W**  
WBr<sub>2</sub>  
Reaction with HF: 2.11.4.1
- Br<sub>2</sub>Zn**  
ZnBr<sub>2</sub>  
Anhydrous: 2.8.19  
Fluorination: 2.11.2.3  
Formation from Zn and HBr: 2.8.14.3  
Formation from Zn and Br<sub>2</sub>: 2.8.14.1  
Formation from ZnO and CF<sub>3</sub>BrCl:  
2.8.15.3  
Formation from ZnO and HBr: 2.8.15.2  
Reaction with HF: 2.8.18  
Stability in H<sub>2</sub>O: 2.8.19
- Br<sub>3</sub>\*Al  
Br<sub>3</sub>\*As  
Br<sub>3</sub>\*Au  
Br<sub>3</sub>\*B  
Br<sub>3</sub>\*C<sub>18</sub>H<sub>15</sub>AsAu  
**Br<sub>3</sub>CdCs**  
Cs[CdBr<sub>3</sub>]  
Formation: 2.8.22
- Br<sub>3</sub>CdCu**  
Cu[CdBr<sub>3</sub>]  
Formation from melt: 2.8.22
- Br<sub>3</sub>CdH<sub>2</sub>KO**  
K[CdBr<sub>3</sub>]·H<sub>2</sub>O  
Formation: 2.8.22
- Br<sub>3</sub>CdH<sub>4</sub>N**  
[NH<sub>4</sub>][CdBr<sub>3</sub>]  
Formation: 2.8.22
- Br<sub>3</sub>CdRb**  
Rb[CdBr<sub>3</sub>]  
Formation: 2.8.22
- Br<sub>3</sub>Cl<sub>2</sub>CrCuH<sub>18</sub>N<sub>6</sub>**  
[Cr(NH<sub>3</sub>)<sub>6</sub>][CuBr<sub>3</sub>Cl<sub>2</sub>]  
Formation: 2.8.10
- Br<sub>3</sub>Cr**  
CrBr<sub>3</sub>  
Electrochemical formation: 2.9.3.7  
Formation: 2.9.2.3  
Reaction with Cr<sub>2</sub>S<sub>3</sub>: 2.9.14.2
- Br<sub>3</sub>CsCu**  
Cs[CuBr<sub>3</sub>]  
Formation: 2.8.10
- Br<sub>3</sub>CsCu<sub>2</sub>**  
Cs[Cu<sub>2</sub>Br<sub>3</sub>]  
Formation: 2.8.12
- Br<sub>3</sub>CsHg**  
Cs[HgBr<sub>3</sub>]  
Formation: 2.8.22
- Br<sub>3</sub>CuN<sub>2</sub>\*C<sub>16</sub>H<sub>40</sub>  
Br<sub>3</sub>CuP<sub>2</sub>\*C<sub>38</sub>H<sub>36</sub>  
Br<sub>3</sub>Cu<sub>2</sub>N<sub>2</sub>\*C<sub>6</sub>H<sub>5</sub>  
Br<sub>3</sub>Cu<sub>2</sub>N<sub>4</sub>\*C<sub>4</sub>H<sub>16</sub>  
Br<sub>3</sub>F<sub>5</sub>N\*C<sub>22</sub>H<sub>36</sub>Au
- Br<sub>3</sub>Fe**  
FeBr<sub>3</sub>  
Formation: 2.9.2.3  
Reaction with [NH<sub>4</sub>]F: 2.11.2.2
- Br<sub>3</sub>FeP\*C<sub>22</sub>H<sub>19</sub>Au
- Br<sub>3</sub>Ga**  
GaBr<sub>3</sub>  
Formation: 2.6.2.1, 2.6.3.3
- Br<sub>3</sub>GaN\*C<sub>3</sub>H<sub>9</sub>
- Br<sub>3</sub>H<sub>2</sub>HgKO**  
K[HgBr<sub>3</sub>]·H<sub>2</sub>O  
Formation: 2.8.22
- Br<sub>3</sub>H<sub>2</sub>NaOZn**  
Na[ZnBr<sub>3</sub>]·H<sub>2</sub>O  
Formation: 2.8.22
- Br<sub>3</sub>H<sub>4</sub>HgKO<sub>2</sub>**  
K[HgBr<sub>3</sub>]·2 H<sub>2</sub>O  
Formation: 2.8.22
- Br<sub>3</sub>H<sub>4</sub>HgN**  
[NH<sub>4</sub>][HgBr<sub>3</sub>]  
Formation: 2.8.22
- Br<sub>3</sub>H<sub>4</sub>HgNaO<sub>2</sub>**  
Na[HgBr<sub>3</sub>]·2 H<sub>2</sub>O  
Formation: 2.8.22
- Br<sub>3</sub>H<sub>4</sub>KO<sub>2</sub>Zn**  
K[ZnBr<sub>3</sub>]·2 H<sub>2</sub>O  
Formation: 2.8.22

**Br<sub>3</sub>H<sub>10</sub>NO<sub>3</sub>Zn**[NH<sub>4</sub>][ZnBr<sub>3</sub>]·3 H<sub>2</sub>O

Formation: 2.8.22

**Br<sub>3</sub>HgK**K[HgBr<sub>3</sub>]

Formation from melt: 2.8.22

**Br<sub>3</sub>HgNa**Na[HgBr<sub>3</sub>]

Formation from melt and solution:

2.8.22

**Br<sub>3</sub>In**InBr<sub>3</sub>

Formation: 2.6.2.1, 2.6.13.1, 2.6.14.1

Reaction with NH<sub>4</sub>F: 2.6.12.3**Br<sub>3</sub>In<sub>7</sub>**In<sub>7</sub>Br<sub>3</sub>

Formation: 2.6.14.1

**Br<sub>3</sub>Ir**IrBr<sub>3</sub>Reaction of MBr in BrF<sub>3</sub>: 2.11.4.2**Br<sub>3</sub>Mo**MoBr<sub>3</sub>

Formation: 2.9.2.3, 2.9.6

Reaction with CsBr: 2.9.10.1

Reaction with elemental S: 2.9.14.3

**Br<sub>3</sub>Mo<sub>2</sub>S<sub>5</sub>**Mo<sub>2</sub>S<sub>4</sub>Br<sub>3</sub>

Formation: 2.9.14.2, 2.9.14.3

**Br<sub>3</sub>N<sup>+</sup>C<sub>8</sub>H<sub>20</sub>Ag<sub>2</sub>****Br<sub>3</sub>N<sub>3</sub><sup>+</sup>C<sub>3</sub>H<sub>9</sub>B<sub>3</sub>****Br<sub>3</sub>NbO**NbOBr<sub>3</sub>

Formation: 2.9.12.1, 2.9.12.4, 2.9.12.5

**Br<sub>3</sub>NbS**NbSBr<sub>3</sub>

Formation: 2.9.14.4

**Br<sub>3</sub>NbSe**NbSeBr<sub>3</sub>

Formation: 2.9.14.4

**Br<sub>3</sub>Nd**NdBr<sub>3</sub>

Formation: 2.9.7

**Br<sub>3</sub>OTa**TaOBr<sub>3</sub>

Formation: 2.9.12.4

**Br<sub>3</sub>OTc**TcOBr<sub>3</sub>

Formation: 2.9.12.1

**Br<sub>3</sub>OV**VBr<sub>3</sub>O

Formation: 2.9.2.3

VOBr<sub>3</sub>

Formation: 2.9.12.1

**Br<sub>3</sub>OW**WOBr<sub>3</sub>

Formation: 2.9.11.3, 2.9.12.7

**Br<sub>3</sub>P**PBr<sub>3</sub>Reaction with R<sub>2</sub>Hg: 2.8.23.5Reaction with R<sub>2</sub> $\overline{\text{NBX}}-\text{NR}'\text{BX}_2$ :

2.6.8.3

Reaction with Hg: 2.8.14.4

**Br<sub>3</sub>P<sup>+</sup>C<sub>3</sub>H<sub>9</sub>Au****Br<sub>3</sub>P<sup>+</sup>C<sub>6</sub>H<sub>15</sub>Au****Br<sub>3</sub>P<sup>+</sup>C<sub>18</sub>H<sub>15</sub>Au****Br<sub>3</sub>P<sup>+</sup>C<sub>20</sub>H<sub>17</sub>Au****Br<sub>3</sub>P<sup>+</sup>C<sub>21</sub>H<sub>19</sub>Au****Br<sub>3</sub>Ru**RuBr<sub>3</sub>

Formation: 2.9.2.3, 2.9.4.3

**Br<sub>3</sub>S<sup>+</sup>C<sub>2</sub>H<sub>6</sub>Au****Br<sub>3</sub>S<sup>+</sup>C<sub>14</sub>H<sub>14</sub>Au****Br<sub>3</sub>S<sub>3</sub><sup>+</sup>B<sub>3</sub>****Br<sub>3</sub>Sb**SbBr<sub>3</sub>Reaction with R<sub>2</sub> $\overline{\text{NBX}}-\text{NR}'\text{BX}_2$ :

2.6.8.3

**Br<sub>3</sub>SeW**WSeBr<sub>3</sub>

Formation: 2.9.14.4

**Br<sub>3</sub>Sm**SmBr<sub>3</sub>

Formation: 2.9.7

**Br<sub>3</sub>Tl**TlBr<sub>3</sub>

Formation: 2.6.2.1

**Br<sub>3</sub>V**VBr<sub>3</sub>

Formation: 2.9.2.3

**Br<sub>4</sub><sup>+</sup>B<sub>2</sub>****Br<sub>4</sub><sup>+</sup>C****Br<sub>4</sub>C**CBr<sub>4</sub>

Use as halogenating agent: 2.9.12.4

**Br<sub>4</sub><sup>+</sup>C<sub>2</sub>H<sub>6</sub>Au<sub>2</sub>****Br<sub>4</sub>CdCs<sub>2</sub>**Cs<sub>2</sub>[CdBr<sub>4</sub>]

Formation: 2.8.22

**Br<sub>4</sub>CdH<sub>2</sub>O<sup>+</sup>Ba****Br<sub>4</sub>CdH<sub>8</sub>N<sub>2</sub>**[NH<sub>4</sub>]<sub>2</sub>[CdBr<sub>4</sub>]

Formation from melt: 2.8.22

**Br<sub>4</sub>CdK<sub>2</sub>**K<sub>2</sub>[CdBr<sub>4</sub>]

Formation from melt: 2.8.22

- Br<sub>4</sub>CdNa<sub>2</sub>**  
 Na<sub>2</sub>[CdBr<sub>4</sub>]  
 Formation from melt: 2.8.22
- Br<sub>4</sub>Cl<sub>2</sub>P<sub>2</sub>\*C<sub>25</sub>H<sub>22</sub>Au<sub>2</sub>**  
**Br<sub>4</sub>CoN<sub>2</sub>\*C<sub>16</sub>H<sub>40</sub>**
- Br<sub>4</sub>Cs<sub>2</sub>Hg**  
 Cs<sub>2</sub>[HgBr<sub>4</sub>]  
 Formation: 2.8.22
- Br<sub>4</sub>Cs<sub>2</sub>Zn**  
 Cs<sub>2</sub>[ZnBr<sub>4</sub>]  
 Formation: 2.8.22
- Br<sub>4</sub>CuN<sub>2</sub>\*C<sub>16</sub>H<sub>40</sub>**  
**Br<sub>4</sub>Cu<sub>2</sub>N<sub>2</sub>\*C<sub>16</sub>H<sub>40</sub>**  
**Br<sub>4</sub>FeN\*C<sub>8</sub>H<sub>20</sub>**
- Br<sub>4</sub>H<sub>4</sub>K<sub>2</sub>O<sub>2</sub>Zn**  
 K<sub>2</sub>[ZnBr<sub>4</sub>]\*2 H<sub>2</sub>O  
 Formation: 2.8.22
- Br<sub>4</sub>H<sub>8</sub>HgN<sub>2</sub>**  
 [NH<sub>4</sub>]<sub>2</sub>[HgBr<sub>4</sub>]  
 Formation: 2.8.22
- Br<sub>4</sub>H<sub>8</sub>N<sub>2</sub>Zn**  
 [NH<sub>4</sub>]<sub>2</sub>[ZnBr<sub>4</sub>]  
 Formation: 2.8.22
- Br<sub>4</sub>H<sub>9</sub>O<sub>4</sub>\*Au**  
**Br<sub>4</sub>H<sub>10</sub>N<sub>2</sub>OZn**  
 [NH<sub>4</sub>]<sub>2</sub>[ZnBr<sub>4</sub>]\*H<sub>2</sub>O  
 Formation: 2.8.22
- Br<sub>4</sub>Hf**  
 HfBr<sub>4</sub>  
 Electrochemical formation: 2.9.3.7  
 Formation: 2.9.4.1
- Br<sub>4</sub>Hg\*Ba**  
**Br<sub>4</sub>HgK<sub>2</sub>**  
 K<sub>2</sub>[HgBr<sub>4</sub>]  
 Formation from melt and solution:  
 2.8.22
- Br<sub>4</sub>HgNa<sub>2</sub>**  
 Na<sub>2</sub>[HgBr<sub>4</sub>]  
 Formation from melt and solution:  
 2.8.22
- Br<sub>4</sub>HgSr**  
 Sr[HgBr<sub>4</sub>]  
 Formation: 2.8.22
- Br<sub>4</sub>Ir**  
 IrBr<sub>4</sub>  
 Formation: 2.9.4.3
- Br<sub>4</sub>K\*Au**
- Br<sub>4</sub>Mo**  
 MoBr<sub>4</sub>  
 Formation: 2.9.6
- Br<sub>4</sub>MoO**  
 [MoOBr<sub>4</sub>]<sup>-</sup>  
 Formation: 2.9.13, 2.9.13.2
- Br<sub>4</sub>Mo<sub>3</sub>S<sub>7</sub>**  
 Mo<sub>3</sub>S<sub>7</sub>Br<sub>4</sub>  
 Formation: 2.9.14.3
- Br<sub>4</sub>Mo<sub>3</sub>Se<sub>7</sub>**  
 Mo<sub>3</sub>Se<sub>7</sub>Br<sub>4</sub>  
 Formation: 2.9.14.3
- Br<sub>4</sub>N\*C<sub>8</sub>H<sub>20</sub>Au**  
**Br<sub>4</sub>N<sub>2</sub>Ni\*C<sub>16</sub>H<sub>40</sub>**  
**Br<sub>4</sub>N<sub>4</sub>Ni\*C<sub>4</sub>H<sub>16</sub>Ag<sub>2</sub>**
- Br<sub>4</sub>Nb<sub>2</sub>S<sub>3</sub>**  
 Nb<sub>2</sub>S<sub>3</sub>Br<sub>4</sub>  
 Formation: 2.9.14.4
- Br<sub>4</sub>ORe**  
 ReOBr<sub>4</sub>  
 Formation: 2.9.11.2, 2.9.12.1
- Br<sub>4</sub>OV**  
 [VOBr<sub>4</sub>]<sup>2-</sup>  
 Formation: 2.9.13.4
- Br<sub>4</sub>OW**  
 WOBr<sub>4</sub>  
 Formation: 2.9.11.2, 2.9.12.4, 2.9.12.5,  
 2.9.12.7  
 Reaction with WBr<sub>5</sub>: 2.9.11.3
- Br<sub>4</sub>O<sub>2</sub>Os**  
 [OsO<sub>2</sub>Br<sub>4</sub>]<sup>2-</sup>  
 Formation: 2.9.13
- Br<sub>4</sub>O<sub>2</sub>Ru**  
 [RuO<sub>2</sub>Br<sub>4</sub>]<sup>2-</sup>  
 Formation: 2.9.13
- Br<sub>4</sub>O<sub>4</sub>\*H<sub>9</sub>Au**
- Br<sub>4</sub>Os**  
 OsBr<sub>4</sub>  
 Formation: 2.9.2.3
- Br<sub>4</sub>P<sub>2</sub>\*C<sub>48</sub>H<sub>40</sub>Ag<sub>2</sub>**  
**Br<sub>4</sub>P<sub>3</sub>\*C<sub>57</sub>H<sub>54</sub>Ag**
- Br<sub>4</sub>Pt**  
 PtBr<sub>4</sub>  
 Formation: 2.9.2.3
- Br<sub>4</sub>Rb\*Au**
- Br<sub>4</sub>SW**  
 WSBBr<sub>4</sub>  
 Formation: 2.9.14.4
- Br<sub>4</sub>S<sub>2</sub>\*C<sub>2</sub>H<sub>6</sub>B<sub>2</sub>**
- Br<sub>4</sub>Se**  
 SeBr<sub>4</sub>  
 Reaction with R<sub>2</sub>Hg: 2.8.23.5
- Br<sub>4</sub>SeW**  
 WSeBr<sub>4</sub>  
 Formation: 2.9.14.4
- Br<sub>4</sub>Si**  
 SiBr<sub>4</sub>  
 Reaction with MX: 2.7.9



**Br<sub>4</sub>Ti**

Electrochemical formation: 2.9.3.7

Formation: 2.9.2.3, 2.9.4.1

**Br<sub>4</sub>Tl<sub>2</sub>**

Formation: 2.6.6.1

**Br<sub>4</sub>U**

Formation: 2.9.5

**Br<sub>4</sub>W**

Formation: 2.9.6

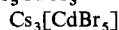
**Br<sub>4</sub>Xe**

Formation: 2.10.1

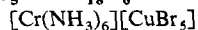
**Br<sub>4</sub>Zr**

Electrochemical formation: 2.9.3.7

Formation: 2.9.4.1

**Br<sub>5</sub>CdCs<sub>3</sub>**

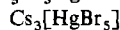
Formation: 2.8.22

**Br<sub>5</sub>CrCuH<sub>18</sub>N<sub>6</sub>**

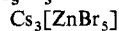
Formation: 2.8.10

**Br<sub>5</sub>CrO**

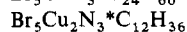
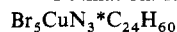
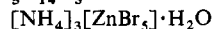
Formation: 2.9.13.2

**Br<sub>5</sub>Cs<sub>3</sub>Hg**

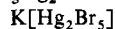
Formation: 2.8.22

**Br<sub>5</sub>Cs<sub>3</sub>Zn**

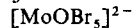
Formation: 2.8.22

**Br<sub>5</sub>H<sub>14</sub>N<sub>3</sub>OZn**

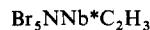
Formation: 2.8.22

**Br<sub>5</sub>Hg<sub>2</sub>K**

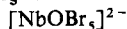
Formation from melt: 2.8.22

**Br<sub>5</sub>MoO**

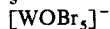
Formation: 2.9.13, 2.9.13.2, 2.9.13.3

**Br<sub>5</sub>Nb**

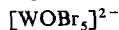
Formation: 2.9.2.3, 2.9.4.1, 2.9.4.6, 2.9.4.8

Reaction with [R<sub>4</sub>N]X: 2.9.10.1Reaction with Sb<sub>2</sub>Y<sub>3</sub>: 2.9.14.4**Br<sub>5</sub>NbO**

Formation: 2.9.13.3

**Br<sub>5</sub>OW**

Formation: 2.9.13.4



Formation: 2.9.13.3

**Br<sub>5</sub>P**Reaction with M<sub>2</sub>O<sub>3</sub>: 2.6.6.4**Br<sub>5</sub>Re**

Formation: 2.9.2.3

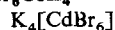
**Br<sub>5</sub>Ta**

Formation: 2.9.2.3, 2.9.3.2, 2.9.4.1,

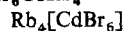
2.9.4.6, 2.9.4.8

Reaction with [R<sub>4</sub>N]X: 2.9.10.1Reaction with Sb<sub>2</sub>S<sub>3</sub>: 2.9.14.4**Br<sub>5</sub>W**

Formation: 2.9.2.3, 2.9.6

Reaction with Sb<sub>2</sub>Y<sub>3</sub>: 2.9.14.4Reaction with WOBr<sub>4</sub>: 2.9.11.3Reaction with M(CO)<sub>6</sub>: 2.9.6**Br<sub>6</sub>CdK<sub>4</sub>**

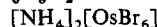
Formation: 2.8.22

**Br<sub>6</sub>CdRb<sub>4</sub>**

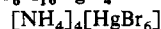
Formation: 2.8.22

**Br<sub>6</sub>Ga<sub>2</sub>**

Formation: 2.6.13.3

**Br<sub>6</sub>H<sub>8</sub>N<sub>2</sub>Os**

Formation: 2.9.10.2

**Br<sub>6</sub>H<sub>16</sub>HgN<sub>4</sub>**

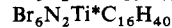
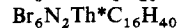
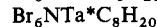
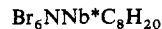
Formation from melt: 2.8.22

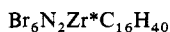
**Br<sub>6</sub>K<sub>2</sub>Re**

Formation: 2.9.10.2

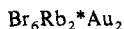
**Br<sub>6</sub>K<sub>2</sub>Ru**

Formation: 2.9.10.2



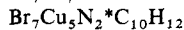


Reaction with Nb-CsBr: 2.9.10.1

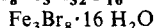


Formation: 2.9.4.6, 2.9.11.3

Reaction with  $\text{Sb}_2\text{Y}_3$ : 2.9.14.4



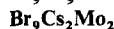
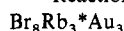
Formation: 2.6.14.1



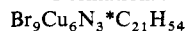
Reaction with  $\text{MCO}_3$ : 2.7.9



Reaction with RbBr: 2.9.10.1



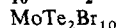
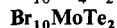
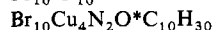
Formation: 2.9.10.1



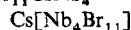
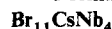
Formation: 2.9.2.3

Reaction with  $\text{ReSe}_2$ : 2.9.14.2

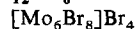
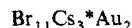
Reaction with elemental S, Se: 2.9.14.3



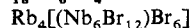
Formation: 2.9.14.2



Formation: 2.9.10.1



Reaction with elemental S, Se: 2.9.14.3



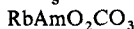
Formation: 2.9.10.1



Reaction with  $\text{F}_2$ : 2.8.8.2



Reaction with  $\text{F}_2$ : 2.8.8.2



Reaction with RbF: 2.11.5.2



Reaction with  $\text{AuCl}_3$ : 2.8.8.1



Reaction with  $\text{F}_2$ : 2.8.3.1.3



Reaction with  $\text{X}_2$ : 2.7.8

Reaction with  $\text{HX}$ : 2.7.8



Reaction with  $\text{CdO}$ : 2.8.15.3

Reaction with  $\text{ZnO}$ : 2.8.15.3



Formation: 2.8.23.3



Reaction with Hg: 2.8.21.3

Reaction with  $\text{MX}$ : 2.7.9

Reaction with  $\text{MO}$ : 2.9.4.6



Reaction with  $\text{HCl}$ : 2.8.17.1

Reaction with  $\text{HI}$ : 2.8.17.1

Reaction with  $\text{HBr}$ : 2.8.17.1

Reaction with  $\text{HF}$ : 2.8.17.1



Formation: 2.8.23.3



Reaction with  $\text{MO}$ : 2.7.7

Reaction with  $(\text{HBNR})_3$ : 2.6.5.3

Reaction with  $\text{MO}$ : 2.9.4.6

Reaction with  $(\text{R}_2\text{N})_3\text{B}$ : 2.6.8.3

Reaction with  $\text{ZnO}$ : 2.8.15.3

Reaction with  $\text{ZrO}_2$ : 2.9.4.7



Reaction with  $(\text{R}_2\text{N})_3\text{B}$ : 2.6.8.3



Reaction with Al: 2.6.3.2

Reaction with  $\text{FeS}_2$ ,  $\text{FeS}$ : 2.9.5

Reaction with  $\text{MO}$ : 2.9.4.6

Reaction with  $\text{MX}$ : 2.7.9

- Reaction with MO: 2.7.7, 2.9.4.6  
 Reaction with  $\text{Os}_3(\text{CO})_{12}$ : 2.9.15.1.1  
 Reaction with  $\text{Ph}_2\text{Hg}$ : 2.8.23.5  
 Reaction with Hg: 2.8.21.3  
 Reaction with  $\text{WS}_2$ ,  $\text{MoS}_3$ ,  $\text{Re}_2\text{S}_7$ : 2.9.5  
 Reaction with  $\text{ZnO}$ : 2.8.15.3  
 Use as halogenating agent: 2.9.12.4
- $\text{CCsO}_3$**   
 $\text{CsCO}_3$   
 Reaction with  $\text{X}_2\text{-N}_2\text{H}_4$ : 2.7.4
- $\text{CCuO}_3$**   
 $\text{CuCO}_3$   
 Reactions with hydrohalic acids: 2.8.8.3
- CFO**  
 COF  
 Fluorinating agent: 2.9.12.3
- $\text{CF}_2\text{Se}$**   
 $\text{SeCF}_2$   
 Formation: 2.6.7.3
- $\text{CHCl}_3$**   
 $\text{CHCl}_3$   
 Reaction with MO: 2.9.4.6
- $\text{CH}_2\text{Cu}_2\text{O}_8$**   
 $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$   
 Reaction with HF: 2.11.2.3
- $\text{CH}_3\text{BCl}_2$**   
 $\text{CH}_3\text{BCl}_2$   
 Formation: 2.6.16
- $\text{CH}_3\text{BeCl}$**   
 $\text{CH}_3\text{BeCl}$   
 Formation: 2.7.3.2.2
- $\text{CH}_3\text{Cl}_3\text{Si}$**   
 $\text{CH}_3\text{SiCl}_3$   
 Reaction with  $\text{K}_2[\text{R}_6\text{Ga}_2]$ : 2.6.10.3
- $\text{CH}_3\text{Cl}_3\text{Ti}$**   
 $\text{CH}_3\text{TiCl}_3$   
 Formation: 2.6.10.3
- $\text{CH}_3\text{GaI}_2$**   
 $\text{CH}_3\text{GaI}_2$   
 Formation: 2.6.10.1
- $\text{CH}_3\text{GaI}_2\text{S}$**   
 $\text{I}_2\text{GaSCH}_3$   
 Reaction with  $\text{I}_2$ : 2.6.7.3
- $\text{CH}_3\text{I}$**   
 $\text{CH}_3\text{I}$   
 Reaction with  $\text{Hg}[\text{CH}_3\text{C}(\text{O})\text{O}]_2$ : 2.8.17.3  
 Reaction with  $\text{HgCl}_2$ : 2.8.18  
 Reaction with  $\text{HgI}_2$ : 2.8.22  
 Reaction with elemental Hg: 2.8.23.1
- $\text{CH}_3\text{BrGe}$**   
 $\text{CH}_3\text{GeH}_2\text{Br}$   
 Reaction with  $\text{Li}[\text{Al}(\text{AsH}_2)_4]$ : 2.6.9.3
- $\text{CH}_3\text{BrSi}$**   
 $\text{CH}_3\text{SiH}_2\text{Br}$   
 Reaction with  $\text{Li}[\text{Al}(\text{AsH}_2)_4]$ : 2.6.9.3
- $\text{CH}_3\text{P}$**   
 $\text{CH}_3\text{PH}_2$   
 Reaction with  $\text{Li}[\text{AlH}_4]$ : 2.6.9.3
- $\text{CH}_6\text{BrHgIN}$**   
 $[\text{CH}_3\text{NH}_3][\text{HgBrI}_2]$   
 Formation: 2.8.22
- $\text{CH}_6\text{Br}_2\text{HgIN}$**   
 $[\text{CH}_3\text{NH}_3][\text{HgBr}_2\text{I}]$   
 Formation: 2.8.22
- $\text{CH}_6\text{GeS}$**   
 $\text{CH}_3\text{SGeH}_3$   
 Formation: 2.6.7.3
- $\text{CH}_6\text{SSI}$**   
 $\text{CH}_3\text{SSiH}_3$   
 Formation: 2.6.7.3
- $\text{CH}_7\text{AsGe}$**   
 $\text{CH}_3\text{GeH}_2\text{AsH}_2$   
 Formation: 2.6.9.3
- $\text{CH}_7\text{AsSi}$**   
 $\text{CH}_3\text{SiH}_2\text{AsH}_2$   
 Formation: 2.6.9.3
- $\text{CH}_7\text{PSi}$**   
 $\text{CH}_3\text{P}(\text{H})\text{SiH}_3$   
 Formation: 2.6.9.3
- $\text{CH}_8\text{SSI}_2$**   
 $\text{Si}_2\text{H}_5(\text{SCH}_3)$   
 Formation: 2.6.7.3
- CHF**  
 HfC  
 Fluorination: 2.11.4.1
- $\text{CHg}_2\text{O}_3$**   
 $\text{Hg}_2[\text{CO}_3]$   
 Reaction with HF: 2.8.21.1
- $\text{Cl}_4$**   
 $\text{Cl}_4$   
 Formation: 2.6.12.2  
 Reaction with Hg: 2.8.21.3  
 Reaction with MX: 2.7.9
- $\text{CNa}_2\text{O}_3$**   
 $\text{Na}_2[\text{CO}_3]$   
 Reaction with  $\text{X}_2$ : 2.7.4
- COS**  
 OCS  
 Formation from HgS and  $\text{COCl}_2$ : 2.8.16.2
- $\text{CO}_3\text{Zn}$**   
 $\text{Zn}[\text{CO}_3]$   
 Reaction with HF: 2.8.17.1  
 Reaction with HCl: 2.8.17.1

- Reaction with HF: 2.11.2.3
- CPa**
- PaC
- Fluorination: 2.11.5.2
- C<sub>2</sub>AuBr<sub>2</sub>KN<sub>2</sub>**
- K[Au(CN)<sub>2</sub>Br<sub>2</sub>]
- Formation: 2.8.4.2
- Reaction with Cl<sup>-</sup>: 2.8.4.2
- C<sub>2</sub>AuCl<sub>2</sub>KN<sub>2</sub>**
- K[Au(CN)<sub>2</sub>Cl<sub>2</sub>]
- Formation: 2.8.4.2
- C<sub>2</sub>AuI<sub>2</sub>KN<sub>2</sub>**
- K[Au(CN)<sub>2</sub>I<sub>2</sub>]
- Formation: 2.8.4.2
- C<sub>2</sub>AuKN<sub>2</sub>**
- K[Au(CN)<sub>2</sub>]
- Reaction with I<sub>2</sub>: 2.8.4.2
- Reaction with halogens: 2.8.4.2
- C<sub>2</sub>Cl<sub>4</sub>**
- C<sub>2</sub>Cl<sub>4</sub>
- Reaction with B: 2.6.3.2
- C<sub>2</sub>H<sub>2</sub>AuCl<sub>2</sub>KN<sub>2</sub>O**
- K[Au(CN)<sub>2</sub>Cl<sub>2</sub>]·H<sub>2</sub>O
- Structure: 2.8.4.2
- C<sub>2</sub>H<sub>3</sub>BrO**
- CH<sub>3</sub>C(O)Br
- Reaction with Cd[OAc]<sub>2</sub>: 2.8.17.3
- C<sub>2</sub>H<sub>3</sub>Br<sub>2</sub>O<sub>2</sub>Tl**
- Tl[O<sub>2</sub>CCH<sub>3</sub>]<sub>2</sub>Br<sub>2</sub>
- Formation: 2.6.6.1
- C<sub>2</sub>H<sub>3</sub>Br<sub>5</sub>NNb**
- CH<sub>3</sub>CNNbBr<sub>5</sub>
- Reaction with [R<sub>4</sub>N]X: 2.9.10.1
- C<sub>2</sub>H<sub>3</sub>CHg**
- CH<sub>2</sub>CHHgCl
- Formation: 2.8.23.5
- C<sub>2</sub>H<sub>3</sub>ClO**
- CH<sub>3</sub>C(O)Cl
- Reaction with Hg[NO<sub>3</sub>]<sub>2</sub>: 2.8.17.3
- Reaction with MO: 2.9.4.6, 2.7.7
- Reaction with Cd[OAc]<sub>2</sub>: 2.8.17.3
- Reaction with Zn: 2.8.14.4
- Reaction with ZnO: 2.8.15.3
- C<sub>2</sub>H<sub>3</sub>Cl<sub>3</sub>Si**
- CH<sub>2</sub>CHSiCl<sub>3</sub>
- Formation: 2.8.23.5
- C<sub>2</sub>H<sub>3</sub>Cl<sub>5</sub>NNb**
- CH<sub>3</sub>CNNbCl<sub>5</sub>
- Reaction with [R<sub>4</sub>N]X: 2.9.10.1
- C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>Tl**
- Tl[O<sub>2</sub>CCH<sub>3</sub>]
- Reaction with X<sub>2</sub>: 2.6.6.1
- C<sub>2</sub>H<sub>5</sub>AlI<sub>2</sub>**
- C<sub>2</sub>H<sub>5</sub>AlI<sub>2</sub>
- Formation: 2.6.3.2
- C<sub>2</sub>H<sub>5</sub>I**
- C<sub>2</sub>H<sub>5</sub>I
- Reaction with Hg<sub>2</sub>[NO<sub>3</sub>]<sub>2</sub>: 2.8.21.1
- Reaction with elemental Zn: 2.8.23.1
- C<sub>2</sub>H<sub>6</sub>AlCl<sub>2</sub>N**
- (CH<sub>3</sub>)<sub>2</sub>AlCl<sub>2</sub>
- Formation: 2.6.8.3
- C<sub>2</sub>H<sub>6</sub>AuBr<sub>3</sub>S**
- AuBr[S(CH<sub>3</sub>)<sub>2</sub>]
- Formation: 2.8.6.2
- C<sub>2</sub>H<sub>6</sub>AuCl<sub>2</sub>Cs**
- Cs[(CH<sub>3</sub>)<sub>2</sub>AuCl<sub>2</sub>]
- Formation: 2.8.5
- C<sub>2</sub>H<sub>6</sub>Au<sub>2</sub>Br<sub>4</sub>**
- [CH<sub>3</sub>AuBr<sub>2</sub>]<sub>2</sub>
- Formation: 2.8.5
- Structure: 2.8.5
- C<sub>2</sub>H<sub>6</sub>BCl**
- (CH<sub>3</sub>)<sub>2</sub>BCl
- Formation: 2.6.7.3
- C<sub>2</sub>H<sub>6</sub>BCl<sub>2</sub>N**
- (CH<sub>3</sub>)<sub>2</sub>NBCl<sub>2</sub>
- Formation: 2.6.8.3
- C<sub>2</sub>H<sub>6</sub>BF**
- (CH<sub>3</sub>)<sub>2</sub>BF
- Formation: 2.6.8.3
- C<sub>2</sub>H<sub>6</sub>B<sub>2</sub>Br<sub>4</sub>S<sub>2</sub>**
- (Br<sub>2</sub>BSCH<sub>3</sub>)<sub>2</sub>
- Formation: 2.6.7.3
- C<sub>2</sub>H<sub>6</sub>B<sub>2</sub>Cl<sub>4</sub>S<sub>2</sub>**
- (Cl<sub>2</sub>BSCH<sub>3</sub>)<sub>2</sub>
- Formation: 2.6.7.3
- C<sub>2</sub>H<sub>6</sub>B<sub>5</sub>Cl**
- 5-Cl-2, 4-C<sub>2</sub>B<sub>5</sub>H<sub>6</sub>
- Formation: 2.6.5.1
- C<sub>2</sub>H<sub>6</sub>BrTi**
- (CH<sub>3</sub>)<sub>2</sub>TiBr
- Formation: 2.6.8.3
- Reaction with X<sub>2</sub>: 2.6.10.1
- C<sub>2</sub>H<sub>6</sub>Cd**
- (CH<sub>3</sub>)<sub>2</sub>Cd
- Reaction with CdBr<sub>2</sub>: 2.8.23.2
- C<sub>2</sub>H<sub>6</sub>ClTi**
- (CH<sub>3</sub>)<sub>2</sub>TiCl
- Formation: 2.6.8.3, 2.6.9.2, 2.6.13.2, 2.6.13.3
- C<sub>2</sub>H<sub>6</sub>Cl<sub>3</sub>NP**
- (CH<sub>3</sub>)<sub>2</sub>NPCl<sub>3</sub>
- Formation: 2.6.8.3

- C<sub>2</sub>H<sub>6</sub>GaI**  
(CH<sub>3</sub>)<sub>2</sub>GaI  
Formation: 2.6.10.1
- C<sub>2</sub>H<sub>6</sub>ITl**  
(CH<sub>3</sub>)<sub>2</sub>TlI  
Formation: 2.6.9.3, 2.6.10.2, 2.6.13.3
- C<sub>2</sub>H<sub>6</sub>I<sub>2</sub>Si**  
(CH<sub>3</sub>)<sub>2</sub>SiI<sub>2</sub>  
Reaction with Mo(CO)<sub>6</sub>, W(CO)<sub>6</sub>:  
2.9.15.1.1
- C<sub>2</sub>H<sub>6</sub>O<sub>4</sub>**  
(CH<sub>3</sub>COO)<sub>2</sub>  
Initiator in aryl exchange: 2.8.23.5
- C<sub>2</sub>H<sub>7</sub>B<sub>5</sub>**  
2, 4-C<sub>2</sub>B<sub>5</sub>H<sub>7</sub>  
Reaction with X<sub>2</sub>-AlCl<sub>3</sub>: 2.6.5.1
- C<sub>2</sub>H<sub>7</sub>ClSi**  
(CH<sub>3</sub>)<sub>2</sub>Si(H)Cl  
Reaction with M(SeR)<sub>4</sub>: 2.6.7.3
- C<sub>2</sub>H<sub>7</sub>Ga**  
(CH<sub>3</sub>)<sub>2</sub>GaH  
Formation: 2.6.5.2
- C<sub>2</sub>H<sub>7</sub>P**  
C<sub>2</sub>H<sub>5</sub>PH<sub>2</sub>  
Formation: 2.6.9.3
- C<sub>2</sub>H<sub>6</sub>AlCl<sub>4</sub>P**  
[(CH<sub>3</sub>)<sub>2</sub>PH<sub>2</sub>][AlCl<sub>4</sub>]  
Formation: 2.6.9.2
- C<sub>2</sub>H<sub>6</sub>BClS**  
H<sub>2</sub>ClB·S(CH<sub>3</sub>)<sub>2</sub>  
Formation: 2.6.5.3
- C<sub>2</sub>H<sub>6</sub>Cl<sub>3</sub>Cu<sub>2</sub>N**  
[(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>][Cu<sub>2</sub>Cl<sub>3</sub>]  
Formation: 2.8.12
- C<sub>2</sub>H<sub>6</sub>Ge**  
(CH<sub>3</sub>)<sub>2</sub>GeH<sub>2</sub>  
Formation: 2.6.9.3
- C<sub>2</sub>H<sub>6</sub>BS**  
H<sub>3</sub>B·S(CH<sub>3</sub>)<sub>2</sub>  
Reaction with CCl<sub>4</sub>: 2.6.5.3
- C<sub>2</sub>H<sub>6</sub>PSi**  
(CH<sub>3</sub>)<sub>2</sub>PSiH<sub>3</sub>  
Formation: 2.6.9.3
- C<sub>2</sub>H<sub>10</sub>Ge<sub>2</sub>**  
(CH<sub>3</sub>GeH<sub>2</sub>)<sub>2</sub>  
Formation: 2.6.9.3
- C<sub>2</sub>H<sub>11</sub>AsB<sub>10</sub>Cl<sub>2</sub>**  
(9-C<sub>2</sub>H<sub>2</sub>B<sub>10</sub>H<sub>9</sub>)AsCl<sub>2</sub>  
Reaction with X<sub>2</sub>: 2.6.9.1
- C<sub>2</sub>H<sub>12</sub>BrCl<sub>3</sub>CuN<sub>2</sub>**  
[CH<sub>3</sub>NH<sub>3</sub>]<sub>2</sub>[CuCl<sub>3</sub>Br]  
Formation: 2.8.10
- C<sub>2</sub>H<sub>12</sub>Br<sub>2</sub>HgI<sub>2</sub>N<sub>2</sub>**  
[(CH<sub>3</sub>NH<sub>3</sub>)<sub>2</sub>HgBr<sub>2</sub>I<sub>2</sub>]  
Formation: 2.8.22
- C<sub>2</sub>H<sub>12</sub>Cl<sub>2</sub>HgI<sub>2</sub>N<sub>2</sub>**  
[CH<sub>3</sub>NH<sub>3</sub>]<sub>2</sub>HgCl<sub>2</sub>I<sub>2</sub>  
Formation: 2.8.22
- C<sub>2</sub>H<sub>12</sub>Cl<sub>3</sub>CuN<sub>2</sub>**  
[CH<sub>3</sub>NH<sub>3</sub>]<sub>2</sub>[CuCl<sub>3</sub>]  
Oxidation by Br<sub>2</sub>: 2.8.10
- C<sub>2</sub>H<sub>18</sub>B<sub>10</sub>Sn**  
(CH<sub>3</sub>)<sub>2</sub>SnB<sub>10</sub>H<sub>12</sub>  
Reaction with X<sub>2</sub>: 2.6.11.1
- C<sub>3</sub>AuBrKN<sub>3</sub>**  
K[Au(CN)<sub>3</sub>Br]  
Formation: 2.8.4.2
- C<sub>3</sub>AuClKN<sub>3</sub>**  
K[Au(CN)<sub>3</sub>Cl]  
Formation: 2.8.4.2  
Reaction with KBr: 2.8.4.2
- C<sub>3</sub>BF<sub>9</sub>S<sub>3</sub>**  
B(SCF<sub>3</sub>)<sub>3</sub>  
Reaction with KF: 2.6.7.3
- C<sub>3</sub>CoNO<sub>4</sub>**  
Co(CO)<sub>3</sub>NO  
Reaction with [R<sub>4</sub>N]X or X<sub>2</sub>: 2.9.15.1.2  
Reaction with X<sub>2</sub>: 2.9.15.1.2
- C<sub>3</sub>F<sub>3</sub>MnO<sub>3</sub>**  
Mn(CO)<sub>3</sub>F<sub>3</sub>  
Formation: 2.9.15.1.1
- C<sub>3</sub>F<sub>3</sub>O<sub>3</sub>Re**  
Re(CO)<sub>3</sub>F<sub>3</sub>  
Formation: 2.9.15.1.1
- C<sub>3</sub>F<sub>3</sub>O<sub>3</sub>Ru**  
Ru(CO)<sub>3</sub>F<sub>3</sub>  
Formation: 2.9.15.1.1
- C<sub>3</sub>H<sub>6</sub>ClNO**  
(CH<sub>3</sub>)<sub>2</sub>NC(O)Cl  
Formation: 2.6.8.3
- C<sub>3</sub>H<sub>6</sub>CINS**  
(CH<sub>3</sub>)<sub>2</sub>NC(S)Cl  
Formation: 2.6.8.3
- C<sub>3</sub>H<sub>9</sub>AsBr<sub>2</sub>**  
(CH<sub>3</sub>)<sub>3</sub>AsBr<sub>2</sub>  
Reaction with R<sub>3</sub>In: 2.6.10.3
- C<sub>3</sub>H<sub>9</sub>Au**  
(CH<sub>3</sub>)<sub>3</sub>Au  
Reaction with AuBr<sub>3</sub>: 2.8.5  
Reaction with HCl: 2.8.5
- C<sub>3</sub>H<sub>9</sub>AuBrP**  
AuBr·P(CH<sub>3</sub>)<sub>3</sub>  
Reaction with X<sub>2</sub>: 2.8.6.1
- C<sub>3</sub>H<sub>9</sub>AuBr<sub>3</sub>P**  
AuBr<sub>3</sub>·P(CH<sub>3</sub>)<sub>3</sub>  
Formation: 2.8.6.1

- C<sub>3</sub>H<sub>9</sub>B**  
(CH<sub>3</sub>)<sub>3</sub>B  
Reaction with BX<sub>3</sub>: 2.6.16
- C<sub>3</sub>H<sub>9</sub>BO<sub>3</sub>**  
B(OCH<sub>3</sub>)<sub>3</sub>  
Reaction with Cl<sub>2</sub>: 2.6.6.1
- C<sub>3</sub>H<sub>9</sub>BS**  
(CH<sub>3</sub>)<sub>2</sub>BSCH<sub>3</sub>  
Reaction with BX<sub>3</sub>, SbCl<sub>5</sub>: 2.6.7.3
- C<sub>3</sub>H<sub>9</sub>B<sub>3</sub>Br<sub>3</sub>N<sub>3</sub>**  
(BrBNCH<sub>3</sub>)<sub>3</sub>  
Formation: 2.6.11.1
- C<sub>3</sub>H<sub>9</sub>B<sub>3</sub>Cl<sub>3</sub>N<sub>3</sub>**  
(ClBNCH<sub>3</sub>)<sub>3</sub>  
Reaction with TiF<sub>4</sub>: 2.6.12.3
- C<sub>3</sub>H<sub>9</sub>B<sub>3</sub>F<sub>3</sub>N<sub>3</sub>**  
(FBNCH<sub>3</sub>)<sub>3</sub>  
Formation: 2.6.12.3
- C<sub>3</sub>H<sub>9</sub>BrSn**  
(CH<sub>3</sub>)<sub>3</sub>SnBr  
Reaction with Li[Al(AsH<sub>2</sub>)<sub>4</sub>]: 2.6.9.3
- C<sub>3</sub>H<sub>9</sub>Br<sub>3</sub>GaN**  
Br<sub>3</sub>Ga·N(CH<sub>3</sub>)<sub>3</sub>  
Formation: 2.6.5.2
- C<sub>3</sub>H<sub>9</sub>ClGe**  
(CH<sub>3</sub>)<sub>3</sub>GeCl  
Reaction with Li[Al(SCH<sub>3</sub>)<sub>4</sub>]: 2.6.7.3
- C<sub>3</sub>H<sub>9</sub>ClSi**  
(CH<sub>3</sub>)<sub>3</sub>SiCl  
Formation: 2.6.11.2  
Reaction with Li[Al(SCH<sub>3</sub>)<sub>4</sub>]: 2.6.7.3
- C<sub>3</sub>H<sub>9</sub>ClSn**  
(CH<sub>3</sub>)<sub>3</sub>SnCl  
Reaction with Li[Al(SCH<sub>3</sub>)<sub>4</sub>]: 2.6.7.3
- C<sub>3</sub>H<sub>9</sub>Cl<sub>3</sub>GaN**  
Cl<sub>3</sub>Ga·N(CH<sub>3</sub>)<sub>3</sub>  
Formation: 2.6.5.2
- C<sub>3</sub>H<sub>9</sub>Cu<sub>2</sub>I<sub>3</sub>S**  
[(CH<sub>3</sub>)<sub>3</sub>S][Cu<sub>2</sub>I<sub>3</sub>]  
Structure: 2.8.12
- C<sub>3</sub>H<sub>9</sub>FSi**  
(CH<sub>3</sub>)<sub>3</sub>SiF  
Reaction with R<sub>3</sub>Al: 2.6.10.3
- C<sub>3</sub>H<sub>9</sub>FSn**  
(CH<sub>3</sub>)<sub>3</sub>SnF  
Reaction with R<sub>3</sub>Ga: 2.6.10.3
- C<sub>3</sub>H<sub>9</sub>Ga**  
(CH<sub>3</sub>)<sub>3</sub>Ga  
Reaction with X<sub>2</sub>: 2.6.10.1  
Reaction with HX: 2.6.10.2
- C<sub>3</sub>H<sub>9</sub>GaI<sub>4</sub>S**  
[(CH<sub>3</sub>)<sub>3</sub>S][GaI<sub>4</sub>]  
Formation: 2.6.7.3
- C<sub>3</sub>H<sub>9</sub>Ge**  
(CH<sub>3</sub>)<sub>3</sub>Ge  
Reaction with Li[Al(AsH<sub>2</sub>)<sub>4</sub>]: 2.6.9.3
- C<sub>3</sub>H<sub>9</sub>In**  
(CH<sub>3</sub>)<sub>3</sub>In  
Reaction with R<sub>3</sub>AsX<sub>2</sub>: 2.6.10.3  
Reaction with R<sub>3</sub>SnX: 2.6.10.3
- C<sub>3</sub>H<sub>9</sub>Si**  
(CH<sub>3</sub>)<sub>3</sub>Si  
Reaction with Li[Al(AsH<sub>2</sub>)<sub>4</sub>]: 2.6.9.3
- C<sub>3</sub>H<sub>9</sub>Tl**  
(CH<sub>3</sub>)<sub>3</sub>Tl  
Reaction with HX: 2.6.10.2
- C<sub>3</sub>H<sub>10</sub>Si**  
(CH<sub>3</sub>)<sub>3</sub>SiH  
Formation: 2.6.11.2
- C<sub>3</sub>H<sub>11</sub>AsGe**  
(CH<sub>3</sub>)<sub>3</sub>GeAsH<sub>2</sub>  
Formation: 2.6.9.3
- C<sub>3</sub>H<sub>11</sub>AsSi**  
(CH<sub>3</sub>)<sub>3</sub>SiAsH<sub>2</sub>  
Formation: 2.6.9.3
- C<sub>3</sub>H<sub>11</sub>AsSn**  
(CH<sub>3</sub>)<sub>3</sub>SnAsH<sub>2</sub>  
Formation: 2.6.9.3
- C<sub>3</sub>H<sub>11</sub>GeP**  
(CH<sub>3</sub>)<sub>3</sub>GePH<sub>2</sub>  
Formation: 2.6.9.3
- C<sub>3</sub>H<sub>11</sub>PSi**  
(CH<sub>3</sub>)<sub>3</sub>SiPH<sub>2</sub>  
Formation: 2.6.9.3
- C<sub>3</sub>H<sub>12</sub>GaN**  
H<sub>3</sub>Ga·N(CH<sub>3</sub>)<sub>3</sub>  
Reaction with HX: 2.6.5.2
- C<sub>3</sub>H<sub>13</sub>AlIP<sub>3</sub>**  
Li[HAL(HPCH<sub>3</sub>)<sub>3</sub>]  
Formation: 2.6.9.3  
Reaction with H<sub>3</sub>SiX: 2.6.9.3
- C<sub>4</sub>AuKN<sub>4</sub>**  
K[Au(CN)<sub>4</sub>]  
Reaction with K[AuCl<sub>4</sub>]: 2.8.4.2  
Reaction with Cl<sub>2</sub>: 2.8.4.2
- C<sub>4</sub>BaN<sub>4</sub>Ni**  
BaNi(CN)<sub>4</sub>  
Fluorination: 2.11.2.2
- C<sub>4</sub>Br<sub>2</sub>FeO<sub>4</sub>**  
Fe(CO)<sub>4</sub>Br<sub>2</sub>  
Formation: 2.6.13.1, 2.9.15.1.1
- C<sub>4</sub>Br<sub>2</sub>MoO<sub>4</sub>**  
Mo(CO)<sub>4</sub>Br<sub>2</sub>  
Formation: 2.9.15.1.1
- C<sub>4</sub>Br<sub>2</sub>O<sub>4</sub>Ru**  
Ru(CO)<sub>4</sub>Br<sub>2</sub>  
Formation: 2.9.15.1.1

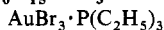
- C<sub>4</sub>Br<sub>2</sub>O<sub>4</sub>W**  
W(CO)<sub>4</sub>Br<sub>2</sub>  
Formation: 2.9.15.1.1
- C<sub>4</sub>Cl<sub>2</sub>FeO<sub>4</sub>**  
Fe(CO)<sub>4</sub>Cl<sub>2</sub>  
Formation: 2.9.15.1.1
- C<sub>4</sub>Cl<sub>2</sub>MoO<sub>4</sub>**  
Mo(CO)<sub>4</sub>Cl<sub>2</sub>  
Formation: 2.9.15.1.1
- C<sub>4</sub>Cl<sub>2</sub>O<sub>4</sub>Os**  
Os(CO)<sub>4</sub>Cl<sub>2</sub>  
Formation: 2.9.15.1.1
- C<sub>4</sub>Cl<sub>2</sub>O<sub>4</sub>Ru**  
Ru(CO)<sub>4</sub>Cl<sub>2</sub>  
Formation: 2.9.15.1.1
- C<sub>4</sub>Cl<sub>2</sub>O<sub>4</sub>W**  
W(CO)<sub>4</sub>Cl<sub>2</sub>  
Formation: 2.9.15.1.1
- C<sub>4</sub>CoO<sub>4</sub>Tl**  
Tl[Co(CO)<sub>4</sub>]  
Reaction with R<sub>3</sub>SnX: 2.6.13.3
- C<sub>4</sub>F<sub>2</sub>MoO<sub>4</sub>**  
Mo(CO)<sub>4</sub>F<sub>2</sub>  
Formation: 2.9.15.1.1
- C<sub>4</sub>FeI<sub>2</sub>O<sub>4</sub>**  
Fe(CO)<sub>4</sub>I<sub>2</sub>  
Thermal decomposition: 2.9.6
- C<sub>4</sub>H<sub>3</sub>BrMg**  
C<sub>4</sub>H<sub>3</sub>MgBr  
Reaction with CdCl<sub>2</sub>: 2.8.23.2
- C<sub>4</sub>H<sub>3</sub>CdCl**  
C<sub>4</sub>H<sub>3</sub>CdCl  
Formation from CdCl<sub>2</sub>: 2.8.23.2
- C<sub>4</sub>H<sub>3</sub>ClHgSe**  
C<sub>4</sub>H<sub>3</sub>HgClSe  
Formation: 2.8.23.6
- C<sub>4</sub>H<sub>4</sub>Se**  
C<sub>4</sub>H<sub>4</sub>Se  
Mercuration of: 2.8.23.6
- C<sub>4</sub>H<sub>6</sub>Au<sub>2</sub>Cl<sub>6</sub>**  
[Au<sub>2</sub>Cl<sub>6</sub>(CH<sub>3</sub>C≡CCH<sub>3</sub>)]  
Rearrangement: 2.8.5
- C<sub>4</sub>H<sub>6</sub>Au<sub>2</sub>Cl<sub>7</sub>**  
{Au<sub>2</sub>Cl<sub>6</sub>[CH<sub>3</sub>C≡C(Cl)CH<sub>3</sub>] }  
Formation: 2.8.5
- C<sub>4</sub>H<sub>6</sub>CdO<sub>4</sub>**  
Cd[CH<sub>3</sub>C(O)O]<sub>2</sub>  
Reaction with CH<sub>3</sub>C(O)X: 2.8.17.3  
Reaction with X<sub>2</sub>: 2.8.17.3
- C<sub>4</sub>H<sub>6</sub>Cl<sub>2</sub>Hg<sub>2</sub>**  
(CH<sub>3</sub>)<sub>2</sub>C<sub>2</sub>(HgCl)<sub>2</sub>  
Formation: 2.8.23.2
- C<sub>4</sub>H<sub>6</sub>Hg**  
(C<sub>2</sub>H<sub>3</sub>)<sub>2</sub>Hg  
Reaction with SiCl<sub>4</sub>: 2.8.23.5
- C<sub>4</sub>H<sub>6</sub>HgO<sub>4</sub>**  
Hg[CH<sub>3</sub>C(O)O]<sub>2</sub>  
Reaction with η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>Cr(CO)<sub>3</sub>: 2.8.23.6  
Reaction with (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe: 2.8.23.6  
Reaction with η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Mn(CO)<sub>3</sub>:  
2.8.23.6  
Reaction with I<sub>2</sub>: 2.8.17.3  
Reaction with CH<sub>3</sub>I: 2.8.17.3
- C<sub>4</sub>H<sub>6</sub>N<sub>4</sub>Na<sub>2</sub>NiO<sub>3</sub>**  
Na<sub>2</sub>[Ni(CN)<sub>4</sub>]·3 H<sub>2</sub>O  
Fluorination: 2.11.2.2
- C<sub>4</sub>H<sub>6</sub>BaNa<sub>4</sub>NiO<sub>4</sub>**  
Ba[Ni(CN)<sub>4</sub>]·4 H<sub>2</sub>O  
Fluorination: 2.11.2.2
- C<sub>4</sub>H<sub>9</sub>BCl<sub>2</sub>O**  
n-C<sub>4</sub>H<sub>9</sub>OBCl<sub>2</sub>  
Formation: 2.6.6.3, 2.6.6.4
- C<sub>4</sub>H<sub>10</sub>Ag<sub>2</sub>I<sub>3</sub>N**  
[CH<sub>3</sub>NH=C(CH<sub>3</sub>)<sub>2</sub>][Ag<sub>2</sub>I<sub>3</sub>]  
Formation: 2.8.12
- C<sub>4</sub>H<sub>10</sub>AlBr**  
(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>AlBr  
Formation: 2.6.5.1
- C<sub>4</sub>H<sub>10</sub>AlCl**  
(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>AlCl  
Formation: 2.6.5.2
- C<sub>4</sub>H<sub>10</sub>AlF**  
(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>AlF  
Formation: 2.6.10.3
- C<sub>4</sub>H<sub>10</sub>AlI**  
(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>AlI  
Formation: 2.6.3.2, 2.6.10.1
- C<sub>4</sub>H<sub>10</sub>BCl**  
(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>BCl  
Formation: 2.6.10.3
- C<sub>4</sub>H<sub>10</sub>BCl<sub>2</sub>N**  
(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NBCl<sub>2</sub>  
Formation: 2.6.8.2, 2.6.9.2
- C<sub>4</sub>H<sub>10</sub>BCl<sub>2</sub>P**  
Cl<sub>2</sub>BP(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>  
Formation: 2.6.9.3
- C<sub>4</sub>H<sub>10</sub>BF<sub>2</sub>N**  
(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NBF<sub>2</sub>  
Formation: 2.6.8.3
- C<sub>4</sub>H<sub>10</sub>BI<sub>2</sub>N**  
(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NBI<sub>2</sub>  
Formation: 2.6.9.3
- C<sub>4</sub>H<sub>10</sub>B<sub>2</sub>S<sub>5</sub>**  
(C<sub>2</sub>H<sub>5</sub>SB)<sub>2</sub>S<sub>3</sub>  
Reaction with BX<sub>3</sub>, AsX<sub>3</sub>: 2.6.7.3

- C<sub>4</sub>H<sub>10</sub>Be**  
 (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Be  
 Reaction with BeX<sub>2</sub>: 2.7.3.2.2
- C<sub>4</sub>H<sub>10</sub>BrTi**  
 (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>TiBr  
 Reaction with X<sub>2</sub>: 2.6.10.1
- C<sub>4</sub>H<sub>10</sub>GaIS<sub>2</sub>**  
 (C<sub>2</sub>H<sub>5</sub>S)<sub>2</sub>GaI  
 Formation: 2.6.7.1
- C<sub>4</sub>H<sub>10</sub>ITi**  
 (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>TiI  
 Formation: 2.6.13.3
- C<sub>4</sub>H<sub>11</sub>Al**  
 (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>AlH  
 Reaction with X<sub>2</sub>: 2.6.5.1  
 Reaction with HCl: 2.6.5.2
- C<sub>4</sub>H<sub>11</sub>BCl<sub>3</sub>N**  
 (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>HN·BCl<sub>3</sub>  
 Formation: 2.6.8.2
- C<sub>4</sub>H<sub>11</sub>P**  
 (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>PH  
 Formation: 2.6.9.2
- C<sub>4</sub>H<sub>12</sub>AgBr<sub>2</sub>N**  
 [(CH<sub>3</sub>)<sub>4</sub>N][AgBr<sub>2</sub>]  
 Structure: 2.8.12
- C<sub>4</sub>H<sub>12</sub>AgCl<sub>2</sub>N**  
 [(CH<sub>3</sub>)<sub>4</sub>N][AgCl<sub>2</sub>]  
 Formation: 2.8.12  
 Structure: 2.8.12
- C<sub>4</sub>H<sub>12</sub>AgI<sub>2</sub>N**  
 [(CH<sub>3</sub>)<sub>4</sub>N][AgI<sub>2</sub>]  
 Formation: 2.8.12
- C<sub>4</sub>H<sub>12</sub>Ag<sub>2</sub>I<sub>3</sub>N**  
 [(CH<sub>3</sub>)<sub>4</sub>N][Ag<sub>2</sub>I<sub>3</sub>]  
 Formation from Ag<sub>2</sub>O and CH<sub>3</sub>I: 2.8.12
- C<sub>4</sub>H<sub>12</sub>AlLiS<sub>4</sub>**  
 Li[Al(SCH<sub>3</sub>)<sub>4</sub>]  
 Reaction with H<sub>3</sub>SiX, H<sub>3</sub>GeX, R<sub>3</sub>SnX:  
 2.6.7.3
- C<sub>4</sub>H<sub>12</sub>AlLiTe<sub>4</sub>**  
 Li[Al(TeCH<sub>3</sub>)<sub>4</sub>]  
 Disproportionation: 2.6.7
- C<sub>4</sub>H<sub>12</sub>AlP**  
 (CH<sub>3</sub>)<sub>2</sub>AlP(CH<sub>3</sub>)<sub>2</sub>  
 Reaction with HX: 2.6.9.2
- C<sub>4</sub>H<sub>12</sub>Au<sub>2</sub>Br<sub>2</sub>**  
 [(CH<sub>3</sub>)<sub>2</sub>AuBr]<sub>2</sub>  
 Formation: 2.8.5  
 Reaction with [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>As]Br: 2.8.5
- C<sub>4</sub>H<sub>12</sub>Au<sub>2</sub>Cl<sub>2</sub>**  
 [(CH<sub>3</sub>)<sub>2</sub>AuCl]<sub>2</sub>  
 Formation: 2.8.5
- Reactions with 2,2'-bipyridine and 1,  
 10-phenanthroline: 2.8.5  
 Reaction with [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>As]Cl: 2.8.5
- C<sub>4</sub>H<sub>12</sub>Au<sub>2</sub>F<sub>2</sub>**  
 [(CH<sub>3</sub>)<sub>2</sub>AuF]<sub>2</sub>  
 Non-existence: 2.8.5
- C<sub>4</sub>H<sub>12</sub>Au<sub>2</sub>I<sub>2</sub>**  
 [(CH<sub>3</sub>)<sub>2</sub>AuI]<sub>2</sub>  
 Formation: 2.8.5  
 Reaction with AgNO<sub>3</sub> and HNO<sub>3</sub>: 2.8.5
- C<sub>4</sub>H<sub>12</sub>BCIN<sub>2</sub>**  
 [(CH<sub>3</sub>)<sub>2</sub>N]<sub>2</sub>BCl  
 Formation: 2.6.8.2, 2.6.8.3, 2.6.9.3
- C<sub>4</sub>H<sub>12</sub>BCl<sub>3</sub>N<sub>2</sub>**  
 [Cl<sub>2</sub>B[N(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>]<sub>2</sub>Cl  
 Formation: 2.6.9.2
- C<sub>4</sub>H<sub>12</sub>BIN<sub>2</sub>**  
 [(CH<sub>3</sub>)<sub>2</sub>N]<sub>2</sub>BI  
 Formation: 2.6.9.3
- C<sub>4</sub>H<sub>12</sub>B<sub>2</sub>O<sub>4</sub>**  
 B<sub>2</sub>(OCH<sub>3</sub>)<sub>4</sub>  
 Reaction with SF<sub>4</sub>: 2.6.14.1
- C<sub>4</sub>H<sub>12</sub>Cl<sub>3</sub>Cu<sub>2</sub>N**  
 [(CH<sub>3</sub>)<sub>4</sub>N][Cu<sub>2</sub>Cl<sub>3</sub>]  
 Formation from Cu[OAc]: 2.8.12  
 Structure: 2.8.12
- C<sub>4</sub>H<sub>12</sub>Cl<sub>3</sub>Cu<sub>2</sub>P**  
 [(CH<sub>3</sub>)<sub>4</sub>P][Cu<sub>2</sub>Cl<sub>3</sub>]  
 Structure: 2.8.12
- C<sub>4</sub>H<sub>12</sub>Cu<sub>2</sub>I<sub>3</sub>N**  
 [(CH<sub>3</sub>)<sub>4</sub>N][Cu<sub>2</sub>I<sub>3</sub>]  
 Formation from Cu: 2.8.12
- C<sub>4</sub>H<sub>12</sub>GeS**  
 (CH<sub>3</sub>)<sub>3</sub>GeSCH<sub>3</sub>  
 Formation: 2.6.7.3
- C<sub>4</sub>H<sub>12</sub>NTi**  
 (CH<sub>3</sub>)<sub>2</sub>TiN(CH<sub>3</sub>)<sub>2</sub>  
 Reaction with RX: 2.6.8.3  
 Reaction with R<sub>3</sub>SnX: 2.6.8.3
- C<sub>4</sub>H<sub>12</sub>SSi**  
 (CH<sub>3</sub>)<sub>3</sub>SiSCH<sub>3</sub>  
 Formation: 2.6.7.3
- C<sub>4</sub>H<sub>12</sub>SSn**  
 (CH<sub>3</sub>)<sub>3</sub>SnSCH<sub>3</sub>  
 Formation: 2.6.7.3
- C<sub>4</sub>H<sub>12</sub>Si**  
 (CH<sub>3</sub>)<sub>4</sub>Si  
 Formation: 2.6.10.3
- C<sub>4</sub>H<sub>14</sub>Au<sub>2</sub>O<sub>2</sub>**  
 [(CH<sub>3</sub>)<sub>2</sub>AuOH]<sub>4</sub>  
 Reaction with CsCl: 2.8.5  
 Reaction with HI, (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>AsCl: 2.8.5

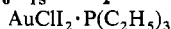


- C<sub>4</sub>H<sub>14</sub>BCl<sub>3</sub>N**  
 [(CH<sub>3</sub>)<sub>2</sub>NH]<sub>2</sub>BCl<sub>2</sub>]Cl  
 Formation: 2.6.8.2
- C<sub>4</sub>H<sub>16</sub>Ag<sub>2</sub>Br<sub>2</sub>CuI<sub>2</sub>N<sub>4</sub>**  
 [Cu(NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>][AgIBr]<sub>2</sub>  
 Formation: 2.8.12
- C<sub>4</sub>H<sub>16</sub>Ag<sub>2</sub>Br<sub>4</sub>N<sub>4</sub>Ni**  
 [Ni(NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>][AgBr<sub>2</sub>]<sub>2</sub>  
 Structure: 2.8.12
- C<sub>4</sub>H<sub>16</sub>Br<sub>3</sub>Cu<sub>2</sub>N<sub>4</sub>**  
 [Cu(NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>][CuBr<sub>3</sub>]  
 Formation: 2.8.12
- C<sub>4</sub>H<sub>17</sub>CoF<sub>4</sub>N<sub>4</sub>**  
 [Coen<sub>2</sub>F<sub>2</sub>][HF<sub>2</sub>]  
 Formation: 2.11.2.2
- C<sub>4</sub>I<sub>2</sub>O<sub>4</sub>W**  
 W(CO)<sub>4</sub>I<sub>2</sub>  
 Formation: 2.9.15.1.1
- C<sub>4</sub>NiO<sub>4</sub>**  
 Ni(CO)<sub>4</sub>  
 Reaction with [R<sub>4</sub>N]X or X<sub>2</sub>: 2.9.15.1.2
- C<sub>5</sub>BCl<sub>2</sub>MnO<sub>5</sub>**  
 Cl<sub>2</sub>BMn(CO)<sub>5</sub>  
 Formation: 2.6.13.2  
 Reaction with HX: 2.6.13.2
- C<sub>5</sub>BrMnO<sub>5</sub>**  
 Mn(CO)<sub>5</sub>Br  
 Formation: 2.6.13.3, 2.9.15.1.1, 2.9.15.11  
 Reaction with [R<sub>4</sub>N]X or X<sub>2</sub>: 2.9.15.1.2
- C<sub>5</sub>BrO<sub>5</sub>Re**  
 Re(CO)<sub>5</sub>Br  
 Formation: 2.9.15.1.1  
 Reaction with [R<sub>4</sub>N]X or X<sub>2</sub>: 2.9.15.1.2
- C<sub>5</sub>BrO<sub>5</sub>Tc**  
 Tc(CO)<sub>5</sub>Br  
 Formation: 2.9.15.1.1
- C<sub>5</sub>Br<sub>2</sub>InMnO<sub>5</sub>**  
 Br<sub>2</sub>InMn(CO)<sub>5</sub>  
 Formation: 2.6.13.1
- C<sub>5</sub>ClMnO<sub>5</sub>**  
 Mn(CO)<sub>5</sub>Cl  
 Formation: 2.6.13.2, 2.9.15.1.1  
 Reaction with [R<sub>4</sub>N]X or X<sub>2</sub>: 2.9.15.1.2
- C<sub>5</sub>ClO<sub>5</sub>Re**  
 Re(CO)<sub>5</sub>Cl  
 Formation: 2.9.15.1.1  
 Reaction with [R<sub>4</sub>N]X or X<sub>2</sub>: 2.9.15.1.2
- C<sub>5</sub>ClO<sub>5</sub>Tc**  
 Tc(CO)<sub>5</sub>Cl  
 Formation: 2.9.15.1.1
- C<sub>5</sub>Cl<sub>2</sub>InMnO<sub>5</sub>**  
 Cl<sub>2</sub>InMn(CO)<sub>5</sub>  
 Formation: 2.6.13.1
- C<sub>5</sub>Cl<sub>6</sub>**  
 C<sub>5</sub>Cl<sub>6</sub>  
 Halogenation reagent: 2.9.12.4
- C<sub>5</sub>Cl<sub>8</sub>**  
 C<sub>5</sub>Cl<sub>8</sub>  
 Halogenation reagent: 2.9.12.4  
 Reaction with MO: 2.9.4.6
- C<sub>5</sub>FO<sub>5</sub>Re**  
 Re(CO)<sub>5</sub>F  
 Formation: 2.9.15.1.1
- C<sub>5</sub>F<sub>6</sub>O<sub>5</sub>Re<sub>2</sub>**  
 Re(CO)<sub>5</sub>F·ReF<sub>5</sub>  
 Formation: 2.9.15.1.1
- C<sub>5</sub>FeO<sub>5</sub>**  
 Fe(CO)<sub>5</sub>  
 Halogenation: 2.9.15.1.1
- C<sub>5</sub>HMnO<sub>5</sub>**  
 HMn(CO)<sub>5</sub>  
 Formation: 2.6.13.2
- C<sub>5</sub>H<sub>8</sub>AuCl<sub>3</sub>N**  
 [AuCl<sub>3</sub>·C<sub>5</sub>H<sub>5</sub>N]  
 Reaction with RMgBr: 2.8.5  
 Reaction with BrMg(CH<sub>2</sub>)<sub>5</sub>MgBr: 2.8.5
- C<sub>5</sub>H<sub>8</sub>ClHg**  
 C<sub>5</sub>H<sub>5</sub>HgCl  
 Formation from (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>ZrCl<sub>2</sub>:  
 2.8.23.2
- C<sub>5</sub>H<sub>5</sub>ClMoN<sub>2</sub>O<sub>2</sub>**  
 η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Mo(NO)<sub>2</sub>Cl  
 Formation: 2.9.15.1.2
- C<sub>5</sub>H<sub>8</sub>AuCl<sub>4</sub>N**  
 [C<sub>5</sub>H<sub>5</sub>NH][AuCl<sub>4</sub>]  
 Formation: 2.8.4.1
- C<sub>5</sub>H<sub>8</sub>BrCuIN**  
 [C<sub>5</sub>H<sub>5</sub>NH][CuBr]  
 Formation: 2.8.12
- C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>Tl**  
 {Tl[OC(Me)CHC(Me)O]}  
 Reaction with dialkyl gold bromides:  
 2.8.5
- C<sub>5</sub>H<sub>10</sub>AuBr<sub>2</sub>NS<sub>2</sub>**  
 Au[S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]Br<sub>2</sub>  
 Formation: 2.8.6.2
- C<sub>5</sub>H<sub>10</sub>AuNS<sub>2</sub>**  
 [Au(S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>)]  
 Reaction with halogens: 2.8.6.2
- C<sub>5</sub>H<sub>17</sub>BCl<sub>2</sub>N<sub>2</sub>**  
 [[(CH<sub>3</sub>)<sub>2</sub>NH]<sub>2</sub>B(CH<sub>3</sub>)Cl]Cl  
 Formation: 2.6.8.2
- C<sub>5</sub>IMnO<sub>5</sub>**  
 Mn(CO)<sub>5</sub>I  
 Formation: 2.9.15.1.1

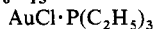
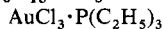
- Reaction with  $[R_4N]X$  or  $X_2$ : 2.9.15.1.2  
 **$C_5IO_3Re$**   
 $Re(CO)_5I$   
 Formation: 2.9.15.1.1  
 Reaction with  $[R_4N]X$  or  $X_2$ : 2.9.15.1.2  
 **$C_5IO_5Tc$**   
 $Tc(CO)_5I$   
 Formation: 2.9.15.1.1  
 **$C_5MnO_5Ti$**   
 $Ti[Mn(CO)_5]$   
 Reaction with  $R_3SnX$ : 2.6.13.3  
 **$C_6Cl_4O_6Os_2$**   
 $[Os(CO)_3Cl_2]_2$   
 Formation: 2.9.15.1.1  
 **$C_6Cl_6$**   
 $C_6Cl_6$   
 Reaction with  $MO$ : 2.9.4.6  
 **$C_6CrF_{21}Sb_2$**   
 $C_6F_6(CrF_4Sb_2F_{11})$   
 Formation: 2.11.2.1  
 **$C_6CrO_6$**   
 $Cr(CO)_6$   
 Reaction with  $[R_4N]X$  or  $X_2$ : 2.9.15.1.2  
 Reaction with  $X_2$ : 2.9.6  
 **$C_6F_5I$**   
 $C_6F_5I$   
 Reaction with elemental  $Cd$ : 2.8.23.1  
 **$C_6F_5Ni$**   
 $C_6F_5NiI$   
 Formation: 2.9.3.8  
 **$C_6F_6$**   
 $C_6F_6$   
 Reaction with  $BX_3$ : 2.6.16  
 **$C_6F_{11}O_6Re_3$**   
 $[Re(CO)_6][Re_2F_{11}]$   
 Formation: 2.9.15.1.1  
 **$C_6H_3MnO_5$**   
 $CH_3Mn(CO)_5$   
 Formation: 2.6.13.3  
 **$C_6H_5BBr_2$**   
 $C_6H_5BBr_2$   
 Formation: 2.6.3.2  
 **$C_6H_5BCl_2$**   
 $C_6H_5BCl_2$   
 Reaction with  $SbF_3$ : 2.6.12.3  
 **$C_6H_5Br$**   
 $C_6H_5Br$   
 Formation: 2.8.23.5  
 **$C_6H_5BrHg$**   
 $C_6H_5HgBr$   
 Formation: 2.8.23.3, 2.8.23.5  
 **$C_6H_5Br_3Cu_2N_2$**   
 $C_6H_5N_2[Cu_2Br_3]$   
 Structure: 2.8.12  
 **$C_6H_5Cl$**   
 $C_6H_5Cl$   
 Formation: 2.8.23.5  
 **$C_6H_5ClHg$**   
 $C_6H_5HgCl$   
 Formation: 2.8.23.3, 2.8.23.5  
 **$C_6H_5Cl_2Ga$**   
 $C_6H_5GaCl_2$   
 Formation: 2.6.10.2  
 **$C_6H_5Cl_2I$**   
 $C_6H_5ICl_2$   
 Reaction with  $(C_6H_5)_2Hg$ : 2.8.23.5  
 **$C_6H_5Cl_2OV$**   
 $C_6H_5VOCl_2$   
 Formation: 2.8.23.5  
 **$C_6H_5Cl_2Ti$**   
 $C_6H_5TiCl_2$   
 Reaction with  $HgX_2$ : 2.6.10.3  
 **$C_6H_5Cl_3V$**   
 $C_6H_5VCl_3$   
 Formation: 2.8.23.5  
 **$C_6H_7P$**   
 $C_6H_5PH_2$   
 Formation: 2.6.9.2  
 **$C_6H_8CuI_2N$**   
 $[(C_5H_5NCH_3)][CuI_2]$   
 Formation from  $Cu$ : 2.8.12  
 **$C_6H_{12}AuBrClN_3$**   
 $(CH_3)_4N[Au(CN)_2ClBr]$   
 Formation: 2.8.4.2  
 **$C_6H_{14}AlClO_2$**   
 $(i-C_3H_7O)_2AlCl$   
 Formation: 2.6.6.3  
 **$C_6H_{14}BCl$**   
 $(n-C_3H_7)_2BCl$   
 Formation: 2.6.7.3  
 **$C_6H_{15}Al$**   
 $(C_2H_5)_3Al$   
 Reaction with  $SnX_4$ : 2.6.10.3, 2.6.15  
 Reaction with  $HX$ : 2.6.10.2  
 **$C_6H_{15}Al_2I_3$**   
 $(C_2H_5)_3Al_2I_3$   
 Formation: 2.6.3.2  
 **$C_6H_{15}AuBrCl_2P$**   
 $AuBrCl_2 \cdot P(C_2H_5)_3$   
 Formation: 2.8.6.1  
 **$C_6H_{15}AuBrP$**   
 $AuBr \cdot P(C_2H_5)_3$   
 Reaction with  $X_2$ : 2.8.6.1  
 **$C_6H_{15}AuBr_2ClP$**   
 $AuBr_2Cl \cdot P(C_2H_5)_3$   
 Formation: 2.8.6.1

**C<sub>6</sub>H<sub>15</sub>AuBr<sub>3</sub>P**

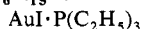
Formation: 2.8.6.1

**C<sub>6</sub>H<sub>15</sub>AuClI<sub>2</sub>P**

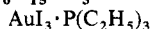
Formation: 2.8.6.1

**C<sub>6</sub>H<sub>15</sub>AuClP**Reaction with X<sub>2</sub>: 2.8.6.1**C<sub>6</sub>H<sub>15</sub>AuCl<sub>3</sub>P**

Formation: 2.8.6.1

**C<sub>6</sub>H<sub>15</sub>AuIP**

Reaction with ICl: 2.8.6.1

**C<sub>6</sub>H<sub>15</sub>AuI<sub>3</sub>P**

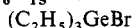
Formation: 2.8.6.1

**C<sub>6</sub>H<sub>15</sub>B**Reaction with SbX<sub>5</sub>: 2.6.10.3

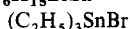
Reaction with ONX: 2.6.16

**C<sub>6</sub>H<sub>15</sub>BCINO**

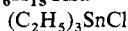
Formation: 2.6.16

**C<sub>6</sub>H<sub>15</sub>BrGe**

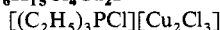
Formation: 2.6.11.3

**C<sub>6</sub>H<sub>15</sub>BrSn**

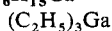
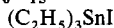
Formation: 2.6.10.3

**C<sub>6</sub>H<sub>15</sub>ClSn**

Formation: 2.6.10.3, 2.6.11.1

**C<sub>6</sub>H<sub>15</sub>Cl<sub>4</sub>Cu<sub>2</sub>P**

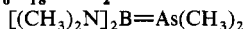
Formation: 2.8.12

**C<sub>6</sub>H<sub>15</sub>Ga**Reaction with R<sub>3</sub>SnX: 2.6.10.3**C<sub>6</sub>H<sub>15</sub>ISn**

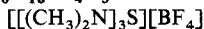
Formation: 2.6.10.3

**C<sub>6</sub>H<sub>16</sub>Cl<sub>2</sub>CuN**

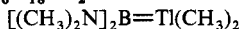
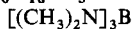
Formation: 2.8.12

**C<sub>6</sub>H<sub>18</sub>AsBN<sub>2</sub>**Reaction with X<sub>2</sub>: 2.6.9.1**C<sub>6</sub>H<sub>18</sub>AsBr<sub>2</sub>In**

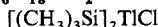
Formation: 2.6.10.3

**C<sub>6</sub>H<sub>18</sub>BF<sub>4</sub>N<sub>3</sub>S**

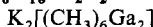
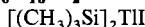
Formation: 2.6.8.3

**C<sub>6</sub>H<sub>18</sub>BN<sub>2</sub>Tl**Reaction with X<sub>2</sub>: 2.6.9.1**C<sub>6</sub>H<sub>18</sub>BN<sub>3</sub>**Reaction with SF<sub>4</sub>: 2.6.8.3Reaction with YCCl<sub>2</sub>: 2.6.8.3

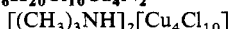
Reaction with HX: 2.6.8.2

**C<sub>6</sub>H<sub>18</sub>ClSi<sub>2</sub>Tl**

Reaction with HX: 2.6.11.2

**C<sub>6</sub>H<sub>18</sub>Ga<sub>2</sub>K<sub>2</sub>**Reaction with RSiX<sub>3</sub>: 2.6.10.3**C<sub>6</sub>H<sub>18</sub>ISi<sub>2</sub>Tl**

Formation: 2.6.11.2

**C<sub>6</sub>H<sub>20</sub>Cl<sub>10</sub>Cu<sub>4</sub>N<sub>2</sub>**

Formation: 2.8.10

**C<sub>6</sub>MoO<sub>6</sub>**

Halogenation: 2.9.15.1.1

Reaction with MoF<sub>6</sub>, MoBr<sub>4</sub>: 2.9.6Reaction with [R<sub>4</sub>N]X or X<sub>2</sub>: 2.9.15.1.2Reaction with X<sub>2</sub>: 2.9.6

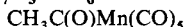
Reaction with ONX: 2.9.15.1.2

**C<sub>6</sub>O<sub>6</sub>W**

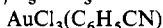
Halogenation: 2.9.15.1.1

Reaction with ReF<sub>6</sub>, IF<sub>5</sub>: 2.9.6Reaction with [R<sub>4</sub>N]X or X<sub>2</sub>: 2.9.15.1.2Reaction with WCl<sub>6</sub>, WCl<sub>5</sub>, WBr<sub>5</sub>: 2.9.6Reaction with ReF<sub>6</sub>: 2.9.6Reaction with X<sub>2</sub>: 2.9.6

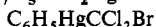
Reaction with ONX: 2.9.15.1.2

Reaction with KI in IF<sub>5</sub>: 2.11.4.1Reaction with moist CsI in IF<sub>5</sub>: 2.11.4.1**C<sub>7</sub>H<sub>3</sub>MnO<sub>6</sub>**

Formation: 2.6.13.3

**C<sub>7</sub>H<sub>8</sub>AuCl<sub>3</sub>N**

Formation: 2.8.5

**C<sub>7</sub>H<sub>5</sub>BrCl<sub>2</sub>Hg**

Reaction with HCl: 2.8.23.3

**C<sub>7</sub>H<sub>5</sub>Br<sub>2</sub>ClHg**

Decomposition: 2.8.23.3

- C<sub>7</sub>H<sub>8</sub>ClO**  
 C<sub>6</sub>H<sub>5</sub>C(O)Cl  
 Reaction with HgO: 2.8.15.3
- C<sub>7</sub>H<sub>8</sub>Cl<sub>3</sub>**  
 C<sub>6</sub>H<sub>5</sub>CCl<sub>3</sub>  
 Reaction with MO: 2.9.4.6
- C<sub>7</sub>H<sub>8</sub>Cl<sub>3</sub>Hg**  
 C<sub>6</sub>H<sub>5</sub>HgCCl<sub>3</sub>  
 Decomposition: 2.8.23.3
- C<sub>7</sub>H<sub>10</sub>AuN<sub>3</sub>S<sub>2</sub>Se<sub>2</sub>**  
 Au[S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>](SeCN)<sub>2</sub>  
 Formation: 2.8.6.2
- C<sub>7</sub>H<sub>10</sub>AuN<sub>3</sub>S<sub>4</sub>**  
 Au[S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>](SCN)<sub>2</sub>  
 Formation: 2.8.6.2
- C<sub>7</sub>H<sub>11</sub>TI**  
 (CH<sub>3</sub>)<sub>2</sub>TlC<sub>5</sub>H<sub>5</sub>  
 Reaction with HX: 2.6.10.2
- C<sub>7</sub>H<sub>13</sub>AuO<sub>2</sub>**  
 {(CH<sub>3</sub>)<sub>2</sub>Au[OC(Me)CHC(Me)O]}  
 Reaction with bromine: 2.8.5
- C<sub>7</sub>H<sub>21</sub>BN<sub>2</sub>Si**  
 [(CH<sub>3</sub>)<sub>2</sub>N]<sub>2</sub>BSi(CH<sub>3</sub>)<sub>3</sub>  
 Reaction with X<sub>2</sub>: 2.6.11.1
- C<sub>8</sub>Br<sub>2</sub>O<sub>8</sub>Tc<sub>2</sub>**  
 [Tc(CO)<sub>4</sub>Br]<sub>2</sub>  
 Formation: 2.9.15.1.1
- C<sub>8</sub>Cl<sub>2</sub>O<sub>4</sub>Tc<sub>2</sub>**  
 [Tc(CO)<sub>4</sub>Cl]<sub>2</sub>  
 Formation: 2.9.15.1.1
- C<sub>8</sub>Cl<sub>2</sub>O<sub>8</sub>Re<sub>2</sub>**  
 [Re(CO)<sub>4</sub>Cl]<sub>2</sub>  
 Reaction with NO: 2.9.15.1.2
- C<sub>8</sub>F<sub>2</sub>Mn<sub>2</sub>O<sub>8</sub>**  
 [Mn(CO)<sub>4</sub>F]<sub>2</sub>  
 Formation: 2.9.15.1.1
- C<sub>8</sub>Fe<sub>2</sub>I<sub>2</sub>O<sub>8</sub>**  
 Fe<sub>2</sub>(CO)<sub>8</sub>I<sub>2</sub>  
 Formation: 2.9.15.1.1
- C<sub>8</sub>H<sub>4</sub>ClHgMnO<sub>3</sub>**  
 (η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>HgClMn(CO))<sub>3</sub>  
 Formation: 2.8.23.6
- C<sub>8</sub>H<sub>4</sub>Cl<sub>6</sub>**  
 C<sub>8</sub>H<sub>4</sub>Cl<sub>6</sub>  
 Reaction with MO: 2.9.4.6
- C<sub>8</sub>H<sub>5</sub>ClHgMoO<sub>3</sub>**  
 η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>3</sub>HgCl  
 Formation: 2.6.13.3
- C<sub>8</sub>H<sub>5</sub>IMoO<sub>3</sub>**  
 η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>3</sub>I  
 Formation: 2.6.13.3
- C<sub>8</sub>H<sub>5</sub>IO<sub>3</sub>W**  
 η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>W(CO)<sub>3</sub>I  
 Formation: 2.6.13.3
- C<sub>8</sub>H<sub>5</sub>MnO<sub>3</sub>**  
 η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Mn(CO)<sub>3</sub>  
 Mercuration of: 2.8.23.6
- C<sub>8</sub>H<sub>5</sub>BF<sub>2</sub>NO<sub>6</sub>S<sub>2</sub>**  
 (CH<sub>3</sub>)<sub>2</sub>NBS<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>  
 Reaction with BX<sub>3</sub>: 2.6.8.3
- C<sub>8</sub>H<sub>6</sub>MoO<sub>3</sub>**  
 η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>MoH(CO)<sub>3</sub>  
 Formation: 2.6.13.2
- C<sub>8</sub>H<sub>10</sub>BBrFeNO<sub>4</sub>**  
 (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NB(Br)Fe(CO)<sub>4</sub>  
 Reaction with X<sub>2</sub>: 2.6.13.1
- C<sub>8</sub>H<sub>11</sub>AuBrP**  
 AuBr·P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>  
 Reaction with X<sub>2</sub>: 2.8.6.1
- C<sub>8</sub>H<sub>11</sub>AuClP**  
 AuCl·P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>  
 Reaction with X<sub>2</sub>: 2.8.6.1
- C<sub>8</sub>H<sub>11</sub>BCIN**  
 (CH<sub>3</sub>)<sub>2</sub>N(C<sub>6</sub>H<sub>5</sub>)BCl  
 Formation: 2.6.13.3
- C<sub>8</sub>H<sub>11</sub>ClOZn**  
 C<sub>6</sub>H<sub>5</sub>ZnCl·C<sub>2</sub>H<sub>5</sub>OH  
 Formation from ZnCl<sub>2</sub>: 2.8.23.2
- C<sub>8</sub>H<sub>11</sub>P**  
 C<sub>2</sub>H<sub>5</sub>P(H)C<sub>6</sub>H<sub>5</sub>  
 Formation: 2.6.9.3
- C<sub>8</sub>H<sub>12</sub>PTI**  
 (CH<sub>3</sub>)<sub>2</sub>TIP(H)C<sub>6</sub>H<sub>5</sub>  
 Reaction with RX: 2.6.9.3  
 Reaction with HX: 2.6.9.2
- C<sub>8</sub>H<sub>12</sub>SeSi**  
 (CH<sub>3</sub>)<sub>2</sub>Si(H)SeC<sub>6</sub>H<sub>5</sub>  
 Formation: 2.6.7.3
- C<sub>8</sub>H<sub>16</sub>Cu<sub>2</sub>O<sub>10</sub>**  
 [Cu(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)]<sub>2</sub>  
 Reactions with RC(O)X: 2.8.8.3
- C<sub>8</sub>H<sub>18</sub>BCl**  
 (C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>BCl  
 Formation: 2.6.10.2
- C<sub>8</sub>H<sub>18</sub>BClO<sub>2</sub>**  
 (n-C<sub>4</sub>H<sub>9</sub>O)<sub>2</sub>BCl  
 Formation: 2.6.6.3
- C<sub>8</sub>H<sub>19</sub>AuCl<sub>4</sub>N<sub>2</sub>O<sub>2</sub>**  
 [{(CH<sub>3</sub>)<sub>2</sub>NC(CH<sub>3</sub>)O}<sub>2</sub>H][AuCl<sub>4</sub>]  
 Formation: 2.8.4.1
- C<sub>8</sub>H<sub>20</sub>Ag<sub>2</sub>Br<sub>3</sub>N**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N][Ag<sub>2</sub>Br<sub>3</sub>]  
 Formation: 2.8.12  
 Structure: 2.8.12
- C<sub>8</sub>H<sub>20</sub>Ag<sub>2</sub>Cl<sub>3</sub>N**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N][Ag<sub>2</sub>Cl<sub>3</sub>]  
 Formation: 2.8.12

- Structure: 2.8.12  
**C<sub>8</sub>H<sub>20</sub>AuBr<sub>2</sub>N**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N][AuBr<sub>2</sub>]  
 Formation: 2.8.12  
**C<sub>8</sub>H<sub>20</sub>AuBr<sub>4</sub>N**  
 (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N[AuBr<sub>4</sub>]  
 Formation: 2.8.4.1  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N][AuBr<sub>4</sub>]  
 Formation: 2.9.10.4  
**C<sub>8</sub>H<sub>20</sub>AuCl<sub>2</sub>N**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N][AuCl<sub>2</sub>]  
 Formation: 2.8.12  
**C<sub>8</sub>H<sub>20</sub>AuCl<sub>4</sub>N**  
 (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N[AuCl<sub>4</sub>]  
 Reaction with HI: 2.8.4.1  
**C<sub>8</sub>H<sub>20</sub>AuI<sub>2</sub>N**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N][AuI<sub>2</sub>]  
 Formation: 2.8.12  
**C<sub>8</sub>H<sub>20</sub>AuI<sub>4</sub>N**  
 (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N[AuI<sub>4</sub>]  
 Formation: 2.8.4.1  
**C<sub>8</sub>H<sub>20</sub>Au<sub>2</sub>Br<sub>2</sub>**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>AuBr]<sub>2</sub>  
 Formation: 2.8.5  
 Structure: 2.8.5  
**C<sub>8</sub>H<sub>20</sub>Au<sub>2</sub>I<sub>2</sub>**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>AuI]<sub>2</sub>  
 Formation: 2.8.5  
**C<sub>8</sub>H<sub>20</sub>BCINP**  
 (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NB(Cl)P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>  
 Formation: 2.6.9.2  
**C<sub>8</sub>H<sub>20</sub>B<sub>2</sub>O<sub>4</sub>**  
 B<sub>2</sub>(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>  
 Reaction with SF<sub>4</sub>: 2.6.6.4  
**C<sub>8</sub>H<sub>20</sub>Br<sub>4</sub>FeN**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N][FeBr<sub>4</sub>]  
 Formation: 2.9.10.4  
**C<sub>8</sub>H<sub>20</sub>Br<sub>6</sub>NNb**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N][NbBr<sub>6</sub>]  
 Formation: 2.9.10.1  
**C<sub>8</sub>H<sub>20</sub>Br<sub>6</sub>NTa**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N][TaBr<sub>6</sub>]  
 Formation: 2.9.10.1  
**C<sub>8</sub>H<sub>20</sub>Cl<sub>3</sub>Cu<sub>2</sub>N**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N][Cu<sub>2</sub>Cl<sub>3</sub>]  
 Electrochemical formation: 2.8.12  
**C<sub>8</sub>H<sub>20</sub>Cl<sub>5</sub>NTi**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N][TiCl<sub>5</sub>]  
 Formation: 2.9.10.1  
**C<sub>8</sub>H<sub>20</sub>Cl<sub>6</sub>NNb**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N][NbCl<sub>6</sub>]  
 Formation: 2.9.10.1  
**C<sub>8</sub>H<sub>20</sub>Cl<sub>6</sub>NTa**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N][TaCl<sub>6</sub>]  
 Formation: 2.9.10.1  
**C<sub>8</sub>H<sub>20</sub>Cl<sub>9</sub>NTi<sub>2</sub>**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N][Ti<sub>2</sub>Cl<sub>9</sub>]  
 Formation: 2.9.10.1  
**C<sub>8</sub>H<sub>20</sub>CuI<sub>2</sub>N**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N][CuI<sub>2</sub>]  
 Electrochemical formation: 2.8.12  
**C<sub>8</sub>H<sub>20</sub>Pb**  
 (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>Pb  
 Reaction with HgCl<sub>2</sub>: 2.8.23.2  
**C<sub>8</sub>H<sub>22</sub>BN<sub>2</sub>P**  
 [(CH<sub>3</sub>)<sub>2</sub>N]<sub>2</sub>BP(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>  
 Reaction with RX: 2.6.9.3  
 Reaction with HX: 2.6.9.2  
 Reaction with BX<sub>3</sub>: 2.6.9.3  
**C<sub>8</sub>H<sub>24</sub>AlLiN<sub>4</sub>**  
 LiAl[N(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>  
 Reaction with BX<sub>3</sub>: 2.6.8.3  
**C<sub>8</sub>I<sub>2</sub>Mo<sub>2</sub>O<sub>8</sub>**  
 [Mo(CO))<sub>4</sub>I]<sub>2</sub>  
 Formation: 2.9.15.1.1  
**C<sub>8</sub>I<sub>2</sub>O<sub>8</sub>Tc<sub>2</sub>**  
 [Tc(CO)<sub>4</sub>I]<sub>2</sub>  
 Formation: 2.9.15.1.1  
**C<sub>8</sub>I<sub>2</sub>O<sub>8</sub>W<sub>2</sub>**  
 [W(CO)<sub>4</sub>I]<sub>2</sub>  
 Formation: 2.9.15.1.1  
**C<sub>9</sub>H<sub>5</sub>ClCrHgO<sub>3</sub>**  
 C<sub>6</sub>H<sub>5</sub>HgClCr(CO)<sub>3</sub>  
 Formation: 2.8.23.6  
**C<sub>9</sub>H<sub>6</sub>CrO<sub>3</sub>**  
 η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>Cr(CO)<sub>3</sub>  
 Mercuration of: 2.8.23.6  
**C<sub>9</sub>H<sub>8</sub>MoO<sub>3</sub>**  
 η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>3</sub>CH<sub>3</sub>  
 Formation: 2.6.13.3  
**C<sub>9</sub>H<sub>10</sub>B<sub>2</sub>FFeIO<sub>3</sub>S**  
 [C<sub>2</sub>H<sub>5</sub>CC(C<sub>2</sub>H<sub>5</sub>)B(I)SBI]Fe(CO)<sub>3</sub>  
 Formation: 2.6.12.2  
**C<sub>9</sub>H<sub>10</sub>B<sub>2</sub>FeI<sub>2</sub>O<sub>3</sub>S**  
 [C<sub>2</sub>H<sub>5</sub>CC(C<sub>2</sub>H<sub>5</sub>)B(I)SBI]Fe(CO)<sub>3</sub>  
 Reaction with AsF<sub>3</sub>: 2.6.12.2  
**C<sub>9</sub>H<sub>11</sub>BCl<sub>3</sub>N**  
 (CH<sub>3</sub>)<sub>2</sub>N(C<sub>6</sub>H<sub>5</sub>)BCCl<sub>3</sub>  
 Formation: 2.6.13.3  
**C<sub>9</sub>H<sub>12</sub>BMnN<sub>2</sub>O<sub>5</sub>**  
 [(CH<sub>3</sub>)<sub>2</sub>N]<sub>2</sub>BMn(CO)<sub>5</sub>  
 Reaction with HX: 2.6.13.2  
**C<sub>9</sub>H<sub>18</sub>AuBr<sub>2</sub>NS<sub>2</sub>**  
 AuBr<sub>2</sub>[S<sub>2</sub>CN(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>]  
 Formation: 2.8.6.2

- C<sub>9</sub>H<sub>18</sub>AuNS<sub>2</sub>**  
 Au[S<sub>2</sub>CN(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>]  
 Reaction with X<sub>2</sub>: 2.8.6.2
- C<sub>9</sub>H<sub>21</sub>Al**  
 (C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>Al  
 Reaction with X<sub>2</sub>: 2.6.10.1
- C<sub>9</sub>H<sub>25</sub>BiN<sub>2</sub>P**  
 [[[CH<sub>3</sub>)<sub>2</sub>N]<sub>2</sub>BP(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>CH<sub>3</sub>]  
 Formation: 2.6.9.3
- C<sub>9</sub>H<sub>27</sub>Si<sub>3</sub>Tl**  
 [(CH<sub>3</sub>)<sub>3</sub>Si]<sub>3</sub>Tl  
 Reaction with RX: 2.6.11.3  
 Reaction with HX: 2.6.11.2
- C<sub>10</sub>BrInMn<sub>2</sub>O<sub>10</sub>**  
 BrIn[Mn(CO)<sub>5</sub>]<sub>2</sub>  
 Formation: 2.6.13.1
- C<sub>10</sub>ClInMn<sub>2</sub>O<sub>10</sub>**  
 ClIn[Mn(CO)<sub>5</sub>]<sub>2</sub>  
 Formation: 2.6.13.1
- C<sub>10</sub>H<sub>4</sub>Au<sub>5</sub>I<sub>2</sub>K<sub>5</sub>N<sub>10</sub>O<sub>2</sub>**  
 K<sub>5</sub>[Au<sub>5</sub>(CN)<sub>10</sub>I<sub>2</sub>]·2 H<sub>2</sub>O  
 Formation and structure: 2.8.4.2
- C<sub>10</sub>H<sub>8</sub>AuBr<sub>2</sub>F<sub>5</sub>S**  
 Au(C<sub>6</sub>F<sub>5</sub>)Br<sub>2</sub>·SC<sub>4</sub>H<sub>8</sub>  
 Formation: 2.8.6.2
- C<sub>10</sub>H<sub>8</sub>AuCl<sub>2</sub>F<sub>5</sub>S**  
 Au(C<sub>6</sub>F<sub>5</sub>)Cl<sub>2</sub>·SC<sub>4</sub>H<sub>8</sub>  
 Formation: 2.8.6.2
- C<sub>10</sub>H<sub>8</sub>AuF<sub>5</sub>S**  
 Au(C<sub>6</sub>F<sub>5</sub>)·SC<sub>4</sub>H<sub>8</sub>  
 Reaction with halogens: 2.8.6.2
- C<sub>10</sub>H<sub>8</sub>Cl<sub>2</sub>FeHg<sub>2</sub>**  
 (η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>HgCl)<sub>2</sub>Fe  
 Formation: 2.8.23.6
- C<sub>10</sub>H<sub>8</sub>MoO<sub>3</sub>**  
 η<sup>6</sup>-C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>Mo(CO)<sub>3</sub>  
 Reaction with [R<sub>4</sub>N]X or X<sub>2</sub>: 2.9.15.1.2
- C<sub>10</sub>H<sub>10</sub>Au<sub>2</sub>Cl<sub>2</sub>N<sub>2</sub>**  
 [Au(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>][AuCl<sub>2</sub>]  
 Structure: 2.8.12
- C<sub>10</sub>H<sub>10</sub>Au<sub>2</sub>I<sub>2</sub>N<sub>2</sub>**  
 [Au(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>][AuI<sub>2</sub>]  
 Structure: 2.8.12
- C<sub>10</sub>H<sub>10</sub>Cl<sub>2</sub>Zr**  
 (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>ZrCl<sub>2</sub>  
 Reaction with HgCl<sub>2</sub>: 2.8.23.2
- C<sub>10</sub>H<sub>10</sub>Fe**  
 (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe  
 Mercuration of: 2.8.23.6
- C<sub>10</sub>H<sub>11</sub>MoO<sub>3</sub>Tl**  
 (CH<sub>3</sub>)<sub>2</sub>TlMo(CO)<sub>3</sub>C<sub>5</sub>H<sub>5</sub>-η<sup>5</sup>  
 Reaction with RI, R<sub>3</sub>SnCl, HgCl<sub>2</sub>, ICl:  
 2.6.13.3
- η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>3</sub>Tl(CH<sub>3</sub>)<sub>2</sub>  
 Reaction with HCl: 2.6.13.2
- C<sub>10</sub>H<sub>11</sub>O<sub>3</sub>TlW**  
 (CH<sub>3</sub>)<sub>2</sub>TlW(CO)<sub>3</sub>C<sub>5</sub>H<sub>5</sub>-η<sup>5</sup>  
 Reaction with ICl: 2.6.13.3
- C<sub>10</sub>H<sub>11</sub>Tl**  
 (CH<sub>3</sub>)<sub>2</sub>TlC≡CC<sub>6</sub>H<sub>5</sub>  
 Reaction with HX: 2.6.10.2
- C<sub>10</sub>H<sub>12</sub>Br<sub>7</sub>Cu<sub>5</sub>N<sub>2</sub>**  
 [C<sub>5</sub>H<sub>5</sub>NH]<sub>2</sub>[Cu<sub>5</sub>Br<sub>7</sub>]  
 Formation: 2.8.12
- C<sub>10</sub>H<sub>12</sub>F<sub>4</sub>HgN<sub>2</sub>**  
 (C<sub>5</sub>H<sub>6</sub>N)<sub>2</sub>HgF<sub>4</sub>  
 Formation: 2.11.4.3
- C<sub>10</sub>H<sub>15</sub>GaS<sub>2</sub>**  
 C<sub>6</sub>H<sub>5</sub>Ga(SC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>  
 Reaction with I<sub>2</sub>: 2.6.7.1
- C<sub>10</sub>H<sub>16</sub>As<sub>2</sub>AuI<sub>3</sub>**  
 [AuI<sub>2</sub>{C<sub>6</sub>H<sub>4</sub>[As(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>}]I  
 Formation: 2.8.6.1
- C<sub>10</sub>H<sub>16</sub>As<sub>4</sub>AuI**  
 [Au{C<sub>6</sub>H<sub>4</sub>[As(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>}]I  
 Reaction with X<sub>2</sub>: 2.8.6.1
- C<sub>10</sub>H<sub>16</sub>F<sub>2</sub>O<sub>4</sub>Ti**  
 TiF<sub>2</sub>[CH<sub>2</sub>(COCH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>  
 Formation: 2.11.2.1
- C<sub>10</sub>H<sub>16</sub>F<sub>4</sub>HgN<sub>2</sub>O<sub>2</sub>**  
 [C<sub>5</sub>H<sub>5</sub>NH]<sub>2</sub>HgF<sub>4</sub>·2 H<sub>2</sub>O  
 Formation: 2.8.22
- C<sub>10</sub>H<sub>20</sub>Au<sub>2</sub>Br<sub>2</sub>**  
 [(CH<sub>2</sub>)<sub>5</sub>AuBr]<sub>2</sub>  
 Formation: 2.8.5
- C<sub>10</sub>H<sub>20</sub>Au<sub>2</sub>Br<sub>2</sub>N<sub>2</sub>S<sub>4</sub>**  
 {Au[S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]}Br<sub>2</sub>  
 Formation: 2.8.6.2
- [Au[S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]][AuBr<sub>2</sub>]  
 Formation: 2.8.6.2
- C<sub>10</sub>H<sub>20</sub>Au<sub>2</sub>I<sub>2</sub>N<sub>2</sub>S<sub>4</sub>**  
 {Au[S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]}I<sub>2</sub>  
 Formation: 2.8.6.2
- [Au[S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]][AuI<sub>2</sub>]  
 Formation: 2.8.6.2
- C<sub>10</sub>H<sub>22</sub>Be**  
 [(CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>]<sub>2</sub>Be  
 Reaction with BeX<sub>2</sub>: 2.7.3.2.2
- C<sub>10</sub>H<sub>27</sub>BN<sub>2</sub>Sn**  
 [(CH<sub>3</sub>)<sub>2</sub>N]<sub>2</sub>BSn(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>  
 Reaction with X<sub>2</sub>: 2.6.11.1
- C<sub>10</sub>H<sub>30</sub>Br<sub>10</sub>Cu<sub>4</sub>N<sub>2</sub>O**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH]<sub>2</sub>[Cu<sub>3</sub>Br<sub>8</sub>]·CuBr<sub>2</sub>·-  
 C<sub>2</sub>H<sub>5</sub>OH  
 Formation: 2.8.10

- C<sub>10</sub>Mn<sub>2</sub>O<sub>10</sub>**  
 Mn<sub>2</sub>(CO)<sub>10</sub>  
 Halogenation: 2.9.15.1.1  
 Reaction with [R<sub>4</sub>N]X or X<sub>2</sub>: 2.9.15.1.2
- C<sub>10</sub>O<sub>10</sub>Re<sub>2</sub>**  
 Re<sub>2</sub>(CO)<sub>10</sub>  
 Halogenation: 2.9.15.1.1
- C<sub>10</sub>O<sub>10</sub>Tc<sub>2</sub>**  
 Tc<sub>2</sub>(CO)<sub>10</sub>  
 Halogenation: 2.9.15.1.1
- C<sub>11</sub>H<sub>14</sub>MoO<sub>3</sub>Sn**  
 η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>3</sub>Sn(CH<sub>3</sub>)<sub>3</sub>  
 Formation: 2.6.13.3
- C<sub>12</sub>BrF<sub>10</sub>Tl**  
 (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>TlBr  
 Reaction with [(C<sub>6</sub>F<sub>5</sub>)AuBr]<sup>-</sup>: 2.8.5
- C<sub>12</sub>ClF<sub>10</sub>Tl**  
 (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>TlCl  
 Formation: 2.6.14.2
- C<sub>12</sub>CoF<sub>10</sub>**  
 (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Co  
 Formation: 2.9.3.8
- C<sub>12</sub>Co<sub>4</sub>O<sub>12</sub>**  
 Co<sub>4</sub>(CO)<sub>12</sub>  
 Reaction with [R<sub>4</sub>N]X or X<sub>2</sub>: 2.9.15.1.2
- C<sub>12</sub>F<sub>8</sub>O<sub>12</sub>Ru<sub>4</sub>**  
 [RuF<sub>2</sub>(CO)<sub>3</sub>]<sub>4</sub>  
 Formation: 2.9.15.1.1
- C<sub>12</sub>F<sub>10</sub>Fe**  
 (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Fe  
 Formation: 2.9.3.8
- C<sub>12</sub>F<sub>10</sub>Ni**  
 (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Ni  
 Formation: 2.9.3.8
- C<sub>12</sub>Fe<sub>3</sub>O<sub>12</sub>**  
 Fe<sub>3</sub>(CO)<sub>12</sub>  
 Halogenation: 2.9.15.1.1
- C<sub>12</sub>HCIF<sub>10</sub>Ge**  
 (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>GeHCl  
 Formation: 2.6.11.2
- C<sub>12</sub>H<sub>5</sub>MnO<sub>6</sub>**  
 C<sub>6</sub>H<sub>5</sub>C(O)Mn(CO)<sub>3</sub>  
 Formation: 2.6.13.3
- C<sub>12</sub>H<sub>10</sub>Au<sub>2</sub>Cl<sub>4</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)AuCl<sub>2</sub>]<sub>2</sub>  
 Formation and analogs: 2.8.5  
 Reaction with Cl<sup>-</sup>: 2.8.5
- C<sub>12</sub>H<sub>10</sub>BBr**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>BBr  
 Formation: 2.6.13.1  
 Reaction with X<sub>2</sub>: 2.6.10.1
- C<sub>12</sub>H<sub>10</sub>ClGa**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>GaCl  
 Formation: 2.6.10.2
- C<sub>12</sub>H<sub>10</sub>Hg**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Hg  
 Reaction with SeBr<sub>4</sub>: 2.8.23.5  
 Reaction with TiCl<sub>4</sub>: 2.8.23.5  
 Reaction with VOCl<sub>3</sub>: 2.8.23.5  
 Reaction with VCl<sub>4</sub>: 2.8.23.5  
 Reaction with C<sub>6</sub>H<sub>5</sub>ICl<sub>2</sub>: 2.8.23.5  
 Reaction with CCl<sub>4</sub>, CHCl<sub>3</sub>: 2.8.23.5
- C<sub>12</sub>H<sub>10</sub>InI**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>InI  
 Formation: 2.6.3.2
- C<sub>12</sub>H<sub>10</sub>Se<sub>2</sub>**  
 (C<sub>6</sub>H<sub>5</sub>Se)<sub>2</sub>  
 Formation: 2.6.7.3
- C<sub>12</sub>H<sub>10</sub>Zn**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Zn  
 Reaction with ZnCl<sub>2</sub>: 2.8.23.2
- C<sub>12</sub>H<sub>15</sub>MoO<sub>3</sub>Tl**  
 (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>TlMo(CO)<sub>3</sub>C<sub>5</sub>H<sub>5</sub>-η<sup>5</sup>  
 Reaction with RI: 2.6.13.3
- C<sub>12</sub>H<sub>15</sub>NbO**  
 (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>NbOC<sub>2</sub>H<sub>5</sub>  
 Formation: 2.6.13.3
- C<sub>12</sub>H<sub>16</sub>CuI<sub>2</sub>N<sub>8</sub>**  
 [CuI<sub>2</sub>(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>4</sub>]  
 Stabilization of CuI<sub>2</sub> in: 2.8.2
- C<sub>12</sub>H<sub>20</sub>Au<sub>2</sub>N<sub>4</sub>S<sub>4</sub>Se<sub>2</sub>**  
 {Au[S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>][SeCN]<sub>2</sub>}  
 Formation: 2.8.6.2  
 Au[S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>[Au(SeCN)<sub>2</sub>]  
 Formation: 2.8.6.2
- C<sub>12</sub>H<sub>20</sub>Au<sub>2</sub>N<sub>4</sub>S<sub>6</sub>**  
 {Au[S<sub>2</sub>Cn(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>][SCN]<sub>2</sub>}  
 Formation: 2.8.6.2  
 [Au[S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>][Au(SCN)<sub>2</sub>]  
 Formation: 2.8.6.2
- C<sub>12</sub>H<sub>24</sub>CuI<sub>2</sub>KO<sub>6</sub>**  
 [K(C<sub>12</sub>H<sub>24</sub>O<sub>6</sub>)] [CuI<sub>2</sub>]  
 Formation: 2.8.12  
 Structure: 2.8.12
- C<sub>12</sub>H<sub>27</sub>B**  
 C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>B  
 Reaction with HX: 2.6.7.2  
 (C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>B  
 Reaction with HX: 2.6.10.2, 2.6.7.1
- C<sub>12</sub>H<sub>27</sub>BO<sub>3</sub>**  
 (n-C<sub>4</sub>H<sub>9</sub>O)<sub>3</sub>B  
 Reaction with HX: 2.6.6.3
- C<sub>12</sub>H<sub>27</sub>B<sub>3</sub>O<sub>6</sub>**  
 (n-C<sub>4</sub>H<sub>9</sub>OBO)<sub>3</sub>  
 Reaction with BCl<sub>3</sub>: 2.6.6.4
- C<sub>12</sub>H<sub>28</sub>Au<sub>2</sub>Br<sub>2</sub>**  
 [(n-C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>AuBr]<sub>2</sub>  
 Formation: 2.8.5

- C<sub>12</sub>H<sub>28</sub>BrCdCl<sub>2</sub>N**  
 [(C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>N]CdCl<sub>2</sub>Br  
 Formation: 2.8.22
- C<sub>12</sub>H<sub>28</sub>BrCdI<sub>2</sub>N**  
 [(C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>N]CdI<sub>2</sub>Br  
 Formation: 2.8.22
- C<sub>12</sub>H<sub>28</sub>Br<sub>2</sub>CdClN**  
 [(C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>N]CdBr<sub>2</sub>Cl  
 Formation: 2.8.22
- C<sub>12</sub>H<sub>28</sub>Br<sub>2</sub>CdIN**  
 [(C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>N]CdBr<sub>2</sub>I  
 Formation: 2.8.22
- C<sub>12</sub>H<sub>28</sub>CdClI<sub>2</sub>N**  
 [(C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>N]CdI<sub>2</sub>Cl  
 Formation: 2.8.22
- C<sub>12</sub>H<sub>28</sub>CdCl<sub>2</sub>IN**  
 [(C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>N]CdCl<sub>2</sub>I  
 Formation: 2.8.22
- C<sub>12</sub>H<sub>28</sub>Cl<sub>2</sub>CuN**  
 [(n-C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>N][CuCl<sub>2</sub>]  
 Structure: 2.8.12
- C<sub>12</sub>H<sub>28</sub>Cu<sub>3</sub>I<sub>4</sub>N**  
 [(n-C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>N][Cu<sub>3</sub>I<sub>4</sub>]  
 Formation from Cu: 2.8.12
- C<sub>12</sub>H<sub>30</sub>BNP<sub>2</sub>**  
 (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NB[P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>  
 Reaction with RX: 2.6.9.3  
 Reaction with HX: 2.6.9.2
- C<sub>12</sub>H<sub>30</sub>BN<sub>3</sub>**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>N]<sub>3</sub>B  
 Reaction with BCl<sub>3</sub>, YPCl<sub>3</sub>: 2.6.8.3  
 Reaction with HX: 2.6.8.2
- C<sub>12</sub>H<sub>33</sub>BrSi<sub>3</sub>Sn**  
 [(CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>]<sub>3</sub>SnBr  
 Formation: 2.6.11.3
- C<sub>12</sub>H<sub>33</sub>Si<sub>3</sub>SnTl**  
 {[(CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>]<sub>3</sub>Sn}Tl  
 Reaction with X<sub>2</sub>: 2.6.11.1
- C<sub>12</sub>H<sub>36</sub>BLiSi<sub>4</sub>**  
 Li{B[Si(CH<sub>3</sub>)<sub>3</sub>]<sub>4</sub>}  
 Reaction with R<sub>3</sub>SiCl, RX, R<sub>2</sub>BX, AlX<sub>3</sub>:  
 2.6.11.3
- C<sub>12</sub>H<sub>36</sub>Br<sub>5</sub>Cu<sub>2</sub>N<sub>3</sub>**  
 [(CH<sub>3</sub>)<sub>4</sub>N]<sub>3</sub>[Cu<sub>2</sub>Br<sub>5</sub>]  
 Structure: 2.8.12
- C<sub>12</sub>H<sub>36</sub>GaLiSi<sub>4</sub>**  
 Li{Ga[Si(CH<sub>3</sub>)<sub>3</sub>]<sub>4</sub>}  
 Reaction with HX: 2.6.11.2
- C<sub>12</sub>H<sub>48</sub>Cl<sub>10</sub>Co<sub>2</sub>Cu<sub>2</sub>N<sub>12</sub>**  
 [Co(NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>3</sub>]<sub>2</sub>[Cu<sub>2</sub>Cl<sub>8</sub>]Cl<sub>2</sub>  
 Formation: 2.8.10
- C<sub>12</sub>O<sub>12</sub>Os<sub>3</sub>**  
 Os<sub>3</sub>(CO)<sub>12</sub>  
 Halogenation: 2.9.15.1.1
- C<sub>12</sub>O<sub>12</sub>Ru<sub>3</sub>**  
 Ru<sub>3</sub>(CO)<sub>12</sub>  
 Halogenation: 2.9.15.1.1
- C<sub>14</sub>H<sub>5</sub>F<sub>10</sub>GeTl**  
 (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>GeTlC<sub>2</sub>H<sub>5</sub>  
 Reaction with HX: 2.6.11.2
- C<sub>14</sub>H<sub>10</sub>O<sub>3</sub>**  
 [C<sub>6</sub>H<sub>5</sub>C(O)]<sub>2</sub>O  
 Formation from HgO and RC(O)X:  
 2.8.15.3
- C<sub>14</sub>H<sub>10</sub>O<sub>4</sub>**  
 (C<sub>6</sub>H<sub>5</sub>COO)<sub>2</sub>  
 Initiator in aryl exchange: 2.8.23.5
- C<sub>14</sub>H<sub>14</sub>AlClO<sub>2</sub>**  
 (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>O)<sub>2</sub>AlCl  
 Formation: 2.6.6.3
- C<sub>14</sub>H<sub>14</sub>AuBrS**  
 AuBr·S(CH<sub>2</sub>Ph)<sub>2</sub>  
 Reaction with X<sub>2</sub>: 2.8.6.2
- C<sub>14</sub>H<sub>14</sub>AuBr<sub>3</sub>S**  
 AuBr<sub>3</sub>·S(CH<sub>2</sub>Ph)<sub>2</sub>  
 Formation: 2.8.6.2
- C<sub>14</sub>H<sub>20</sub>Au<sub>2</sub>Cl<sub>2</sub>N<sub>2</sub>**  
 [(CH<sub>3</sub>)<sub>2</sub>Au(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)][(CH<sub>3</sub>)<sub>2</sub>AuCl<sub>2</sub>]  
 Formation: 2.8.5
- C<sub>15</sub>InMn<sub>3</sub>O<sub>15</sub>**  
 In[Mn(CO)<sub>5</sub>]<sub>3</sub>  
 Reaction with X<sub>2</sub>: 2.6.13.1  
 Reaction with HX: 2.6.13.2
- C<sub>15</sub>In<sub>2</sub>Mn<sub>3</sub>O<sub>15</sub>**  
 In[Mn(CO)<sub>5</sub>]<sub>3</sub>  
 Formation: 2.6.13.3
- C<sub>15</sub>Mn<sub>3</sub>O<sub>15</sub>Tl**  
 Tl[Mn(CO)<sub>5</sub>]<sub>3</sub>  
 Reaction with RX: 2.6.13.3  
 Reaction with HX: 2.6.13.2  
 Reaction with GaX, InX, SbX<sub>3</sub>: 2.6.13.3
- C<sub>16</sub>H<sub>10</sub>HgMo<sub>2</sub>O<sub>6</sub>**  
 [η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>3</sub>]<sub>2</sub>Hg  
 Formation: 2.6.13.3
- C<sub>16</sub>H<sub>10</sub>Mo<sub>2</sub>O<sub>6</sub>**  
 [η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>3</sub>]<sub>2</sub>  
 Reaction with ONX: 2.9.15.1.2
- C<sub>16</sub>H<sub>14</sub>HgO<sub>2</sub>**  
 Hg[CH<sub>2</sub>C(O)C<sub>6</sub>H<sub>5</sub>]<sub>2</sub>  
 Reaction with HgI<sub>2</sub>: 2.8.23.2
- C<sub>16</sub>H<sub>20</sub>AuCl<sub>2</sub>N<sub>3</sub>O<sub>4</sub>**  
 [(CH<sub>3</sub>)<sub>4</sub>N][O-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>]<sub>2</sub>AuCl<sub>2</sub>]  
 Formation: 2.8.5
- C<sub>16</sub>H<sub>20</sub>Au<sub>2</sub>Cl<sub>2</sub>N<sub>2</sub>**  
 [(CH<sub>3</sub>)<sub>2</sub>Au(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)][(CH<sub>3</sub>)<sub>2</sub>AuCl<sub>2</sub>]  
 Formation: 2.8.5



- C<sub>16</sub>H<sub>22</sub>B<sub>2</sub>N<sub>2</sub>**  
 (CH<sub>3</sub>)<sub>2</sub>N(C<sub>6</sub>H<sub>5</sub>)BB(C<sub>6</sub>H<sub>5</sub>)N(CH<sub>3</sub>)<sub>2</sub>  
 Reaction with RX: 2.6.13.3
- C<sub>16</sub>H<sub>32</sub>Cu<sub>4</sub>I<sub>6</sub>K<sub>2</sub>O<sub>8</sub>**  
 [K(C<sub>8</sub>H<sub>16</sub>O<sub>4</sub>)<sub>2</sub>][Cu<sub>4</sub>I<sub>6</sub>]  
 Formation: 2.8.12
- C<sub>16</sub>H<sub>36</sub>Ag<sub>3</sub>I<sub>4</sub>N**  
 [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][Ag<sub>3</sub>I<sub>4</sub>]  
 Formation from AgOAc: 2.8.12
- C<sub>16</sub>H<sub>36</sub>AuBr<sub>2</sub>N**  
 [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][AuBr<sub>2</sub>]  
 Formation: 2.8.12
- C<sub>16</sub>H<sub>36</sub>AuCl<sub>2</sub>N**  
 [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][AuCl<sub>2</sub>]  
 Formation: 2.8.12
- C<sub>16</sub>H<sub>36</sub>AuI<sub>2</sub>N**  
 [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][AuI<sub>2</sub>]  
 Formation: 2.8.12
- C<sub>16</sub>H<sub>36</sub>Br<sub>2</sub>CuN**  
 [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][CuBr<sub>2</sub>]  
 Structure: 2.8.12
- C<sub>16</sub>H<sub>36</sub>Cl<sub>2</sub>CuN**  
 [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][CuCl<sub>2</sub>]  
 Structure: 2.8.12
- C<sub>16</sub>H<sub>36</sub>F<sub>6</sub>NNb**  
 [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]NbF<sub>6</sub>  
 Formation: 2.11.3.1
- C<sub>16</sub>H<sub>36</sub>F<sub>11</sub>NNb<sub>2</sub>**  
 [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]Nb<sub>2</sub>F<sub>11</sub>  
 Formation: 2.11.3.1
- C<sub>16</sub>H<sub>46</sub>Br<sub>3</sub>CuN<sub>2</sub>**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>2</sub>[CuBr<sub>3</sub>]  
 Electrochemical formation: 2.8.12
- C<sub>16</sub>H<sub>46</sub>Br<sub>4</sub>CoN<sub>2</sub>**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>2</sub>[CoBr<sub>4</sub>]  
 Formation: 2.9.10.4
- C<sub>16</sub>H<sub>46</sub>Br<sub>4</sub>CuN<sub>2</sub>**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>2</sub>[CuBr<sub>4</sub>]  
 Electrochemical formation: 2.8.10
- C<sub>16</sub>H<sub>46</sub>Br<sub>4</sub>Cu<sub>2</sub>N<sub>2</sub>**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>2</sub>[Cu<sub>2</sub>Br<sub>4</sub>]  
 Structure: 2.8.12
- C<sub>16</sub>H<sub>40</sub>Br<sub>4</sub>N<sub>2</sub>Ni**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>2</sub>[NiBr<sub>4</sub>]  
 Formation: 2.9.10.4
- C<sub>16</sub>H<sub>40</sub>Br<sub>6</sub>N<sub>2</sub>Th**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>2</sub>[ThBr<sub>6</sub>]  
 Formation: 2.9.10.1
- C<sub>16</sub>H<sub>40</sub>Br<sub>6</sub>N<sub>2</sub>Ti**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>2</sub>[TiBr<sub>6</sub>]  
 Formation: 2.9.10.1
- C<sub>16</sub>H<sub>40</sub>Br<sub>6</sub>N<sub>2</sub>U**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>2</sub>[UBr<sub>6</sub>]  
 Formation: 2.9.10.1
- C<sub>16</sub>H<sub>40</sub>Br<sub>6</sub>N<sub>2</sub>Zr**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>2</sub>[ZrBr<sub>6</sub>]  
 Formation: 2.9.10.1
- C<sub>16</sub>H<sub>40</sub>Cl<sub>2</sub>InN<sub>2</sub>**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>2</sub>[InCl<sub>5</sub>]  
 Formation: 2.6.3.2
- C<sub>16</sub>H<sub>40</sub>Cl<sub>6</sub>N<sub>2</sub>Th**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>2</sub>[ThCl<sub>6</sub>]  
 Formation: 2.9.10.1
- C<sub>16</sub>H<sub>40</sub>Cl<sub>6</sub>N<sub>2</sub>Ti**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>2</sub>[TiCl<sub>6</sub>]  
 Formation: 2.9.10.1
- C<sub>16</sub>H<sub>40</sub>Cl<sub>6</sub>N<sub>2</sub>U**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>2</sub>[UCl<sub>6</sub>]  
 Formation: 2.9.10.1
- C<sub>16</sub>H<sub>40</sub>Cl<sub>6</sub>N<sub>2</sub>Zr**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>2</sub>[ZrCl<sub>6</sub>]  
 Formation: 2.9.10.1
- C<sub>16</sub>H<sub>40</sub>Cu<sub>2</sub>I<sub>4</sub>N<sub>2</sub>**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>2</sub>[Cu<sub>2</sub>I<sub>4</sub>]  
 Formation from Cu: 2.8.12
- C<sub>16</sub>H<sub>40</sub>I<sub>6</sub>N<sub>2</sub>Ti**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>2</sub>[TiI<sub>6</sub>]  
 Formation: 2.9.10.1
- C<sub>17</sub>H<sub>5</sub>AuClF<sub>10</sub>N**  
 (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>AuCl(C<sub>5</sub>H<sub>5</sub>N)  
 Formation: 2.8.5
- C<sub>18</sub>ClF<sub>15</sub>Ge**  
 (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>GeCl  
 Formation: 2.6.13.3
- C<sub>18</sub>HF<sub>15</sub>Ge**  
 (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>GeH  
 Formation: 2.6.13.3
- C<sub>18</sub>H<sub>15</sub>Al**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Al  
 Reaction with HgCl<sub>2</sub>: 2.6.15
- C<sub>18</sub>H<sub>15</sub>AlSe<sub>3</sub>**  
 (C<sub>6</sub>H<sub>5</sub>Se)<sub>3</sub>Al  
 Reaction with MCl<sub>3</sub>: 2.6.7.3
- C<sub>18</sub>H<sub>15</sub>AsAuBr<sub>3</sub>**  
 AuBr<sub>3</sub>·As(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Formation: 2.8.6.1
- C<sub>18</sub>H<sub>15</sub>AsAuI**  
 AuI·As(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Formation: 2.8.6.1
- C<sub>18</sub>H<sub>15</sub>AsAuI<sub>3</sub>**  
 AuI<sub>3</sub>·As(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Formation: 2.8.6.1
- C<sub>18</sub>H<sub>15</sub>AuBrCl<sub>2</sub>P**  
 AuCl<sub>2</sub>Br·P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Formation: 2.8.6.1
- C<sub>18</sub>H<sub>15</sub>AuBrP**  
 AuBr·P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Reaction with X<sub>2</sub>: 2.8.6.1

- C<sub>18</sub>H<sub>15</sub>AuBr<sub>2</sub>ClP**  
 AuClBr<sub>2</sub>·P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Formation: 2.8.6.1
- C<sub>18</sub>H<sub>15</sub>AuBr<sub>3</sub>P**  
 AuBr<sub>3</sub>·P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Formation: 2.8.6.1
- C<sub>18</sub>H<sub>15</sub>AuClP**  
 AuCl·P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Reaction with X<sub>2</sub>: 2.8.6.1
- C<sub>18</sub>H<sub>15</sub>AuCl<sub>3</sub>P**  
 AuCl<sub>3</sub>·P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Formation: 2.8.6.1
- C<sub>18</sub>H<sub>15</sub>BSe<sub>3</sub>**  
 (C<sub>6</sub>H<sub>5</sub>Se)<sub>3</sub>B  
 Reaction with HX: 2.6.7.2
- C<sub>18</sub>H<sub>15</sub>BrSi**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiBr  
 Formation: 2.6.11.1
- C<sub>18</sub>H<sub>15</sub>ClSn**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnCl  
 Reaction with Ti[Co(CO)<sub>4</sub>]: 2.6.13.3
- C<sub>18</sub>H<sub>15</sub>Ga**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Ga  
 Reaction with GaX<sub>3</sub>: 2.6.15  
 Reaction with HX: 2.6.10.2
- C<sub>18</sub>H<sub>24</sub>AuCl<sub>2</sub>N<sub>3</sub>O<sub>4</sub>**  
 [(CH<sub>3</sub>)<sub>4</sub>N][(-2-CH<sub>3</sub>-6-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>AuCl<sub>2</sub>]  
 Formation: 2.8.5
- C<sub>18</sub>H<sub>25</sub>Cl<sub>2</sub>CuNOP**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(O)(CH<sub>2</sub>)<sub>2</sub>NH(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>][CuCl<sub>2</sub>]  
 Formation: 2.8.12
- C<sub>18</sub>H<sub>45</sub>Ge<sub>3</sub>Tl**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Ge]<sub>3</sub>Tl  
 Reaction with RX: 2.6.11.3
- C<sub>19</sub>H<sub>15</sub>AsAuBr<sub>2</sub>NO**  
 Au(NCO)Br<sub>2</sub>As(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Formation: 2.8.6.1
- C<sub>19</sub>H<sub>15</sub>AsAuNO**  
 Au(NCO)As(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Reaction with X<sub>2</sub>: 2.8.6.1
- C<sub>19</sub>H<sub>15</sub>AuBr<sub>2</sub>NOP**  
 Au(NCO)Br<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Formation: 2.8.6.1
- C<sub>19</sub>H<sub>15</sub>AuNOP**  
 Au(NCO)P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Reaction with X<sub>2</sub>: 2.8.6.1
- C<sub>19</sub>H<sub>16</sub>LiP**  
 LiC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>  
 Reaction with HgBr<sub>2</sub>: 2.8.23.2
- C<sub>19</sub>H<sub>18</sub>AsCu<sub>3</sub>I<sub>4</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>(CH<sub>3</sub>)As][Cu<sub>3</sub>I<sub>4</sub>]  
 Formation: 2.8.12
- C<sub>19</sub>H<sub>18</sub>Cu<sub>2</sub>I<sub>3</sub>P**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>(CH<sub>3</sub>)P][Cu<sub>2</sub>I<sub>3</sub>]  
 Formation: 2.8.12
- C<sub>20</sub>H<sub>15</sub>BMoO<sub>3</sub>**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>BMo(CO)<sub>3</sub>C<sub>5</sub>H<sub>5</sub>-η<sup>5</sup>  
 Reaction with X<sub>2</sub>: 2.6.13.1
- C<sub>20</sub>H<sub>17</sub>AuBrP**  
 AuBr[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>CH=CH<sub>2</sub>]  
 Reaction with X<sub>2</sub>: 2.8.6.1
- C<sub>20</sub>H<sub>17</sub>AuBr<sub>3</sub>P**  
 AuBr<sub>2</sub>[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>CHCH<sub>2</sub>Br]  
 Formation: 2.8.6.1
- C<sub>20</sub>H<sub>20</sub>Br<sub>2</sub>CuP**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>(C<sub>2</sub>H<sub>5</sub>)P][CuBr<sub>2</sub>]  
 Formation: 2.8.12
- C<sub>20</sub>H<sub>32</sub>As<sub>4</sub>Au<sub>2</sub>I<sub>2</sub>**  
 [Au(o-C<sub>6</sub>H<sub>4</sub>{As(CH<sub>3</sub>)<sub>2</sub>})<sub>2</sub>][AuI<sub>2</sub>]  
 Formation: 2.8.12
- C<sub>20</sub>H<sub>40</sub>Cu<sub>4</sub>I<sub>6</sub>K<sub>2</sub>O<sub>10</sub>**  
 [K(C<sub>10</sub>H<sub>20</sub>O<sub>5</sub>)<sub>2</sub>][Cu<sub>4</sub>I<sub>6</sub>]  
 Formation: 2.8.12
- C<sub>20</sub>H<sub>44</sub>Au<sub>2</sub>Br<sub>2</sub>**  
 {[C(CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>]<sub>2</sub>AuBr}<sub>2</sub>  
 Formation: 2.8.5
- C<sub>21</sub>H<sub>19</sub>AuBrP**  
 AuBr[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH=CH<sub>2</sub>]  
 Reaction with X<sub>2</sub>: 2.8.6.1
- C<sub>21</sub>H<sub>19</sub>AuBr<sub>3</sub>P**  
 AuBr<sub>2</sub>[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CHCH<sub>2</sub>Br]  
 Formation: 2.8.6.1
- C<sub>21</sub>H<sub>22</sub>Br<sub>2</sub>CuP**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>(n-C<sub>3</sub>H<sub>7</sub>)P][CuBr<sub>2</sub>]  
 Formation: 2.8.12
- C<sub>21</sub>H<sub>54</sub>AlP<sub>9</sub>**  
 Al{C[P(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>}<sub>3</sub>  
 Formation: 2.6.9.3
- C<sub>21</sub>H<sub>54</sub>Br<sub>9</sub>Cu<sub>6</sub>N<sub>3</sub>**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>(CH<sub>3</sub>)N]<sub>3</sub>[Cu<sub>6</sub>Br<sub>9</sub>]  
 Formation: 2.8.12
- C<sub>22</sub>H<sub>15</sub>CoO<sub>4</sub>Sn**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnCo(CO)<sub>4</sub>  
 Formation: 2.6.13.3
- C<sub>22</sub>H<sub>19</sub>AuBrFeP**  
 AuBr·P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(η<sup>5</sup>C<sub>5</sub>H<sub>4</sub>FeC<sub>5</sub>H<sub>5</sub>η<sup>5</sup>)  
 Reaction with X<sub>2</sub>: 2.8.6.1
- C<sub>22</sub>H<sub>19</sub>AuBr<sub>3</sub>FeP**  
 AuBr<sub>3</sub>·P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>FeC<sub>5</sub>H<sub>5</sub>η<sup>5</sup>)  
 Formation: 2.8.6.1
- C<sub>22</sub>H<sub>24</sub>Br<sub>2</sub>CuP**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>(n-C<sub>4</sub>H<sub>9</sub>)P][CuBr<sub>2</sub>]  
 Formation: 2.8.12
- C<sub>22</sub>H<sub>24</sub>Cu<sub>2</sub>I<sub>6</sub>N<sub>4</sub>**  
 [(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>CH<sub>2</sub>]<sub>2</sub>[Cu<sub>2</sub>I<sub>6</sub>]  
 Formation: 2.8.12

- C<sub>22</sub>H<sub>25</sub>O<sub>2</sub>Sb**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Sb(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>  
 Formation: 2.6.13.3
- C<sub>22</sub>H<sub>36</sub>AuBrF<sub>5</sub>N**  
 [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][C<sub>6</sub>F<sub>5</sub>AuBr]  
 Reactions with Br<sub>2</sub> and (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>TlBr:  
 2.8.5
- C<sub>22</sub>H<sub>36</sub>AuBr<sub>3</sub>F<sub>5</sub>N**  
 [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][C<sub>6</sub>F<sub>5</sub>AuBr<sub>3</sub>]  
 Formation: 2.8.5
- C<sub>22</sub>H<sub>41</sub>AuI<sub>3</sub>N**  
 [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][C<sub>6</sub>H<sub>5</sub>AuI<sub>3</sub>]  
 Formation: 2.8.5
- C<sub>24</sub>Au<sub>2</sub>Br<sub>2</sub>F<sub>20</sub>**  
 [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>AuBr]<sub>2</sub>  
 Formation: 2.8.5
- C<sub>24</sub>Au<sub>2</sub>Cl<sub>2</sub>F<sub>20</sub>**  
 [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>AuCl]<sub>2</sub>  
 Formation: 2.8.5
- C<sub>24</sub>Au<sub>2</sub>F<sub>20</sub>N<sub>6</sub>**  
 [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>AuN<sub>3</sub>]<sub>2</sub>  
 Formation: 2.8.5
- C<sub>24</sub>H<sub>15</sub>AsAuBr<sub>2</sub>F<sub>5</sub>**  
 Au(C<sub>6</sub>F<sub>5</sub>)Br<sub>2</sub>·As(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Formation: 2.8.6.1
- C<sub>24</sub>H<sub>15</sub>AsAuCl<sub>5</sub>**  
 Au(C<sub>6</sub>Cl<sub>5</sub>)·As(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Reaction with TiCl<sub>3</sub> or Cl<sub>2</sub>: 2.8.6.1
- C<sub>24</sub>H<sub>15</sub>AsAuCl<sub>7</sub>**  
 Au(C<sub>6</sub>Cl<sub>5</sub>)Cl<sub>2</sub>·As(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Formation: 2.8.6.1
- C<sub>24</sub>H<sub>15</sub>AsAuF<sub>5</sub>**  
 Au(C<sub>6</sub>F<sub>5</sub>)·As(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Reaction with X<sub>2</sub>: 2.8.6.1
- C<sub>24</sub>H<sub>15</sub>AuBr<sub>2</sub>F<sub>5</sub>P**  
 Au(C<sub>6</sub>F<sub>5</sub>)Br<sub>2</sub>·P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Formation: 2.8.6.1
- C<sub>24</sub>H<sub>15</sub>AuF<sub>5</sub>P**  
 Au(C<sub>6</sub>F<sub>5</sub>)·P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Reaction with X<sub>2</sub>: 2.8.6.1
- C<sub>24</sub>H<sub>20</sub>AgBr<sub>2</sub>P**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>P][AgBr<sub>2</sub>]  
 Formation: 2.8.12
- C<sub>24</sub>H<sub>20</sub>AlLiSe<sub>4</sub>**  
 LiAl(SeC<sub>6</sub>H<sub>5</sub>)<sub>4</sub>  
 Reaction with R<sub>3</sub>SiX: 2.6.7.3
- C<sub>24</sub>H<sub>20</sub>AsAuCl<sub>4</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>As][AuCl<sub>4</sub>]  
 Formation: 2.8.4.1
- C<sub>24</sub>H<sub>20</sub>AsF<sub>2</sub>O<sub>2</sub>V**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>As]VO<sub>2</sub>F<sub>2</sub>  
 Formation: 2.11.2.1
- C<sub>24</sub>H<sub>20</sub>AuP**  
 Au(C<sub>6</sub>H<sub>5</sub>)·P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Reaction with X<sub>2</sub>: 2.8.6.1
- C<sub>24</sub>H<sub>20</sub>Br<sub>2</sub>CuP**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>P][CuBr<sub>2</sub>]  
 Formation: 2.8.12  
 Structure: 2.8.12
- C<sub>24</sub>H<sub>20</sub>Cl<sub>2</sub>CuP**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>P][CuCl<sub>2</sub>]  
 Structure: 2.8.12
- C<sub>24</sub>H<sub>20</sub>Cl<sub>3</sub>CuP**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>P][CuCl<sub>3</sub>]  
 Formation: 2.8.10
- C<sub>24</sub>H<sub>20</sub>F<sub>2</sub>O<sub>2</sub>PV**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>P]VO<sub>2</sub>F<sub>2</sub>  
 Formation: 2.11.2.1
- C<sub>24</sub>H<sub>20</sub>Se<sub>4</sub>Ti**  
 Ti(SeC<sub>6</sub>H<sub>5</sub>)<sub>4</sub>  
 Formation: 2.6.7.3
- C<sub>24</sub>H<sub>20</sub>Se<sub>4</sub>Zr**  
 Zr(SeC<sub>6</sub>H<sub>5</sub>)<sub>4</sub>  
 Formation: 2.6.7.3
- C<sub>24</sub>H<sub>21</sub>Au<sub>2</sub>Cl<sub>2</sub>NP<sub>2</sub>**  
 Au<sub>2</sub>Cl<sub>2</sub>[μ-(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PNHP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]  
 Reaction with X<sub>2</sub>: 2.8.6.1
- C<sub>24</sub>H<sub>21</sub>Au<sub>2</sub>Cl<sub>6</sub>NP<sub>2</sub>**  
 Au<sub>2</sub>Cl<sub>6</sub>[μ-(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PNHP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]  
 Formation: 2.8.6.1
- C<sub>24</sub>H<sub>40</sub>BClP<sub>2</sub>Pt**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>BPtCl[P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>  
 Reaction with X<sub>2</sub>: 2.6.13.1
- C<sub>24</sub>H<sub>56</sub>Cu<sub>2</sub>I<sub>4</sub>N<sub>2</sub>**  
 [(n-C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>N]<sub>2</sub>[Cu<sub>2</sub>I<sub>4</sub>]  
 Formation: 2.8.12  
 Structure: 2.8.12
- C<sub>24</sub>H<sub>56</sub>Cu<sub>5</sub>I<sub>7</sub>N<sub>2</sub>**  
 [(n-C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>N]<sub>2</sub>[Cu<sub>5</sub>I<sub>7</sub>]  
 Formation: 2.8.12
- C<sub>24</sub>H<sub>60</sub>Br<sub>5</sub>CuN<sub>3</sub>**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>3</sub>[CuBr<sub>5</sub>]  
 Formation: 2.9.10.4
- C<sub>24</sub>H<sub>60</sub>Cl<sub>5</sub>Cu<sub>2</sub>N<sub>3</sub>**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>3</sub>[Cu<sub>2</sub>Cl<sub>5</sub>]  
 Electrochemical formation: 2.8.12
- C<sub>24</sub>H<sub>60</sub>CuI<sub>4</sub>N<sub>3</sub>**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>3</sub>[CuI<sub>4</sub>]  
 Electrochemical formation: 2.8.12
- C<sub>24</sub>H<sub>63</sub>AlP<sub>6</sub>Si<sub>3</sub>**  
 Al{C[P(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>}<sub>3</sub>  
 Formation: 2.6.9.3
- C<sub>24</sub>H<sub>72</sub>Cl<sub>3</sub>Cu<sub>2</sub>N<sub>18</sub>P<sub>6</sub>**  
 [N<sub>6</sub>P<sub>6</sub>{N(CH<sub>3</sub>)<sub>2</sub>}]<sub>12</sub>CuCl][CuCl<sub>2</sub>]  
 Formation: 2.8.12

- C<sub>25</sub>H<sub>22</sub>Au<sub>2</sub>Br<sub>4</sub>Cl<sub>2</sub>P<sub>2</sub>**  
 Au<sub>2</sub>Br<sub>4</sub>Cl<sub>2</sub>[μ-(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PCH<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]  
 Formation: 2.8.6.1
- C<sub>25</sub>H<sub>22</sub>Au<sub>2</sub>Cl<sub>2</sub>P<sub>2</sub>**  
 Au<sub>2</sub>Cl<sub>2</sub>[μ-(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PCH<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]  
 Reactions with Cl<sub>2</sub> and Br<sub>2</sub>: 2.8.6.1
- C<sub>25</sub>H<sub>22</sub>Au<sub>2</sub>Cl<sub>6</sub>P<sub>2</sub>**  
 Au<sub>2</sub>Cl<sub>6</sub>[μ-(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PCH<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]  
 Formation: 2.8.6.1
- C<sub>26</sub>Au<sub>2</sub>F<sub>20</sub>N<sub>2</sub>S<sub>2</sub>**  
 [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Au(SCN)]<sub>2</sub>  
 Formation: 2.8.5
- C<sub>26</sub>H<sub>20</sub>AsAuBr<sub>2</sub>N<sub>2</sub>O<sub>2</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>As][Au(CNO)<sub>2</sub>Br<sub>2</sub>]  
 Formation: 2.8.4.2
- C<sub>26</sub>H<sub>20</sub>AsAuCl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>As][Au(CNO)<sub>2</sub>Cl<sub>2</sub>]  
 Formation: 2.8.4.2
- C<sub>26</sub>H<sub>20</sub>AsAuN<sub>2</sub>O<sub>2</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>As][Au(CNO)<sub>2</sub>]  
 Reaction with halogens: 2.8.4.2
- C<sub>26</sub>H<sub>26</sub>AsAuBr<sub>2</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>As][(CH<sub>3</sub>)<sub>2</sub>AuBr<sub>2</sub>]  
 Formation: 2.8.5
- C<sub>26</sub>H<sub>26</sub>AsAuCl<sub>2</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>As][(CH<sub>3</sub>)<sub>2</sub>AuCl<sub>2</sub>]  
 Formation: 2.8.5
- C<sub>26</sub>H<sub>26</sub>AsAuI<sub>2</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>As][(CH<sub>3</sub>)<sub>2</sub>AuI<sub>2</sub>]  
 Formation: 2.8.5
- C<sub>27</sub>H<sub>26</sub>Au<sub>2</sub>Cl<sub>2</sub>P<sub>2</sub>**  
 Au<sub>2</sub>Cl<sub>2</sub>[μ-(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]  
 Reaction with X<sub>2</sub>: 2.8.6.1
- C<sub>27</sub>H<sub>26</sub>Au<sub>2</sub>Cl<sub>6</sub>P<sub>2</sub>**  
 Au<sub>2</sub>Cl<sub>6</sub>[μ-(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]  
 Formation: 2.8.6.1
- C<sub>28</sub>Au<sub>2</sub>F<sub>26</sub>O<sub>4</sub>**  
 [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Au(O<sub>2</sub>CCF<sub>3</sub>)]<sub>2</sub>  
 Formation: 2.8.5
- C<sub>28</sub>H<sub>36</sub>AuBr<sub>2</sub>F<sub>10</sub>N**  
 [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>AuBr<sub>2</sub>]  
 Reactions: 2.8.5
- C<sub>28</sub>H<sub>36</sub>AuCl<sub>2</sub>F<sub>10</sub>N**  
 [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>AuCl<sub>2</sub>]  
 Reactions: 2.8.5
- C<sub>32</sub>H<sub>72</sub>Cu<sub>2</sub>I<sub>4</sub>N<sub>2</sub>**  
 [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>2</sub>[Cu<sub>2</sub>I<sub>4</sub>]  
 Structure: 2.8.12
- C<sub>32</sub>H<sub>80</sub>Cl<sub>12</sub>Cu<sub>4</sub>N<sub>4</sub>**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>4</sub>[Cu<sub>4</sub>Cl<sub>12</sub>]  
 Formation: 2.8.10
- C<sub>32</sub>H<sub>88</sub>Ag<sub>31</sub>I<sub>39</sub>N<sub>8</sub>**  
 [(CH<sub>3</sub>)<sub>3</sub>N(CH<sub>2</sub>)<sub>2</sub>N(CH<sub>3</sub>)<sub>3</sub>]<sub>4</sub>[Ag<sub>31</sub>I<sub>39</sub>]  
 Formation: 2.8.12
- C<sub>34</sub>H<sub>8</sub>Au<sub>2</sub>Cl<sub>2</sub>F<sub>20</sub>N<sub>2</sub>**  
 [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Au(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)][(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>AuCl<sub>2</sub>]  
 Formation: 2.8.5
- C<sub>34</sub>H<sub>14</sub>Au<sub>2</sub>F<sub>20</sub>O<sub>4</sub>**  
 [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Au{OC(CH<sub>3</sub>)CHC(CH<sub>3</sub>)O}]  
 Formation: 2.8.5
- C<sub>34</sub>H<sub>25</sub>BMnO<sub>4</sub>P**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>BMn(CO)<sub>4</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Reaction with X<sub>2</sub>: 2.6.13.1
- C<sub>34</sub>H<sub>36</sub>AuBrF<sub>15</sub>N**  
 [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>AuBr]  
 Formation: 2.8.5
- C<sub>36</sub>F<sub>30</sub>Ge<sub>2</sub>Hg**  
 [(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Ge]<sub>2</sub>Hg  
 Formation: 2.6.13.3
- C<sub>36</sub>H<sub>8</sub>Au<sub>2</sub>Cl<sub>2</sub>F<sub>20</sub>N<sub>2</sub>**  
 [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Au(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)][(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>AuCl<sub>2</sub>]  
 Formation: 2.8.5
- C<sub>36</sub>H<sub>99</sub>Si<sub>9</sub>Sn<sub>3</sub>Tl**  
 {[ (CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>]<sub>3</sub>Sn]<sub>3</sub>Tl  
 Reaction with RX: 2.6.11.3
- C<sub>38</sub>H<sub>36</sub>AgI<sub>3</sub>P<sub>2</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>(CH<sub>3</sub>)P]<sub>2</sub>[AgI<sub>3</sub>]  
 Structure: 2.8.12
- C<sub>38</sub>H<sub>36</sub>Br<sub>3</sub>CuP<sub>2</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>(CH<sub>3</sub>)P]<sub>2</sub>[CuBr<sub>3</sub>]  
 Formation: 2.8.12  
 Structure: 2.8.12
- C<sub>38</sub>H<sub>36</sub>CuI<sub>3</sub>P<sub>2</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>(CH<sub>3</sub>)P]<sub>2</sub>[CuI<sub>3</sub>]  
 Formation: 2.8.12  
 Structure: 2.8.12
- C<sub>48</sub>H<sub>40</sub>Ag<sub>2</sub>Br<sub>4</sub>P<sub>2</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>P]<sub>2</sub>[Ag<sub>2</sub>Br<sub>4</sub>]  
 Formation: 2.8.12  
 Structure: 2.8.12
- C<sub>48</sub>H<sub>40</sub>Ag<sub>2</sub>Cl<sub>4</sub>P<sub>2</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>P]<sub>2</sub>[Ag<sub>2</sub>Cl<sub>4</sub>]  
 Formation: 2.8.12  
 Structure: 2.8.12
- C<sub>48</sub>H<sub>40</sub>As<sub>2</sub>Cl<sub>8</sub>Re<sub>2</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>As]<sub>2</sub>[Re<sub>2</sub>Cl<sub>8</sub>]  
 Formation: 2.9.10.3
- C<sub>48</sub>H<sub>64</sub>Cu<sub>4</sub>I<sub>6</sub>K<sub>2</sub>O<sub>16</sub>**  
 [K(C<sub>24</sub>H<sub>32</sub>O<sub>8</sub>)]<sub>2</sub>[Cu<sub>4</sub>I<sub>6</sub>]  
 Formation: 2.8.12
- C<sub>48</sub>H<sub>120</sub>Cu<sub>6</sub>I<sub>12</sub>N<sub>6</sub>**  
 [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>6</sub>[Cu<sub>6</sub>I<sub>12</sub>]  
 Formation from Cu: 2.8.12
- C<sub>54</sub>H<sub>45</sub>AlClIKSi<sub>3</sub>**  
 K[C<sub>6</sub>H<sub>5</sub>Al[Si(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>][(C<sub>6</sub>H<sub>5</sub>)<sub>5</sub>Si<sub>2</sub>Cl]  
 Reaction with HX: 2.6.11.2

**C<sub>54</sub>H<sub>45</sub>CuFP<sub>3</sub>**  
 CuF[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>3</sub>  
 Stabilization of CuF: 2.8.2

**C<sub>54</sub>H<sub>48</sub>Cl<sub>6</sub>LnP<sub>3</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PH]<sub>3</sub>[LnCl<sub>6</sub>]  
 Formation: 2.9.10.2

**C<sub>57</sub>H<sub>54</sub>AgBr<sub>4</sub>P<sub>3</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>CH<sub>3</sub>P]<sub>3</sub>[AgBr<sub>4</sub>]  
 Formation: 2.8.12

**C<sub>57</sub>H<sub>54</sub>B<sub>3</sub>N<sub>3</sub>Si<sub>3</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiBNCH<sub>3</sub>]<sub>3</sub>  
 Reaction with X<sub>2</sub>: 2.6.11.1

**C<sub>72</sub>H<sub>60</sub>Ag<sub>2</sub>As<sub>3</sub>Cl<sub>5</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>As]<sub>3</sub>[Ag<sub>2</sub>Cl<sub>5</sub>]  
 Formation: 2.8.12

**C<sub>84</sub>H<sub>12</sub>CrF<sub>60</sub>Ge<sub>4</sub>Hg**  
 [Cr(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]{[(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Ge]<sub>4</sub>Hg}  
 Formation: 2.6.13.3

**C<sub>108</sub>CoF<sub>90</sub>Ge<sub>6</sub>Hg<sub>2</sub>**  
 Co{[(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Ge]<sub>3</sub>Hg}<sub>2</sub>  
 Formation: 2.6.13.3

**C<sub>108</sub>F<sub>90</sub>Ge<sub>6</sub>Hg<sub>2</sub>Mn**  
 Mn{[(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Ge]<sub>3</sub>Hg}<sub>2</sub>  
 Formation: 2.6.13.3

**C<sub>108</sub>F<sub>90</sub>Ge<sub>6</sub>Hg<sub>2</sub>Ni**  
 Ni{[(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Ge]<sub>3</sub>Hg}<sub>2</sub>  
 Formation: 2.6.13.3

**C<sub>108</sub>H<sub>20</sub>F<sub>90</sub>Ge<sub>6</sub>Hg<sub>2</sub>Ti<sub>2</sub>**  
 (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ti{[(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Ge]<sub>3</sub>Hg}<sub>2</sub>  
 Formation: 2.6.13.3

**C<sub>120</sub>H<sub>144</sub>Cu<sub>36</sub>I<sub>60</sub>N<sub>24</sub>**  
 [(C<sub>5</sub>H<sub>5</sub>NH)<sub>24</sub>][Cu<sub>36</sub>I<sub>56</sub>]<sub>4</sub>  
 Formation: 2.8.12  
 Structure: 2.8.12

**Ca**  
 Ca  
 Reaction with X<sub>2</sub>: 2.7.2  
 Reaction with HX: 2.7.3.1

**Ca\*Br<sub>2</sub>**  
**CaCd<sub>2</sub>Cl<sub>6</sub>H<sub>14</sub>O<sub>7</sub>**  
 CaCd<sub>2</sub>Cl<sub>6</sub>·7 H<sub>2</sub>O  
 Formation: 2.8.22

**CaCl<sub>2</sub>**  
 CaCl<sub>2</sub>  
 Formation: 2.7.2, 2.7.5  
 Reaction with ZnSO<sub>4</sub>: 2.8.17.2

**CaF<sub>2</sub>**  
 CaF<sub>2</sub>  
 Fluorinating agent: 2.6.12.3  
 Formation: 2.7.2, 2.7.5

**CaF<sub>4</sub>\*Ag**  
**CaF<sub>12</sub>\*Au<sub>2</sub>**

**CaI<sub>2</sub>**  
 CaI<sub>2</sub>  
 Formation: 2.7.2

**CaO**  
 CaO  
 Reaction with HX: 2.7.5

**Cd**  
 Cd  
 Fluorination: 2.11.3.3  
 Reaction with CuI: 2.8.14.5  
 Reaction with CuBr: 2.8.14.5  
 Reaction with Hg<sub>2</sub>Cl<sub>2</sub>: 2.8.14.5  
 Reaction with SF<sub>6</sub>: 2.8.14.4  
 Reaction with S<sub>2</sub>Cl<sub>2</sub>: 2.8.14.4  
 Reaction with AlI<sub>3</sub>: 2.8.14.5  
 Reaction with ONF·3 HF: 2.8.14.4  
 Reaction with I<sub>2</sub>: 2.8.14.1  
 Reaction with F<sub>2</sub>: 2.8.14.1  
 Reaction with IF<sub>5</sub>: 2.8.14.4  
 Reaction with Br<sub>2</sub>: 2.8.14.1  
 Reaction with Cl<sub>2</sub>: 2.8.14.1  
 Reaction with HF: 2.8.14.3  
 Reaction with HI: 2.8.14.3

**Cd\*Br<sub>2</sub>**  
**Cd\*C<sub>2</sub>H<sub>6</sub>**  
**CdCl\*C<sub>4</sub>H<sub>3</sub>**  
**CdClI<sub>2</sub>N\*C<sub>12</sub>H<sub>28</sub>**  
**CdClIN\*C<sub>12</sub>H<sub>28</sub>Br<sub>2</sub>**  
**CdCl<sub>2</sub>**  
 CdCl<sub>2</sub>  
 Anhydrous: 2.8.19  
 Dehydration by OSCl<sub>2</sub>: 2.8.19  
 Fluorination: 2.11.3.3  
 Formation: 2.8.23.4  
 Formation from Cd[OAc]<sub>2</sub> and AcCl: 2.8.17.3  
 Formation from Cd[NO<sub>3</sub>]<sub>2</sub> and HCl: 2.8.17.1  
 Formation from Cd[CO<sub>3</sub>] and HCl: 2.8.17.1  
 Formation from Cd and HCl: 2.8.14.2  
 Formation from Cd and Cl<sub>2</sub>: 2.8.14.1  
 Formation from CdO and S<sub>2</sub>Cl<sub>2</sub>: 2.8.15.3  
 Formation from CdO and NH<sub>4</sub>Cl: 2.8.15.3  
 Formation from CdO and CF<sub>2</sub>BrCl: 2.8.15.3  
 Formation from CdO and HCl: 2.8.15.2  
 Formation from CdO and Cl<sub>2</sub>: 2.8.15.1  
 Formation from CdS and AlCl<sub>3</sub>: 2.8.16.2  
 Reaction with BBr<sub>3</sub>: 2.8.18

- Reaction with  $\text{RMgX}$ : 2.8.23.2  
 Reaction with  $\text{NH}_4\text{F}$ : 2.8.18
- $\text{CdCl}_2\text{H}_2\text{O}$**   
 $\text{CdCl}_2 \cdot \text{H}_2\text{O}$   
 Stability: 2.8.19
- $\text{CdCl}_2\text{H}_8\text{O}_4$**   
 $\text{CdCl}_2 \cdot 4 \text{H}_2\text{O}$   
 Stability: 2.8.19
- $\text{CdCl}_2\text{IN}^*\text{C}_{12}\text{H}_{28}$**
- $\text{CdCl}_2\text{I}_2\text{K}_2$**   
 $\text{K}_2[\text{CdCl}_2\text{I}_2]$   
 Formation: 2.8.22
- $\text{CdCl}_2\text{N}^*\text{C}_{12}\text{H}_{28}\text{Br}$**
- $\text{CdCl}_3\text{Cs}$**   
 $\text{Cs}[\text{CdCl}_3]$   
 Formation from melt and solution: 2.8.22
- $\text{CdCl}_3\text{H}_2\text{KO}$**   
 $\text{K}[\text{CdCl}_3] \cdot \text{H}_2\text{O}$   
 Formation: 2.8.22
- $\text{CdCl}_3\text{H}_4\text{N}$**   
 $[\text{NH}_4][\text{CdCl}_3]$   
 Formation from melt and solution: 2.8.22
- $\text{CdCl}_3\text{K}$**   
 $\text{K}[\text{CdCl}_3]$   
 Formation: 2.8.22
- $\text{CdCl}_3\text{Rb}$**   
 $\text{Rb}[\text{CdCl}_3]$   
 Formation: 2.8.22
- $\text{CdCl}_4\text{Cs}_2$**   
 $\text{Cs}_2[\text{CdCl}_4]$   
 Formation from melt and solution: 2.8.22
- $\text{CdCl}_4\text{H}_{16}\text{O}_7$**   
 $\text{H}_2[\text{CdCl}_4] \cdot 7 \text{H}_2\text{O}$   
 Formation: 2.8.22
- $\text{CdCl}_4\text{H}_{16}\text{O}_8^*\text{Ba}$**
- $\text{CdCl}_4\text{Na}_2$**   
 $\text{Na}_2[\text{CdCl}_4]$   
 Formation from melt: 2.8.22
- $\text{CdCl}_5\text{CoH}_{18}\text{N}_6$**   
 $[\text{Co}(\text{NH}_3)_6][\text{CdCl}_5]$   
 Formation: 2.8.22
- $\text{CdCl}_6\text{Cs}_4$**   
 $\text{Cs}_4[\text{CdCl}_6]$   
 Formation from melt: 2.8.22
- $\text{CdCl}_6\text{Cu}_2\text{H}_8\text{O}_4$**   
 $\text{Cu}_2\text{CdCl}_6 \cdot 4 \text{H}_2\text{O}$   
 Formation: 2.8.22
- $\text{CdCl}_6\text{H}_{16}\text{N}_4$**   
 $[\text{NH}_4]_4[\text{CdCl}_6]$   
 Formation from melt and solution: 2.8.22
- $\text{CdCl}_6\text{K}_4$**   
 $\text{K}_4[\text{CdCl}_6]$   
 Formation from melt and solution: 2.8.22
- $\text{CdCl}_6\text{Rb}_4$**   
 $\text{Rb}_4[\text{CdCl}_6]$   
 Formation: 2.8.22
- $\text{CdCs}^*\text{Br}_3$**
- $\text{CdCsH}_2\text{I}_3\text{O}$**   
 $\text{Cs}[\text{CdI}_3] \cdot \text{H}_2\text{O}$   
 Formation: 2.8.22
- $\text{CdCsI}_3$**   
 $\text{Cs}[\text{CdI}_3]$   
 Formation: 2.8.22
- $\text{CdCs}_2^*\text{Br}_4$**
- $\text{CdCs}_2\text{F}_4$**   
 $\text{Cs}_2[\text{CdF}_4]$   
 Formation from melt: 2.8.22
- $\text{CdCs}_2\text{I}_4$**   
 $\text{Cs}_2[\text{CdI}_4]$   
 Formation from melt and solution: 2.8.22
- $\text{CdCs}_3^*\text{Br}_5$**
- $\text{CdCs}_3\text{I}_5$**   
 $\text{Cs}_3[\text{CdI}_5]$   
 Formation: 2.8.22
- $\text{CdCu}^*\text{Br}_3$**
- $\text{CdF}_2$**   
 $\text{CdF}_2$   
 Anhydrous: 2.8.19  
 Formation: 2.11.3.3  
 Formation from  $\text{Cd}[\text{CO}_3]$  and  $\text{HF}$ : 2.8.17.1  
 Formation from  $\text{Cd}$  and  $\text{S}_2\text{Cl}_2$ : 2.8.14.4  
 Formation from  $\text{Cd}$  and  $\text{ONF} \cdot 3 \text{HF}$ : 2.8.14.4  
 Formation from  $\text{Cd}$  and  $\text{F}_2$ : 2.8.14.1, 2.8.14.3  
 Formation from  $\text{Cd}$  and  $\text{IF}_5$ : 2.8.14.4  
 Formation from  $\text{Cd}$  and  $\text{HF}$ : 2.8.14.2  
 Formation from  $\text{CdO}$  and  $\text{F}_2$ : 2.8.15.1  
 Formation from  $\text{CdS}$  and  $\text{F}_2$ : 2.8.16.1  
 Formation from  $\text{Cd}$  and  $\text{SF}_6$ : 2.8.14.4  
 Formation from  $\text{CdO}$  and  $\text{CF}_2\text{BrCl}$ : 2.8.15.3  
 Formation from  $\text{CdO}$  and  $\text{HF}$ : 2.8.15.2  
 Formation from  $\text{CdCl}_2$  and  $[\text{NH}_4]\text{F}$ : 2.8.18  
 Reaction with  $\text{MF}$ : 2.11.3.3  
 Reaction with  $\text{Re}$ : 2.9.3.6
- $\text{CdF}_2\text{H}_4\text{O}_2$**   
 $\text{CdF}_2 \cdot 2 \text{H}_2\text{O}$   
 Dehydration: 2.8.19

- Formation from  $\text{Cd}[\text{NO}_3]_2$  and  $\text{NH}_4\text{F}$ :  
2.8.17.2
- $\text{CdF}_3\text{H}_4\text{N}$**   
 $[\text{NH}_4][\text{CdF}_3]$   
 Formation: 2.8.22
- $\text{CdF}_3\text{K}$**   
 $\text{K}[\text{CdF}_3]$   
 Formation: 2.8.22, 2.11.3.3
- $\text{CdF}_3\text{Rb}$**   
 $\text{Rb}[\text{CdF}_3]$   
 Formation: 2.8.22
- $\text{CdF}_3\text{Tl}$**   
 $\text{Tl}[\text{CdF}_3]$   
 Formation: 2.8.22
- $\text{CdF}_4^*\text{Ag}$**
- $\text{CdF}_4\text{K}_2$**   
 $\text{K}_2[\text{CdF}_4]$   
 Formation from melt: 2.8.22
- $\text{CdF}_4\text{Rb}_2$**   
 $\text{Rb}_2[\text{CdF}_4]$   
 Formation from melt and solution:  
2.8.22
- $\text{CdHO}^*\text{Br}$**
- $\text{CdH}_2\text{KO}^*\text{Br}_3$**
- $\text{CdH}_2\text{O}^*\text{BaBr}_4$**
- $\text{CdH}_2\text{O}^*\text{Br}_2$**
- $\text{CdH}_4\text{N}^*\text{Br}_3$**
- $\text{CdH}_8\text{N}_2^*\text{Br}_4$**
- $\text{CdH}_8\text{O}_4^*\text{Br}_2$**
- $\text{CdH}_{10}\text{I}_4\text{O}_5^*\text{Ba}$**
- $\text{CdH}_{12}\text{I}_4\text{N}_2\text{O}_2$**   
 $[\text{NH}_4]_2[\text{CdI}_4] \cdot 2 \text{H}_2\text{O}$   
 Formation: 2.8.22
- $\text{CdH}_{12}\text{I}_4\text{Na}_2\text{O}_6$**   
 $\text{Na}_2[\text{CdI}_4] \cdot 6 \text{H}_2\text{O}$   
 Formation: 2.8.22
- $\text{CdH}_{16}\text{I}_4\text{O}_8\text{Sr}$**   
 $\text{Sr}[\text{CdI}_4] \cdot 8 \text{H}_2\text{O}$   
 Formation: 2.8.22
- $\text{CdHgI}_4$**   
 $\text{Cd}[\text{HgI}_4]$   
 Formation: 2.8.22
- $\text{CdIN}^*\text{C}_{12}\text{H}_{28}\text{Br}_2$**
- $\text{CdI}_2$**   
 $\text{CdI}_2$   
 Anhydrous: 2.8.19  
 Formation from  $\text{Cd}[\text{OAc}]_2$  and  $\text{I}_2$ :  
2.8.17.3  
 Formation from  $\text{CdCO}_3$  and  $\text{HI}$ :  
2.8.17.1  
 Formation from  $\text{Cd}$  and  $\text{CuI}$ : 2.8.14.5  
 Formation from  $\text{Cd}$  and  $\text{I}_2$ : 2.8.14.3
- Formation from  $\text{CdO}$  and  $\text{HI}$ : 2.8.15.2  
 Formation from  $\text{Cd}$  and  $\text{AlI}_3$ : 2.8.14.5  
 Formation from  $\text{Cd}$  and  $\text{I}_2$ : 2.8.14.1  
 Formation from  $\text{KI}$  and  $\text{Cd}[\text{SO}_4]$ :  
2.8.17.2
- $\text{CdI}_2\text{N}^*\text{C}_{12}\text{H}_{28}\text{Br}$**
- $\text{CdI}_3\text{K}$**   
 $\text{K}[\text{CdI}_3]$   
 Formation: 2.8.22
- $\text{CdI}_4\text{K}_2$**   
 $\text{K}_2[\text{CdI}_4]$   
 Formation from melt and solution:  
2.8.22
- $\text{CdI}_6\text{K}_4$**   
 $\text{K}_4[\text{CdI}_6]$   
 Formation from melt: 2.8.22
- $\text{CdK}_2^*\text{Br}_4$**
- $\text{CdK}_4^*\text{Br}_6$**
- $\text{CdN}_2\text{O}_6$**   
 $\text{Cd}[\text{NO}_3]_2$   
 Reaction with  $\text{AcX}$ : 2.8.17.3  
 Reaction with  $\text{NH}_4\text{F}$ : 2.8.17.2  
 Reaction with  $\text{HCl}$ : 2.8.17.1
- $\text{CdNa}_2^*\text{Br}_4$**
- $\text{CdO}$**   
 $\text{CdO}$   
 Reaction with  $\text{HI}$ : 2.8.15.2  
 Reaction with  $\text{F}_2$ : 2.8.15.1  
 Reaction with  $\text{HCl}$ : 2.8.15.2  
 Reaction with  $\text{Cl}_2$ : 2.8.15.1  
 Reaction with  $\text{HF}$ : 2.8.15.2
- $\text{CdO}_3^*\text{C}$**
- $\text{CdO}_4^*\text{C}_4\text{H}_6$**
- $\text{CdO}_4\text{S}$**   
 $\text{Cd}[\text{SO}_4]$   
 Reaction with  $\text{KI}$ : 2.8.17.2
- $\text{CdRb}^*\text{Br}_3$**
- $\text{CdRb}_4^*\text{Br}_6$**
- $\text{CdS}$**   
 $\text{CdS}$   
 Fluorination: 2.11.3.3  
 Reaction with  $\text{AlCl}_3$ : 2.8.16.2  
 Reaction with  $\text{F}_2$ : 2.8.16.1
- $\text{Cd}_2\text{Cl}_2\text{H}_4\text{N}$**   
 $[\text{NH}_4][\text{Cd}_2\text{Cl}_5]$   
 Formation from melt: 2.8.22
- $\text{Cd}_2\text{Cl}_6\text{H}_{10}\text{O}_5^*\text{Ba}$**
- $\text{Cd}_2\text{Cl}_6\text{H}_{14}\text{O}_7^*\text{Ca}$**
- $\text{Cd}_2\text{Cl}_6\text{H}_{14}\text{O}_7\text{Sr}$**   
 $\text{Sr}[\text{Cd}_2\text{Cl}_6] \cdot 7 \text{H}_2\text{O}$   
 Formation: 2.8.22
- $\text{Cd}_2\text{F}_7\text{Rb}_3$**   
 $\text{Rb}_3[\text{Cd}_2\text{F}_7]$   
 Formation from melt: 2.8.22

- Ce**  
**Ce**  
 Reaction with HX: 2.9.14.1.1  
**CeClS**  
**CeSCl**  
 Formation: 2.9.14.1.1  
**CeCl<sub>3</sub>**  
**CeCl<sub>3</sub>**  
 Fluorination of MCl mixture: 2.11.5.1  
 Formation: 2.9.9.1  
**CeFS**  
**CeSF**  
 Formation: 2.9.14.1.1  
**CeFSe**  
**CeSeF**  
 Formation: 2.9.14.2  
**CeF<sub>3</sub>**  
**CeF<sub>3</sub>**  
 Fluorination: 2.11.5.1  
 Reaction with Ce<sub>2</sub>S<sub>3</sub>, Ce<sub>2</sub>Se<sub>3</sub>: 2.9.14.2  
 Reaction with ClF<sub>3</sub>-HF: 2.11.5.1  
**CeF<sub>4</sub>**  
**CeF<sub>4</sub>**  
 Formation: 2.11.5.1  
**CeIS**  
**CeSI**  
 Formation: 2.9.14.1.1  
**CeO<sub>2</sub>**  
**CeO<sub>2</sub>**  
 Fluorination of MCl mixture: 2.11.5.1  
 Reaction with ClF<sub>3</sub>-HF: 2.11.5.1  
**CeS\*Br**  
**Ce<sub>2</sub>F<sub>4</sub>Se**  
 Ce<sub>2</sub>[SeF<sub>4</sub>]  
 Formation: 2.9.14.2  
**CfF<sub>3</sub>**  
**CfF<sub>3</sub>**  
 Fluorination: 2.11.5.2  
**CfF<sub>4</sub>**  
**CfF<sub>4</sub>**  
 Formation: 2.11.5.2  
**Cl**  
**Cl**  
 Reaction with Zn: 2.8.14.1  
**Cl\*Ag**  
**Cl\*Al**  
**Cl\*Au**  
**Cl\*B**  
**Cl\*BBr<sub>2</sub>**  
**Cl\*CH<sub>3</sub>Be**  
**Cl\*C<sub>2</sub>H<sub>6</sub>B**  
**Cl\*C<sub>2</sub>H<sub>6</sub>B<sub>5</sub>**  
**Cl\*C<sub>4</sub>H<sub>3</sub>Cd**  
**Cl\*C<sub>4</sub>H<sub>10</sub>Al**  
**Cl\*C<sub>4</sub>H<sub>10</sub>B**  
**Cl\*C<sub>6</sub>H<sub>5</sub>**  
**Cl\*C<sub>6</sub>H<sub>14</sub>B**  
**Cl\*C<sub>8</sub>H<sub>18</sub>B**  
**ClCrHgO<sub>3</sub>\*C<sub>9</sub>H<sub>5</sub>**  
**ClCrO**  
**CrOCl**  
 Formation: 2.9.12.6  
**ClCrO<sub>3</sub>**  
 [CrO<sub>3</sub>Cl]<sup>-</sup>  
 Formation: 2.9.13.4  
**ClCrO<sub>5</sub>**  
 [CrO<sub>3</sub>Cl]<sup>-</sup>  
 Formation: 2.9.13.2  
**ClCu**  
**CuCl**  
 Formation: 2.8.2, 2.8.7.2, 2.9.8.  
 Formation by reduction of Cu<sup>2+</sup>:  
 2.8.11.2  
 Formation from Cu[OAc]<sub>2</sub>: 2.8.11.2  
 Formation from Cu: 2.8.11.1  
 Formation from CuCl<sub>2</sub>: 2.8.11.2  
 Reaction with X<sub>2</sub>: 2.8.8.1  
 Reaction with Zn: 2.8.14.5  
 Reaction with F<sub>2</sub>: 2.8.8.1  
 Reaction with BrF<sub>3</sub>: 2.8.8.1  
 Reaction with elemental Te, Se: 2.9.14.3  
**ClCu\*Br**  
**ClCuI**  
**CuICl**  
 Formation: 2.8.8.1  
**ClCuSe<sub>2</sub>**  
**CuSe<sub>2</sub>Cl**  
 Formation: 2.9.14.3  
**ClCuTe**  
**CuTeCl**  
 Formation: 2.9.14.3  
**ClCuTe<sub>2</sub>**  
**CuTe<sub>2</sub>Cl**  
 Formation: 2.9.14.3  
**ClF**  
**ClF**  
 Fluorinating agent: 2.9.12.3  
**ClF<sub>2</sub>\*B**  
**ClF<sub>2</sub>\*CBr**  
**ClF<sub>3</sub>**  
**ClF<sub>3</sub>**  
 Reaction with BX<sub>3</sub>: 2.6.15  
 Reaction with Hg: 2.8.14.4  
 Reaction with MO: 2.7.7



- Reaction with  $\text{WO}_3$ ,  $\text{MoO}_3$ ,  $\text{NiO}_2$ :  
2.9.4.4  
Reaction with transition-metals: 2.9.3.4
- $\text{ClF}_5\text{NRe}$**   
 $\text{ReF}_5(\text{NCl})$   
Formation: 2.11.4.1
- $\text{ClF}_5\text{W}$**   
 $\text{WF}_5\text{Cl}$   
Formation: 2.11.4.1
- $\text{ClF}_6\text{IrO}_2$**   
 $[\text{ClO}_2][\text{IrF}_6]$   
Formation: 2.11.4.2
- $\text{ClF}_8\text{OPt}$**   
 $[\text{ClF}_2\text{O}]\text{PtF}_6$   
Formation: 2.11.4.2
- $\text{ClF}_{10}\text{Ge}^*\text{C}_{12}\text{H}$   
 $\text{ClF}_{10}\text{N}^*\text{C}_{17}\text{H}_5\text{Au}$   
 $\text{ClF}_{10}\text{Ti}^*\text{C}_{12}$   
 $\text{ClF}_{15}\text{Ge}^*\text{C}_{18}$
- $\text{ClFeO}$**   
 $\text{FeOCl}$   
Formation: 2.9.12.6
- $\text{ClGa}$**   
 $\text{GaCl}$   
Formation: 2.6.14.1
- $\text{ClGa}^*\text{C}_{12}\text{H}_{10}$
- $\text{ClGe}$**   
 $\text{GeCl}$   
Formation: 2.6.3.3
- $\text{ClGe}^*\text{C}_3\text{H}_9$
- $\text{ClGeH}_3$**   
 $\text{H}_3\text{GeCl}$   
Reaction with  $\text{Li}[\text{Al}(\text{SCH}_3)_4]$ : 2.6.7.3
- $\text{ClH}$**   
 $\text{HCl}$   
Metathesis: 2.6.12.1  
Reaction with B, Al, Ga, In, Tl: 2.6.3.1  
Reaction with  $\text{H}_3\text{Ga}\cdot\text{NR}_3$ : 2.6.5.2  
Reaction with  $\text{HgSO}_4$ : 2.8.17.1  
Reaction with  $[\text{B}_3\text{H}_8]^-$ : 2.6.4.2  
Reaction with  $\text{Cd}[\text{NO}_3]_2$ : 2.8.17.1  
Reaction with  $\text{CdCO}_3$ : 2.8.17.1  
Reaction with Cd: 2.8.14.2  
Reaction with  $\text{CdO}$ : 2.8.15.2  
Reaction with Group IIIB–Group IVB  
bonds: 2.6.11.2  
Reaction with Hg: 2.8.14.2, 2.8.14.3  
Reaction with  $\text{HgO}$ : 2.8.15.2  
Reaction with  $\text{Hg}_2(\text{NO}_3)_2$ : 2.8.20.1  
Reaction with  $\text{Hg}_2\text{O}$ : 2.8.21.1  
Reaction with MO, MOH,  $\text{MCO}_3$ : 2.7.5  
Reaction with  $\text{M}_2\text{S}_3$ ,  $\text{M}_2\text{Se}_3$ : 2.6.7.2
- Reaction with  $\text{M}_2\text{O}_3$ : 2.6.6.3  
Reaction with  $(\text{RO})_3\text{B}$ : 2.6.6.3  
Reaction with  $\text{R}_2\text{AlPR}_2$ : 2.6.9.2  
Reaction with  $\text{R}_2\text{NBPR}_2$ : 2.6.9.2  
Reaction with  $\text{R}_2\text{TlPR}_2$ : 2.6.9.2  
Reaction with  $\text{R}_3\text{B} \dots \text{R}_3\text{Tl}$ : 2.6.10.2  
Reaction with  $\text{ZnSO}_4$ : 2.8.17.1  
Reaction with  $\text{ZnCO}_3$ : 2.8.17.1  
Reaction with Zn: 2.8.14.1, 2.8.14.2  
Reaction with  $\text{ZnO}$ : 2.8.15.2  
Reaction with  $\text{ZnS}$ : 2.8.16.2  
Reaction with group-IA and group-IIA  
metals: 2.7.3.1  
Reaction with transition-metal oxides:  
2.9.4.3  
Reaction with transition-metals: 2.9.3.2,  
2.9.3.3, 2.9.14.1.1  
Use in dehydration: 2.8.19
- $\text{ClHHgI}_2$**   
 $\text{HHgClI}_2$   
Formation: 2.8.22
- $\text{ClHMgO}$**   
 $\text{Mg}(\text{OH})\text{Cl}$   
Formation: 2.7.5
- $\text{ClHO}$**   
 $\text{HClO}$   
Reaction with Hg: 2.8.14.1
- $\text{ClHOZn}$**   
 $\text{ZnOHCl}$   
Decomposition with heat: 2.8.19
- $\text{ClHO}_3\text{S}$**   
 $\text{HSO}_3\text{Cl}$   
Halogenation agent: 2.9.12.5
- $\text{ClHO}_4$**   
 $\text{H}[\text{ClO}_4]$   
Reaction with  $\text{Au}_2\text{O}_3$ : 2.8.3.1.4
- $\text{ClH}_2^*\text{Al}$
- $\text{ClH}_2\text{HgN}$**   
 $\text{NH}_2\text{HgCl}$   
Conversion to salts: 2.8.22
- $\text{ClH}_3\text{Li}^*\text{Al}$
- $\text{ClH}_3\text{OS}$**   
 $\text{H}_3\text{SOCl}$   
Reaction with  $\text{Li}[\text{Al}(\text{SCH}_3)_4]$ : 2.6.7.3
- $\text{ClH}_4\text{N}$**   
 $[\text{NH}_4]\text{Cl}$   
Reaction with  $\text{CdO}$ : 2.8.15.3  
Reaction with  $\text{ZnO}$ : 2.8.15.3
- $\text{ClH}_4\text{N}_2$**   
 $\text{N}_2\text{H}_4\cdot\text{HCl}$   
Reaction with  $\text{HgCl}_2$  and x-rays:  
2.8.21.2

- ClH<sub>5</sub>Si<sub>2</sub>**  
 Si<sub>2</sub>H<sub>5</sub>Cl  
 Reaction with Li[Al(SCH<sub>3</sub>)<sub>4</sub>]: 2.6.7.3  
**ClHg\*Br**  
**ClHg\*C<sub>2</sub>H<sub>3</sub>**  
**ClHg\*C<sub>5</sub>H<sub>5</sub>**  
**ClHg\*C<sub>6</sub>H<sub>5</sub>**  
**ClHg\*C<sub>7</sub>H<sub>3</sub>Br<sub>2</sub>**  
**ClHgMnO<sub>3</sub>\*C<sub>8</sub>H<sub>4</sub>**  
**ClHgMoO<sub>3</sub>\*C<sub>8</sub>H<sub>5</sub>**  
**ClHgSe\*C<sub>4</sub>H<sub>3</sub>**  
**ClI**  
 ICl  
 Reaction with Au: 2.8.3.1.2  
 Reaction with HgBr<sub>2</sub>: 2.8.18  
**ClI<sub>2</sub>N\*C<sub>12</sub>H<sub>28</sub>Cd**  
**ClI<sub>2</sub>P\*C<sub>6</sub>H<sub>15</sub>Au**  
**ClInMn<sub>2</sub>O<sub>10</sub>\*C<sub>10</sub>**  
**ClK**  
 KCl  
 Reaction with BX<sub>3</sub>: 2.6.12.2  
**ClKN<sub>3</sub>\*C<sub>3</sub>Au**  
**ClKO<sub>4</sub>**  
 KClO<sub>4</sub>  
 Use in formation of [RuOCl<sub>10</sub>]<sup>4-</sup>:  
 2.9.13  
**ClKSi<sub>3</sub>\*C<sub>54</sub>H<sub>45</sub>Al**  
**ClLaS**  
 LaSCl  
 Formation: 2.9.14.1.1  
**ClMnO<sub>3</sub>**  
 MnO<sub>3</sub>Cl  
 Formation: 2.9.12.5  
**ClMnO<sub>5</sub>\*C<sub>5</sub>**  
**ClMoN<sub>2</sub>O<sub>2</sub>\*C<sub>5</sub>H<sub>5</sub>**  
**ClMoO<sub>3</sub>**  
 [MoO<sub>3</sub>Cl]<sup>-</sup>  
 Formation: 2.9.13  
**ClMoS**  
 MoSCl  
 Formation: 2.9.14.1.2  
**ClN\*C<sub>8</sub>H<sub>11</sub>B**  
**ClN\*C<sub>12</sub>H<sub>28</sub>Br<sub>2</sub>Cd**  
**ClNO**  
 ONCl  
 Reaction with Al, Ga, In, Tl: 2.6.3.3  
 Reaction with Mo(CO)<sub>6</sub>, W(CO)<sub>6</sub>:  
 2.9.15.1.2  
 Reaction with R<sub>3</sub>B: 2.6.16  
 Reaction with Hg: 2.8.14.4  
 Reaction with R<sub>3</sub>B: 2.6.10.3  
**ClNO\*C<sub>3</sub>H<sub>6</sub>**
- ClNO\*C<sub>6</sub>H<sub>15</sub>B**  
**ClNP\*C<sub>8</sub>H<sub>20</sub>B**  
**ClNS\*C<sub>3</sub>H<sub>6</sub>**  
**ClN<sub>2</sub>\*C<sub>4</sub>H<sub>12</sub>B**  
**ClN<sub>3</sub>\*C<sub>6</sub>H<sub>12</sub>AuBr**  
**ClNa**  
 NaCl  
 Reaction with HgSO<sub>4</sub>: 2.8.17.2  
 Reaction with Hg, MnO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>:  
 2.8.21.3  
 Reaction with Hg, and HgSO<sub>4</sub>: 2.8.21.3  
 Reaction with HgO: 2.8.15.3  
 Reaction with Hg<sub>2</sub>[NO<sub>3</sub>]<sub>2</sub>: 2.8.21.1  
 Reaction with ZnS: 2.8.16.2  
**ClO\*Al**  
**ClO\*Au**  
**ClO\*CAu**  
**ClO\*C<sub>2</sub>H<sub>3</sub>**  
**ClO\*C<sub>7</sub>H<sub>5</sub>**  
**ClOTi**  
 TiOCl  
 Formation: 2.9.12.6  
**ClOV**  
 VOCl  
 Formation: 2.9.12.6  
**ClOZn\*C<sub>8</sub>H<sub>11</sub>**  
**ClO<sub>2</sub>\*C<sub>6</sub>H<sub>14</sub>Al**  
**ClO<sub>2</sub>\*C<sub>8</sub>H<sub>18</sub>B**  
**ClO<sub>2</sub>\*C<sub>14</sub>H<sub>14</sub>Al**  
**ClO<sub>2</sub>Ta**  
 TaO<sub>2</sub>Cl  
 Formation: 2.9.12.4  
**ClO<sub>2</sub>V**  
 O<sub>2</sub>VCl  
 Fluorination: 2.11.2.1  
**ClO<sub>3</sub>Re**  
 ReO<sub>3</sub>Cl  
 Formation: 2.9.12.1  
 Reaction with HF: 2.11.4.1  
**ClO<sub>3</sub>Re\*C<sub>5</sub>**  
**ClO<sub>3</sub>Tc\*C<sub>5</sub>**  
**ClP\*C<sub>6</sub>H<sub>15</sub>Au**  
**ClP\*C<sub>6</sub>H<sub>15</sub>AuBr<sub>2</sub>**  
**ClP\*C<sub>8</sub>H<sub>11</sub>Au**  
**ClP\*C<sub>18</sub>H<sub>15</sub>Au**  
**ClP\*C<sub>18</sub>H<sub>15</sub>AuBr<sub>2</sub>**  
**ClP<sub>2</sub>Pt\*C<sub>24</sub>H<sub>40</sub>B**  
**ClS\*Al**  
**ClS\*C<sub>2</sub>H<sub>8</sub>B**  
**ClS\*Ce**  
**ClSV**  
 VSCl  
 Formation: 2.9.14.4

- ClSe\*Al  
 ClSe\*Au  
 ClSi\*C<sub>2</sub>H<sub>7</sub>  
 ClSi\*C<sub>3</sub>H<sub>9</sub>  
 ClSi<sub>2</sub>Tl\*C<sub>6</sub>H<sub>18</sub>  
 ClSn\*C<sub>3</sub>H<sub>9</sub>  
 ClSn\*C<sub>6</sub>H<sub>15</sub>  
 ClSn\*C<sub>18</sub>H<sub>15</sub>  
 ClTe\*Al  
 ClTe<sub>2</sub>\*Au  
**ClTi**  
   TlCl  
     Formation: 2.6.3.1, 2.6.13.2  
     Reaction with X<sub>2</sub>: 2.6.14.2  
 ClTi\*C<sub>2</sub>H<sub>6</sub>  
**Cl<sub>x</sub>CrF<sub>5+x</sub>O**  
   CrOF<sub>5</sub>·X ClF (X=0.10–0.21)  
     Fluorination: 2.11.2.1  
     Formation: 2.11.2.1  
**Cl<sub>2</sub>**  
   Cl<sub>2</sub>  
     Reaction with Al, Ga, In, Tl: 2.6.2.1  
     Reaction with AlN: 2.6.8.1  
     Reaction with Hg[NO<sub>3</sub>]<sub>2</sub>: 2.8.17.3  
     Reaction with B<sub>2</sub>X<sub>4</sub>: 2.6.13.1  
     Reaction with B<sub>2</sub>H<sub>6</sub>: 2.6.5.1  
     Reaction with [B<sub>12</sub>H<sub>12</sub>]<sup>2-</sup>: 2.6.4.1  
     Reaction with Cd: 2.8.14.1  
     Reaction with CdO: 2.8.15.1  
     Reaction with η<sup>5</sup>-CpMoNO(CO)<sub>2</sub>: 2.9.15.1.2  
     Reaction with Fe(CO)<sub>5</sub>: 2.9.15.1.1  
     Reaction with Group IIIB–Group IVB bonds: 2.6.11.1  
     Reaction with HgI<sub>2</sub>: 2.8.18  
     Reaction with Hg: 2.8.14.1, 2.8.21.3  
     Reaction with HgO: 2.8.15.1  
     Reaction with HgS: 2.8.16.1  
     Reaction with HgO·HgCl<sub>2</sub>: 2.8.14.1  
     Reaction with Hg<sub>3</sub>F<sub>2</sub>: 2.8.20.1  
     Reaction with Hg<sub>2</sub>Cl<sub>2</sub>: 2.8.20.1  
     Reaction with Mn<sub>2</sub>(CO)<sub>10</sub>, Tc<sub>2</sub>(CO)<sub>10</sub>: 2.9.15.1.1  
     Reaction with MoY<sub>2</sub>: 2.9.14.2  
     Reaction with Mo: 2.9.11.1  
     Reaction with M[BH<sub>4</sub>]: 2.6.5.1  
     Reaction with M(CO)<sub>6</sub>: 2.9.6  
     Reaction with MO: 2.7.6  
     Reaction with M<sub>2</sub>O<sub>3</sub>: 2.6.6.2  
     Reaction with R<sub>2</sub>AlH: 2.6.5.1  
     Reaction with R<sub>3</sub>B ... R<sub>3</sub>Tl: 2.6.10.1  
     Reaction with ZnS: 2.8.16.1  
     Reaction with MoS<sub>2</sub>, Fe<sub>2</sub>S, FeS: 2.9.5  
     Reaction with WS<sub>3</sub>, Re<sub>2</sub>S<sub>7</sub>, ReS<sub>2</sub>: 2.9.5  
     Reaction with Zn: 2.8.14.1  
     Reaction with ZnO: 2.8.15.1  
     Reaction with group-IA and -IIA metals: 2.7.2  
     Reaction with transition-metal oxides: 2.9.4.1  
     Reaction with transition-metals: 2.9.2.2  
     Safety: 2.7.1  
     Use in dehydration: 2.8.19  
   Cl<sub>2</sub>\*BBr  
   Cl<sub>2</sub>\*Ba  
   Cl<sub>2</sub>\*Be  
   Cl<sub>2</sub>\*C  
   Cl<sub>2</sub>\*CH<sub>3</sub>B  
   Cl<sub>2</sub>\*C<sub>2</sub>H<sub>11</sub>AsB<sub>10</sub>  
   Cl<sub>2</sub>\*C<sub>4</sub>H<sub>12</sub>Au<sub>2</sub>  
   Cl<sub>2</sub>\*C<sub>6</sub>H<sub>5</sub>B  
   Cl<sub>2</sub>\*C<sub>26</sub>H<sub>26</sub>AsAu  
   Cl<sub>2</sub>\*Ca  
   Cl<sub>2</sub>\*Cd  
   Cl<sub>2</sub>Co  
     CoCl<sub>2</sub>  
       Fluorination: 2.11.2.2  
       Formation: 2.9.3.3, 2.9.4.3, 2.9.4.6, 2.9.7, 2.9.9.1, 2.9.9.2  
       Reaction with BX<sub>3</sub>: 2.6.12.2  
       Reaction with XeF<sub>2</sub>: 2.11.2.2  
       Reaction with ClF<sub>3</sub>: 2.11.2.2  
   Cl<sub>2</sub>Cr  
     CrCl<sub>2</sub>  
       Formation: 2.9.3.2, 2.9.7  
   Cl<sub>2</sub>CrCuH<sub>18</sub>N<sub>6</sub>\*Br<sub>3</sub>  
   Cl<sub>2</sub>CrO<sub>2</sub>  
     CrO<sub>2</sub>Cl<sub>2</sub>: 2.9.12.2  
       Formation: 2.9.12.5  
       Reaction with ClF: 2.11.2.1  
   Cl<sub>2</sub>Cs\*Ag  
   Cl<sub>2</sub>Cs\*C<sub>2</sub>H<sub>6</sub>Au  
   Cl<sub>2</sub>Cu  
     CuCl<sub>2</sub>  
       Fluorination: 2.11.2.3  
       Formation: 2.8.2, 2.8.7.1, 2.8.8.1, 2.8.8.2, 2.8.8.3, 2.8.9, 2.9.7, 2.9.9.2  
       Reactions with BBr<sub>3</sub>: 2.8.8.1  
       Reactions with F<sub>2</sub> and ClF<sub>3</sub>: 2.8.8.1  
       Reaction with BX<sub>3</sub>: 2.6.12.2  
       Reaction with ZnS: 2.8.16.2  
   Cl<sub>2</sub>CuH<sub>4</sub>O<sub>2</sub>  
     CuCl<sub>2</sub>·2 H<sub>2</sub>O  
       Dehydration by SOCl<sub>2</sub>: 2.8.9

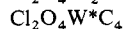
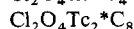
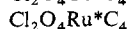
- Dehydration by HCl: 2.8.9  
 Dehydration by triethylorthoformate: 2.8.9  
 Dehydration by 2,2-dimethoxypropane: 2.8.9  
 Formation: 2.8.7.1, 2.8.7.3, 2.8.8.3  
 Thermal dehydration: 2.8.9
- Cl<sub>2</sub>CuK**  
 K[CuCl<sub>2</sub>]  
 Formation from Cu<sup>2+</sup>: 2.8.12
- Cl<sub>2</sub>CuN\*C<sub>6</sub>H<sub>16</sub>  
 Cl<sub>2</sub>CuN\*C<sub>12</sub>H<sub>28</sub>  
 Cl<sub>2</sub>CuN\*C<sub>16</sub>H<sub>36</sub>  
 Cl<sub>2</sub>CuNOP\*C<sub>18</sub>H<sub>25</sub>  
 Cl<sub>2</sub>CuP\*C<sub>24</sub>H<sub>20</sub>
- Cl<sub>2</sub>Cu<sub>2</sub>**  
 Cu<sub>2</sub>Cl<sub>2</sub>  
 Reaction with Al: 2.6.3.3
- Cl<sub>2</sub>F\*B**
- Cl<sub>2</sub>F<sub>2</sub>Ti**  
 TiF<sub>2</sub>Cl<sub>2</sub>  
 Reaction with Cl<sub>2</sub>O: 2.11.2.1
- Cl<sub>2</sub>F<sub>5</sub>S\*C<sub>10</sub>H<sub>8</sub>Au  
 Cl<sub>2</sub>F<sub>10</sub>N\*C<sub>28</sub>H<sub>36</sub>Au  
 Cl<sub>2</sub>F<sub>20</sub>\*C<sub>24</sub>Au<sub>2</sub>  
 Cl<sub>2</sub>F<sub>20</sub>N<sub>2</sub>\*C<sub>34</sub>H<sub>8</sub>Au<sub>2</sub>  
 Cl<sub>2</sub>F<sub>20</sub>N<sub>2</sub>\*C<sub>36</sub>H<sub>8</sub>Au<sub>2</sub>
- Cl<sub>2</sub>Fe**  
 FeCl<sub>2</sub>  
 Electrochemical formation: 2.9.3.7  
 Formation: 2.9.3.2  
 Formation from FeCl<sub>3</sub> and Hg: 2.8.21.3  
 Reaction with HgCl<sub>2</sub>: 2.8.21.2
- Cl<sub>2</sub>FeHg<sub>2</sub>\*C<sub>10</sub>H<sub>8</sub>  
 Cl<sub>2</sub>FeO<sub>4</sub>\*C<sub>4</sub>  
 Cl<sub>2</sub>Ga\*C<sub>6</sub>H<sub>5</sub>
- Cl<sub>2</sub>Ge**  
 GeCl<sub>2</sub>  
 Formation: 2.6.3.3
- Cl<sub>2</sub>H\*Al  
 Cl<sub>2</sub>H<sub>2</sub>O\*Cd
- Cl<sub>2</sub>H<sub>2</sub>OZn**  
 ZnCl<sub>2</sub>·H<sub>2</sub>O  
 Stability: 2.8.19
- Cl<sub>2</sub>H<sub>4</sub>HgN\*Br  
**Cl<sub>2</sub>H<sub>6</sub>O<sub>3</sub>Zn**  
 ZnCl<sub>2</sub>·3 H<sub>2</sub>O  
 Stability: 2.8.19
- Cl<sub>2</sub>H<sub>8</sub>HgN<sub>2</sub>\*Br<sub>2</sub>  
 Cl<sub>2</sub>H<sub>8</sub>O<sub>4</sub>\*Cd
- Cl<sub>2</sub>H<sub>8</sub>O<sub>4</sub>Zn**  
 ZnCl<sub>2</sub>·4 H<sub>2</sub>O  
 Stability: 2.8.19
- Cl<sub>2</sub>H<sub>9</sub>**  
 H<sub>9</sub>Cl<sub>2</sub>  
 Reaction with (HBNR)<sub>3</sub>: 2.6.5.3
- Cl<sub>2</sub>H<sub>10</sub>O<sub>9</sub>Zn<sub>5</sub>**  
 ZnCl<sub>2</sub>·4 Zn(OH)<sub>2</sub>·H<sub>2</sub>O  
 Decomposition with heat: 2.8.19
- Cl<sub>2</sub>H<sub>14</sub>O<sub>7</sub>Zn**  
 ZnCl<sub>2</sub>·7 H<sub>2</sub>O  
 Dehydration: 2.8.19
- Cl<sub>2</sub>Hg**  
 HgCl<sub>2</sub>  
 Fluorination: 2.11.4.3  
 Formation from HgSO<sub>4</sub> and NaCl: 2.8.17.2  
 Formation from Hg[NO<sub>3</sub>]<sub>2</sub> and HCl: 2.8.17.1  
 Formation from Hg[NO<sub>3</sub>]<sub>2</sub> and Cl<sub>2</sub>: 2.8.17.3  
 Formation from HgBr<sub>2</sub> and ICl: 2.8.18  
 Formation from HgI<sub>2</sub> and Cl<sub>2</sub>: 2.8.18  
 Formation from Hg, MnO and NaCl: 2.8.14.5  
 Formation from Hg and PCl<sub>5</sub>: 2.8.14.4  
 Formation from Hg and OSOCl<sub>2</sub>: 2.8.14.4  
 Formation from Hg and O<sub>2</sub>SOCl<sub>2</sub>: 2.8.14.4  
 Formation from Hg and S<sub>2</sub>Cl<sub>2</sub>: 2.8.14.4  
 Formation from Hg and NOCl: 2.8.14.4  
 Formation from Hg and Cl<sub>2</sub>: 2.8.14.1, 2.8.14.3  
 Formation from HgO and TiCl<sub>4</sub>: 2.8.15.3  
 Formation from HgO and NaCl: 2.8.15.3  
 Formation from HgO and HCl: 2.8.15.2  
 Formation from HgO and Cl<sub>2</sub>: 2.8.15.1  
 Formation from HgO and C<sub>6</sub>H<sub>5</sub>C(O)\*Cl: 2.8.15.3  
 Formation from HgS and AlCl<sub>3</sub>: 2.8.16.2  
 Formation from HgS and OCOCl<sub>2</sub>: 2.8.16.2  
 Formation from HgS and Cl<sub>2</sub>: 2.8.16.1  
 Formation from HgS and S<sub>2</sub>Cl<sub>2</sub>: 2.8.16.2  
 Formation from Hg<sub>2</sub>[NO<sub>3</sub>]<sub>2</sub> and HCl: 2.8.20.1  
 Formation from Hg<sub>2</sub>F<sub>2</sub> and Cl<sub>2</sub>: 2.8.20.1  
 Formation from Hg<sub>2</sub>Cl<sub>2</sub>: 2.8.20.1, 2.8.20.2, 2.8.21.2  
 Formation from Hg<sub>2</sub>Cl<sub>2</sub> and HCl: 2.8.20.1  
 Formation from Hg<sub>2</sub>Cl<sub>2</sub> and Cl<sub>2</sub>: 2.8.20.1

- Formation from Zn and  $\text{Hg}_2\text{Cl}_2$ : 2.8.14.5  
 Formation from HCl and Hg: 2.8.14.2  
 Reaction with Al: 2.6.3.3  
 Reaction with  $\text{Fe}[\text{SO}_4]$  and  $\text{H}_2\text{SO}_4$ : 2.8.21.2  
 Reaction with  $\text{FeCl}_2$ : 2.8.21.2  
 Reaction with Hg: 2.8.21.2  
 Reaction with  $\text{H}_3\text{PO}_2$ : 2.8.21.2  
 Reaction with  $\text{H}_3\text{PO}_3$ : 2.8.21.2  
 Reaction with RTIX<sub>2</sub>: 2.6.10.3  
 Reaction with  $\text{R}_3\text{Al}$ : 2.6.15  
 Reaction with  $\text{R}_2\text{NBX}-\text{NR}'\text{BX}_2$ : 2.6.8.3  
 Reaction with  $\text{R}_3\text{B}$ : 2.6.10.3  
 Reaction with  $\text{C}_4\text{H}_4\text{Se}$ : 2.8.23.6  
 Reaction with  $\text{SnCl}_2$ : 2.8.21.2  
 Reaction with  $\text{SO}_2$ : 2.8.21.2  
 Reaction with  $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$ : 2.8.23.2  
 Reaction with  $\text{N}_2\text{H}_4 \cdot \text{HCl}$  and x-rays: 2.8.21.2  
 Reaction with  $\text{F}_2$ : 2.8.18  
 Reaction with  $\text{IF}_3$ : 2.8.18  
 Reaction with KI: 2.8.18  
 Reaction with Mg: 2.7.3.2.1  
 Reaction with  $\text{Br}_2$ : 2.8.18  
 Reaction with  $\text{I}_2$ : 2.8.18  
 Reaction with  $\text{CH}_3\text{I}$ : 2.8.18  
 Reaction with HI: 2.8.18  
 **$\text{Cl}_2\text{Hg} \cdot \text{C}_7\text{H}_5\text{Br}$**   
 **$\text{Cl}_2\text{HgI}_2\text{N}_2 \cdot \text{C}_2\text{H}_{12}$**   
 **$\text{Cl}_2\text{HgK}_2 \cdot \text{Br}_2$**   
 **$\text{Cl}_2\text{HgNa}_2 \cdot \text{Br}_2$**   
 **$\text{Cl}_2\text{HgO}_6$**   
      $\text{Hg}[\text{ClO}_3]_2$   
     Formation from HgO and  $\text{Cl}_2$ : 2.8.15.1  
 **$\text{Cl}_2\text{HgO}_8$**   
      $\text{Hg}[\text{ClO}_4]_2$   
     Reaction with KI: 2.8.17.2  
 **$\text{Cl}_2\text{Hg}_2$**   
      $\text{Hg}_2\text{Cl}_2$   
         Disproportionation: 2.8.20.1, 2.8.20.2  
         Formation from  $\text{FeCl}_3$  and Hg: 2.8.21.3  
         Formation from  $\text{HgCl}_2$ ,  $\text{Fe}[\text{SO}_4]$  and  $\text{H}_2\text{SO}_4$ : 2.8.21.2  
         Formation from  $\text{HgCl}_2$ ,  $\text{N}_2\text{H}_4 \cdot \text{HCl}$  and x-rays: 2.8.21.2  
         Formation from  $\text{HgCl}_2$  and  $\text{FeCl}_2$ : 2.8.21.2  
         Formation from  $\text{HgCl}_2$  and Hg: 2.8.21.2  
         Formation from  $\text{HgCl}_2$  and  $\text{H}_2\text{PO}_2$ : 2.8.21.2  
 Formation from  $\text{HgCl}_2$  and  $\text{H}_3\text{PO}_2$ : 2.8.21.2  
 Formation from  $\text{HgCl}_2$  and  $\text{SO}_2$ : 2.8.21.2  
 Formation from  $\text{HgCl}_2$  and  $\text{Li}_2\text{SO}_3$ : 2.8.21.2  
 Formation from  $\text{HgCl}_2 \cdot 2 \text{HgS}$ : 2.8.21.2  
 Formation from Hg,  $\text{MnO}_2$ , NaCl and  $\text{H}_2\text{SO}_4$ : 2.8.21.3  
 Formation from Hg, HCl and  $\text{O}_2$ : 2.8.21.3  
 Formation from Hg and  $\text{Cl}_2$ : 2.8.21.3  
 Formation from Hg and  $\text{CCl}_4$ : 2.8.21.3  
 Formation from  $\text{Hg}_2\text{SO}_4$  and NaCl: 2.8.21.1  
 Formation from  $\text{Hg}_2(\text{NO}_3)_2$  and NaCl: 2.8.21.1  
 Formation from  $\text{Hg}_2[\text{NO}_3]_2$  and NaCl: 2.8.21.1  
 Formation from  $\text{Hg}_2\text{O}$  and HCl: 2.8.21.1  
 Formation from  $\text{SnCl}_2$  and  $\text{HgCl}_2$ : 2.8.21.2  
 Formation from Hg,  $\text{HgSO}_4$ , and NaCl: 2.8.21.3  
 Reaction with AgF: 2.8.21.1  
 Reaction with KBr: 2.8.21.1  
 Reaction with KI: 2.8.21.1  
 Reaction with  $\text{Br}_2$ : 2.8.20.1  
 Reaction with HCl: 2.8.20.1  
 Reaction with  $\text{Cl}_2$ : 2.8.20.1  
 Reaction with  $\text{I}_2$ : 2.8.20.1  
 **$\text{Cl}_2\text{Hg}_2 \cdot \text{C}_4\text{H}_6$**   
 **$\text{Cl}_2\text{Hg}_2\text{O}$**   
      $\text{HgO} \cdot \text{HgCl}_2$   
     Reaction with  $\text{Cl}_2$ : 2.8.14.1  
 **$\text{Cl}_2\text{Hg}_3\text{S}_2$**   
      $\text{HgCl}_2 \cdot 2 \text{HgS}$   
     reaction of heating: 2.8.21.2  
 **$\text{Cl}_2\text{I} \cdot \text{C}_6\text{H}_5$**   
 **$\text{Cl}_2\text{IN} \cdot \text{C}_{12}\text{H}_{28}\text{Cd}$**   
 **$\text{Cl}_2\text{I}_2\text{K}_2 \cdot \text{Cd}$**   
 **$\text{Cl}_2\text{In}$**   
      $\text{InCl}_2$   
         Formation: 2.6.3.1  
 **$\text{Cl}_2\text{InMnO}_5 \cdot \text{C}_5$**   
 **$\text{Cl}_2\text{KN}_2 \cdot \text{C}_2\text{Au}$**   
 **$\text{Cl}_2\text{KN}_2\text{O} \cdot \text{C}_2\text{H}_2\text{Au}$**   
 **$\text{Cl}_2\text{Mg}$**   
      $\text{MgCl}_2$   
         Formation: 2.7.3.1, 2.7.3.2.1, 2.7.5  
 **$\text{Cl}_2\text{Mn}$**   
      $\text{MnCl}_2$   
         Formation: 2.9.2.2, 2.9.3.3, 2.9.4.6, 2.9.7

- Cl<sub>2</sub>MnO<sub>2</sub>**  
 MnO<sub>2</sub>Cl<sub>2</sub>  
 Formation: 2.9.12.5  
**Cl<sub>2</sub>MnO<sub>3</sub>\*C<sub>5</sub>B**  
**Cl<sub>2</sub>Mo**  
 MoCl<sub>2</sub>  
 Formation: 2.9.7  
**Cl<sub>2</sub>MoO**  
 MoOCl<sub>2</sub>  
 Formation: 2.9.12.6  
**Cl<sub>2</sub>MoO<sub>2</sub>**  
 MoO<sub>2</sub>Cl<sub>2</sub>  
 Formation: 2.9.11.2, 2.9.12.1, 2.9.12.4,  
 2.9.12.5  
 Reaction with XeF<sub>2</sub>: 2.11.3.1  
 Reaction with HF: 2.11.3.1  
**Cl<sub>2</sub>MoO<sub>4</sub>\*C<sub>4</sub>**  
**Cl<sub>2</sub>MoS**  
 MoSCl<sub>2</sub>  
 Formation: 2.9.14.2  
**Cl<sub>2</sub>MoS<sub>2</sub>**  
 MoS<sub>2</sub>Cl<sub>2</sub>  
 Formation: 2.9.14.1.2  
**Cl<sub>2</sub>Mo<sub>6</sub>S<sub>6</sub>**  
 Mo<sub>6</sub>S<sub>6</sub>Cl<sub>2</sub>  
 Formation: 2.9.14.1.2  
**Cl<sub>2</sub>N\*C<sub>2</sub>H<sub>6</sub>Al**  
**Cl<sub>2</sub>N\*C<sub>2</sub>H<sub>6</sub>B**  
**Cl<sub>2</sub>N\*C<sub>4</sub>H<sub>10</sub>B**  
**Cl<sub>2</sub>N\*C<sub>4</sub>H<sub>12</sub>Ag**  
**Cl<sub>2</sub>N\*C<sub>8</sub>H<sub>20</sub>Au**  
**Cl<sub>2</sub>N\*C<sub>12</sub>H<sub>28</sub>BrCd**  
**Cl<sub>2</sub>N\*C<sub>16</sub>H<sub>36</sub>Au**  
**Cl<sub>2</sub>NP<sub>2</sub>\*C<sub>24</sub>H<sub>21</sub>Au<sub>2</sub>**  
**Cl<sub>2</sub>N<sub>2</sub>\*C<sub>5</sub>H<sub>17</sub>B**  
**Cl<sub>2</sub>N<sub>2</sub>\*C<sub>10</sub>H<sub>10</sub>Au<sub>2</sub>**  
**Cl<sub>2</sub>N<sub>2</sub>\*C<sub>14</sub>H<sub>20</sub>Au<sub>2</sub>**  
**Cl<sub>2</sub>N<sub>2</sub>\*C<sub>16</sub>H<sub>20</sub>Au<sub>2</sub>**  
**Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>\*C<sub>26</sub>H<sub>20</sub>AsAu**  
**Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>W**  
 W(NO)<sub>2</sub>Cl<sub>2</sub>  
 Formation: 2.9.15.1.2  
**Cl<sub>2</sub>N<sub>3</sub>O<sub>4</sub>\*C<sub>16</sub>H<sub>20</sub>Au**  
**Cl<sub>2</sub>N<sub>3</sub>O<sub>4</sub>\*C<sub>18</sub>H<sub>24</sub>Au**  
**Cl<sub>2</sub>NbO**  
 NbOCl<sub>2</sub>  
 Formation: 2.9.11.4  
**Cl<sub>2</sub>NbS**  
 NbSCl<sub>2</sub>  
 Formation: 2.9.14.3  
**Cl<sub>2</sub>NbS<sub>2</sub>**  
 NbS<sub>2</sub>Cl<sub>2</sub>  
 Formation: 2.9.14.1.2  
**Cl<sub>2</sub>NbSe<sub>2</sub>**  
 NbSe<sub>2</sub>Cl<sub>2</sub>  
 Formation: 2.9.14.1.2  
**Cl<sub>2</sub>Nd**  
 NdCl<sub>2</sub>  
 Formation: 2.9.9.2  
**Cl<sub>2</sub>Ni**  
 NiCl<sub>2</sub>  
 Electrochemical formation: 2.9.3.7  
 Fluorination: 2.11.2.2  
 Formation: 2.9.2.2, 2.9.4.2, 2.9.7, 2.9.9.2  
**Cl<sub>2</sub>O\*C**  
**Cl<sub>2</sub>O\*C<sub>4</sub>H<sub>9</sub>B**  
**Cl<sub>2</sub>ORe**  
 ReOCl<sub>2</sub>  
 Formation: 2.9.12.6  
**Cl<sub>2</sub>OS**  
 OSCl<sub>2</sub>  
 Halogenation agent: 2.9.12.5  
 Reaction with (HBNR)<sub>3</sub>: 2.6.5.3  
 Reaction with Hg: 2.8.14.4  
 Reaction with MO: 2.7.7  
 Reaction with Ta<sub>2</sub>O<sub>5</sub>, CrO<sub>3</sub>, ReO<sub>2</sub>:  
 2.9.4.5  
 Use as dehydrating agent: 2.8.19  
**Cl<sub>2</sub>OSW**  
 WOSCl<sub>2</sub>  
 Formation: 2.9.14.4  
**Cl<sub>2</sub>OTa**  
 TaOCl<sub>2</sub>  
 Formation: 2.9.11.4  
**Cl<sub>2</sub>OTi**  
 TiOCl<sub>2</sub>  
 Formation: 2.9.12.7  
 Formation from HgO and TiCl<sub>4</sub>:  
 2.8.15.3  
**Cl<sub>2</sub>OV**  
 VOCl<sub>2</sub>  
 Formation: 2.9.12.6, 2.9.12.7  
**Cl<sub>2</sub>OV\*C<sub>6</sub>H<sub>5</sub>**  
**Cl<sub>2</sub>OW**  
 WOCl<sub>2</sub>  
 Formation: 2.9.11.4  
**Cl<sub>2</sub>O<sub>2</sub>S**  
 O<sub>2</sub>SCl<sub>2</sub>  
 Reaction with Hg: 2.8.14.4  
 Reaction with Zn: 2.8.14.4  
**Cl<sub>2</sub>O<sub>2</sub>Ta**  
 [TaO<sub>2</sub>Cl<sub>2</sub>]<sup>-</sup>  
 Formation: 2.9.13.3  
**Cl<sub>2</sub>O<sub>2</sub>V**  
 [VO<sub>2</sub>Cl<sub>2</sub>]<sup>-</sup>  
 Formation: 2.9.13.2

**Cl<sub>2</sub>O<sub>2</sub>W**

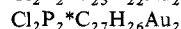
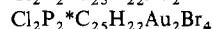
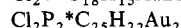
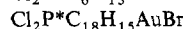
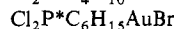
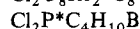
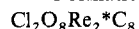
Formation: 2.9.12.1, 2.9.12.4, 2.9.12.6,  
2.9.12.7

**Cl<sub>2</sub>O<sub>5</sub>**

Reaction with VO<sub>2</sub>, V<sub>2</sub>O<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>:  
2.9.4.5

**Cl<sub>2</sub>O<sub>6</sub>Zn**

Formation with ZnO and Cl<sub>2</sub>: 2.8.15.1

**Cl<sub>2</sub>Pb**

Reaction with Al: 2.6.3.3

Reaction with Zn: 2.8.14.5

**Cl<sub>2</sub>Pd**

Formation: 2.9.2.2

**Cl<sub>2</sub>Pt**

Fluorination: 2.11.4.2

Formation: 2.9.2.2, 2.9.4.2

**Cl<sub>2</sub>Ra**

Formation: 2.7.2

**Cl<sub>2</sub>ReS**

Formation: 2.9.14.3

**Cl<sub>2</sub>ReSe**

Formation: 2.9.14.3

**Cl<sub>2</sub>S**

Formation: 2.9.12.5

Formation from Hg and OSCl<sub>2</sub>: 2.8.14.4

Reaction with OsO<sub>4</sub>: 2.9.4.5

**Cl<sub>2</sub>SSeW**

Formation: 2.9.14.4

**Cl<sub>2</sub>S<sub>2</sub>**

Formation from HgS and Cl<sub>2</sub>: 2.8.16.1

Halogenation agent: 2.9.12.5

Reaction with Cd: 2.8.14.4

Reaction with CdO: 2.8.15.3

Reaction with Hg: 2.8.14.4

Reaction with MoS<sub>3</sub>: 2.9.14.2

Reaction with MO: 2.7.7

Reaction with M<sub>2</sub>O<sub>3</sub>: 2.6.6.2

Reaction with Re: 2.9.3.5

Reaction with ZnO: 2.8.15.3

Reaction with Zn: 2.8.14.4

Reaction with ZnS: 2.8.16.2

Reaction with ZrO<sub>2</sub>, HfO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>:

2.9.4.5

Reaction with transition-metals:

2.9.14.1.2

**Cl<sub>2</sub>S<sub>2</sub>Ta**

Formation: 2.9.14.3

**Cl<sub>2</sub>S<sub>2</sub>W**

Formation: 2.9.14.4

**Cl<sub>2</sub>Se<sub>2</sub>**

Reaction with Al<sub>2</sub>Y<sub>3</sub>: 2.6.7.3

**Cl<sub>2</sub>Sn**

Reaction with HgCl<sub>2</sub>: 2.8.21.2

**Cl<sub>2</sub>Sr**

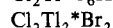
Formation: 2.7.2

**Cl<sub>2</sub>Te**

Formation: 2.6.7.1

**Cl<sub>2</sub>Tl**

Formation: 2.6.14.2

**Cl<sub>2</sub>V**

Electrochemical formation: 2.9.3.7

Formation: 2.9.3.2

**Cl<sub>2</sub>Xe**

Formation: 2.10.1, 2.10.2.2, 2.10.2.2.2

**Cl<sub>2</sub>Zn**

Anhydrous: 2.8.19

Dehydration by OSCl<sub>2</sub>: 2.8.19

Formation from ZnSO<sub>4</sub> and CaCl<sub>2</sub>:

2.8.17.2

Formation from ZnSO<sub>4</sub> and HCl:

2.8.17.1

- Formation from  $\text{ZnOHCl}$ : 2.8.19  
 Formation from  $\text{ZnCO}_3$  and  $\text{HCl}$ : 2.8.17.1  
 Formation from  $\text{ZnCl}_2 \cdot 4 \text{Zn(OH)}_2 \cdot \text{H}_2\text{O}$ : 2.8.19  
 Formation from  $\text{Zn}$  and  $\text{CuBr}$ : 2.8.14.5  
 Formation from  $\text{Zn}$  and  $\text{CuI}$ : 2.8.14.5  
 Formation from  $\text{Zn}$  and  $\text{CuCl}_2$ : 2.8.14.5  
 Formation from  $\text{Zn}$  and  $\text{HgI}_2$ : 2.8.14.5  
 Formation from  $\text{Zn}$  and  $\text{Hg}_2\text{Cl}_2$ : 2.8.14.5  
 Formation from  $\text{Zn}$  and  $\text{PbCl}_2$ : 2.8.14.5  
 Formation from  $\text{Zn}$  and  $\text{POCl}_3$ : 2.8.14.4  
 Formation from  $\text{Zn}$  and  $\text{SiCl}_4$ : 2.8.14.4  
 Formation from  $\text{Zn}$  and  $\text{SO}_2\text{Cl}_2$ : 2.8.14.4  
 Formation from  $\text{Zn}$  and  $\text{S}_2\text{Cl}_2$ : 2.8.14.4  
 Formation from  $\text{Zn}$  and  $\text{CH}_3\text{COCl}$ : 2.8.14.4  
 Formation from  $\text{Zn}$  and  $\text{HCl}$ : 2.8.14.2, 2.8.14.3  
 Formation from  $\text{Zn}$  and  $\text{Cl}_2$ : 2.8.14.1  
 Formation from  $\text{ZnO}$  and  $\text{BCl}_3$ : 2.8.15.3  
 Formation from  $\text{ZnO}$  and  $\text{S}_2\text{Cl}_2$ : 2.8.15.3  
 Formation from  $\text{ZnO}$  and  $[\text{NH}_4]\text{Cl}$ : 2.8.15.3  
 Formation from  $\text{ZnO}$  and  $\text{CF}_3\text{BrCl}$ : 2.8.15.3  
 Formation from  $\text{ZnO}$  and  $\text{HCl}$ : 2.8.15.2  
 Formation from  $\text{ZnO}$  and  $\text{Cl}_2$ : 2.8.15.1  
 Formation from  $\text{ZnO}$  and  $\text{CCl}_4$ : 2.8.15.3  
 Formation from  $\text{ZnO}$  and  $\text{CH}_3\text{C(O)Cl}$ : 2.8.15.3  
 Formation from  $\text{ZnO}$  and  $\text{COCl}_2$ : 2.8.15.3  
 Formation from  $\text{ZnS}$  and  $\text{AlCl}_3$ : 2.8.16.2  
 Formation from  $\text{ZnS}$  and  $\text{CuCl}_2$ : 2.8.16.2  
 Formation from  $\text{ZnS}$  and  $\text{FeCl}_3$ : 2.8.16.2  
 Formation from  $\text{ZnS}$  and  $\text{NaCl}$ : 2.8.16.2  
 Formation from  $\text{ZnS}$  and  $\text{HCl}$ : 2.8.16.2  
 Formation from  $\text{ZnS}$  and  $\text{Cl}_2$ : 2.8.16.1  
 Formation from  $\text{ZnS}$  and  $\text{S}_2\text{Cl}_2$ : 2.8.16.2  
 Reaction with  $\text{Zn(C}_6\text{H}_5)_2$ : 2.8.23.2  
 Reaction with  $\text{RMgX}$ : 2.8.23.2  
 Reaction with  $\text{R}_3\text{B}$ : 2.6.10.3  
 Reaction with  $\text{NH}_4\text{F}$ : 2.8.18  
 Reaction with  $\text{HF}$ : 2.8.18  
 Stability in  $\text{H}_2\text{O}$ : 2.8.19  
 $\text{Cl}_2\text{Zr} \cdot \text{C}_{10}\text{H}_{10}$
- $\text{Cl}_3 \cdot \text{Al}$   
 $\text{Cl}_3 \cdot \text{As}$   
 $\text{Cl}_3 \cdot \text{Au}$   
 $\text{Cl}_3 \cdot \text{B}$   
 $\text{Cl}_3 \cdot \text{CH}$   
 $\text{Cl}_3 \cdot \text{C}_7\text{H}_5$   
 $\text{Cl}_3 \cdot \text{Ce}$   
 $\text{Cl}_3\text{Cr}$   
 $\text{CrCl}_3$   
 Formation: 2.9.2.2, 2.9.4.2, 2.9.4.5, 2.9.4.6, 2.9.5, 2.9.6, 2.9.7, 2.9.9.2  
 Reaction with  $\text{CsCl}$ : 2.9.10.1  
 $\text{Cl}_3\text{CrO}$   
 $\text{CrOCl}_3$   
 Formation: 2.9.12.5  
 $\text{Cl}_3\text{Cs} \cdot \text{Cd}$   
 $\text{Cl}_3\text{CsCu}$   
 $\text{Cs}[\text{CuCl}_3]$   
 Fluorination: 2.8.4.1, 2.11.2.3  
 Formation: 2.8.10  
 Reaction with  $\text{F}_2$ : 2.9.10.5  
 $\text{Cl}_3\text{CsCu}_2$   
 $\text{Cs}[\text{Cu}_2\text{Cl}_3]$   
 Formation: 2.8.12  
 Structure: 2.8.12  
 $\text{Cl}_3\text{CsCu}_4\text{I}_2$   
 $\text{Cs}[\text{Cu}_4\text{Cl}_3\text{I}_2]$   
 Formation: 2.8.12  
 $\text{Cl}_3\text{Cs}_3\text{Hg} \cdot \text{Br}_2$   
 $\text{Cl}_3\text{Cu} \cdot \text{Ag}$   
 $\text{Cl}_3\text{CuH}_4\text{N}$   
 $\text{NH}_4[\text{CuCl}_3]$   
 Formation: 2.8.10  
 $\text{Cl}_3\text{CuK}$   
 $\text{K}[\text{CuCl}_3]$   
 Formation: 2.8.10  
 $\text{Cl}_3\text{CuK}_2$   
 $\text{K}_2[\text{CuCl}_3]$   
 Formation: 2.8.12  
 Structure: 2.8.12  
 $\text{Cl}_3\text{CuN}_2 \cdot \text{C}_2\text{H}_{12}$   
 $\text{Cl}_3\text{CuN}_2 \cdot \text{C}_2\text{H}_{12}\text{Br}$   
 $\text{Cl}_3\text{CuP} \cdot \text{C}_{24}\text{H}_{20}$   
 $\text{Cl}_3\text{CuRb}_2$   
 $\text{Rb}_2[\text{CuCl}_3]$   
 Formation from  $\text{Cu}[\text{OAc}]$ : 2.8.12  
 $\text{Cl}_3\text{Cu}_2\text{N} \cdot \text{C}_2\text{H}_8$   
 $\text{Cl}_3\text{Cu}_2\text{N} \cdot \text{C}_4\text{H}_{12}$   
 $\text{Cl}_3\text{Cu}_2\text{N} \cdot \text{C}_8\text{H}_{20}$   
 $\text{Cl}_3\text{Cu}_2\text{N}_{18}\text{P}_6 \cdot \text{C}_{24}\text{H}_{72}$   
 $\text{Cl}_3\text{Cu}_2\text{P} \cdot \text{C}_4\text{H}_{12}$   
 $\text{Cl}_3\text{Dy}$   
 $\text{DyCl}_3$   
 Formation: 2.9.9.1



**Cl<sub>3</sub>Fe**

Fluorination: 2.11.2.2

Formation: 2.9.4.2, 2.9.4.6, 2.9.5, 2.9.9.2

Formation from HgCl<sub>2</sub> and FeCl<sub>2</sub>:

2.8.21.2

Reaction with Hg: 2.8.21.3

Reaction with BrF<sub>3</sub>: 2.11.2.2

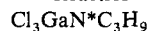
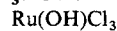
Reaction with ZnS: 2.8.16.2

Reaction with ClF<sub>3</sub>: 2.11.2.2

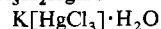
Reaction with HF: 2.11.2.2

**Cl<sub>3</sub>Ga**

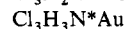
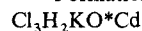
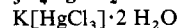
Formation: 2.6.2.1, 2.6.3.1, 2.6.6.3, 2.6.6.4

Reaction with R<sub>3</sub>Ga: 2.6.15**Cl<sub>3</sub>HORu**

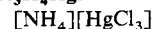
Formation: 2.9.4.3

**Cl<sub>3</sub>H<sub>2</sub>HgKO**

Formation: 2.8.22

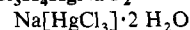
**Cl<sub>3</sub>H<sub>4</sub>HgKO<sub>2</sub>**

Formation: 2.8.22

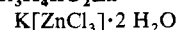
**Cl<sub>3</sub>H<sub>4</sub>HgN**

Formation from melt and solution:

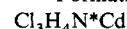
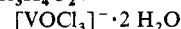
2.8.22

**Cl<sub>3</sub>H<sub>4</sub>HgNaO<sub>2</sub>**

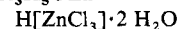
Formation: 2.8.22

**Cl<sub>3</sub>H<sub>4</sub>KO<sub>2</sub>Zn**

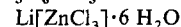
Formation: 2.8.22

**Cl<sub>3</sub>H<sub>4</sub>O<sub>2</sub>V**

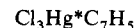
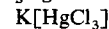
Formation: 2.9.13

**Cl<sub>3</sub>H<sub>5</sub>OZn**

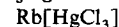
Formation: 2.8.22

**Cl<sub>3</sub>H<sub>6</sub>LiO<sub>3</sub>Zn**

Formation: 2.8.22

**Cl<sub>3</sub>HgK**

Formation: 2.8.22

**Cl<sub>3</sub>HgRb**

Formation: 2.8.22

**Cl<sub>3</sub>Ho**

Formation: 2.9.9.1

**Cl<sub>3</sub>I**Formation from HgCl<sub>2</sub> and IF<sub>3</sub>: 2.8.18**Cl<sub>3</sub>In**

Formation: 2.6.2.1, 2.6.6.3, 2.6.13.1,

2.6.13.2

**Cl<sub>3</sub>In<sub>2</sub>**

Formation: 2.6.14.1

**Cl<sub>3</sub>K\*Cd****Cl<sub>3</sub>La**

Formation: 2.9.9.1

**Cl<sub>3</sub>Mn**

Formation: 2.9.4.2

**Cl<sub>3</sub>Mo**

Reaction with CsCl: 2.9.10.1

Reaction with elemental S, Se: 2.9.14.3

**Cl<sub>3</sub>MoO**

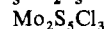
Formation: 2.9.12.4, 2.9.12.5, 2.9.12.7

**Cl<sub>3</sub>MoS**

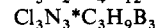
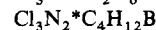
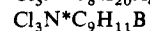
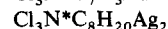
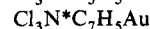
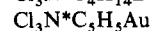
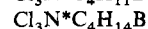
Formation: 2.6.7.3, 2.9.14.4

**Cl<sub>3</sub>MoSe**

Formation: 2.9.14.4

**Cl<sub>3</sub>Mo<sub>2</sub>S<sub>3</sub>**

Formation: 2.9.14.3

**Cl<sub>3</sub>NbO**

Formation: 2.9.12.1, 2.9.12.4, 2.9.12.5,

2.9.12.6

**Cl<sub>3</sub>NbS**

Formation: 2.6.7.3, 2.9.14.4

- Cl<sub>3</sub>Nd**  
 NdCl<sub>3</sub>  
 Formation: 2.9.7, 2.9.9.1
- Cl<sub>3</sub>OP**  
 OPCl<sub>3</sub>  
 Reaction with AlX<sub>3</sub>: 2.6.12.2  
 Reaction with (R<sub>2</sub>NBNH)<sub>3</sub>: 2.6.8.3  
 Reaction with (R<sub>2</sub>N)<sub>3</sub>B: 2.6.8.3  
 Reaction with Zn: 2.8.14.4
- Cl<sub>3</sub>OTa**  
 TaOCl<sub>3</sub>  
 Formation: 2.9.12.6
- Cl<sub>3</sub>OTc**  
 TcOCl<sub>3</sub>  
 Formation: 2.9.12.1
- Cl<sub>3</sub>OV**  
 VOCl<sub>3</sub>  
 Formation: 2.9.12.1, 2.9.12.4, 2.9.12.5
- Cl<sub>3</sub>OW**  
 WOCl<sub>3</sub>  
 Formation: 2.9.11.4, 2.9.12.7
- Cl<sub>3</sub>O<sub>3</sub>\*B<sub>3</sub>**  
**Cl<sub>3</sub>O<sub>3</sub>Re**  
 [ReO<sub>3</sub>Cl<sub>3</sub>]<sup>2-</sup>  
 Formation: 2.9.13.4
- Cl<sub>3</sub>P**  
 PCl<sub>3</sub>  
 Formation from Hg and PCl<sub>5</sub>: 2.8.14.4  
 Reaction with AlH<sub>3</sub>: 2.6.5.3  
 Reaction with R<sub>2</sub>Hg: 2.8.23.5  
 Reaction with R<sub>2</sub>NBX—NR'BX<sub>2</sub>:  
 2.6.8.3  
 Reaction with (R<sub>2</sub>NBNH)<sub>3</sub>: 2.6.8.3
- Cl<sub>3</sub>P\*C<sub>6</sub>H<sub>15</sub>Au**  
**Cl<sub>3</sub>P\*C<sub>18</sub>H<sub>15</sub>Au**  
**Cl<sub>3</sub>PS**  
 SPCl<sub>3</sub>  
 Reaction with (R<sub>2</sub>N)<sub>3</sub>B: 2.6.8.3
- Cl<sub>3</sub>Pr**  
 PrCl<sub>3</sub>  
 Fluorination of MCl mixture: 2.11.5.1  
 Formation: 2.9.9.1
- Cl<sub>3</sub>Rb\*Cd**  
**Cl<sub>3</sub>Re**  
 ReCl<sub>3</sub>  
 Formation: 2.9.2.2, 2.9.3.5
- Cl<sub>3</sub>Rh**  
 RhCl<sub>3</sub>  
 Formation: 2.9.2.2
- Cl<sub>3</sub>Ru**  
 α-RuCl<sub>3</sub>  
 Formation: 2.9.2.2
- RuCl<sub>3</sub>  
 Fluorination: 2.11.3.2  
 β-RuCl<sub>3</sub>  
 Formation: 2.9.2.2
- Cl<sub>3</sub>STa**  
 TaSCl<sub>3</sub>  
 Formation: 2.6.7.3, 2.9.14.4
- Cl<sub>3</sub>SW**  
 WSCl<sub>3</sub>  
 Formation: 2.9.14.4
- Cl<sub>3</sub>S<sub>3</sub>\*B<sub>3</sub>**  
**Cl<sub>3</sub>Sb**  
 SbCl<sub>3</sub>  
 Formation: 2.9.3.6  
 Reaction with R<sub>2</sub>NBX—NR'BX<sub>2</sub>:  
 2.6.8.3
- Cl<sub>3</sub>SeWY**  
 WYSeCl<sub>3</sub>  
 Formation: 2.9.14.4
- Cl<sub>3</sub>Si\*CH<sub>3</sub>**  
**Cl<sub>3</sub>Si\*C<sub>2</sub>H<sub>3</sub>**  
**Cl<sub>3</sub>Sm**  
 SmCl<sub>3</sub>  
 Formation: 2.9.7, 2.9.9.1
- Cl<sub>3</sub>Tb**  
 TbCl<sub>3</sub>  
 Fluorination of MCl mixture: 2.11.5.1
- Cl<sub>3</sub>Ti**  
 TiCl<sub>3</sub>  
 Formation: 2.8.23.5  
 Reaction with CsCl: 2.9.10.1
- Cl<sub>3</sub>Ti\*CH<sub>3</sub>**  
**Cl<sub>3</sub>Tl**  
 TlCl<sub>3</sub>  
 Formation: 2.6.2.1, 2.6.6.3, 2.6.10.3,  
 2.6.11.2, 2.6.13.2, 2.6.14.2  
 Reaction with HMn(CO)<sub>5</sub>: 2.6.13.2  
 Reaction with R<sub>2</sub>Hg: 2.8.23.5
- Cl<sub>3</sub>Tm**  
 TmCl<sub>3</sub>  
 Formation: 2.9.9.1
- Cl<sub>3</sub>V**  
 VCl<sub>3</sub>  
 Formation: 2.9.4.5, 2.9.4.6  
 Reaction with CsCl: 2.9.10.1
- Cl<sub>3</sub>V\*C<sub>6</sub>H<sub>5</sub>**  
**Cl<sub>3</sub>Yb**  
 YbCl<sub>3</sub>  
 Formation: 2.9.9.1
- Cl<sub>4</sub>\*B<sub>2</sub>**  
**Cl<sub>4</sub>\*B<sub>4</sub>**  
**Cl<sub>4</sub>\*C**

- $\text{Cl}_4^*\text{C}_2$   
 $\text{Cl}_4^*\text{C}_{12}\text{H}_{10}\text{Au}_2$   
 $\text{Cl}_4^*\text{C}_{24}\text{H}_{20}\text{AsAu}$   
 $\text{Cl}_4\text{CoCs}_2$   
 $\text{Cs}_2[\text{CoCl}_4]$   
 Fluorination: 2.11.2.2  
 **$\text{Cl}_4\text{CrO}$**   
 $[\text{CrOCl}_4]^-$   
 Formation: 2.9.13, 2.9.13.4  
 $\text{Cl}_4\text{Cs}^*\text{Au}$   
 $\text{Cl}_4\text{Cs}_2^*\text{Cd}$   
 **$\text{Cl}_4\text{Cs}_2\text{Cu}$**   
 $\text{Cs}_2[\text{CuCl}_4]$   
 Formation: 2.8.10  
 **$\text{Cl}_4\text{Cs}_2\text{Hg}$**   
 $\text{Cs}_2[\text{HgCl}_4]$   
 Formation: 2.8.22  
 **$\text{Cl}_4\text{Cs}_2\text{Zn}$**   
 $\text{Cs}_2[\text{ZnCl}_4]$   
 Formation: 2.8.22  
 **$\text{Cl}_4\text{CuH}_8\text{N}_2$**   
 $[\text{NH}_4]_2[\text{CuCl}_4]$   
 Formation: 2.8.10  
 $\text{Cl}_4\text{Cu}_2\text{P}^*\text{C}_6\text{H}_{15}$   
 **$\text{Cl}_4\text{Cu}_3\text{H}_{12}\text{N}_4$**   
 $[\text{Cu}(\text{NH}_3)_4][\text{CuCl}_2]_2$   
 Formation: 2.8.12  
 Structure: 2.8.12  
 **$\text{Cl}_4\text{Cu}_3\text{Rb}$**   
 $\text{Rb}[\text{Cu}_3\text{Cl}_4]$   
 Formation: 2.8.12  
 **$\text{Cl}_4\text{Ge}$**   
 $\text{GeCl}_4$   
 Reaction with  $(\text{C}_2\text{H}_5)_2\text{Hg}$ : 2.8.23.5  
 Reaction with B: 2.6.3.3  
 Reaction with  $\text{R}_3\text{Al}$ : 2.6.10.3  
 **$\text{Cl}_4\text{H}_2\text{HgK}_2\text{O}$**   
 $\text{K}_2[\text{HgCl}_4]\cdot\text{H}_2\text{O}$   
 Formation: 2.8.22  
 $\text{Cl}_4\text{H}_4\text{KO}_2^*\text{Au}$   
 $\text{Cl}_4\text{H}_4\text{N}^*\text{Au}$   
 $\text{Cl}_4\text{H}_4\text{NaO}_2^*\text{Au}$   
 **$\text{Cl}_4\text{H}_4\text{O}_3\text{V}$**   
 $[\text{VOCl}_4]^{2-}\cdot 2\text{H}_2\text{O}$   
 Formation: 2.9.13, 2.9.13.2, 2.9.13.3  
 **$\text{Cl}_4\text{H}_6\text{Na}_2\text{O}_3\text{Zn}$**   
 $\text{Na}_2[\text{ZnCl}_4]\cdot 3\text{H}_2\text{O}$   
 Formation: 2.8.22  
 **$\text{Cl}_4\text{H}_8\text{HgN}_2$**   
 $[\text{NH}_4]_2[\text{HgCl}_4]$   
 Formation from melt: 2.8.22  
 **$\text{Cl}_4\text{H}_8\text{N}_2\text{Zn}$**   
 $[\text{NH}_4]_2[\text{ZnCl}_4]$   
 Formation: 2.8.22  
 $\text{Cl}_4\text{H}_8\text{O}_4\text{Zn}^*\text{Ba}$   
 $\text{Cl}_4\text{H}_9\text{O}_4^*\text{Au}$   
 **$\text{Cl}_4\text{H}_{12}\text{MgO}_6\text{Zn}$**   
 $\text{Mg}[\text{ZnCl}_4]\cdot 6\text{H}_2\text{O}$   
 Formation: 2.8.22  
 $\text{Cl}_4\text{H}_{12}\text{O}_6\text{Zn}^*\text{Ba}$   
 $\text{Cl}_4\text{H}_{16}\text{O}_7^*\text{Cd}$   
 $\text{Cl}_4\text{H}_{16}\text{O}_8^*\text{BaCd}$   
 **$\text{Cl}_4\text{Hf}$**   
 $\text{HfCl}_4$   
 Electrochemical formation: 2.9.3.7  
 Formation: 2.9.2.2, 2.9.4.1, 2.9.4.5  
 **$\text{Cl}_4\text{HgK}_2$**   
 $\text{K}_2[\text{HgCl}_4]$   
 Formation: 2.8.22  
 **$\text{Cl}_4\text{HgRb}_2$**   
 $\text{Rb}_2[\text{HgCl}_4]$   
 Formation: 2.8.22  
 **$\text{Cl}_4\text{In}_3$**   
 $\text{In}_3\text{Cl}_4$   
 Formation: 2.6.14.1  
 $\text{Cl}_4\text{K}^*\text{Au}$   
 **$\text{Cl}_4\text{K}_2\text{Zn}$**   
 $\text{K}_2[\text{ZnCl}_4]$   
 Formation: 2.8.22  
 **$\text{Cl}_4\text{Mo}$**   
 $\text{MoCl}_4$   
 Formation: 2.9.4.6  
 **$\text{Cl}_4\text{MoO}$**   
 $\text{MoOCl}_4$   
 Contamination of  $\text{MoCl}_3$ : 2.9.11.1  
 Formation: 2.9.11.2, 2.9.12.5  
 $[\text{MoOCl}_4]^-$   
 Formation: 2.9.13.3  
 $\text{Cl}_4\text{MoO}^*\text{Br}$   
 **$\text{Cl}_4\text{MoO}_2$**   
 $[\text{MoO}_2\text{Cl}_4]^{2-}$   
 Formation: 2.9.13.2  
 **$\text{Cl}_4\text{Mo}_3\text{Y}$**   
 $\text{Mo}_3\text{Y}_7\text{Cl}_4$   
 Formation: 2.9.14.3  
 $\text{Cl}_4\text{N}^*\text{C}_5\text{H}_6\text{Au}$   
 $\text{Cl}_4\text{N}^*\text{C}_6\text{H}_{20}\text{Au}$   
 $\text{Cl}_4\text{NO}^*\text{Al}$   
 $\text{Cl}_4\text{N}_2\text{O}_2^*\text{C}_8\text{H}_{19}\text{Au}$   
 $\text{Cl}_4\text{Na}^*\text{Au}$   
 $\text{Cl}_4\text{Na}_2^*\text{Cd}$   
 **$\text{Cl}_4\text{NbO}$**   
 $[\text{NbOCl}_4]^-$   
 Formation: 2.9.13.3, 2.9.13.4  
 **$\text{Cl}_4\text{Nb}_2\text{S}_3$**   
 $\text{Nb}_2\text{S}_3\text{Cl}_4$   
 Formation: 2.9.14.4

**Cl<sub>4</sub>OOs**

Formation: 2.9.11.2

**Cl<sub>4</sub>ORe**

Formation: 2.9.12.6

**Cl<sub>4</sub>OTa**

Formation: 2.9.13.3

**Cl<sub>4</sub>OTi**

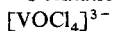
Formation: 2.9.13.4

**Cl<sub>4</sub>OV**

Formation: 2.9.13, 2.9.13.4



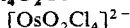
Formation: 2.9.13.4



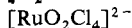
Formation: 2.9.13.3

**Cl<sub>4</sub>OW**Formation: 2.9.12.1, 2.9.12.4, 2.9.12.5,  
2.9.12.6, 2.9.12.7**Cl<sub>4</sub>OZr**

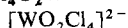
Formation: 2.9.13.3

**Cl<sub>4</sub>O<sub>2</sub>Os**

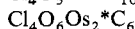
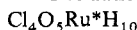
Formation: 2.9.13

**Cl<sub>4</sub>O<sub>2</sub>Ru**

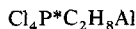
Formation: 2.9.13

**Cl<sub>4</sub>O<sub>2</sub>W**

Formation: 2.9.13.2, 2.9.13.3

**Cl<sub>4</sub>Os**

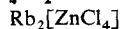
Formation: 2.9.2.2

**Cl<sub>4</sub>P<sub>2</sub>**

Formation: 2.6.3.3

**Cl<sub>4</sub>Pt**

Formation: 2.9.2.2

**Cl<sub>4</sub>Rb<sub>2</sub>Zn**

Formation: 2.8.22

**Cl<sub>4</sub>Re**

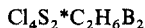
Formation: 2.9.3.6, 2.9.4.5

**Cl<sub>4</sub>Re<sub>2</sub>S<sub>3</sub>**

Formation: 2.9.14.3

**Cl<sub>4</sub>SW**

Formation: 2.6.7.3, 2.9.14.3, 2.9.14.4

Reaction with Sb<sub>2</sub>Y<sub>3</sub>: 2.9.14.4

Formation: 2.9.14.1.2

**Cl<sub>4</sub>Se**

Formation: 2.6.7.1

**Cl<sub>4</sub>SeW**Reaction with Sb<sub>2</sub>Y<sub>3</sub>: 2.9.14.4**Cl<sub>4</sub>Si**Reaction with (C<sub>2</sub>H<sub>3</sub>)<sub>2</sub>Hg: 2.8.23.5

Reaction with MX: 2.7.9

Reaction with Zn: 2.8.14.4

**Cl<sub>4</sub>Sn**Formation from SnCl<sub>2</sub> and HgCl<sub>2</sub>:  
2.8.21.2Reaction with BX<sub>3</sub>: 2.6.12.2Reaction with (HBNR)<sub>3</sub>: 2.6.5.3Reaction with R<sub>3</sub>Al: 2.6.10.3, 2.6.15**Cl<sub>4</sub>Tc**

Formation: 2.9.2.2

**Cl<sub>4</sub>Te**

Formation: 2.9.4.6

**Cl<sub>4</sub>Th**

Formation: 2.9.9.2

**Cl<sub>4</sub>Ti**

Electrochemical formation: 2.9.3.7

Formation: 2.9.2.2, 2.9.4.1, 2.9.4.6

Reaction with BX<sub>3</sub>: 2.6.12.2

Reaction with HgO: 2.8.15.3

Reaction with R<sub>3</sub>Al: 2.6.10.3Reaction with (R<sub>3</sub>NBNH)<sub>3</sub>: 2.6.8.3

Reaction with HF: 2.11.2.1

**Cl<sub>4</sub>V**

Formation: 2.9.2.2, 2.9.4.1, 2.9.4.6

**Cl<sub>4</sub>W**

Formation: 2.9.6, 2.9.12.4

- Cl<sub>4</sub>Xe**  
 XeCl<sub>4</sub>  
 Formation: 2.10.1, 2.10.2.2, 2.10.2.2.2
- Cl<sub>4</sub>Zn\*Ba**
- Cl<sub>4</sub>Zr**  
 ZrCl<sub>4</sub>  
 Electrochemical formation: 2.9.3.7  
 Formation: 2.9.2.2, 2.9.4.1, 2.9.4.5, 2.9.4.7  
 Formation from (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>ZrCl<sub>2</sub>: 2.8.23.2  
 Reaction with HF: 2.11.3.1
- Cl<sub>5</sub>\*C<sub>24</sub>H<sub>15</sub>AsAu**
- Cl<sub>5</sub>\*C<sub>72</sub>H<sub>60</sub>Ag<sub>2</sub>As<sub>3</sub>**
- Cl<sub>5</sub>CoH<sub>18</sub>N<sub>6</sub>\*Cd**
- Cl<sub>5</sub>CrO**  
 [CrOCl<sub>5</sub>]<sup>2-</sup>  
 Formation: 2.9.13
- Cl<sub>5</sub>Cs<sub>3</sub>Cu<sub>2</sub>**  
 Cs<sub>3</sub>[Cu<sub>2</sub>Cl<sub>5</sub>]  
 Formation from Cu[OAc]: 2.8.12
- Cl<sub>5</sub>Cs<sub>3</sub>Zn**  
 Cs<sub>3</sub>[ZnCl<sub>5</sub>]  
 Formation: 2.8.22
- Cl<sub>5</sub>Cu<sub>2</sub>N<sub>3</sub>\*C<sub>24</sub>H<sub>60</sub>**
- Cl<sub>5</sub>H<sub>4</sub>N\*Cd<sub>2</sub>**
- Cl<sub>5</sub>H<sub>5</sub>O<sub>2</sub>Zn<sub>2</sub>**  
 HZn<sub>2</sub>Cl<sub>5</sub>·2 H<sub>2</sub>O  
 Formation: 2.8.22
- Cl<sub>5</sub>H<sub>12</sub>N<sub>3</sub>Zn**  
 [NH<sub>4</sub>]<sub>3</sub>[ZnCl<sub>5</sub>]  
 Formation: 2.8.22
- Cl<sub>5</sub>InN<sub>2</sub>\*C<sub>16</sub>H<sub>40</sub>**
- Cl<sub>5</sub>MO**  
 MoCl<sub>5</sub>  
 Formation: 2.9.5
- Cl<sub>5</sub>Mo**  
 MoCl<sub>5</sub>  
 Formation: 2.9.2.2, 2.9.4.6, 2.9.11.1, 2.9.12.5  
 Reaction with B<sub>2</sub>S<sub>3</sub>: 2.6.7.3  
 Reaction with [R<sub>4</sub>N]X, MX: 2.9.10.1  
 Reaction with Sb<sub>2</sub>Y<sub>3</sub>: 2.9.14.4
- Cl<sub>5</sub>MoO**  
 [MoOCl<sub>5</sub>]<sup>2-</sup>  
 Formation: 2.9.13, 2.9.13.2, 2.9.13.3, 2.9.13.4
- Cl<sub>5</sub>Mo<sub>2</sub>S<sub>4</sub>**  
 Mo<sub>2</sub>S<sub>4</sub>Cl<sub>5</sub>  
 Formation: 2.9.14.2
- Cl<sub>5</sub>NNb\*C<sub>2</sub>H<sub>3</sub>**
- Cl<sub>5</sub>NTi\*C<sub>8</sub>H<sub>20</sub>**
- Cl<sub>5</sub>Nb**  
 NbCl<sub>5</sub>  
 Formation: 2.9.2.2, 2.9.4.1, 2.9.4.5, 2.9.4.6
- Reaction with B<sub>2</sub>S<sub>3</sub>: 2.6.7.3  
 Reaction with Nb-Nb<sub>2</sub>O<sub>5</sub>: 2.9.11.4  
 Reaction with [R<sub>4</sub>N]X: 2.9.10.1  
 Reaction with Sb<sub>2</sub>Y<sub>3</sub>, B<sub>2</sub>S<sub>3</sub>: 2.9.14.4  
 Reaction with HF: 2.11.3.1  
 Reaction with elemental S: 2.9.14.3
- Cl<sub>5</sub>NbO**  
 [NbOCl<sub>5</sub>]<sup>2-</sup>  
 Formation: 2.9.13.3, 2.9.13.4
- Cl<sub>5</sub>ORe**  
 [ReOCl<sub>5</sub>]<sup>-</sup>  
 Formation: 2.9.13.2, 2.9.13.3  
 [ReOCl<sub>5</sub>]<sup>2-</sup>  
 Formation: 2.9.13.2, 2.9.13.3, 2.9.13.4
- Cl<sub>5</sub>OV**  
 [VOCl<sub>5</sub>]<sup>2-</sup>  
 Formation: 2.9.13.4
- Cl<sub>5</sub>OW**  
 [WOC<sub>5</sub>]<sup>-</sup>  
 Formation: 2.9.13.4  
 [WOC<sub>5</sub>]<sup>2-</sup>  
 Formation: 2.9.13, 2.9.13.2, 2.9.13.3
- Cl<sub>5</sub>Os**  
 OsCl<sub>5</sub>  
 Formation: 2.9.4.5
- Cl<sub>5</sub>P**  
 PCl<sub>5</sub>  
 Reaction with Hg: 2.8.14.4  
 Reaction with MO: 2.7.7  
 Reaction with M<sub>2</sub>O<sub>3</sub>: 2.6.6.4  
 Reaction with AuCl<sub>3</sub>: 2.8.4.1  
 Reaction with ZrO<sub>2</sub>, HfO<sub>2</sub>: 2.9.4.5
- Cl<sub>5</sub>Pa**  
 PaCl<sub>5</sub>  
 Fluorination: 2.11.5.2
- Cl<sub>5</sub>Pr\*Ba**
- Cl<sub>5</sub>Re**  
 ReCl<sub>5</sub>  
 Formation: 2.9.2.2, 2.9.4.6, 2.9.5  
 Reaction with elemental S: 2.9.14.3
- Cl<sub>5</sub>S<sub>2</sub>\*Al**
- Cl<sub>5</sub>Sb**  
 SbCl<sub>5</sub>  
 Reaction with R<sub>3</sub>B, R<sub>3</sub>In: 2.6.10.3
- Cl<sub>5</sub>Ta**  
 TaCl<sub>5</sub>  
 Formation: 2.9.2.2, 2.9.3.2, 2.9.4.1, 2.9.4.5, 2.9.4.6, 2.9.4.8, 2.9.12.4  
 Reaction with Al-KCl: 2.9.10.1  
 Reaction with B<sub>2</sub>S<sub>3</sub>: 2.6.7.3  
 Reaction with [R<sub>4</sub>N]X: 2.9.10.1  
 Reaction with Sb<sub>2</sub>S<sub>3</sub>: 2.9.14.4

- Reaction with Ta-SiO<sub>2</sub>: 2.9.11.4  
 Reaction with Ta-Ta<sub>2</sub>O<sub>5</sub>: 2.9.11.4  
 Reaction with elemental S: 2.9.14.3
- Cl<sub>5</sub>V**  
 VCl<sub>5</sub>  
 Reaction with B<sub>2</sub>S<sub>3</sub>: 2.9.14.4
- Cl<sub>5</sub>W**  
 WCl<sub>5</sub>  
 Formation: 2.9.6  
 Reaction with M(CO)<sub>6</sub>: 2.9.6  
 Reaction with Sb<sub>2</sub>Y<sub>3</sub>: 2.9.14.4
- Cl<sub>6</sub>\*C<sub>4</sub>H<sub>6</sub>Au<sub>2</sub>**  
**Cl<sub>6</sub>\*C<sub>5</sub>**  
**Cl<sub>6</sub>\*C<sub>6</sub>**  
**Cl<sub>6</sub>\*C<sub>8</sub>H<sub>4</sub>**  
**Cl<sub>6</sub>CsNb**  
 Cs[NbCl<sub>6</sub>]  
 Reaction with HI: 2.9.10.1
- Cl<sub>6</sub>CsTa**  
 Cs[TaCl<sub>6</sub>]  
 Reaction with HI: 2.9.10.1
- Cl<sub>6</sub>Cs<sub>2</sub>\*AgAu**  
**Cl<sub>6</sub>Cs<sub>2</sub>\*Au<sub>2</sub>**  
**Cl<sub>6</sub>Cs<sub>2</sub>Pd**  
 Cs<sub>2</sub>[PdCl<sub>6</sub>]  
 Fluorination: 2.11.3.2
- Cl<sub>6</sub>Cs<sub>2</sub>Ta**  
 Cs<sub>2</sub>[TaCl<sub>6</sub>]  
 Formation: 2.9.10.1
- Cl<sub>6</sub>Cs<sub>2</sub>W**  
 Cs<sub>2</sub>[WCl<sub>6</sub>]  
 Formation: 2.9.10.5
- Cl<sub>6</sub>Cs<sub>4</sub>\*Cd**  
**Cl<sub>6</sub>Cu<sub>2</sub>H<sub>8</sub>O<sub>4</sub>\*Cd**  
**Cl<sub>6</sub>Ga<sub>2</sub>K<sub>2</sub>**  
 K<sub>2</sub>[Ga<sub>2</sub>Cl<sub>6</sub>]  
 Formation: 2.6.10.3
- Cl<sub>6</sub>H<sub>8</sub>N<sub>2</sub>Os**  
 [NH<sub>4</sub>]<sub>2</sub>[OsCl<sub>6</sub>]  
 Formation: 2.9.10.2
- Cl<sub>6</sub>H<sub>10</sub>O<sub>5</sub>\*BaCd<sub>2</sub>**  
**Cl<sub>6</sub>H<sub>12</sub>Hg<sub>2</sub>MgO<sub>6</sub>**  
 Mg[Hg<sub>2</sub>Cl<sub>6</sub>]·6 H<sub>2</sub>O  
 Formation: 2.8.22
- Cl<sub>6</sub>H<sub>12</sub>Hg<sub>2</sub>O<sub>6</sub>\*Ba**  
**Cl<sub>6</sub>H<sub>14</sub>O<sub>7</sub>\*CaCd<sub>2</sub>**  
**Cl<sub>6</sub>H<sub>14</sub>O<sub>7</sub>Sr\*Cd<sub>2</sub>**  
**Cl<sub>6</sub>H<sub>16</sub>HgN<sub>4</sub>**  
 [NH<sub>4</sub>]<sub>4</sub>HgCl<sub>6</sub>  
 Formation from melt: 2.8.22
- Cl<sub>6</sub>H<sub>16</sub>N<sub>4</sub>\*Cd**  
**Cl<sub>6</sub>IrK<sub>2</sub>**  
 K<sub>2</sub>[IrCl<sub>6</sub>]  
 Formation: 2.9.10.2
- Cl<sub>6</sub>KW**  
 K[WCl<sub>6</sub>]  
 Formation: 2.9.10.1
- Cl<sub>6</sub>K<sub>2</sub>Mn**  
 K<sub>2</sub>[MnCl<sub>6</sub>]  
 Formation: 2.9.10.3
- Cl<sub>6</sub>K<sub>2</sub>Mo**  
 K<sub>2</sub>[MoCl<sub>6</sub>]  
 Formation: 2.9.10.1
- Cl<sub>6</sub>K<sub>2</sub>Pd**  
 K<sub>2</sub>[PdCl<sub>6</sub>]  
 Fluorination: 2.11.3.2
- Cl<sub>6</sub>K<sub>2</sub>Re**  
 K<sub>2</sub>[ReCl<sub>6</sub>]  
 Formation: 2.9.10.2
- Cl<sub>6</sub>K<sub>2</sub>W**  
 K<sub>2</sub>[WCl<sub>6</sub>]  
 Formation: 2.9.10.5
- Cl<sub>6</sub>K<sub>3</sub>Mo**  
 K<sub>3</sub>[MoCl<sub>6</sub>]  
 Formation: 2.9.10.4
- Cl<sub>6</sub>K<sub>4</sub>\*Cd**  
**Cl<sub>6</sub>LnP<sub>3</sub>\*C<sub>54</sub>H<sub>48</sub>**  
**Cl<sub>6</sub>MoRb<sub>3</sub>**  
 Rb<sub>3</sub>[MoCl<sub>6</sub>]  
 Formation: 2.9.10.3
- Cl<sub>6</sub>NNb\*C<sub>8</sub>H<sub>20</sub>**  
**Cl<sub>6</sub>NP<sub>2</sub>\*C<sub>24</sub>H<sub>21</sub>Au<sub>2</sub>**  
**Cl<sub>6</sub>NTa\*C<sub>6</sub>H<sub>20</sub>**  
**Cl<sub>6</sub>N<sub>2</sub>Th\*C<sub>16</sub>H<sub>40</sub>**  
**Cl<sub>6</sub>N<sub>2</sub>Ti\*C<sub>16</sub>H<sub>40</sub>**  
**Cl<sub>6</sub>N<sub>2</sub>U\*C<sub>16</sub>H<sub>40</sub>**  
**Cl<sub>6</sub>N<sub>2</sub>Zr\*C<sub>16</sub>H<sub>40</sub>**  
**Cl<sub>6</sub>P<sub>2</sub>\*C<sub>25</sub>H<sub>22</sub>Au<sub>2</sub>**  
**Cl<sub>6</sub>P<sub>2</sub>\*C<sub>27</sub>H<sub>26</sub>Au<sub>2</sub>**  
**Cl<sub>6</sub>PdRb<sub>2</sub>**  
 Rb<sub>2</sub>[PdCl<sub>6</sub>]  
 Fluorination: 2.11.3.2
- Cl<sub>6</sub>Rb<sub>4</sub>\*Cd**  
**Cl<sub>6</sub>Re**  
 ReCl<sub>6</sub>  
 Formation: 2.9.2.2
- Cl<sub>6</sub>Tc**  
 TcCl<sub>6</sub>  
 Formation: 2.9.2.2
- Cl<sub>6</sub>W**  
 WCl<sub>6</sub>  
 Formation: 2.9.2.2, 2.9.4.6, 2.9.5, 2.9.12.4  
 Reaction with B<sub>2</sub>S<sub>3</sub>: 2.6.7.3  
 Reaction with M(CO)<sub>6</sub>: 2.9.6  
 Reaction with MI: 2.9.10.1  
 Reaction with Sb<sub>2</sub>S<sub>3</sub>: 2.9.14.4

- Reaction with W-WO<sub>3</sub>: 2.9.11.4  
 Reaction with elements: 2.9.14.3  
**Cl<sub>7</sub>\*C<sub>4</sub>H<sub>6</sub>Au<sub>2</sub>**  
**Cl<sub>7</sub>\*C<sub>24</sub>H<sub>15</sub>AsAu**  
**Cl<sub>7</sub>Cu<sub>2</sub>Rb<sub>3</sub>**  
   Rb<sub>3</sub>[Cu<sub>2</sub>Cl<sub>7</sub>]  
     Formation: 2.8.10  
**Cl<sub>7</sub>Nb<sub>3</sub>Se<sub>5</sub>**  
   Nb<sub>3</sub>Se<sub>5</sub>Cl<sub>7</sub>  
     Formation: 2.9.14.1.2  
**Cl<sub>7</sub>S\*Al**  
**Cl<sub>7</sub>S\*Au**  
**Cl<sub>7</sub>Se\*Au**  
**Cl<sub>7</sub>Te\*Au**  
**Cl<sub>8</sub>\*Au<sub>2</sub>Ba**  
**Cl<sub>8</sub>\*Au<sub>4</sub>**  
**Cl<sub>8</sub>\*B<sub>8</sub>**  
**Cl<sub>8</sub>\*C<sub>5</sub>**  
**Cl<sub>8</sub>H<sub>4</sub>Hg<sub>3</sub>SrO<sub>2</sub>**  
   SrHg<sub>3</sub>Cl<sub>8</sub>·7 H<sub>2</sub>O  
     Formation: 2.8.22  
**Cl<sub>9</sub>H<sub>10</sub>HgN<sub>2</sub>O**  
   [NH<sub>4</sub>]<sub>2</sub>[HgCl<sub>4</sub>]·H<sub>2</sub>O  
     Formation: 2.8.22  
**Cl<sub>8</sub>H<sub>11</sub>N<sub>2</sub>O<sub>3</sub>\*Au<sub>2</sub>**  
**Cl<sub>8</sub>Hg<sub>3</sub>O<sub>2</sub>\*BaH<sub>4</sub>**  
**Cl<sub>8</sub>P\*Al**  
**Cl<sub>8</sub>P\*Au**  
**Cl<sub>8</sub>P\*B**  
**Cl<sub>8</sub>Re<sub>2</sub>\*C<sub>48</sub>H<sub>40</sub>As<sub>2</sub>**  
**Cl<sub>9</sub>\*B<sub>9</sub>**  
**Cl<sub>9</sub>Cr<sub>2</sub>Cs**  
   Cs[Cr<sub>2</sub>Cl<sub>9</sub>]  
     Formation: 2.9.10.1  
**Cl<sub>9</sub>CsTi<sub>2</sub>**  
   Cs[Ti<sub>2</sub>Cl<sub>9</sub>]  
     Formation: 2.9.10.1  
**Cl<sub>9</sub>CsV<sub>2</sub>**  
   Cs[V<sub>2</sub>Cl<sub>9</sub>]  
     Formation: 2.9.10.1  
**Cl<sub>9</sub>Cs<sub>3</sub>In<sub>2</sub>**  
   Cs<sub>3</sub>[In<sub>2</sub>Cl<sub>9</sub>]  
     Formation: 2.6.14.1  
**Cl<sub>9</sub>Cs<sub>3</sub>Mo<sub>2</sub>**  
   Cs<sub>3</sub>[Mo<sub>2</sub>Cl<sub>9</sub>]  
     Formation: 2.9.10.1  
**Cl<sub>9</sub>In<sub>5</sub>**  
   In<sub>5</sub>Cl<sub>9</sub>  
     Formation: 2.6.14.1  
**Cl<sub>9</sub>K<sub>3</sub>W<sub>3</sub>**  
   K<sub>3</sub>[W<sub>3</sub>Cl<sub>9</sub>]  
     Formation: 2.9.10.4  
**Cl<sub>9</sub>K<sub>3</sub>W<sub>3</sub>**  
   K<sub>3</sub>[W<sub>3</sub>Cl<sub>9</sub>]  
     Formation: 2.9.10.2  
**Cl<sub>9</sub>NTi<sub>2</sub>\*C<sub>8</sub>H<sub>20</sub>**  
**Cl<sub>9</sub>Re<sub>3</sub>**  
   Re<sub>3</sub>Cl<sub>9</sub>  
     Reaction with ReSe<sub>2</sub>: 2.9.14.2  
     Reaction with elemental S, Se: 2.9.14.3  
**Cl<sub>10</sub>\*B<sub>10</sub>**  
**Cl<sub>10</sub>Co<sub>2</sub>Cu<sub>2</sub>N<sub>12</sub>\*C<sub>12</sub>H<sub>48</sub>**  
**Cl<sub>10</sub>Cu<sub>4</sub>N<sub>2</sub>\*C<sub>6</sub>H<sub>20</sub>**  
**Cl<sub>10</sub>ORu**  
   [RuOCl<sub>10</sub>]<sup>4-</sup>  
     Formation: 2.9.13  
**Cl<sub>10</sub>ORu<sub>2</sub>**  
   [Ru<sub>2</sub>OCl<sub>10</sub>]<sup>4-</sup>  
     Formation: 2.9.13.3  
**Cl<sub>10</sub>OZr<sub>2</sub>**  
   [Zr<sub>2</sub>OCl<sub>10</sub>]<sub>4</sub><sup>-</sup>  
     Formation: 2.9.13.4  
**Cl<sub>11</sub>\*B<sub>11</sub>**  
**Cl<sub>12</sub>\*B<sub>12</sub>**  
**Cl<sub>12</sub>Cu<sub>4</sub>N<sub>4</sub>\*C<sub>32</sub>H<sub>80</sub>**  
**Cl<sub>12</sub>Mo<sub>6</sub>**  
   [Mo<sub>6</sub>Cl<sub>8</sub>]Cl<sub>4</sub>  
     Reaction with elemental S: 2.9.14.3  
   Mo<sub>6</sub>Cl<sub>12</sub>  
     Formation: 2.9.7  
**Cl<sub>17</sub>H<sub>24</sub>N<sub>6</sub>\*Ag<sub>2</sub>Au<sub>3</sub>**  
**Cl<sub>18</sub>K<sub>4</sub>Ta<sub>6</sub>**  
   K<sub>4</sub>[(Ta<sub>6</sub>Cl<sub>12</sub>)Cl<sub>6</sub>]  
     Formation: 2.9.10.1  
**Cl<sub>30</sub>O<sub>6</sub>P<sub>6</sub>\*Al<sub>4</sub>**  
**CmF<sub>3</sub>**  
   CmF<sub>3</sub>  
     Fluorination: 2.11.5.2  
**CmF<sub>4</sub>**  
   CmF<sub>4</sub>  
     Formation: 2.11.5.2  
**Co**  
   Co  
     Reaction with XeF<sub>2</sub>: 2.11.2.2  
     Reaction with I<sub>2</sub>: 2.9.2.4  
     Reaction with C<sub>6</sub>F<sub>5</sub>X: 2.9.3.8  
     Reaction with ag HX: 2.9.3.3  
**Co\*Br<sub>2</sub>**  
**Co\*Cl<sub>2</sub>**  
**CoCs<sub>2</sub>\*Cl<sub>4</sub>**  
**CoCs<sub>2</sub>F<sub>6</sub>**  
   Cs<sub>2</sub>[CoF<sub>6</sub>]  
     Formation: 2.11.2.2  
**CoCs<sub>2</sub>O<sub>8</sub>S<sub>2</sub>**  
   Cs<sub>2</sub>Co[SO<sub>4</sub>]<sub>2</sub>  
     Fluorination: 2.11.2.2

- CoF<sub>2</sub>**  
 CoF<sub>2</sub>  
 Air oxidation in aq en followed by addition of HF: 2.11.2.2  
 Electrolytic oxidation in HF: 2.11.2.2  
 Formation: 2.9.3.2  
 Reaction with XeF<sub>2</sub>: 2.11.2.2  
 Reaction with XeF<sub>6</sub>: 2.11.2.2
- CoF<sub>3</sub>**  
 CoF<sub>3</sub>  
 Fluorinating agent: 2.9.12.3  
 Formation: 2.11.2.2
- CoF<sub>3</sub>H<sub>5</sub>N<sub>2</sub>**  
 [N<sub>2</sub>H<sub>5</sub>][CoF<sub>3</sub>]  
 Reaction with XeF<sub>6</sub>: 2.11.2.2
- CoF<sub>3</sub>H<sub>18</sub>N<sub>6</sub>**  
 [Co(NH<sub>3</sub>)<sub>6</sub>][F<sub>3</sub>]  
 Heating: 2.11.2.2
- CoF<sub>3</sub>O<sub>3.5</sub>\*H<sub>7</sub>**  
**CoF<sub>4</sub>N<sub>4</sub>\*C<sub>4</sub>H<sub>17</sub>**  
**CoF<sub>9</sub>Xe**  
 XeF<sub>6</sub>·CoF<sub>3</sub>  
 Formation: 2.11.2.2
- CoF<sub>10</sub>\*C<sub>12</sub>**  
**CoF<sub>90</sub>Ge<sub>6</sub>Hg<sub>2</sub>\*C<sub>108</sub>**  
**CoH<sub>18</sub>N<sub>6</sub>\*CdCl<sub>5</sub>**  
**CoI<sub>2</sub>**  
 CoI<sub>2</sub>  
 Formation: 2.9.2.4, 2.9.3.2, 2.9.3.8, 2.9.4.8, 2.9.7
- CoNO<sub>4</sub>\*C<sub>3</sub>**  
**CoN<sub>2</sub>\*C<sub>16</sub>H<sub>40</sub>Br<sub>4</sub>**  
**CoO<sub>4</sub>Sn\*C<sub>22</sub>H<sub>15</sub>**  
**CoO<sub>4</sub>Tl\*C<sub>4</sub>**  
**Co<sub>2</sub>Cu<sub>2</sub>N<sub>12</sub>\*C<sub>12</sub>H<sub>48</sub>Cl<sub>10</sub>**  
**Co<sub>2</sub>F<sub>6</sub>H<sub>19</sub>N<sub>6</sub>O<sub>0.5</sub>**  
 [Co(NH<sub>3</sub>)<sub>6</sub>][CoF<sub>6</sub>]·0.5 H<sub>2</sub>O  
 Formation: 2.11.2.2
- Co<sub>2</sub>O<sub>3</sub>**  
 Co<sub>2</sub>O<sub>3</sub>  
 Fluorination: 2.11.2.2
- Co<sub>3</sub>O<sub>4</sub>**  
 Co<sub>3</sub>O<sub>4</sub>  
 Reaction with AlI<sub>3</sub>: 2.9.4.8  
 Reaction with RX: 2.9.4.6  
 Reaction with ag HX: 2.9.4.3
- Co<sub>4</sub>O<sub>12</sub>\*C<sub>12</sub>**  
**Cr**  
 Cr  
 Fluorination: 2.11.2.1  
 Fluorination in a flow system: 2.11.2.1  
 Reaction with NO<sub>2</sub>F: 2.11.2.1
- Reaction with HX: 2.9.3.2  
 Reaction with F<sub>2</sub>: 2.9.11.1, 2.9.2.1  
 Reaction with Br<sub>2</sub>: 2.9.2.3  
 Reaction with Cl<sub>2</sub>: 2.9.2.2  
 Reaction with I<sub>2</sub>: 2.9.2.4  
 Cr\*Br<sub>2</sub>  
 Cr\*Br<sub>3</sub>  
 Cr\*Cl<sub>2</sub>  
 Cr\*Cl<sub>3</sub>  
 CrCuH<sub>18</sub>N<sub>6</sub>\*Br<sub>3</sub>Cl<sub>2</sub>  
 CrCuH<sub>18</sub>N<sub>6</sub>\*Br<sub>5</sub>  
**CrF<sub>2</sub>**  
 CrF<sub>2</sub>  
 Formation: 2.9.3.2, 2.9.3.6
- CrF<sub>2</sub>O<sub>2</sub>**  
 CrO<sub>2</sub>F<sub>2</sub>  
 Formation: 2.9.12.1, 2.9.12.2, 2.9.12.3, 2.9.12.6  
 From fluorination of CrO<sub>3</sub>: 2.9.12.3  
 Preparation: 2.11.2.1  
 Reaction with XeF<sub>2</sub>: 2.11.2.1
- CrF<sub>3</sub>**  
 CrF<sub>3</sub>  
 Fluorination: 2.11.2.1  
 Formation: 2.9.3.2
- CrF<sub>3</sub>K**  
 K[CrF<sub>3</sub>]  
 Formation: 2.9.10.3
- CrF<sub>3</sub>O**  
 CrOF<sub>3</sub>  
 Formation: 2.11.2.1
- CrF<sub>4</sub>O**  
 CrOF<sub>4</sub>  
 Formation: 2.9.11.1, 2.9.12.1  
 [CrOF<sub>4</sub>]<sup>-</sup>  
 Formation: 2.9.13.2  
 CrOF<sub>4</sub>  
 Formation: 2.11.2.1
- CrF<sub>4</sub>O<sub>2</sub>**  
 [CrO<sub>2</sub>F<sub>4</sub>]<sup>2-</sup>  
 Formation: 2.9.13.4
- CrF<sub>5</sub>**  
 CrF<sub>5</sub>  
 Formation: 2.9.2.1, 2.9.4.2, 2.11.2.1
- CrF<sub>5+x</sub>O\*Cl<sub>x</sub>**  
**CrF<sub>6</sub>**  
 CrF<sub>6</sub>  
 Formation: 2.9.2.1, 2.9.4.2, 2.11.2.1  
 Thermal decomposition: 2.11.2.1
- CrF<sub>15</sub>O<sub>2</sub>Sb<sub>2</sub>**  
 O<sub>2</sub>[CrF<sub>4</sub>][Sb<sub>2</sub>F<sub>11</sub>]  
 Formation: 2.11.2.1



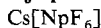
- CrF<sub>18</sub>Sb<sub>2</sub>**  
 CrF<sub>4</sub>[Sb<sub>2</sub>F<sub>11</sub>]  
 Reaction with Xe: 2.11.2.1  
 Reaction with O<sub>2</sub>: 2.11.2.1  
 Reaction with C<sub>6</sub>F<sub>6</sub>: 2.11.2.1  
**CrF<sub>21</sub>Sb<sub>2</sub>\*C<sub>6</sub>**  
**CrF<sub>60</sub>Ge<sub>4</sub>Hg\*C<sub>84</sub>H<sub>12</sub>**  
**CrHgO<sub>3</sub>\*C<sub>9</sub>H<sub>5</sub>Cl**  
**CrISe**  
 CrSeI  
 Formation: 2.9.14.2  
**CrI<sub>2</sub>**  
 CrI<sub>2</sub>  
 Formation: 2.9.2.4  
**CrI<sub>3</sub>**  
 CrI<sub>3</sub>  
 Formation: 2.9.2.4, 2.9.7  
 Reaction with CrY: 2.9.14.2  
**CrO\*Br<sub>5</sub>**  
**CrO\*Cl**  
**CrO\*Cl<sub>3</sub>**  
**CrO\*Cl<sub>4</sub>**  
**CrO\*Cl<sub>5</sub>**  
**CrO<sub>2</sub>\*Br<sub>2</sub>**  
**CrO<sub>2</sub>\*Cl<sub>2</sub>**  
**CrO<sub>3</sub>**  
 CrO<sub>3</sub>  
 Fluorination: 2.11.2.1  
 Reaction with MoF<sub>6</sub>: 2.11.2.1  
 Reaction with MoF<sub>6</sub>, WF<sub>6</sub>: 2.9.12.6  
 Reaction with RCl: 2.9.4.6  
 Reaction with SOX<sub>2</sub>, AlX<sub>3</sub>: 2.9.12.5  
 Reaction with SOCl<sub>2</sub>, S<sub>2</sub>Cl<sub>2</sub>: 2.9.4.5  
 Reaction with SF<sub>4</sub>: 2.11.2.1  
 Reaction with WF<sub>6</sub>: 2.11.2.1  
 Reaction with X<sub>2</sub>: 2.9.12.1  
 Reaction with X<sub>2</sub> or C-X<sub>2</sub>: 2.9.4.2  
 Reaction with CoF<sub>3</sub>: 2.11.2.1  
 Reaction with COF<sub>2</sub>: 2.11.2.1  
 Reaction with ClF, OCF<sub>2</sub>, ClF<sub>3</sub>, BrF<sub>3</sub>, BrF<sub>5</sub>: 2.9.12.3  
 Reaction with IF<sub>5</sub>: 2.11.2.1  
 Reaction with ClF: 2.11.2.1  
 Reaction with HF: 2.9.12.2  
**CrO<sub>3</sub>\*C<sub>9</sub>H<sub>6</sub>**  
**CrO<sub>3</sub>\*Cl**  
**CrO<sub>3</sub>X**  
 [CrO<sub>3</sub>F]<sup>-</sup>  
 Formation: 2.9.13.2  
**CrO<sub>5</sub>\*Cl**  
**CrO<sub>6</sub>\*C<sub>6</sub>**  
**CrS**  
 CrS  
 Reaction with CrI<sub>3</sub>: 2.9.14.2  
**CrS\*Br**  
**CrSe**  
 CrSe  
 Reaction with CrI<sub>3</sub>: 2.9.14.2  
**CrTe**  
 CrTe  
 Reaction with CrI<sub>3</sub>: 2.9.14.2  
**Cr<sub>2</sub>Cs\*Cl<sub>9</sub>**  
**Cr<sub>2</sub>F<sub>30</sub>Sb<sub>4</sub>Xe**  
 Xe(CrF<sub>4</sub>Sb<sub>2</sub>F<sub>11</sub>)<sub>2</sub>  
 Formation: 2.11.2.1  
**Cr<sub>2</sub>O<sub>3</sub>**  
 Cr<sub>2</sub>O<sub>3</sub>  
 Reaction with CrCl<sub>3</sub>: 2.9.12.6  
**Cr<sub>2</sub>S<sub>3</sub>**  
 Cr<sub>2</sub>S<sub>3</sub>  
 Reaction with AlI<sub>3</sub>: 2.9.5  
 Reaction with CrBr<sub>3</sub>: 2.9.14.2  
 Reaction with Cl<sub>2</sub>: 2.9.5  
**Cs**  
 Cs  
 Reaction with X<sub>2</sub>: 2.7.2  
 Reaction with HX: 2.7.3.1  
**Cs\*AgCl<sub>2</sub>**  
**Cs\*AuCl<sub>4</sub>**  
**Cs\*Br**  
**Cs\*Br<sub>3</sub>Cd**  
**Cs\*C<sub>2</sub>H<sub>6</sub>AuCl<sub>2</sub>**  
**Cs\*CdCl<sub>3</sub>**  
**Cs\*Cl<sub>9</sub>Cr<sub>2</sub>**  
**CsCu\*Br<sub>3</sub>**  
**CsCu\*Cl<sub>3</sub>**  
**CsCuF<sub>4</sub>**  
 Cs[CuF<sub>4</sub>]  
 Formation: 2.8.4.1  
**CsCuI<sub>3</sub>**  
 Cs[CuI<sub>3</sub>]  
 Structure: 2.8.12  
**CsCu<sub>2</sub>\*Br<sub>3</sub>**  
**CsCu<sub>2</sub>\*Cl<sub>3</sub>**  
**CsCu<sub>4</sub>I<sub>2</sub>\*Cl<sub>3</sub>**  
**CsF**  
 CsF  
 Formation: 2.7.2  
**CsFO<sub>4</sub>S**  
 Cs[SO<sub>4</sub>F]  
 Formation: 2.7.4  
**CsF<sub>3</sub>\*Ag**  
**CsF<sub>4</sub>\*Ag**  
**CsF<sub>4</sub>\*Au**  
**CsF<sub>4</sub>OV**  
 Cs[VOF<sub>4</sub>]  
 Formation: 2.11.2.1

**CsF<sub>5</sub>OW**

Formation: 2.11.4.1

**CsF<sub>5</sub>Zr**

Formation: 2.11.3.1

**CsF<sub>6</sub>\*Au****CsF<sub>6</sub>Np**

Formation: 2.11.5.2

**CsF<sub>6</sub>Pt**

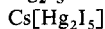
Formation: 2.11.4.2

**CsF<sub>6</sub>Rh**

Formation: 2.11.3.2

**CsH<sub>2</sub>I<sub>3</sub>O\*Cd****CsHg\*Br<sub>3</sub>****CsHgI<sub>3</sub>**

Formation: 2.8.22

**CsHg<sub>2</sub>I<sub>5</sub>**Formation from melt and solution:  
2.8.22**CsI**

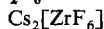
Formation: 2.7.4

**CsI<sub>3</sub>**

Coproducts At: 2.7.9

**CsI<sub>3</sub>\*Ag<sub>2</sub>****CsI<sub>3</sub>\*At****CsI<sub>3</sub>\*Cd****CsNb\*Cl<sub>6</sub>****CsNb<sub>4</sub>\*Br<sub>11</sub>****CsO<sub>3</sub>\*C****CsTa\*Cl<sub>6</sub>****CsTi<sub>2</sub>\*Cl<sub>9</sub>****CsV<sub>4</sub>\*Cl<sub>9</sub>****Cs<sub>2</sub>\*AgAuCl<sub>6</sub>****Cs<sub>2</sub>\*Au<sub>2</sub>Cl<sub>6</sub>****Cs<sub>2</sub>\*Br<sub>4</sub>Cd****Cs<sub>2</sub>\*CdCl<sub>4</sub>****Cs<sub>2</sub>\*Cl<sub>4</sub>Co****Cs<sub>2</sub>Cu\*Cl<sub>4</sub>****Cs<sub>2</sub>CuF<sub>6</sub>**

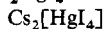
Formation: 2.8.2, 2.9.10.5

**Cs<sub>2</sub>F<sub>4</sub>\*Ag****Cs<sub>2</sub>F<sub>4</sub>\*Cd****Cs<sub>2</sub>F<sub>6</sub>\*Ag****Cs<sub>2</sub>F<sub>6</sub>\*Co****Cs<sub>2</sub>F<sub>6</sub>K\*Ag****Cs<sub>2</sub>F<sub>6</sub>Ni**Reaction with [NF<sub>4</sub>][SbF<sub>6</sub>]: 2.11.2.2**Cs<sub>2</sub>F<sub>6</sub>Zr**

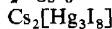
Formation: 2.11.3.1

**Cs<sub>2</sub>HfI<sub>6</sub>**

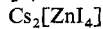
Formation: 2.9.10.1

**Cs<sub>2</sub>Hg\*Br<sub>4</sub>****Cs<sub>2</sub>Hg\*Cl<sub>4</sub>****Cs<sub>2</sub>HgI<sub>4</sub>**

Formation: 2.8.22

**Cs<sub>2</sub>Hg<sub>3</sub>I<sub>8</sub>**

Formation: 2.8.22

**Cs<sub>2</sub>I<sub>3</sub>\*Ag****Cs<sub>2</sub>I<sub>4</sub>\*Cd****Cs<sub>2</sub>I<sub>4</sub>Zn**

Formation: 2.8.22

**Cs<sub>2</sub>I<sub>6</sub>\*Au<sub>2</sub>****Cs<sub>2</sub>I<sub>6</sub>Nb**

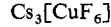
Formation: 2.9.10.1

**Cs<sub>2</sub>I<sub>6</sub>Ti**

Formation: 2.9.10.1

**Cs<sub>2</sub>I<sub>6</sub>Zr**

Formation: 2.9.10.1

**Cs<sub>2</sub>Mo<sub>2</sub>\*Br<sub>9</sub>****Cs<sub>2</sub>O<sub>4</sub>S**Reaction with F<sub>2</sub>: 2.7.4**Cs<sub>2</sub>O<sub>8</sub>S<sub>2</sub>\*Co****Cs<sub>2</sub>Pd\*Cl<sub>6</sub>****Cs<sub>2</sub>Ta\*Cl<sub>6</sub>****Cs<sub>2</sub>W\*Cl<sub>6</sub>****Cs<sub>2</sub>Zn\*Br<sub>4</sub>****Cs<sub>2</sub>Zn\*Cl<sub>4</sub>****Cs<sub>3</sub>\*Au<sub>2</sub>Br<sub>11</sub>****Cs<sub>3</sub>\*Br<sub>5</sub>Cd****Cs<sub>3</sub>CuF<sub>6</sub>**

Formation: 2.11.2.3

**Cs<sub>3</sub>Cu<sub>2</sub>\*Cl<sub>5</sub>****Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>**

Formation: 2.8.12

- Cs<sub>3</sub>F<sub>7</sub>Zr**  
 Cs<sub>3</sub>[ZrF<sub>7</sub>]  
 Formation: 2.11.3.1
- Cs<sub>3</sub>Hg\*Br<sub>2</sub>Cl<sub>3</sub>**  
**Cs<sub>3</sub>Hg\*Br<sub>5</sub>**  
**Cs<sub>3</sub>HgI<sub>8</sub>**  
 Cs<sub>3</sub>[HgI<sub>5</sub>]  
 Formation: 2.8.22
- Cs<sub>3</sub>I<sub>3</sub>\*Cd**  
**Cs<sub>3</sub>I<sub>5</sub>Zn**  
 Cs<sub>3</sub>[ZnI<sub>5</sub>]  
 Formation: 2.8.22
- Cs<sub>3</sub>In<sub>2</sub>\*Cl<sub>9</sub>**  
**Cs<sub>3</sub>Mo<sub>2</sub>\*Cl<sub>9</sub>**  
**Cs<sub>3</sub>Zn\*Br<sub>5</sub>**  
**Cs<sub>3</sub>Zn\*Cl<sub>5</sub>**  
**Cs<sub>4</sub>\*CdCl<sub>6</sub>**  
**Cs<sub>4</sub>Cu<sub>3</sub>F<sub>10</sub>**  
 Cs<sub>4</sub>[Cu<sub>3</sub>F<sub>10</sub>]  
 Formation: 2.8.10
- Cs<sub>7</sub>Cu<sub>6</sub>F<sub>19</sub>**  
 Cs<sub>7</sub>[Cu<sub>6</sub>F<sub>19</sub>]  
 Formation: 2.8.10
- Cu**  
 Cu  
 Fluorination: 2.11.2.3
- Cu\*AgCl<sub>3</sub>**  
**Cu\*Br**  
**Cu\*BrCl**  
**Cu\*Br<sub>2</sub>**  
**Cu\*Br<sub>3</sub>Cd**  
**Cu\*Br<sub>3</sub>Cs**  
**Cu\*Cl**  
**Cu\*Cl<sub>2</sub>**  
**Cu\*Cl<sub>3</sub>Cs**  
**Cu\*Cl<sub>4</sub>Cs<sub>2</sub>**
- CuF**  
 CuF  
 Non-existence: 2.8.2
- CuFHO**  
 Cu(OH)F  
 Formation: 2.11.2.3
- CuFP<sub>3</sub>\*Cs<sub>4</sub>H<sub>45</sub>**  
**CuF<sub>2</sub>**  
 CuF<sub>2</sub>  
 Formation: 2.8.2, 2.8.7.1, 2.8.7.2, 2.8.8.1, 2.8.8.2, 2.8.8.3, 2.11.2.3  
 Reaction with Cr: 2.9.3.6  
 Reaction with metal fluorides: 2.11.2.3
- CuF<sub>2</sub>H<sub>4</sub>O**  
 CuF<sub>2</sub>·2 H<sub>2</sub>O  
 Thermal decomposition: 2.11.2.3
- CuF<sub>2</sub>H<sub>4</sub>O<sub>2</sub>**  
 CuF<sub>2</sub>·2 H<sub>2</sub>O  
 Boiling in aq solution: 2.11.2.3  
 Dehydration by HF: 2.8.9  
 Formation: 2.8.7.3, 2.11.2.3  
 Thermal decomposition: 2.8.9
- CuF<sub>2</sub>O<sub>2</sub>\*H<sub>4</sub>**  
**CuF<sub>3</sub>H<sub>4</sub>N**  
 [NH<sub>4</sub>]CuF<sub>3</sub>  
 Formation: 2.8.10
- CuF<sub>3</sub>K**  
 K[CuF<sub>3</sub>]  
 Formation: 2.8.10
- CuF<sub>3</sub>Rb**  
 Rb[CuF<sub>3</sub>]  
 Formation: 2.8.10
- CuF<sub>4</sub>\*Cs**  
**CuF<sub>4</sub>H<sub>8</sub>N<sub>2</sub>**  
 [NH<sub>4</sub>]<sub>2</sub>CuF<sub>4</sub>  
 Formation: 2.8.10
- CuF<sub>4</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>**  
 [NH<sub>4</sub>]<sub>2</sub>CuF<sub>4</sub>·2 H<sub>2</sub>O  
 Formation: 2.8.10
- CuF<sub>6</sub>\*Ba<sub>2</sub>**  
**CuF<sub>6</sub>\*Cs<sub>2</sub>**  
**CuF<sub>6</sub>\*Cs<sub>3</sub>**  
**CuF<sub>6</sub>K<sub>2</sub>Na**  
 NaK<sub>2</sub>[CuF<sub>6</sub>]  
 Formation: 2.8.2
- CuF<sub>6</sub>K<sub>3</sub>**  
 K<sub>3</sub>[CuF<sub>6</sub>]  
 Formation: 2.8.2, 2.11.2.3
- CuF<sub>6</sub>Na<sub>3</sub>**  
 Na<sub>3</sub>[CuF<sub>6</sub>]  
 Formation: 2.11.2.3
- CuH<sub>2</sub>O<sub>2</sub>**  
 Cu(OH)<sub>2</sub>  
 Reactions with hydrohalic acids: 2.8.8.3
- CuH<sub>4</sub>N\*Cl<sub>3</sub>**  
**CuH<sub>4</sub>O<sub>2</sub>\*Cl<sub>2</sub>**  
**CuH<sub>8</sub>N<sub>2</sub>\*Cl<sub>4</sub>**  
**CuH<sub>8</sub>O<sub>4</sub>\*Br<sub>2</sub>**  
**CuH<sub>18</sub>N<sub>6</sub>\*Br<sub>3</sub>Cl<sub>2</sub>Cr**  
**CuH<sub>18</sub>N<sub>6</sub>\*Br<sub>5</sub>Cr**
- CuI**  
 CuI  
 Formation: 2.8.7.3, 2.9.8.  
 Formation by addition of I<sup>-</sup> to Cu<sup>2+</sup>: 2.8.11.2  
 Formation from Cu[OAc]: 2.8.11.2  
 Formation from Cu<sup>2+</sup>: 2.8.2  
 Formation from the elements: 2.8.2

- Formation from the metal: 2.8.11.1  
 Reaction with Cd: 2.8.14.5  
 Reaction with Zn: 2.8.14.5  
 Reaction with  $F_2$ : 2.8.8.1  
 Reaction with elemental Te, Se: 2.9.14.3  
**CuI\*Cl**  
**CuIN\*C<sub>5</sub>H<sub>6</sub>Br**  
**CuISe<sub>3</sub>**  
 CuSe<sub>3</sub>I  
 Formation: 2.9.14.3  
**CuI<sub>2</sub>**  
 CuI<sub>2</sub>  
 Formation: 2.9.7  
**CuI<sub>2</sub>K**  
 K[CuI<sub>2</sub>]  
 Formation from  $Cu^{2+}$ : 2.8.12  
 CuI<sub>2</sub>KO<sub>6</sub>\*C<sub>12</sub>H<sub>24</sub>  
 CuI<sub>2</sub>N\*C<sub>6</sub>H<sub>8</sub>  
 CuI<sub>2</sub>N\*C<sub>8</sub>H<sub>20</sub>  
 CuI<sub>2</sub>N<sub>4</sub>\*C<sub>4</sub>H<sub>16</sub>Ag<sub>2</sub>Br<sub>2</sub>  
 CuI<sub>2</sub>N<sub>8</sub>\*C<sub>12</sub>H<sub>16</sub>  
 CuI<sub>3</sub>\*Cs  
 CuI<sub>3</sub>P<sub>2</sub>\*C<sub>38</sub>H<sub>36</sub>  
 CuI<sub>4</sub>N<sub>3</sub>\*C<sub>24</sub>H<sub>60</sub>  
 CuK\*Br<sub>2</sub>  
 CuK\*Cl<sub>2</sub>  
 CuK\*Cl<sub>3</sub>  
 CuK<sub>2</sub>\*Cl<sub>3</sub>  
 CuN\*C<sub>6</sub>H<sub>16</sub>Cl<sub>2</sub>  
 CuN\*C<sub>12</sub>H<sub>28</sub>Cl<sub>2</sub>  
 CuN\*C<sub>16</sub>H<sub>36</sub>Br<sub>2</sub>  
 CuN\*C<sub>16</sub>H<sub>36</sub>Cl<sub>2</sub>  
 CuNOP\*C<sub>18</sub>H<sub>25</sub>Cl<sub>2</sub>  
 CuN<sub>2</sub>\*C<sub>2</sub>H<sub>12</sub>BrCl<sub>3</sub>  
 CuN<sub>2</sub>\*C<sub>2</sub>H<sub>12</sub>Cl<sub>3</sub>  
 CuN<sub>2</sub>\*C<sub>16</sub>H<sub>40</sub>Br<sub>3</sub>  
 CuN<sub>2</sub>\*C<sub>16</sub>H<sub>40</sub>Br<sub>4</sub>  
 CuN<sub>3</sub>\*C<sub>24</sub>H<sub>60</sub>Br<sub>5</sub>  
**CuO**  
 CuO  
 Reactions with ClF<sub>3</sub> and BrF<sub>3</sub>: 2.8.8.2  
 Reaction with S<sub>2</sub>Cl<sub>2</sub>: 2.8.8.2  
 Reaction with HF: 2.11.2.3  
 Reaction with F<sub>2</sub>: 2.8.8.2  
 Reaction with HF: 2.8.8.3  
 Reaction with aq HCl: 2.8.8.3  
 Reaction with aq HBr: 2.8.8.3  
 Reaction with aq HF: 2.8.8.3  
**CuO<sub>3</sub>\*C**  
**CuO<sub>4</sub>S**  
 CuSO<sub>4</sub>  
 Fluorination: 2.11.2.3  
 Reaction with F<sub>2</sub>: 2.8.8.2  
 CuP\*C<sub>20</sub>H<sub>20</sub>Br<sub>2</sub>  
 CuP\*C<sub>21</sub>H<sub>22</sub>Br<sub>2</sub>  
 CuP\*C<sub>22</sub>H<sub>24</sub>Br<sub>2</sub>  
 CuP\*C<sub>24</sub>H<sub>20</sub>Br<sub>2</sub>  
 CuP\*C<sub>24</sub>H<sub>20</sub>Cl<sub>2</sub>  
 CuP\*C<sub>24</sub>H<sub>20</sub>Cl<sub>3</sub>  
 CuP<sub>2</sub>\*C<sub>38</sub>H<sub>36</sub>Br<sub>3</sub>  
 CuRb<sub>2</sub>\*Cl<sub>3</sub>  
**CuS**  
 CuS  
 Formation from ZnS and CuCl<sub>2</sub>:  
 2.8.16.2  
 Reaction with SF<sub>4</sub>: 2.11.2.3  
 Reaction with F<sub>2</sub>: 2.8.8.2  
 CuSe<sub>2</sub>\*Cl  
 CuSe<sub>3</sub>\*Br  
 CuTe\*Cl  
 CuTe<sub>2</sub>\*Cl  
 Cu<sub>2</sub>\*Br<sub>3</sub>Cs  
 Cu<sub>2</sub>\*Cl<sub>2</sub>  
 Cu<sub>2</sub>\*Cl<sub>3</sub>Cs  
 Cu<sub>2</sub>\*Cl<sub>2</sub>Cs<sub>3</sub>  
**Cu<sub>2</sub>F<sub>3</sub>HO**  
 Cu(OH)F·CuF<sub>2</sub>  
 Formation: 2.8.9, 2.11.2.3  
 Thermal decomposition: 2.11.2.3  
**Cu<sub>2</sub>F<sub>7</sub>K<sub>3</sub>**  
 K<sub>3</sub>[Cu<sub>2</sub>F<sub>7</sub>]  
 Formation: 2.8.10  
 Cu<sub>2</sub>H<sub>8</sub>O<sub>4</sub>\*CdCl<sub>6</sub>  
**Cu<sub>2</sub>Hgl<sub>4</sub>**  
 Cu<sub>2</sub>[HgI<sub>4</sub>]  
 Formation: 2.8.22  
 Cu<sub>2</sub>I<sub>3</sub>N\*C<sub>4</sub>H<sub>12</sub>  
 Cu<sub>2</sub>I<sub>3</sub>P\*C<sub>19</sub>H<sub>18</sub>  
 Cu<sub>2</sub>I<sub>3</sub>S\*C<sub>3</sub>H<sub>9</sub>  
 Cu<sub>2</sub>I<sub>4</sub>N<sub>2</sub>\*C<sub>16</sub>H<sub>40</sub>  
 Cu<sub>2</sub>I<sub>4</sub>N<sub>2</sub>\*C<sub>24</sub>H<sub>56</sub>  
 Cu<sub>2</sub>I<sub>4</sub>N<sub>2</sub>\*C<sub>32</sub>H<sub>72</sub>  
 Cu<sub>2</sub>I<sub>5</sub>\*Cs<sub>3</sub>  
 Cu<sub>2</sub>I<sub>6</sub>N<sub>4</sub>\*C<sub>22</sub>H<sub>24</sub>  
 Cu<sub>2</sub>N\*C<sub>2</sub>H<sub>8</sub>Cl<sub>3</sub>  
 Cu<sub>2</sub>N\*C<sub>4</sub>H<sub>12</sub>Cl<sub>3</sub>  
 Cu<sub>2</sub>N\*C<sub>8</sub>H<sub>20</sub>Cl<sub>3</sub>  
 Cu<sub>2</sub>N<sub>2</sub>\*C<sub>6</sub>H<sub>5</sub>Br<sub>3</sub>  
 Cu<sub>2</sub>N<sub>2</sub>\*C<sub>16</sub>H<sub>40</sub>Br<sub>4</sub>  
 Cu<sub>2</sub>N<sub>3</sub>\*C<sub>12</sub>H<sub>36</sub>Br<sub>5</sub>  
 Cu<sub>2</sub>N<sub>3</sub>\*C<sub>24</sub>H<sub>60</sub>Cl<sub>5</sub>  
 Cu<sub>2</sub>N<sub>4</sub>\*C<sub>4</sub>H<sub>16</sub>Br<sub>3</sub>  
 Cu<sub>2</sub>N<sub>12</sub>\*C<sub>12</sub>H<sub>48</sub>Cl<sub>10</sub>Co<sub>2</sub>  
 Cu<sub>2</sub>N<sub>18</sub>P<sub>6</sub>\*C<sub>24</sub>H<sub>72</sub>Cl<sub>3</sub>

**Cu<sub>2</sub>O****Cu<sub>2</sub>O**Reaction with X<sub>2</sub>: 2.8.8.2Reaction with F<sub>2</sub>: 2.8.8.2

Reaction with aq HF: 2.8.8.3

**Cu<sub>2</sub>O<sub>5</sub>\*CH<sub>2</sub>****Cu<sub>2</sub>O<sub>10</sub>\*C<sub>8</sub>H<sub>16</sub>****Cu<sub>2</sub>P\*C<sub>4</sub>H<sub>12</sub>Cl<sub>3</sub>****Cu<sub>2</sub>P\*C<sub>6</sub>H<sub>15</sub>Cl<sub>4</sub>****Cu<sub>2</sub>Rb<sub>3</sub>\*Cl<sub>7</sub>****Cu<sub>2</sub>S****Cu<sub>2</sub>S**Reaction with F<sub>2</sub>: 2.8.8.2**Cu<sub>3</sub>F<sub>10</sub>\*Cs<sub>4</sub>****Cu<sub>3</sub>H<sub>12</sub>N<sub>4</sub>\*Cl<sub>4</sub>****Cu<sub>3</sub>I<sub>4</sub>\*C<sub>19</sub>H<sub>18</sub>As****Cu<sub>3</sub>I<sub>4</sub>N\*C<sub>12</sub>H<sub>28</sub>****Cu<sub>3</sub>Rb\*Cl<sub>4</sub>****Cu<sub>4</sub>I<sub>2</sub>\*Cl<sub>3</sub>Cs****Cu<sub>4</sub>I<sub>6</sub>K<sub>2</sub>O<sub>8</sub>\*C<sub>16</sub>H<sub>32</sub>****Cu<sub>4</sub>I<sub>6</sub>K<sub>2</sub>O<sub>10</sub>\*C<sub>20</sub>H<sub>40</sub>****Cu<sub>4</sub>I<sub>6</sub>K<sub>2</sub>O<sub>16</sub>\*C<sub>48</sub>H<sub>64</sub>****Cu<sub>4</sub>N<sub>2</sub>\*C<sub>6</sub>H<sub>20</sub>Cl<sub>10</sub>****Cu<sub>4</sub>N<sub>2</sub>O\*C<sub>10</sub>H<sub>30</sub>Br<sub>10</sub>****Cu<sub>4</sub>N<sub>4</sub>\*C<sub>32</sub>H<sub>80</sub>Cl<sub>12</sub>****Cu<sub>4</sub>I<sub>7</sub>N<sub>2</sub>\*C<sub>24</sub>H<sub>56</sub>****Cu<sub>5</sub>N<sub>2</sub>\*C<sub>10</sub>H<sub>12</sub>Br<sub>7</sub>****Cu<sub>6</sub>F<sub>19</sub>\*Cs<sub>7</sub>****Cu<sub>6</sub>I<sub>12</sub>N<sub>6</sub>\*C<sub>48</sub>H<sub>120</sub>****Cu<sub>6</sub>N<sub>3</sub>\*C<sub>21</sub>H<sub>54</sub>Br<sub>9</sub>****Cu<sub>36</sub>I<sub>60</sub>N<sub>24</sub>\*C<sub>120</sub>H<sub>144</sub>****Dy****Dy**

Reaction with HX: 2.9.14.1.1

**Dy\*Cl<sub>3</sub>****DyS\*Br****Er****Er**

Reaction with HX: 2.9.14.1.1

**ErFS****ErSF**

Formation: 2.9.14.1.1

**ErFSe****ErSeF**

Formation: 2.9.14.2

**ErF<sub>3</sub>****ErF<sub>3</sub>**Reaction with Er<sub>2</sub>S<sub>3</sub>, Er<sub>2</sub>Se<sub>3</sub>: 2.9.14.2**ErS\*Br****Eu****Eu**

Reaction with HX: 2.9.14.1.1

**EuFS****EuSF**

Formation: 2.9.14.1.1

**F\*Ag****F\*Ag<sub>2</sub>****F\*Al****F\*Au****F\*B****F\*BCl<sub>2</sub>****F\*C<sub>2</sub>H<sub>6</sub>B****F\*C<sub>4</sub>H<sub>10</sub>Al****F\*Cl****F\*Cs****F\*Cu****FFeIO<sub>3</sub>S\*C<sub>9</sub>H<sub>10</sub>B<sub>2</sub>****FFeO****FeOF**

Formation: 2.11.2.2

**FFr****FrF**

Formation: 2.7.2

**FGa****GaF**

Formation: 2.6.14.1

**FGdSe****GdSeF**

Formation: 2.9.14.2

**FH****HF**

Fluorinating agent: 2.6.12.3

Metathesis: 2.6.12.1

Reaction with BN: 2.6.8.2

Reaction with B, Al, Ga, In, Tl: 2.6.3.1

Reaction with Cd: 2.8.14.2, 2.8.14.3

Reaction with CdO: 2.8.15.2

Reaction with HgO: 2.8.15.2

Reaction with Hg<sub>2</sub>CO<sub>3</sub>: 2.8.21.1Reaction with MO, MOH, MCO<sub>3</sub>: 2.7.5Reaction with M<sub>2</sub>O<sub>3</sub>: 2.6.6.3

Reaction with group-IA and group-IIA metals: 2.7.3.1

Reaction with R<sub>3</sub>B... R<sub>3</sub>Tl: 2.6.10.2

Reaction with Group IIIB-group IVB bonds: 2.6.11.2

Reaction with ZnCO<sub>3</sub>: 2.8.17.1Reaction with ZnBr<sub>2</sub>: 2.8.18Reaction with ZnCl<sub>2</sub>: 2.8.18

Reaction with Zn: 2.8.14.2

Reaction with ZnO: 2.8.15.2

Reaction with transition-metal oxides: 2.9.4.3, 2.9.13.1.1

Reaction with transition-metals: 2.9.3.2, 2.9.14.1.1

- Safety: 2.7.1
- FHHgO**  
 $\text{Hg}(\text{OH})\text{F}$   
 Formation: 2.11.4.3  
 Formation from  $\text{HgF}_2 \cdot 2 \text{H}_2\text{O}$  and heat: 2.8.19
- FHO\*Cu**
- FHO<sub>3</sub>S**  
 $\text{HSO}_3\text{F}$   
 Halogenation agent: 2.9.12.5
- FH<sub>2</sub>IO\*Ag<sub>2</sub>**
- FH<sub>4</sub>N**  
 $[\text{NH}_4]\text{F}$   
 Fluorinating agent: 2.6.12.3  
 Reaction with  $\text{Cd}[\text{NO}_3]_2$ : 2.8.17.2  
 Reaction with  $\text{CdCl}_2$ : 2.8.18  
 $[\text{NH}_4]\text{F}$   
 Reaction with  $\text{MO}$ : 2.7.7  
 $[\text{NH}_4]\text{F}$   
 Reaction with  $\text{ZnCl}_2$ : 2.8.18
- FH<sub>4</sub>NO<sub>6</sub>V<sub>3</sub>**  
 $\text{NH}_4[\text{V}_3\text{O}_6\text{F}]$   
 Formation: 2.9.13.2
- FH<sub>6</sub>Mo<sub>4</sub>O<sub>16</sub>**  
 $[\text{Mo}_4\text{O}_{13}\text{F}]^{3-} \cdot 3 \text{H}_2\text{O}$   
 Formation: 2.9.13
- FHg\*Br**
- FHoS**  
 $\text{HoSF}$   
 Formation: 2.9.14.1.1
- FIn**  
 $\text{InF}$   
 Formation: 2.6.14.1
- FInO**  
 $\text{InOF}$   
 Formation: 2.6.6.4
- FK**  
 $\text{KF}$   
 Fluorinating agent: 2.6.12.3, 2.9.13  
 Formation: 2.7.2
- FKr**  
 $\text{KrF}$   
 Formation: 2.10.2
- FLaS**  
 $\text{LaSF}$   
 Formation: 2.9.14.1.1
- FLaSe**  
 $\text{LaSeF}$   
 Formation: 2.9.14.2
- FLi**  
 $\text{LiF}$   
 Formation: 2.7.2
- FLuS**  
 $\text{LuSF}$   
 Formation: 2.9.14.1.1
- FLuSe**  
 $\text{LuSeF}$   
 Formation: 2.9.14.2
- FMnO<sub>3</sub>**  
 $\text{MnO}_3\text{F}$   
 Formation: 2.9.12.3, 2.9.12.5, 2.11.2.1
- FNO**  
 $\text{ONF}$   
 Reaction with  $\text{MF}_6$ : 2.9.10.1
- FNa**  
 $\text{NaF}$   
 Fluorinating agent: 2.6.12.3  
 Formation: 2.7.2  
 Reaction with  $\text{Hg}_2[\text{NO}_3]_2$ : 2.8.21.1
- FNbO<sub>2</sub>**  
 $\text{NbO}_2\text{F}$   
 Formation: 2.9.12.2, 2.11.3.1  
 Thermal decomposition: 2.11.3.1
- FNdSe**  
 $\text{NdSeF}$   
 Formation: 2.9.14.2
- FO\*Ac**
- FO\*C**
- FOSc**  
 $\text{ScOF}$   
 Formation: 2.11.2.1
- FOTl**  
 $\text{TlOF}$   
 Formation: 2.6.6.3
- FOY**  
 $\text{YOF}$   
 Formation: 2.11.3.1
- FO<sub>2</sub>Ta**  
 $\text{TaO}_2\text{F}$   
 Decomposition: 2.11.4.1  
 Formation: 2.9.12.2, 2.11.4.1
- FO<sub>2</sub>V**  
 $\text{O}_2\text{VF}$   
 Formation: 2.11.2.1
- FO<sub>3</sub>Os**  
 $\text{OsO}_3\text{F}$   
 Formation: 2.9.12.3
- FO<sub>3</sub>Re**  
 $\text{ReO}_3\text{F}$   
 Formation: 2.9.12.2, 2.9.12.3, 2.11.4.1
- FO<sub>3</sub>Tc**  
 $\text{TcO}_3\text{F}$   
 Formation: 2.9.12.1, 2.11.3.1  
 Reaction with  $\text{KrF}_2$ : 2.11.3.1

- Reaction with  $\text{XeF}_6$ : 2.11.3.1  
 $\text{FO}_3\text{V}^*\text{Ba}$   
 $\text{FO}_4\text{S}^*\text{Cs}$   
 $\text{FO}_5\text{Re}^*\text{C}_5$   
 $\text{FO}_6\text{V}_3$   
 $[\text{V}_3\text{O}_6\text{F}]^-$   
 Formation: 2.9.13.2  
 $\text{FO}_7\text{Ta}_3$   
 $\text{Ta}_3\text{O}_7\text{F}$   
 Formation: 2.11.4.1  
 $\text{FP}_3^*\text{C}_{54}\text{H}_{45}\text{Cu}$   
 $\text{FPrSe}$   
 $\text{PrSeF}$   
 Formation: 2.9.14.2  
**FRb**  
 $\text{RbF}$   
 Formation: 2.7.2  
**FRn**  
 $\text{RnF}$   
 Formation: 2.10.2.2.2  
 $\text{FS}^*\text{Ce}$   
 $\text{FS}^*\text{Er}$   
 $\text{FS}^*\text{Eu}$   
 $\text{FSY}$   
 $\text{YSF}$   
 Formation: 2.9.14.1.1, 2.9.14.2  
**FSYb**  
 $\text{YbSF}$   
 Formation: 2.9.14.1.1  
 $\text{FSe}^*\text{Ce}$   
 $\text{FSe}^*\text{Er}$   
 $\text{FSeSm}$   
 $\text{SmSeF}$   
 Formation: 2.9.14.2  
 $\text{FSeTm}$   
 $\text{TmSeF}$   
 Formation: 2.9.14.2  
 $\text{FSeY}$   
 $\text{YSeF}$   
 Formation: 2.9.14.2  
 $\text{FSeYb}$   
 $\text{YbSeF}$   
 Formation: 2.9.14.2  
 $\text{FSi}^*\text{C}_3\text{H}_9$   
 $\text{FSn}^*\text{C}_3\text{H}_9$   
**FTl**  
 $\text{TlF}$   
 Formation: 2.6.3.1, 2.6.14.2  
 $\text{F}_2$   
 $\text{F}_2$   
 Reaction with  $\text{BN}$ : 2.6.8.1  
 Reaction with  $\text{CdO}$ : 2.8.15.1  
 Reaction with  $\text{Cd}$ : 2.8.14.1  
 Reaction with  $\text{CdS}$ : 2.8.16.1  
 Reaction with Group IIIB-Group IVB bonds: 2.6.11.1  
 Reaction with  $\text{HgCl}_2$ : 2.8.18  
 Reaction with  $\text{Hg}$ : 2.8.14.1  
 Reaction with  $\text{M}(\text{CO})_6$ : 2.9.6  
 Reaction with  $\text{MO}$ : 2.7.6, 2.7.7  
 Reaction with  $\text{M}_2\text{S}_3$ : 2.6.7.1  
 Reaction with  $\text{M}_2\text{O}_3$ : 2.6.6.1  
 Reaction with  $\text{Os}$ ,  $\text{Cr}$ : 2.9.11.1  
 Reaction with  $\text{R}_3\text{B} \dots \text{R}_3\text{Ti}$ : 2.6.10.1  
 Reaction with group-IA and -IIA metals: 2.7.2  
 Reaction with  $\text{Xe}$ : 2.10.2.2  
 Reaction with  $\text{ZnS}$ : 2.8.16.1  
 Reaction with  $\text{Zn}$ : 2.8.14.1  
 Reaction with  $\text{ZnO}$ : 2.8.15.1  
 Reaction with transition-metal oxides: 2.9.4.1  
 Reaction with transition-metals: 2.9.2.1  
 Safety: 2.7.1  
 $\text{F}_2^*\text{Ag}$   
 $\text{F}_2^*\text{B}$   
 $\text{F}_2^*\text{BCl}$   
 $\text{F}_2^*\text{Ba}$   
 $\text{F}_2^*\text{Be}$   
 $\text{F}_2^*\text{CBrCl}$   
 $\text{F}_2^*\text{C}_4\text{H}_{12}\text{Au}_2$   
 $\text{F}_2^*\text{Ca}$   
 $\text{F}_2^*\text{Cd}$   
 $\text{F}_2^*\text{Co}$   
 $\text{F}_2^*\text{Cr}$   
 $\text{F}_2^*\text{Cu}$   
 $\text{F}_2\text{Fe}$   
 $\text{FeF}_2$   
 Fluorination: 2.11.2.2  
 Formation: 2.9.3.2, 2.9.4.2  
 **$\text{F}_2\text{HK}$**   
 $\text{KHF}_2$   
 Fluorinating agent: 2.9.13  
 $\text{F}_2\text{HO}_8^*\text{Ag}_7$   
 $\text{F}_2\text{H}_2\text{MoO}_4$   
 $[\text{MoO}_3\text{F}_2]^{2-} \cdot \text{H}_2\text{O}$   
 Formation: 2.9.13  
 $\text{F}_2\text{H}_4\text{HgO}_2$   
 $\text{HgF}_2 \cdot 2 \text{H}_2\text{O}$   
 Formation: 2.11.4.3  
 Formation from  $\text{HgO}$  and aq  $\text{HF}$ : 2.8.15.2  
 $\text{F}_2\text{H}_4\text{O}^*\text{Cu}$   
 $\text{F}_2\text{H}_4\text{O}_2^*\text{Cd}$

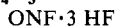
- F<sub>2</sub>H<sub>4</sub>O<sub>2</sub>\*Cu**  
**F<sub>2</sub>H<sub>4</sub>O<sub>2</sub>Zn**  
     ZnF<sub>2</sub>·2 H<sub>2</sub>O  
         Dehydration: 2.8.19  
**F<sub>2</sub>H<sub>5</sub>N**  
     [NH<sub>4</sub>][HF<sub>2</sub>]  
         Reaction with MO: 2.7.7  
**F<sub>2</sub>H<sub>6</sub>O<sub>4</sub>Zn**  
     ZnF<sub>2</sub>·4 H<sub>2</sub>O  
         Dehydration: 2.8.19  
**F<sub>2</sub>H<sub>6</sub>O<sub>4</sub>Zn**  
     ZnF<sub>2</sub>·4 H<sub>2</sub>O  
         Formation: 2.11.2.3  
**F<sub>2</sub>Hg**  
     HgF<sub>2</sub>  
         Formation: 2.11.4.3  
         Formation from HgF<sub>2</sub>·2 H<sub>2</sub>O and heat:  
             2.8.19  
         Formation from HgO and HF: 2.8.15.2  
         Formation from Hg and ONF·3 HF:  
             2.8.14.4  
         Formation from Hg and F<sub>2</sub>: 2.8.14.1  
         Formation from Hg and ClF<sub>3</sub>: 2.8.14.4  
         Formation from HgCl<sub>2</sub> and F<sub>2</sub>: 2.8.18  
         Formation from HgCl<sub>2</sub> and IF<sub>3</sub>: 2.8.18  
         Formation from Hg and ONF·3 HF:  
             2.8.14.4  
         Formation from Hg<sub>2</sub>F<sub>2</sub>: 2.8.20.2  
         Formation from Hg<sub>2</sub>F<sub>2</sub> and Br<sub>2</sub>:  
             2.8.20.1  
         Formation from Hg<sub>2</sub>F<sub>2</sub> and Cl<sub>2</sub>: 2.8.20.1  
**F<sub>2</sub>HgH<sub>4</sub>O<sub>2</sub>**  
     HgF<sub>2</sub>·2 H<sub>2</sub>O  
         Reaction of heating: 2.8.19  
**F<sub>2</sub>Hg<sub>2</sub>**  
     Hg<sub>2</sub>F<sub>2</sub>  
         Disproportionation: 2.8.20.2  
         Formation from Hg and ONF·3 HF:  
             2.8.14.4  
         Formation from Hg<sub>2</sub>[NO<sub>3</sub>]<sub>2</sub> and NaF:  
             2.8.21.1  
         Formation from Hg<sub>2</sub>Cl<sub>2</sub> and AgF:  
             2.8.21.1  
         Formation from HF and Hg<sub>2</sub>CO<sub>3</sub>:  
             2.8.21.1  
         Reaction with Br<sub>2</sub>: 2.8.20.1  
         Reaction with Cl<sub>2</sub>: 2.8.20.1  
**F<sub>2</sub>KO<sub>2</sub>Re**  
     K[ReO<sub>2</sub>F<sub>2</sub>]  
         Formation: 2.11.4.1  
**F<sub>2</sub>Kr**  
     KrF<sub>2</sub>  
         Formation: 2.10.2  
         Total bond energy: 2.10.1  
         ΔH<sub>f</sub>: 2.10.2  
**F<sub>2</sub>Mg**  
     MgF<sub>2</sub>  
         Formation: 2.7.2, 2.7.5  
**F<sub>2</sub>Mn**  
     MnF<sub>2</sub>  
         Electrolytic oxidation in KHF<sub>2</sub>-HF(aq):  
             2.11.2.1  
         Fluorination: 2.11.2.1  
         Formation: 2.9.3.2  
         Reaction with XeF<sub>2</sub>: 2.11.2.1  
         Reaction with XeF<sub>6</sub>: 2.11.2.1  
         Reaction with F<sub>2</sub>-O<sub>2</sub>: 2.11.2.1  
**F<sub>2</sub>Mn<sub>2</sub>O<sub>8</sub>\*C<sub>8</sub>**  
**F<sub>2</sub>MoO<sub>2</sub>**  
     [MoO<sub>2</sub>F<sub>2</sub>]<sup>-</sup>  
         Formation: 2.9.13.3  
     MoO<sub>2</sub>F<sub>2</sub>  
         Formation: 2.11.3.1  
         Reaction with XeF<sub>2</sub> in HF: 2.11.3.1  
**F<sub>2</sub>MoO<sub>3</sub>**  
     [MoO<sub>3</sub>F<sub>2</sub>]<sup>2-</sup>  
         Formation: 2.9.13.3  
**F<sub>2</sub>MoO<sub>4</sub>\*C<sub>4</sub>**  
**F<sub>2</sub>N\*C<sub>4</sub>H<sub>10</sub>B**  
**F<sub>2</sub>NaO<sub>2</sub>Re**  
     NaReO<sub>2</sub>F<sub>2</sub>  
         Formation: 2.11.4.1  
**F<sub>2</sub>NbO<sub>2</sub>**  
     [NbO<sub>2</sub>F<sub>2</sub>]<sup>-</sup>  
         Formation: 2.9.13.4  
**F<sub>2</sub>Ni**  
     NiF<sub>2</sub>  
         Catalyst for the fluorination of CrF<sub>3</sub>:  
             2.11.2.1  
         Formation: 2.9.2.1, 2.9.3.2, 2.9.4.2, 2.9.4.4  
         Reaction with F<sub>2</sub>-NOF: 2.11.2.2  
**F<sub>2</sub>NpO<sub>2</sub>**  
     NpO<sub>2</sub>F<sub>2</sub>  
         Formation: 2.11.5.2  
**F<sub>2</sub>OSW**  
     WOSF<sub>2</sub>  
         Formation: 2.9.14.1.2  
**F<sub>2</sub>OTh**  
     ThOF<sub>2</sub>  
         Formation: 2.11.5.2  
**F<sub>2</sub>OTi**  
     TiOF<sub>2</sub>  
         Formation: 2.11.2.1  
**F<sub>2</sub>OW**  
     WOF<sub>2</sub>  
         Formation: 2.9.12.2



- $F_2O_2^*Am$   
 $F_2O_2^*Cr$   
 $F_2O_2^*H_4Cu$   
 $F_2O_2PV^*C_{24}H_{20}$   
 $F_2O_2Pu$   
 $PuO_2F_2$   
 Formation: 2.11.5.2  
 $F_2O_2Rb^*Am$   
 $F_2O_2U$   
 $UO_2F_2$   
 Formation: 2.11.5.2  
 Reaction with  $SF_4$ : 2.11.5.2  
 Reaction with  $XeF_2$ : 2.11.5.2  
 $F_2O_2V$   
 $[VO_2F_2]^-$   
 Formation: 2.9.13.2  
 $F_2O_2V^*C_{24}H_{20}As$   
 $F_2O_2W$   
 $WO_2F_2$   
 Formation: 2.11.4.1  
 $F_2O_2Xe$   
 $XeO_2F_2$   
 Formation: 2.10.2.2.1  
 $F_2O_3Os$   
 $OsO_3F_2$   
 Formation: 2.9.11.2, 2.11.4.2  
 Reaction with  $MF$ : 2.11.4.2  
 $F_2O_3SXe$   
 $FXeOSO_2F$   
 Formation: 2.10.2.2.1  
 $F_2O_4Os$   
 $[OsO_4F_2]^{2-}$   
 Formation: 2.9.13  
 $F_2O_4Ti^*C_{10}H_{16}$   
 $F_2Pb$   
 $PbF_2$   
 Reaction with  $Cr$ : 2.9.3.6  
 $F_2Ra$   
 $RaF_2$   
 Formation: 2.7.2, 2.7.5  
 $F_2Rn$   
 $RnF_2$   
 Formation: 2.10.2.2.2  
 Total bond energy: 2.10.1  
 $F_2SW$   
 $WSF_2$   
 Formation: 2.9.14.1.2  
 $F_2S_3^*B_2$   
 $F_2Se^*C$   
 $F_2Sn$   
 $SnF_2$   
 Reaction with  $Cr$ ,  $Nb$ : 2.9.3.6
- $F_2Sr$   
 $SrF_2$   
 Formation: 2.7.2, 2.7.5  
 $F_2Ti^*Cl_2$   
 $F_2V$   
 $VF_2$   
 Formation: 2.9.3.2  
 $F_2Xe$   
 $XeF_2$   
 Formation: 2.10.2.2  
 Reaction with  $MO$ : 2.7.7  
 Reaction with  $Re_2(CO)_{10}$ ,  $Ru_3(CO)_{12}$ :  
 2.9.15.1.1  
 Reaction with  $HOSO_2F$ : 2.10.2.2.1  
 Reaction with  $H_2O$ : 2.10.2.2.1  
 Total bond energy: 2.10.1  
 $F_2Zn$   
 $ZnF_2$   
 Formation: 2.11.2.3  
 Formation from  $ZnS$  and  $F_2$ : 2.8.16.1  
 Formation from  $ZnCO_3$  and  $HF$ :  
 2.8.17.1  
 Formation from  $ZnBr_2$  and  $HF$ : 2.8.18  
 Formation from  $ZnCl_2$  and  $NH_4F$ :  
 2.8.18  
 Formation from  $ZnCl_2$  and  $HF$ : 2.8.18  
 Formation from  $Zn$  and  $NOF \cdot 3 HF$ :  
 2.8.14.4  
 Formation from  $Zn$  and  $F_2$ : 2.8.14.1  
 Formation from  $ZnO$  and  $PF_3$ : 2.8.15.3  
 Formation from  $Zn$  and  $HF$ : 2.8.14.2  
 Formation from  $ZnO$  and  $CF_2BrCl$ :  
 2.8.15.3  
 Formation from  $ZnO$  and  $F_2$ : 2.8.15.1  
 Formation from  $ZnO$  and  $HF$ : 2.8.15.2  
 Reaction with  $AgF$ : 2.11.2.3  
 Reaction with  $MF$ : 2.11.2.3  
 $F_3^*Ac$   
 $F_3^*Ag$   
 $F_3^*AgCs$   
 $F_3^*Al$   
 $F_3^*As$   
 $F_3^*Au$   
 $F_3^*B$   
 $F_3^*Bi$   
 $F_3^*Br$   
 $F_3^*Ce$   
 $F_3^*Cf$   
 $F_3^*Cl$   
 $F_3^*Cm$   
 $F_3^*Co$   
 $F_3^*Cr$

- F<sub>3</sub>\*Er**  
**F<sub>3</sub>Fe**  
   FeF<sub>3</sub>  
     Formation: 2.9.2.1, 2.9.5, 2.11.2.2  
     Reaction with Fe<sub>2</sub>O<sub>3</sub>-O<sub>2</sub>: 2.11.2.2  
     Reaction with NH<sub>4</sub>F: 2.11.2.2  
**F<sub>3</sub>Ga**  
   GaF<sub>3</sub>  
     Formation: 2.6.3.1, 2.6.7.1  
**F<sub>3</sub>Gd**  
   GdF<sub>3</sub>  
     Reaction with Gd<sub>2</sub>S<sub>3</sub>, Gd<sub>2</sub>Se<sub>3</sub>: 2.9.14.2  
**F<sub>3</sub>HO\*Cu<sub>2</sub>**  
**F<sub>3</sub>H<sub>2</sub>MoO<sub>3</sub>**  
   [MoO<sub>2</sub>F<sub>3</sub>]<sup>-</sup>·H<sub>2</sub>O  
     Formation: 2.9.13  
**F<sub>3</sub>H<sub>2</sub>MoO<sub>4</sub>**  
   [MoO<sub>3</sub>F<sub>3</sub>]<sup>3-</sup>·H<sub>2</sub>O  
     Formation: 2.9.13  
**F<sub>3</sub>H<sub>2</sub>O<sub>2</sub>Ti**  
   [TiOF<sub>3</sub>]<sup>-</sup>·H<sub>2</sub>O  
     Formation: 2.9.13  
**F<sub>3</sub>H<sub>2</sub>O<sub>3</sub>W**  
   [WO<sub>2</sub>F<sub>3</sub>]<sup>-</sup>·H<sub>2</sub>O  
     Formation: 2.9.13.2  
**F<sub>3</sub>H<sub>4</sub>HfO<sub>3</sub>**  
   [HfOF<sub>3</sub>]<sup>-</sup>·2 H<sub>2</sub>O  
     Formation: 2.9.13.3  
**F<sub>3</sub>H<sub>4</sub>N\*Be**  
**F<sub>3</sub>H<sub>4</sub>N\*Cd**  
**F<sub>3</sub>H<sub>4</sub>N\*Cu**  
**F<sub>3</sub>H<sub>4</sub>NZn**  
   [NH<sub>4</sub>]ZnF<sub>3</sub>  
     Formation: 2.8.22  
**F<sub>3</sub>H<sub>4</sub>O<sub>3</sub>Zr**  
   [ZrOF<sub>3</sub>]<sup>-</sup>·2 H<sub>2</sub>O  
     Formation: 2.9.13.3  
**F<sub>3</sub>H<sub>5</sub>N<sub>2</sub>\*Co**  
**F<sub>3</sub>H<sub>6</sub>O<sub>3</sub>V**  
   VF<sub>3</sub>·3 H<sub>2</sub>O  
     Formation: 2.9.4.3  
**F<sub>3</sub>H<sub>18</sub>N<sub>6</sub>\*Co**  
**F<sub>3</sub>HgK**  
   K[HgF<sub>3</sub>]  
     Formation: 2.8.22  
**F<sub>3</sub>I**  
   IF<sub>3</sub>  
     Reaction with HgCl<sub>2</sub>: 2.8.18  
**F<sub>3</sub>In**  
   InF<sub>3</sub>  
     Formation: 2.6.12.3  
**F<sub>3</sub>K\*Ag**  
**F<sub>3</sub>K\*Cd**  
**F<sub>3</sub>K\*Cr**  
**F<sub>3</sub>K\*Cu**  
**F<sub>3</sub>KZn**  
   K[ZnF<sub>3</sub>]  
     Formation: 2.8.22  
**F<sub>3</sub>La**  
   LaF<sub>3</sub>  
     Reaction with La<sub>2</sub>S<sub>3</sub>, La<sub>2</sub>Se<sub>3</sub>: 2.9.14.2  
**F<sub>3</sub>Lu**  
   LuF<sub>3</sub>  
     Reaction with Lu<sub>2</sub>S<sub>3</sub>, Lu<sub>2</sub>Se<sub>3</sub>: 2.9.14.2  
**F<sub>3</sub>Mn**  
   MnF<sub>3</sub>  
     Formation: 2.9.4.1, 2.9.4.2  
     Reaction with F<sub>2</sub>-O<sub>2</sub>: 2.11.2.1  
**F<sub>3</sub>MnO<sub>3</sub>\*C<sub>3</sub>**  
**F<sub>3</sub>Mo**  
   MoF<sub>3</sub>  
     Formation: 2.9.3.2  
**F<sub>3</sub>MoNO<sub>3</sub>**  
   NO[MoO<sub>2</sub>F<sub>3</sub>]  
     Formation: 2.11.3.1  
**F<sub>3</sub>MoO<sub>2</sub>**  
   [MoO<sub>2</sub>F<sub>3</sub>]<sup>-</sup>  
     Formation: 2.9.13  
   [MoO<sub>2</sub>F<sub>3</sub>]<sup>2-</sup>  
     Formation: 2.9.13.3  
**F<sub>3</sub>NO\*Ag**  
**F<sub>3</sub>N<sub>3</sub>\*C<sub>3</sub>H<sub>9</sub>B<sub>3</sub>**  
**F<sub>3</sub>NaZn**  
   Na[ZnF<sub>3</sub>]  
     Formation: 2.8.22  
**F<sub>3</sub>Nb**  
   NbF<sub>3</sub>  
     Formation: 2.9.3.2  
     Reaction with Nd<sub>2</sub>S<sub>3</sub>, Md<sub>2</sub>Se<sub>3</sub>: 2.9.14.2  
**F<sub>3</sub>Ni**  
   NiF<sub>3</sub>  
     Formation: 2.11.2.2  
**F<sub>3</sub>O\*Cr**  
**F<sub>3</sub>OPt**  
   PtOF<sub>3</sub>  
     Formation: 2.11.4.2

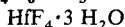
- F<sub>3</sub>OTa**  
 TaOF<sub>3</sub>  
 Formation: 2.11.4.1  
**F<sub>3</sub>OV**  
 OVF<sub>3</sub>  
 Formation: 2.11.2.1  
**F<sub>3</sub>O<sub>2</sub>Os**  
 OsO<sub>2</sub>F<sub>3</sub>  
 Formation: 2.11.4.2  
**F<sub>3</sub>O<sub>2</sub>Re**  
 ReO<sub>2</sub>F<sub>3</sub>  
 Formation: 2.9.12.1, 2.11.4.1  
**F<sub>3</sub>O<sub>2</sub>Tc**  
 TcO<sub>2</sub>F<sub>3</sub>  
 Formation: 2.11.3.1  
**F<sub>3</sub>O<sub>2</sub>V\*Ba**  
**F<sub>3</sub>O<sub>3</sub>Os**  
 [OsO<sub>3</sub>F<sub>3</sub>]<sup>-</sup>  
 Formation: 2.9.13  
**F<sub>3</sub>O<sub>3</sub>Re\*C<sub>3</sub>**  
**F<sub>3</sub>O<sub>3</sub>Ru\*C<sub>3</sub>**  
**F<sub>3</sub>O<sub>3.5</sub>\*H<sub>7</sub>Co**  
**F<sub>3</sub>P**  
 PF<sub>3</sub>  
 Reaction with ZnO: 2.8.15.3  
**F<sub>3</sub>Pr**  
 PrF<sub>3</sub>  
 Fluorination of a SrF<sub>2</sub> mixture: 2.11.5.1  
 Reaction with Pr<sub>2</sub>S<sub>3</sub>, Pr<sub>2</sub>Se<sub>3</sub>: 2.9.14.2  
**F<sub>3</sub>Pu**  
 PuF<sub>3</sub>  
 Fluorination: 2.11.5.2  
**F<sub>3</sub>Rb\*Ag**  
**F<sub>3</sub>Rb\*Cd**  
**F<sub>3</sub>Rb\*Cd**  
**F<sub>3</sub>ReS**  
 ReF<sub>3</sub>S  
 Formation: 2.9.14.4  
**F<sub>3</sub>Rh**  
 RhF<sub>3</sub>  
 Fluorination: 2.11.3.2  
 Formation: 2.9.2.1  
**F<sub>3</sub>SW**  
 WSF<sub>3</sub>  
 Formation: 2.9.14.1.2  
**F<sub>3</sub>Sb**  
 SbF<sub>3</sub>  
 Fluorinating agent: 2.6.12.3  
 Reaction with B<sub>2</sub>Cl<sub>4</sub>: 2.6.14.1  
 Reaction with RBX<sub>2</sub>: 2.6.12.3  
 Reaction with R<sub>3</sub>B: 2.6.10.3  
**F<sub>3</sub>Sc**  
 ScF<sub>3</sub>  
 Formation: 2.11.2.1  
 Partial hydrolysis: 2.11.2.1  
 Reaction with MF: 2.11.2.1  
**F<sub>3</sub>Sm**  
 SmF<sub>3</sub>  
 Reaction with Sm<sub>2</sub>S<sub>3</sub>, Sm<sub>2</sub>Se<sub>3</sub>: 2.9.14.2  
**F<sub>3</sub>Ta**  
 TaF<sub>3</sub>  
 Formation: 2.9.3.2  
**F<sub>3</sub>Tb**  
 TbF<sub>3</sub>  
 Fluorination: 2.11.5.1  
 Reaction with ClF<sub>3</sub>-HF: 2.11.5.1  
**F<sub>3</sub>Ti**  
 TiF<sub>3</sub>  
 Formation: 2.9.3.2  
**F<sub>3</sub>Tl**  
 TlF<sub>3</sub>  
 Formation: 2.6.14.2  
**F<sub>3</sub>Tl\*Cd**  
**F<sub>3</sub>Tm**  
 TmF<sub>3</sub>  
 Reaction with Tm<sub>2</sub>S<sub>3</sub>, Tm<sub>2</sub>Se<sub>3</sub>: 2.9.14.2  
**F<sub>3</sub>V**  
 VF<sub>3</sub>  
 Formation: 2.9.3.2  
**F<sub>3</sub>Y**  
 YF<sub>3</sub>  
 Formation: 2.11.3.1  
 Reaction with MF: 2.11.3.1  
 Reaction with Y<sub>2</sub>S<sub>3</sub>, Y<sub>2</sub>Se<sub>3</sub>: 2.9.14.2  
 Reaction with Y<sub>2</sub>O<sub>3</sub>: 2.11.3.1  
 Reaction with NaF: 2.11.3.1  
**F<sub>3</sub>Yb**  
 YbF<sub>3</sub>  
 Reaction with Yb<sub>2</sub>S<sub>3</sub>, Yb<sub>2</sub>Se<sub>3</sub>: 2.9.14.2  
**F<sub>3</sub>Zn\*Ag**  
**F<sub>4</sub>\*AgAu**  
**F<sub>4</sub>\*AgBa**  
**F<sub>4</sub>\*AgCa**  
**F<sub>4</sub>\*AgCd**  
**F<sub>4</sub>\*AgCs**  
**F<sub>4</sub>\*AgCs<sub>2</sub>**  
**F<sub>4</sub>\*Am**  
**F<sub>4</sub>\*AuCs**  
**F<sub>4</sub>\*B<sub>2</sub>**  
**F<sub>4</sub>\*Bk**  
**F<sub>4</sub>\*CdCs<sub>2</sub>**  
**F<sub>4</sub>\*Ce**  
**F<sub>4</sub>\*Cf**  
**F<sub>4</sub>\*Cm**  
**F<sub>4</sub>\*CsCu**  
**F<sub>4</sub>H<sub>2</sub>MoO<sub>3</sub>**  
 [MoO<sub>2</sub>F<sub>4</sub>]<sup>2-</sup>·H<sub>2</sub>O  
 Formation: 2.9.13

**F<sub>4</sub>H<sub>3</sub>NO**

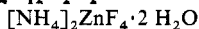
Reaction with Cd: 2.8.14.4

Reaction with Hg: 2.8.14.4

Reaction with Zn: 2.8.14.4

**F<sub>4</sub>H<sub>4</sub>N\*Be****F<sub>4</sub>H<sub>6</sub>HfO<sub>3</sub>**

Heating: 2.11.4.1

**F<sub>4</sub>H<sub>8</sub>N<sub>2</sub>\*Be****F<sub>4</sub>H<sub>8</sub>N<sub>2</sub>\*Cu****F<sub>4</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>\*Cu****F<sub>4</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>Zn**

Formation: 2.8.22

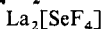
**F<sub>4</sub>Hf**Formation: 2.9.2.1, 2.9.3.2, 2.9.4.1,  
2.11.4.1

Reaction with MF-HF: 2.11.4.1

Reaction with an MF: 2.11.4.1

**F<sub>4</sub>Hg\*Ag****F<sub>4</sub>HgN<sub>2</sub>\*C<sub>10</sub>H<sub>12</sub>****F<sub>4</sub>HgN<sub>2</sub>O<sub>2</sub>\*C<sub>10</sub>H<sub>16</sub>****F<sub>4</sub>K\*Ag****F<sub>4</sub>K\*Au****F<sub>4</sub>K\*B****F<sub>4</sub>K<sub>2</sub>\*Ag****F<sub>4</sub>K<sub>2</sub>\*Cd****F<sub>4</sub>K<sub>2</sub>Zn**

Formation: 2.8.22

**F<sub>4</sub>La<sub>2</sub>Se**

Formation: 2.9.14.2

**F<sub>4</sub>MO**

Formation: 2.9.5

**F<sub>4</sub>Mn**

Formation: 2.9.2.1, 2.11.2.1

Reaction with F<sub>2</sub>-O<sub>2</sub>: 2.11.2.1**F<sub>4</sub>Mo**

Formation: 2.9.6

Reaction with ONF: 2.11.3.1

**F<sub>4</sub>MoO**

Formation: 2.9.11.2, 2.11.3.1

Reaction with SbF<sub>5</sub>: 2.11.3.1**F<sub>4</sub>MoS**

Formation: 2.11.3.1

**F<sub>4</sub>MoSe**

Formation: 2.11.3.1

**F<sub>4</sub>Mo<sub>2</sub>O<sub>4</sub>**

Formation: 2.9.13.3

**F<sub>4</sub>NO\*Au****F<sub>4</sub>NO\*B****F<sub>4</sub>NO<sub>2</sub>\*Au****F<sub>4</sub>NO<sub>2</sub>V**

Formation: 2.11.2.1

**F<sub>4</sub>N<sub>3</sub>S\*C<sub>6</sub>H<sub>18</sub>B****F<sub>4</sub>N<sub>4</sub>\*C<sub>4</sub>H<sub>17</sub>Co****F<sub>4</sub>Na\*Ag****F<sub>4</sub>NaSc**

Formation: 2.11.2.1

**F<sub>4</sub>NaY**

Formation: 2.11.3.1

**F<sub>4</sub>Nd<sub>2</sub>Se**

Formation: 2.9.14.2

**F<sub>4</sub>NpO**Reaction with KrF<sub>2</sub> in HF: 2.11.5.2**F<sub>4</sub>O\*Cr****F<sub>4</sub>OOs**

Formation: 2.9.11.1

**F<sub>4</sub>OPu**

Rearrangement in HF: 2.11.5.2

**F<sub>4</sub>ORe**

Fluorination: 2.11.4.1

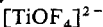
Formation: 2.11.4.1

Reaction with SbF<sub>5</sub>: 2.11.4.1**F<sub>4</sub>ORu**

Formation: 2.11.3.2

**F<sub>4</sub>OTc**

Formation: 2.11.3.1

**F<sub>4</sub>OTi**

Formation: 2.9.13

**F<sub>4</sub>OU**

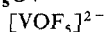
Formation: 2.11.5.2

**F<sub>4</sub>OV**

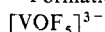
Formation: 2.9.13

- $[\text{VOF}_4]^{2-}$   
 Formation: 2.9.13, 2.9.13.2  
**F<sub>4</sub>OV\*Cs**  
**F<sub>4</sub>OW**  
**WOF<sub>4</sub>**  
 Formation: 2.9.11.2, 2.11.4.1  
 Reaction with SbF<sub>5</sub>: 2.11.4.1  
 Reaction with [NF<sub>4</sub>][HF<sub>2</sub>] in HF:  
 2.11.4.1  
 Reaction with H<sub>2</sub>O–HF: 2.11.4.1  
**F<sub>4</sub>OXe**  
**XeOF<sub>4</sub>**  
 Formation: 2.10.2.2.1  
 Reaction with SiO<sub>2</sub>: 2.10.2.2.1  
**F<sub>4</sub>O<sub>2</sub>\*Ag**  
**F<sub>4</sub>O<sub>2</sub>\*Cr**  
**F<sub>4</sub>O<sub>2</sub>V**  
 $[\text{VO}_2\text{F}_4]^{3-}$   
 Formation: 2.9.13  
**F<sub>4</sub>O<sub>2</sub>Xe**  
**XeO<sub>2</sub>F<sub>4</sub>**  
 Reaction with SiO<sub>2</sub>: 2.10.2.2.1  
**F<sub>4</sub>O<sub>5</sub>Tc<sub>2</sub>**  
**Tc<sub>2</sub>O<sub>5</sub>F<sub>4</sub>**  
 Formation: 2.11.3.1  
 Reaction with KrF<sub>2</sub>: 2.11.3.1  
**F<sub>4</sub>O<sub>9</sub>Ta<sub>4</sub>**  
 $[\text{Ta}_4\text{O}_9\text{F}_4]^{2-}$   
 Formation: 2.9.13  
**F<sub>4</sub>Pa**  
**PaF<sub>4</sub>**  
 Fluorination: 2.11.5.2  
**F<sub>4</sub>Pd**  
**PdF<sub>4</sub>**  
 Formation: 2.11.3.2  
**F<sub>4</sub>Pr**  
**PrF<sub>4</sub>**  
 Formation: 2.11.5.1  
**F<sub>4</sub>Pr<sub>2</sub>Se**  
**Pr<sub>2</sub>SeF<sub>4</sub>**  
 Formation: 2.9.14.2  
**F<sub>4</sub>Pu**  
**PuF<sub>4</sub>**  
 Irradiation in F<sub>2</sub>: 2.11.5.2  
 Reaction with O<sub>2</sub>F<sub>2</sub>: 2.11.5.2  
**F<sub>4</sub>Rb\*Ag**  
**F<sub>4</sub>Rb<sub>2</sub>\*Ag**  
**F<sub>4</sub>Rb<sub>2</sub>\*Cd**  
**F<sub>4</sub>ReS**  
**ReF<sub>4</sub>S**  
 Formation: 2.9.14.3  
**F<sub>4</sub>Rn**  
**RnF<sub>4</sub>**  
 Formation: 2.10.2.2.2  
**F<sub>4</sub>S**  
**SF<sub>4</sub>**  
 Fluorinating agent: 2.9.12.3  
 Reaction with B<sub>2</sub>(OR)<sub>4</sub>, BO: 2.6.14.1  
 Reaction with MoS<sub>2</sub>, FeS<sub>2</sub>: 2.9.5  
 Reaction with MoO<sub>3</sub>: 2.9.4.5  
 Reaction with MoO<sub>3</sub>, WO<sub>3</sub>: 2.9.4.4  
 Reaction with M<sub>2</sub>O<sub>3</sub>: 2.6.6.4  
 Reaction with [R<sub>2</sub>N]<sub>3</sub>B: 2.6.8.3  
**F<sub>4</sub>SW**  
**WF<sub>4</sub>S**  
 Formation: 2.9.14.3  
**WSF<sub>4</sub>**  
 Formation: 2.9.14.4, 2.11.4.1  
**F<sub>4</sub>Se**  
**SeF<sub>4</sub>**  
 Fluorinating agent: 2.9.12.3, 2.9.13  
**F<sub>4</sub>Se\*Ce<sub>2</sub>**  
**F<sub>4</sub>SeW**  
**WF<sub>4</sub>Se**  
 Formation: 2.9.14.3  
**WSeF<sub>4</sub>**  
 Formation: 2.11.4.1  
**F<sub>4</sub>SeWY**  
**WYSeF<sub>4</sub>**  
 Formation: 2.9.14.4  
**F<sub>4</sub>Si**  
**SiF<sub>4</sub>**  
 Fluorinating agent: 2.6.12.3  
**F<sub>4</sub>Sr\*Ag**  
**F<sub>4</sub>Tb**  
**TbF<sub>4</sub>**  
 Formation: 2.11.5.1  
**F<sub>4</sub>Th**  
**ThF<sub>4</sub>**  
 Formation: 2.11.5.2  
 Reaction with ThO<sub>4</sub>: 2.11.5.2  
**F<sub>4</sub>Ti**  
**TiF<sub>4</sub>**  
 Fluorinating agent: 2.6.12.3  
 Formation: 2.9.2.1, 2.9.3.2, 2.9.3.4,  
 2.9.4.1, 2.11.2.1  
 Reaction with B<sub>2</sub>Cl<sub>4</sub>: 2.6.14.1  
 Reaction with XeF<sub>2</sub>: 2.11.2.1  
 Reaction with XeF<sub>6</sub>: 2.11.2.1  
 Reaction with KF: 2.9.10.1  
 Reaction with acetylacetone: 2.11.2.1  
 Reaction with aq HF: 2.11.2.1  
**F<sub>4</sub>U**  
**F<sub>4</sub>U**  
 Reaction with XeF<sub>2</sub>: 2.11.5.2  
**UF<sub>4</sub>**  
 Fluorination: 2.11.5.2

- Reaction with  $O_2$ : 2.11.5.2
- F<sub>4</sub>V**  
VF<sub>4</sub>  
Formation: 2.9.2.1
- F<sub>4</sub>Xe**  
XeF<sub>4</sub>  
Formation: 2.10.2.2  
Reaction with H<sub>2</sub>O: 2.10.2.2.1
- F<sub>4</sub>Zr**  
ZrF<sub>4</sub>  
Formation: 2.9.2.1, 2.9.3.2, 2.9.3.4, 2.9.4.1  
Reaction with MF: 2.11.3.1
- F<sub>5</sub>\*AgBa**  
**F<sub>5</sub>\*As**  
**F<sub>5</sub>\*Au**  
**F<sub>5</sub>\*B<sub>3</sub>**  
**F<sub>5</sub>\*Br**  
**F<sub>5</sub>\*C<sub>24</sub>H<sub>15</sub>AsAu**  
**F<sub>5</sub>\*C<sub>24</sub>H<sub>15</sub>AsAuBr<sub>2</sub>**  
**F<sub>5</sub>\*Cr**  
**F<sub>5</sub>H<sub>3</sub>O<sub>2</sub>W**  
[H<sub>3</sub>O][WOF<sub>5</sub>]  
Formation: 2.11.4.1
- F<sub>5</sub>H<sub>4</sub>O<sub>2</sub>Pa**  
PaF<sub>5</sub>·2 H<sub>2</sub>O  
Thermal decomposition: 2.11.5.2
- F<sub>5</sub>H<sub>5</sub>I<sub>2</sub>O<sub>2.5</sub>\*Ag<sub>7</sub>**  
**F<sub>5</sub>H<sub>8</sub>N<sub>2</sub>\*Be<sub>2</sub>**  
**F<sub>5</sub>H<sub>12</sub>N<sub>3</sub>O<sub>2</sub>U**  
[NH<sub>4</sub>]<sub>3</sub>[UO<sub>2</sub>F<sub>5</sub>]  
Formation: 2.11.5.2
- F<sub>5</sub>I**  
IF<sub>5</sub>  
Fluorinating agent: 2.9.12.3  
Reaction with Cd: 2.8.14.4  
Reaction with M(CO)<sub>6</sub>: 2.9.6  
Reaction with WO<sub>3</sub>, MoO<sub>3</sub>: 2.9.4.4  
Reaction with WO<sub>3</sub>, MoO<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>: 2.9.12.3
- F<sub>5</sub>I\*C<sub>6</sub>**  
**F<sub>5</sub>INi\*C<sub>6</sub>**  
**F<sub>5</sub>Ir**  
IrF<sub>5</sub>  
Formation: 2.9.2.1, 2.11.4.2  
Reaction with XeF<sub>2</sub>-BrF<sub>5</sub>: 2.11.4.2  
Reaction with XeF<sub>6</sub>-BrF<sub>5</sub>: 2.11.4.2
- F<sub>5</sub>KOW**  
K[WOF<sub>5</sub>]  
Formation: 2.11.4.1
- F<sub>5</sub>K<sub>2</sub>OV**  
K<sub>2</sub>[VOF<sub>5</sub>]  
Formation: 2.11.2.1
- Reaction with KOH: 2.11.2.1
- F<sub>5</sub>K<sub>3</sub>O<sub>2</sub>Ti**  
K<sub>3</sub>[TiO<sub>2</sub>F<sub>5</sub>]  
Formation: 2.11.2.1
- F<sub>5</sub>K<sub>3</sub>O<sub>2</sub>U**  
K<sub>3</sub>[UO<sub>2</sub>F<sub>5</sub>]  
Formation: 2.11.5.2
- F<sub>5</sub>K<sub>3</sub>O<sub>4</sub>V<sub>2</sub>**  
K<sub>3</sub>[V<sub>2</sub>O<sub>4</sub>F<sub>5</sub>]  
Formation: 2.9.13
- F<sub>5</sub>MnXe<sub>0.5</sub>**  
0.5XeF<sub>2</sub>·MnF<sub>4</sub>  
Formation: 2.11.2.1
- F<sub>5</sub>Mo**  
MoF<sub>5</sub>  
Formation: 2.9.6
- F<sub>5</sub>MoO**  
[MoOF<sub>5</sub>]<sup>-</sup>  
Formation: 2.9.13.3  
[MoOF<sub>5</sub>]<sup>2-</sup>  
Formation: 2.9.13.3
- F<sub>5</sub>N\*C<sub>22</sub>H<sub>36</sub>AuBr**  
**F<sub>5</sub>N\*C<sub>22</sub>H<sub>36</sub>AuBr<sub>3</sub>**  
**F<sub>5</sub>NO<sub>2</sub>W**  
[NO]WOF<sub>5</sub>  
Formation: 2.11.4.1
- F<sub>5</sub>NRe\*Cl**  
**F<sub>5</sub>N<sub>3</sub>W**  
WF<sub>5</sub>N<sub>3</sub>  
Formation: 2.11.4.1
- F<sub>5</sub>NaPr**  
Na[PrF<sub>5</sub>]  
Formation: 2.9.10.5
- F<sub>5</sub>Nb**  
NbF<sub>5</sub>  
Fluorinating agent: 2.6.12.3  
Formation: 2.9.2.1, 2.9.3.2, 2.9.3.4, 2.9.3.6, 2.11.3.1  
Reaction with [R<sub>4</sub>N][BF<sub>4</sub>]: 2.11.3.1  
Reaction with SbF<sub>5</sub>: 2.11.3.1  
Reaction with SeF<sub>4</sub>: 2.11.3.1  
Reaction with KF: 2.9.10.1  
Reaction with aq HF: 2.11.3.1
- F<sub>5</sub>Ni\*Ba**  
**F<sub>5</sub>OOs**  
OsOF<sub>5</sub>  
Formation: 2.11.4.2
- F<sub>5</sub>ORe**  
ReOF<sub>5</sub>  
Formation: 2.9.11.2, 2.9.12.1, 2.11.4.1
- F<sub>5</sub>OTi**  
[TiOF<sub>5</sub>]<sup>3-</sup>  
Formation: 2.9.13.3

**F<sub>5</sub>OV**

Formation: 2.9.13



Formation: 2.9.13

**F<sub>5</sub>OW**

Formation: 2.9.13

**F<sub>5</sub>OW\*Cs****F<sub>5</sub>O<sub>4</sub>V<sub>2</sub>**

Formation: 2.9.13

**F<sub>5</sub>P\*C<sub>24</sub>H<sub>15</sub>Au****F<sub>5</sub>P\*C<sub>24</sub>H<sub>15</sub>AuBr<sub>2</sub>****F<sub>5</sub>Pa**

Formation: 2.11.5.2

**F<sub>5</sub>Pt**

Formation: 2.11.4.2

Reaction with Xe-F<sub>2</sub>: 2.11.4.2Reaction with IF<sub>5</sub>: 2.11.4.2**F<sub>5</sub>Re**

Formation: 2.9.6, 2.9.15.1.1

Reaction with Sb<sub>2</sub>S<sub>3</sub>: 2.9.14.4**F<sub>5</sub>ReS**

Formation: 2.9.14.4

**F<sub>5</sub>Rh**

Formation: 2.11.3.2

Reaction of CsF-IF<sub>5</sub>: 2.11.3.2**F<sub>5</sub>Ru**

Formation: 2.9.2.1, 2.9.3.4, 2.11.3.2

**F<sub>5</sub>S\*C<sub>10</sub>H<sub>8</sub>Au****F<sub>5</sub>S\*C<sub>10</sub>H<sub>8</sub>AuBr<sub>2</sub>****F<sub>5</sub>S\*C<sub>10</sub>H<sub>8</sub>AuCl<sub>2</sub>****F<sub>5</sub>Ta**

Fluorinating agent: 2.6.12.3

Formation: 2.9.2.1, 2.9.3.2, 2.9.3.4,

2.11.4.1

Reaction with AsH<sub>3</sub> in HF: 2.11.4.1

Reaction with MF: 2.11.4.1

Reaction with PH<sub>3</sub> in HF: 2.11.4.1

Reaction with KF: 2.9.10.1

Reaction with H<sub>2</sub>S in HF: 2.11.4.1

Reaction with aq HF: 2.11.4.1

Reaction with silica: 2.11.4.1

**F<sub>5</sub>Tc**

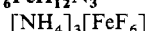
Formation: 2.9.2.1

**F<sub>5</sub>V**

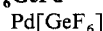
Formation: 2.9.2.1, 2.9.4.1, 2.11.2.1

Reaction with BX<sub>3</sub>: 2.6.12.3Reaction with O<sub>2</sub>F<sub>2</sub>: 2.11.2.1**F<sub>5</sub>W**

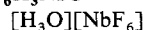
Formation: 2.9.6

**F<sub>5</sub>W\*Cl****F<sub>5+x</sub>O\*Cl<sub>x</sub>Cr****F<sub>5</sub>Zr\*Cs****F<sub>6</sub>\*AgBa<sub>2</sub>****F<sub>6</sub>\*AgCs<sub>2</sub>****F<sub>6</sub>\*AuBr****F<sub>6</sub>\*AuCs****F<sub>6</sub>\*Ba<sub>2</sub>Cu****F<sub>6</sub>\*C<sub>6</sub>****F<sub>6</sub>\*CoCs<sub>2</sub>****F<sub>6</sub>\*Cr****F<sub>6</sub>\*Cs<sub>2</sub>Cu****F<sub>6</sub>\*Cs<sub>3</sub>Cu****F<sub>6</sub>FeH<sub>12</sub>N<sub>3</sub>**

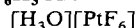
Formation: 2.11.2.2

**F<sub>6</sub>GePd**

Fluorination: 2.11.3.2

**F<sub>6</sub>H<sub>3</sub>NbO**

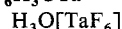
Formation: 2.11.3.1

**F<sub>6</sub>H<sub>3</sub>OPt**

Formation: 2.11.4.2

**F<sub>6</sub>H<sub>3</sub>ORu**

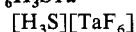
Formation: 2.11.3.2

**F<sub>6</sub>H<sub>3</sub>OTa**

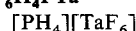
Formation: 2.11.4.1

**F<sub>6</sub>H<sub>3</sub>OTi**

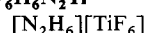
Formation: 2.11.2.1

**F<sub>6</sub>H<sub>3</sub>STa**

Formation: 2.11.4.1

**F<sub>6</sub>H<sub>4</sub>PTa**

Formation: 2.11.4.1

**F<sub>6</sub>H<sub>2</sub>Ta\*As****F<sub>6</sub>H<sub>6</sub>N<sub>2</sub>Ti**Reaction with XeF<sub>2</sub>: 2.11.2.1

- Reaction with  $\text{XeF}_6$ : 2.11.2.1
- $\text{F}_6\text{H}_6\text{O}_2\text{Pt}$**   
 $[\text{H}_3\text{O}]_2[\text{PtF}_6]$   
 Formation: 2.11.4.2
- $\text{F}_6\text{H}_{12}\text{N}_3\text{NbO}$**   
 $[\text{NH}_4]_3[\text{NbOF}_6]$   
 Formation: 2.11.3.1
- $\text{F}_6\text{H}_{12}\text{N}_3\text{OTa}$**   
 $[\text{NH}_4]_3[\text{TaOF}_6]$   
 Formation: 2.11.4.1
- $\text{F}_6\text{H}_{16}\text{N}_6\text{O}_{0.5}\text{*Co}_2$**
- $\text{F}_6\text{Hf}_2\text{O}$**   
 $\text{Hf}_2\text{OF}_6$   
 Formation: 2.11.4.1  
 Heating: 2.11.4.1
- $\text{F}_6\text{Ir}$**   
 $\text{IrF}_6$   
 Formation: 2.9.2.1, 2.11.4.2  
 Reaction with  $\text{ONF}$ : 2.11.4.2  
 Reaction with  $\text{NO}$ : 2.11.4.2  
 Reaction with  $\text{ClO}_2$ : 2.11.4.2
- $\text{F}_6\text{IrNO}$**   
 $[\text{NO}]\text{IrF}_6$   
 Formation: 2.11.4.2
- $\text{F}_6\text{IrN}_2\text{O}_2$**   
 $[\text{NO}]_2\text{IrF}_6$   
 Formation: 2.11.4.2
- $\text{F}_6\text{IrO}_2\text{*Cl}$**
- $\text{F}_6\text{K*AgCs}_2$**
- $\text{F}_6\text{K*Au}$**
- $\text{F}_6\text{KPt}$**   
 $\text{K}[\text{PtF}_6]$   
 Formation: 2.11.4.2
- $\text{F}_6\text{KV}$**   
 $\text{K}[\text{VF}_6]$   
 Formation: 2.9.10.1
- $\text{F}_6\text{KW}$**   
 $\text{K}[\text{WF}_6]$   
 Formation: 2.9.10.1
- $\text{F}_6\text{K}_2\text{Mn}$**   
 $\text{K}_2[\text{MnF}_6]$   
 Dissolution in  $\text{HF-AsF}_3$ : 2.11.2.1  
 Formation: 2.9.10.1, 2.11.2.1
- $\text{F}_6\text{K}_2\text{Na*Cu}$**
- $\text{F}_6\text{K}_2\text{Ni}$**   
 $\text{K}_2[\text{NiF}_6]$   
 Decomposition: 2.11.2.2  
 Reaction with  $\text{AsF}_5\text{-HF}$ : 2.11.2.2  
 Reaction with  $\text{BF}_3\text{-HF}$ : 2.11.2.2
- $\text{F}_6\text{K}_2\text{Pd}$**   
 $\text{K}_2[\text{PdF}_6]$   
 Formation: 2.11.3.2
- $\text{F}_6\text{K}_2\text{Ti}$**   
 $\text{K}_2[\text{TiF}_6]$   
 Formation: 2.9.10.1  
 Reaction with  $\text{H}_2\text{O}$ ,  $\text{KOH}$ : 2.11.2.1
- $\text{F}_6\text{K}_3\text{*Cu}$**
- $\text{F}_6\text{K}_3\text{NbO}$**   
 $\text{K}_3[\text{NbOF}_6]$   
 Formation: 2.11.3.1
- $\text{F}_6\text{K}_3\text{Ni}$**   
 $\text{K}_3[\text{NiF}_6]$   
 Formation: 2.11.2.2
- $\text{F}_6\text{K}_3\text{OTa}$**   
 $\text{K}_3[\text{TaOF}_6]$   
 Formation: 2.11.4.1
- $\text{F}_6\text{K}_3\text{Ti}$**   
 $\text{K}_3[\text{TiF}_6]$   
 Formation: 2.9.10.4
- $\text{F}_6\text{MnN}_2\text{*H}_8$**
- $\text{F}_6\text{MnXe}$**   
 $\text{XeF}_2\text{*MnF}_4$   
 Formation: 2.11.2.1
- $\text{F}_6\text{MnXe}_{0.5}$**   
 $0.5\text{XeF}_4\text{*MnF}_4$   
 Formation: 2.11.2.1
- $\text{F}_6\text{Mo}$**   
 $\text{MoF}_6$   
 Fluorinating agent: 2.6.12.3  
 Formation: 2.9.2.1, 2.9.3.4, 2.9.4.4, 2.9.4.5, 2.9.6, 2.11.3.1  
 Reaction with  $\text{BX}_3$ : 2.6.12.3  
 Reaction with  $\text{CrO}_3$ : 2.11.3.1  
 Reaction with  $\text{M}(\text{CO})_6$ : 2.9.6  
 Reaction with  $\text{Sb}_2\text{Se}_3$ : 2.11.3.1  
 Reaction with  $\text{Sb}_2\text{S}_3$ : 2.11.3.1  
 Reaction with  $\text{CF}_3\text{CH}_2\text{OSi}(\text{CH}_3)_3$ : 2.11.3.1  
 Reaction with  $\text{NOF}$ : 2.11.3.1  
 Reaction with  $\text{NO}_2\text{F}$ : 2.11.3.1  
 Reaction with  $\text{FNO}$ : 2.9.10.1  
 Reaction with  $\text{KF}$  in  $\text{SO}_2(\text{l})$ : 2.11.3.1  
 Reaction with  $\text{H}_2\text{O}$ : 2.11.3.1
- $\text{F}_6\text{MoO}_2\text{Se}$**   
 $\text{MoO}_2\text{F}_2\text{*SeF}_4$   
 Formation: 2.9.12.3
- $\text{F}_6\text{Mo}_2\text{O}_4$**   
 $[\text{Mo}_2\text{O}_4\text{F}_6]^{2-}$   
 Formation: 2.9.13.3
- $\text{F}_6\text{NNb*C}_{16}\text{H}_{36}$**
- $\text{F}_6\text{NO*Au}$**
- $\text{F}_6\text{NOPt}$**   
 $[\text{NO}][\text{PtF}_6]$   
 Formation: 2.11.4.2



- F<sub>6</sub>NORu**  
[NO][RuF<sub>6</sub>]  
Formation: 2.11.3.2
- F<sub>6</sub>NO<sub>2</sub>Pt**  
[NO<sub>2</sub>][PtF<sub>6</sub>]  
Formation: 2.11.4.2
- F<sub>6</sub>NRe**  
ReF<sub>5</sub>(NF)  
Formation: 2.11.4.1
- F<sub>6</sub>N<sub>2</sub>NiO<sub>2</sub>**  
[NO]<sub>2</sub>[NiF<sub>6</sub>]  
Formation: 2.11.2.2  
Pyrolysis in F<sub>2</sub>: 2.11.2.2
- F<sub>6</sub>N<sub>2</sub>O<sub>2</sub>Ti**  
[NO]<sub>2</sub>[TiF<sub>6</sub>]  
Formation: 2.11.2.1
- F<sub>6</sub>Na<sub>2</sub>Ni**  
Na<sub>2</sub>[NiF<sub>6</sub>]  
Formation: 2.11.2.2
- F<sub>6</sub>Na<sub>2</sub>Pr**  
Na<sub>2</sub>[PrF<sub>6</sub>]  
Reaction with HF: 2.11.5.1
- F<sub>6</sub>Na<sub>3</sub>\*Cu**
- F<sub>6</sub>Na<sub>3</sub>Sc**  
3 NaF·ScF<sub>3</sub>  
Formation: 2.11.2.1
- F<sub>6</sub>NbO**  
[NbOF<sub>6</sub>]<sup>3-</sup>  
Formation: 2.9.13
- F<sub>6</sub>NbO<sub>2</sub>**  
[O<sub>2</sub>][NbF<sub>6</sub>]  
Formation: 2.11.3.1
- F<sub>6</sub>Ni\*Ba**
- F<sub>6</sub>Ni\*Cs<sub>2</sub>**
- F<sub>6</sub>No\*Au**
- F<sub>6</sub>Np**  
NpF<sub>6</sub>  
Formation: 2.11.5.2  
Reaction with CsF: 2.11.5.2  
Reaction with aq HF: 2.11.5.2
- F<sub>6</sub>Np\*Cs**
- F<sub>6</sub>OTa**  
[TaOF<sub>6</sub>]<sup>3-</sup>  
Formation: 2.9.13
- F<sub>6</sub>O<sub>2</sub>\*Au**
- F<sub>6</sub>O<sub>2</sub>Pd**  
[O<sub>2</sub>][PdF<sub>6</sub>]  
Formation: 2.11.3.2
- F<sub>6</sub>O<sub>2</sub>Pt**  
[O<sub>2</sub>][PtF<sub>6</sub>]  
Formation: 2.11.4.2  
Reaction with KF-IF<sub>5</sub>: 2.11.4.2
- F<sub>6</sub>O<sub>2</sub>Rh**  
[O<sub>2</sub>][RhF<sub>6</sub>]  
Formation: 2.11.3.2
- F<sub>6</sub>O<sub>2</sub>Ru**  
[O<sub>2</sub>][RuF<sub>6</sub>]  
Formation: 2.11.3.2
- F<sub>6</sub>O<sub>2</sub>SeW**  
WOF<sub>4</sub>·SeOF<sub>2</sub>  
Formation: 2.9.12.3
- F<sub>6</sub>O<sub>3</sub>Re<sub>2</sub>\*C<sub>5</sub>**
- F<sub>6</sub>Os**  
OsF<sub>6</sub>  
Formation: 2.9.2.1, 2.11.4.2  
Reaction with OsO<sub>4</sub>: 2.11.4.2  
Reaction with ONF: 2.11.4.2  
Reaction with N<sub>2</sub>H<sub>6</sub>F<sub>2</sub> in HF: 2.11.4.2  
Reaction with Br<sub>2</sub>: 2.11.4.2
- F<sub>6</sub>Os\*Br<sub>2</sub>**
- F<sub>6</sub>Pd**  
PdF<sub>6</sub>  
Formation: 2.9.2.1, 2.11.3.2
- F<sub>6</sub>PdXe**  
Xe[PdF<sub>6</sub>]  
Formation: 2.11.3.2  
Heating: 2.11.3.2
- F<sub>6</sub>Pd<sub>2</sub>**  
Pd<sub>2</sub>F<sub>6</sub>  
Fluorination: 2.11.3.2  
Reaction with XeF<sub>2</sub>: 2.11.3.2
- F<sub>6</sub>Pr\*Ba**
- F<sub>6</sub>PrSr**  
Sr[PrF<sub>6</sub>]  
Formation: 2.11.5.1
- F<sub>6</sub>Pt**  
PtF<sub>6</sub>  
Formation: 2.9.2.1, 2.11.4.2  
Reaction with KrF<sub>2</sub>: 2.11.4.2  
Reaction with Xe: 2.11.4.2  
Reaction with Xe and CsF; addition of IF<sub>5</sub>: 2.11.4.2  
Reaction with Xe and RbF; addition of IF<sub>5</sub>: 2.11.4.2  
Reaction with ONF: 2.11.4.2  
Reaction with NO<sub>2</sub>F: 2.11.4.2  
Reaction with O<sub>2</sub>: 2.11.4.2  
Reaction with ClF<sub>3</sub>O: 2.11.4.2  
Reaction with aq HF: 2.11.4.2
- F<sub>6</sub>Pt\*Cs**
- F<sub>6</sub>PtRb**  
Rb[PtF<sub>6</sub>]  
Formation: 2.11.4.2
- F<sub>6</sub>PtXe**  
Xe[PtF<sub>6</sub>]  
Formation: 2.10.2.2.1, 2.11.4.2

**F<sub>6</sub>Pu****PuF<sub>6</sub>**

- Formation: 2.11.5.2
- Reaction with aq HF: 2.11.5.2

**F<sub>6</sub>Rb<sub>2</sub>\*Am****F<sub>6</sub>Re****ReF<sub>6</sub>**

- Formation: 2.9.2.1, 2.9.3.4, 2.11.4.1
- Hydrolysis with quartz wool in HF: 2.11.4.1
- Reaction with M(CO)<sub>6</sub>: 2.9.6
- Reaction with Re<sub>2</sub>(CO)<sub>10</sub>: 2.9.15.1.1
- Reaction with Sb<sub>2</sub>Y<sub>3</sub>, B<sub>2</sub>S<sub>3</sub>: 2.9.14.4
- Reaction with (CH<sub>3</sub>)<sub>3</sub>SiN<sub>3</sub> followed by treatment with ClF<sub>3</sub>: 2.11.4.1
- Reaction with ONF: 2.11.4.1
- Reaction with FNO: 2.9.10.1
- Reaction with elemental S: 2.9.14.3

**F<sub>6</sub>Rh****RhF<sub>6</sub>**

- Formation: 2.9.2.1, 2.11.3.2
- Reaction with Xe: 2.11.3.2
- Reaction with O<sub>2</sub>: 2.11.3.2
- Thermal decomposition: 2.11.3.2

**F<sub>6</sub>Rh\*Cs****F<sub>6</sub>RhXe****Xe[RhF<sub>6</sub>]**

- Formation: 2.11.3.2

**F<sub>6</sub>Rn****RnF<sub>6</sub>**

- Formation: 2.10.2.2.2

**F<sub>6</sub>Ru****RuF<sub>6</sub>**

- Formation: 2.9.2.1, 2.11.3.2
- Reaction with ONF: 2.11.3.2
- Reaction with NO: 2.11.3.2
- Reaction with aq HF: 2.11.3.2
- Reaction with dried glass: 2.11.3.2
- Thermal decomposition: 2.11.3.2

**F<sub>6</sub>S****SF<sub>6</sub>**

- Fluorinating agent: 2.6.12.3
- Reaction with Cd: 2.8.14.4
- Reaction with Zn: 2.8.14.4

**F<sub>6</sub>Tc****TcF<sub>6</sub>**

- Formation: 2.9.2.1, 2.11.3.1
- Reaction with ONF: 2.11.3.1
- Reaction with NO<sub>2</sub>F: 2.11.3.1

**F<sub>6</sub>TiXe****XeF<sub>2</sub>·TiF<sub>4</sub>**

- Formation: 2.11.2.1

**F<sub>6</sub>U****UF<sub>6</sub>**

- Fluorinating agent: 2.6.12.3
- Formation: 2.11.5.2
- Reaction with AlCl<sub>3</sub>: 2.6.12.3
- Reaction with (CH<sub>3</sub>)<sub>3</sub>SiOCH<sub>3</sub>: 2.11.5.2
- Reaction with H<sub>2</sub>O from SiO<sub>2</sub> in HF: 2.11.5.2

**F<sub>6</sub>W****WF<sub>6</sub>**

- Fluorinating agent: 2.6.12.3
- Formation: 2.9.2.1, 2.9.3.4, 2.9.4.4, 2.9.6, 2.11.4.1
- Reaction with B(OTeF<sub>5</sub>)<sub>3</sub>: 2.11.4.1
- Reaction with M(CO)<sub>6</sub>: 2.9.6
- Reaction with MI: 2.9.10.1
- Reaction with Sb<sub>2</sub>Se<sub>3</sub>: 2.11.4.1
- Reaction with Sb<sub>2</sub>S<sub>3</sub>: 2.11.4.1
- Reaction with Sb<sub>2</sub>Y<sub>3</sub>, B<sub>2</sub>S<sub>3</sub>: 2.9.14.4
- Reaction with (CH<sub>3</sub>)<sub>3</sub>SiN<sub>3</sub>: 2.11.4.1
- Reaction with SiO<sub>2</sub>-HF: 2.11.4.1
- Reaction with TiCl<sub>4</sub>: 2.11.4.1
- Reaction with NO<sub>2</sub>F: 2.11.4.1
- Reaction with NOF: 2.11.4.1
- Reaction with FNO: 2.9.10.1
- Reaction with aq HF: 2.11.4.1
- Reaction with elemental S, Se: 2.9.14.3

**F<sub>6</sub>Xe****XeF<sub>6</sub>**

- Formation: 2.10.2.2
- Reaction with SiO<sub>2</sub>: 2.10.2.2.1
- Reaction with NH<sub>4</sub>OH: 2.10.2.2.1
- Reaction with H<sub>2</sub>O: 2.10.2.2.1

**F<sub>6</sub>Zr\*Cs<sub>2</sub>****F<sub>7</sub>H<sub>12</sub>N<sub>3</sub>Zr****[NH<sub>4</sub>]<sub>3</sub>[ZrF<sub>7</sub>]**

- Thermal decomposition: 2.11.3.1

**F<sub>7</sub>I****IF<sub>7</sub>**

- Reaction with Xe: 2.10.2.2.1

**F<sub>7</sub>IXe****XeF<sub>2</sub>·IF<sub>5</sub>**

- Formation: 2.10.2.2.1

**F<sub>7</sub>IrXe****[XeF][IrF<sub>6</sub>]**

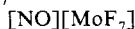
- Formation: 2.11.4.2

**F<sub>7</sub>K<sub>3</sub>\*Cu<sub>2</sub>****F<sub>7</sub>Kr\*Au****F<sub>7</sub>KrPt****[KrF][PtF<sub>6</sub>]**

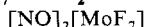
- Formation: 2.11.4.2

**F<sub>7</sub>KrSb****[KrF][SbF<sub>6</sub>]**

- Formation: 2.10.1

**F<sub>7</sub>MoNO**

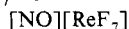
Formation: 2.9.10.1, 2.11.3.1

**F<sub>7</sub>MoNO<sub>2</sub>**

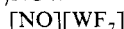
Formation: 2.11.3.1

**F<sub>7</sub>NOOs**

Formation: 2.11.4.2

**F<sub>7</sub>NORe**

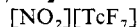
Formation: 2.9.10.1

**F<sub>7</sub>NOW**

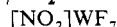
Formation: 2.9.10.1



Formation: 2.11.4.1

**F<sub>7</sub>NO<sub>2</sub>Tc**

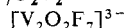
Formation: 2.11.3.1

**F<sub>7</sub>NO<sub>2</sub>W**

Formation: 2.11.4.1

**F<sub>7</sub>NaU**

Thermal decomposition: 2.11.5.2

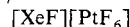
**F<sub>7</sub>O<sub>2</sub>V<sub>2</sub>**

Formation: 2.9.13

**F<sub>7</sub>Os**

Formation: 2.9.2.1, 2.11.4.2

Thermal decomposition: 2.11.4.2

**F<sub>7</sub>PtXe**

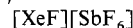
Formation: 2.10.2.2.1

**F<sub>7</sub>Rb<sub>3</sub>\*Cd<sub>2</sub>****F<sub>7</sub>Re**

Formation: 2.9.2.1, 2.11.4.1

Reaction with MF: 2.9.10.1

Reaction with Re: 2.11.4.1

Reaction with Re<sub>2</sub>O<sub>7</sub>: 2.11.4.1Reaction with SbF<sub>5</sub>-F<sub>2</sub>: 2.11.4.1**F<sub>7</sub>SbXe**

Formation: 2.10.1

**F<sub>7</sub>Se\*Au****F<sub>7</sub>Zr\*Cs<sub>3</sub>****F<sub>8</sub>\*Au<sub>2</sub>Ba****F<sub>8</sub>\*B<sub>14</sub>****F<sub>8</sub>Hf<sub>3</sub>O<sub>2</sub>**

Formation: 2.11.4.1

**F<sub>8</sub>KRe**

Formation: 2.9.10.1

**F<sub>8</sub>K<sub>2</sub>Mo**

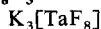
Formation: 2.11.3.1

**F<sub>8</sub>K<sub>2</sub>W**

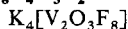
Formation: 2.11.4.1

**F<sub>8</sub>K<sub>3</sub>Nb**

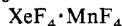
Formation: 2.9.10.1

**F<sub>8</sub>K<sub>3</sub>Ta**

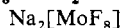
Formation: 2.9.10.1

**F<sub>8</sub>K<sub>4</sub>O<sub>3</sub>V<sub>2</sub>**

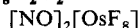
Formation: 2.11.2.1

**F<sub>8</sub>MnXe**

Formation: 2.11.2.1

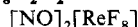
**F<sub>8</sub>MoNa<sub>2</sub>**

Formation: 2.11.3.1

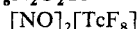
**F<sub>8</sub>N<sub>2</sub>O<sub>2</sub>Os**

Formation: 2.11.4.2

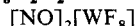
Thermal decomposition: 2.11.4.2

**F<sub>8</sub>N<sub>2</sub>O<sub>2</sub>Re**

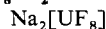
Formation: 2.9.10.1, 2.11.4.1

**F<sub>8</sub>N<sub>2</sub>O<sub>2</sub>Tc**

Formation: 2.11.3.1

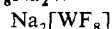
**F<sub>8</sub>N<sub>2</sub>O<sub>2</sub>W**

Formation: 2.9.10.1, 2.11.4.1

**F<sub>8</sub>Na<sub>2</sub>U**

Formation: 2.11.5.2

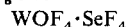
Thermal decomposition: 2.11.5.2

**F<sub>8</sub>Na<sub>2</sub>W**

Formation: 2.11.4.1

**F<sub>8</sub>OPa<sub>2</sub>**

Formation: 2.11.5.2

**F<sub>8</sub>OPt\*Cl****F<sub>8</sub>OSeW**

Formation: 2.9.12.3

**F<sub>8</sub>O<sub>12</sub>Ru<sub>4</sub>\*C<sub>12</sub>**

- F<sub>8</sub>Ru**  
 RuF<sub>8</sub>  
 Formation: 2.11.3.2
- F<sub>9</sub>FeXe**  
 XeF<sub>6</sub>·FeF<sub>3</sub>  
 Formation: 2.11.2.2
- F<sub>9</sub>H<sub>3</sub>O<sub>3</sub>W<sub>2</sub>**  
 [H<sub>3</sub>O]W<sub>2</sub>O<sub>2</sub>F<sub>9</sub>  
 Formation: 2.11.4.1
- F<sub>9</sub>IrXe<sub>2</sub>**  
 [Xe<sub>2</sub>F<sub>3</sub>][IrF<sub>6</sub>]  
 Formation: 2.11.4.2
- F<sub>9</sub>Mn<sub>2</sub>O<sub>2</sub>**  
 O<sub>2</sub>Mn<sub>2</sub>F<sub>9</sub>  
 Formation: 2.11.2.1
- F<sub>9</sub>MoOSb**  
 MoOF<sub>4</sub>·SbF<sub>5</sub>  
 Formation: 2.11.3.1
- F<sub>9</sub>NOW**  
 [NF<sub>4</sub>][WOF<sub>3</sub>]  
 Formation: 2.11.4.1  
 Heating: 2.11.4.1
- F<sub>9</sub>OReSb**  
 ReOF<sub>4</sub>·SbF<sub>5</sub>  
 Formation: 2.11.4.1
- F<sub>9</sub>OSbW**  
 WOF<sub>4</sub>·SbF<sub>5</sub>  
 Formation: 2.11.4.1
- F<sub>9</sub>S<sub>3</sub>\*C<sub>3</sub>B**
- F<sub>9</sub>SbXe**  
 [XeF<sub>3</sub>][SbF<sub>6</sub>]  
 Formation: 2.10.1
- F<sub>9</sub>Xe\*Co**
- F<sub>9</sub>Xe<sub>2</sub>\*Au**
- F<sub>10</sub>\*C<sub>12</sub>Co**
- F<sub>10</sub>\*Cs<sub>4</sub>Cu<sub>3</sub>**
- F<sub>10</sub>\*Ce\*C<sub>12</sub>**
- F<sub>10</sub>Ge\*C<sub>12</sub>HCl**
- F<sub>10</sub>GeTl\*C<sub>14</sub>H<sub>5</sub>**
- F<sub>10</sub>IPt**  
 PtF<sub>5</sub>·IF<sub>5</sub>  
 Formation: 2.11.4.2
- F<sub>10</sub>I<sub>2</sub>O<sub>3</sub>W**  
 WO<sub>3</sub>·2 IF<sub>5</sub>  
 Formation: 2.9.12.3
- F<sub>10</sub>N\*C<sub>17</sub>H<sub>5</sub>AuCl**
- F<sub>10</sub>N\*C<sub>28</sub>H<sub>36</sub>AuBr<sub>2</sub>**
- F<sub>10</sub>N\*C<sub>28</sub>H<sub>36</sub>AuCl<sub>2</sub>**
- F<sub>10</sub>NbSb**  
 [NbF<sub>4</sub>][SbF<sub>6</sub>]  
 Formation: 2.11.3.1
- F<sub>10</sub>Ni\*C<sub>12</sub>**
- F<sub>10</sub>Pd<sub>2</sub>Xe**  
 XePd<sub>2</sub>F<sub>10</sub>  
 Formation: 2.11.3.2  
 Thermal decomposition: 2.11.3.2
- F<sub>10</sub>Ru\*Br**
- F<sub>10</sub>TiXe**  
 XeF<sub>6</sub>·TiF<sub>4</sub>  
 Formation: 2.11.2.1
- F<sub>10</sub>Ti<sub>2</sub>Xe**  
 XeF<sub>2</sub>·2 TiF<sub>4</sub>  
 Formation: 2.11.2.1
- F<sub>10</sub>Tl\*C<sub>12</sub>Br**
- F<sub>10</sub>Tl\*C<sub>12</sub>Cl**
- F<sub>11</sub>H<sub>3</sub>STa<sub>2</sub>**  
 [H<sub>3</sub>S][Ta<sub>2</sub>F<sub>11</sub>]  
 Formation: 2.11.4.1
- F<sub>11</sub>H<sub>4</sub>Ta<sub>2</sub>\*As**
- F<sub>11</sub>IrXe**  
 [XeF<sub>5</sub>][IrF<sub>6</sub>]  
 Formation: 2.11.4.2
- F<sub>11</sub>NNb<sub>2</sub>\*C<sub>16</sub>H<sub>36</sub>**
- F<sub>11</sub>Nb<sub>2</sub>O<sub>2</sub>**  
 [O<sub>2</sub>][Nb<sub>2</sub>F<sub>11</sub>]  
 Formation: 2.11.3.1
- F<sub>11</sub>O<sub>2</sub>Ta<sub>2</sub>**  
 [O<sub>2</sub>][Ta<sub>2</sub>F<sub>11</sub>]  
 Formation: 2.11.4.1
- F<sub>11</sub>O<sub>2</sub>V<sub>2</sub>**  
 [O<sub>2</sub>][V<sub>2</sub>F<sub>11</sub>]  
 Formation: 2.11.2.1
- F<sub>11</sub>O<sub>6</sub>Re<sub>3</sub>\*C<sub>6</sub>**
- F<sub>11</sub>PtXe**  
 [XeF<sub>5</sub>]PtF<sub>6</sub>  
 Formation: 2.11.4.2
- F<sub>11</sub>RuXe**  
 [XeF<sub>5</sub>][RuF<sub>6</sub>]  
 Formation: 2.10.2.2.1
- F<sub>11</sub>SbXe**  
 [XeF<sub>5</sub>][SbF<sub>6</sub>]  
 Formation: 2.10.1
- F<sub>11</sub>Xe\*As**
- F<sub>11</sub>Xe\*Au**
- F<sub>12</sub>\*Au<sub>2</sub>Ca**
- F<sub>12</sub>\*B<sub>8</sub>**
- F<sub>12</sub>H<sub>6</sub>N<sub>2</sub>Os<sub>2</sub>**  
 [N<sub>2</sub>H<sub>6</sub>][OsF<sub>6</sub>]<sub>2</sub>  
 Formation: 2.11.4.2
- F<sub>12</sub>I\*Au**
- F<sub>12</sub>Ir<sub>2</sub>Xe**  
 [XeF][Ir<sub>2</sub>F<sub>11</sub>]  
 Formation: 2.11.4.2
- F<sub>12</sub>KrSb<sub>2</sub>**  
 [KrF][Sb<sub>2</sub>F<sub>11</sub>]  
 Formation: 2.10.2

- F<sub>12</sub>MnXe<sub>2</sub>**  
 $2\text{XeF}_4 \cdot \text{MnF}_4$   
 Formation: 2.11.2.1
- F<sub>12</sub>Na<sub>2</sub>O\*B<sub>4</sub>**
- F<sub>12</sub>PdSe<sub>2</sub>**  
 $[\text{SeF}_3]_2\text{PdF}_6$   
 Reaction with  $\text{KSeF}_5$  in  $\text{SeF}_4$ : 2.11.3.2
- F<sub>12</sub>Pt<sub>2</sub>Xe**  
 $[\text{XeF}][\text{Pt}_2\text{F}_{11}]$   
 Formation: 2.10.2.2.1  
 $\text{Xe}[\text{PtF}_6]_2$   
 Formation: 2.11.4.2
- F<sub>12</sub>ReSb**  
 $[\text{ReF}_6][\text{SbF}_6]$   
 Formation: 2.11.4.1
- F<sub>12</sub>Sr\*Au<sub>2</sub>**
- F<sub>13</sub>NO<sub>2</sub>W<sub>2</sub>**  
 $[\text{NF}_4][\text{W}_2\text{O}_2\text{F}_9]$   
 Formation: 2.11.4.1
- F<sub>14</sub>K<sub>5</sub>O<sub>3</sub>V<sub>3</sub>**  
 $\text{K}_5[\text{V}_3\text{O}_3\text{F}_{14}]$   
 Formation: 2.9.13
- F<sub>14</sub>N<sub>2</sub>Ni**  
 $[\text{NF}_4]_2[\text{NiF}_6]$   
 Formation: 2.11.2.2
- F<sub>14</sub>Nb<sub>2</sub>Se**  
 $[\text{SeF}_3][\text{Nb}_2\text{F}_{11}]$   
 Formation: 2.11.3.1
- F<sub>14</sub>O<sub>2</sub>Te<sub>2</sub>W**  
 $\text{cis-F}_4\text{W}(\text{OTeF}_5)_2$   
 Formation: 2.11.4.1
- F<sub>14</sub>O<sub>3</sub>V<sub>3</sub>**  
 $[\text{V}_3\text{O}_3\text{F}_{14}]^{5-}$   
 Formation: 2.9.13
- F<sub>14</sub>Ti<sub>2</sub>Xe**  
 $\text{XeF}_6 \cdot 2 \text{TiF}_4$   
 Formation: 2.11.2.1
- F<sub>14</sub>Ti<sub>2</sub>Xe<sub>3</sub>**  
 $3 \text{XeF}_2 \cdot 2 \text{TiF}_4$   
 Formation: 2.11.2.1
- F<sub>15</sub>Ge\*C<sub>18</sub>Cl**
- F<sub>15</sub>Ge\*C<sub>18</sub>H**
- F<sub>18</sub>I<sub>3</sub>Mo<sub>2</sub>O<sub>6</sub>**  
 $2\text{MoO}_3 \cdot 3 \text{IF}_5$   
 Formation: 2.9.12.3
- F<sub>15</sub>N\*C<sub>34</sub>H<sub>36</sub>AuBr**
- F<sub>15</sub>O<sub>2</sub>Sb<sub>2</sub>\*Cr**
- F<sub>15</sub>Sb<sub>2</sub>\*Cr**
- F<sub>16</sub>NiXe<sub>2</sub>**  
 $[\text{XeF}_5]_2[\text{NiF}_6]$   
 Formation: 2.10.2.2.1
- F<sub>16</sub>O<sub>3</sub>Ti**  
 $[\text{TiO}_3\text{F}_{16}]^{6-}$   
 Formation: 2.9.13
- F<sub>16</sub>PdXe<sub>2</sub>**  
 $[\text{XeF}_5]_2[\text{PdF}_6]$   
 Formation: 2.10.2.2.1
- F<sub>16</sub>Sb<sub>2</sub>Xe**  
 $[\text{XeF}_5][\text{Sb}_2\text{F}_{11}]$   
 Formation: 2.10.2.2.1
- F<sub>17</sub>IrXe<sub>2</sub>**  
 $[\text{Xe}_2\text{F}_{11}][\text{IrF}_6]$   
 Formation: 2.11.4.2
- F<sub>17</sub>ReSb<sub>2</sub>**  
 $[\text{ReF}_6][\text{Sb}_2\text{F}_{11}]$   
 Formation: 2.11.4.1
- F<sub>17</sub>SbXe<sub>2</sub>**  
 $[\text{Xe}_2\text{F}_{11}][\text{SbF}_6]$   
 Formation: 2.10.2.2.1
- F<sub>17</sub>Xe<sub>2</sub>\*Au**
- F<sub>19</sub>\*C<sub>57</sub>Cu<sub>6</sub>**
- F<sub>20</sub>\*C<sub>24</sub>Au<sub>2</sub>Br<sub>2</sub>**
- F<sub>20</sub>\*C<sub>24</sub>Au<sub>2</sub>Cl<sub>2</sub>**
- F<sub>20</sub>MnXe<sub>4</sub>**  
 $4\text{XeF}_4 \cdot \text{MnF}_4$   
 Formation: 2.11.2.1
- F<sub>20</sub>N<sub>2</sub>\*C<sub>34</sub>H<sub>8</sub>Au<sub>2</sub>Cl<sub>2</sub>**
- F<sub>20</sub>N<sub>2</sub>\*C<sub>36</sub>H<sub>8</sub>Au<sub>2</sub>Cl<sub>2</sub>**
- F<sub>20</sub>N<sub>2</sub>S<sub>2</sub>\*C<sub>26</sub>Au<sub>2</sub>**
- F<sub>20</sub>N<sub>6</sub>\*C<sub>24</sub>Au<sub>2</sub>**
- F<sub>20</sub>O<sub>4</sub>\*C<sub>34</sub>H<sub>14</sub>Au<sub>2</sub>**
- F<sub>21</sub>I<sub>3</sub>O<sub>5</sub>V<sub>2</sub>**  
 $2\text{VOF}_3 \cdot 3 \text{IOF}_5$   
 Formation: 2.9.12.3
- F<sub>21</sub>Sb<sub>2</sub>\*C<sub>6</sub>Cr**
- F<sub>22</sub>O<sub>4</sub>Te<sub>4</sub>W**  
 $\text{cis-F}_2\text{W}(\text{OTeF}_5)_4$   
 Formation: 2.11.4.1
- F<sub>26</sub>O<sub>4</sub>\*C<sub>28</sub>Au<sub>2</sub>**
- F<sub>28</sub>NiXe<sub>4</sub>**  
 $[\text{Xe}_2\text{F}_{11}]_2[\text{NiF}_6]$   
 Formation: 2.10.2.2.1
- F<sub>28</sub>TiXe<sub>4</sub>**  
 $4 \text{XeF}_6 \cdot \text{TiF}_4$   
 Formation: 2.11.2.1
- F<sub>30</sub>Ge<sub>2</sub>Hg\*C<sub>36</sub>**
- F<sub>30</sub>O<sub>2</sub>Ti<sub>7</sub>**  
 $\text{O}_2\text{Ti}_7\text{F}_{30}$   
 Formation: 2.11.2.1
- F<sub>30</sub>Sb<sub>4</sub>Xe\*Cr<sub>2</sub>**
- F<sub>60</sub>Ge<sub>4</sub>Hg\*C<sub>84</sub>H<sub>12</sub>Cr**
- F<sub>90</sub>Ge<sub>6</sub>Hg<sub>2</sub>\*C<sub>108</sub>Co**
- F<sub>90</sub>Ge<sub>6</sub>Hg<sub>2</sub>Mn\*C<sub>108</sub>**
- F<sub>90</sub>Ge<sub>6</sub>Hg<sub>2</sub>Ni\*C<sub>108</sub>**
- F<sub>90</sub>Ge<sub>6</sub>Hg<sub>2</sub>Ti<sub>2</sub>\*C<sub>108</sub>H<sub>20</sub>**
- Fe**  
 Fe  
 Reaction with  $\text{Br}_2$ : 2.9.2.3

- Reaction with  $F_2$ : 2.9.2.1  
 Reaction with  $C_6F_5X$ : 2.9.3.8  
 Reaction with  $I_2$ : 2.9.2.4  
**Fe\*Br<sub>2</sub>**  
**Fe\*Br<sub>3</sub>**  
**Fe\*C<sub>10</sub>H<sub>10</sub>**  
**Fe\*C<sub>12</sub>F<sub>10</sub>**  
**Fe\*Cl<sub>2</sub>**  
**Fe\*Cl<sub>3</sub>**  
**Fe\*F<sub>2</sub>**  
**Fe\*F<sub>3</sub>**  
**FeH<sub>12</sub>N<sub>3</sub>\*F<sub>6</sub>**  
**FeHg<sub>2</sub>\*C<sub>10</sub>H<sub>8</sub>Cl<sub>2</sub>**  
**FeIO<sub>3</sub>S\*C<sub>9</sub>H<sub>10</sub>B<sub>2</sub>F**  
**FeI<sub>2</sub>**  
   **FeI<sub>2</sub>**  
     Electrochemical formation: 2.9.3.7  
     Formation: 2.9.2.4, 2.9.3.8, 2.9.4.8, 2.9.6  
**FeI<sub>2</sub>O<sub>3</sub>S\*C<sub>9</sub>H<sub>10</sub>B<sub>2</sub>**  
**FeI<sub>2</sub>O<sub>4</sub>\*C<sub>4</sub>**  
**FeN\*C<sub>8</sub>H<sub>20</sub>Br<sub>4</sub>**  
**FeNO<sub>4</sub>\*C<sub>8</sub>H<sub>10</sub>BBr**  
**FeO\*Cl**  
**FeO\*F**  
**FeO<sub>4</sub>\*C<sub>4</sub>Br<sub>2</sub>**  
**FeO<sub>4</sub>\*C<sub>4</sub>Cl<sub>2</sub>**  
**FeO<sub>4</sub>S**  
   **Fe[SO<sub>4</sub>]**  
     Reaction with  $HgCl_2$  and  $H_2SO_4$ :  
       2.8.21.2  
**FeO<sub>5</sub>\*C<sub>5</sub>**  
**FeP\*C<sub>22</sub>H<sub>19</sub>AuBr**  
**FeP\*C<sub>22</sub>H<sub>19</sub>AuBr<sub>3</sub>**  
**FeS**  
   **FeS**  
     Reaction with  $CCl_4$ ,  $Cl_2$ : 2.9.5  
**FeS<sub>2</sub>**  
   **FeS<sub>2</sub>**  
     Reaction with  $SF_4$ : 2.9.5, 2.11.2.2  
     Reaction with  $CCl_4$ : 2.9.5  
**FeXe\*F<sub>9</sub>**  
**Fe<sub>2</sub>I<sub>2</sub>O<sub>8</sub>\*C<sub>8</sub>**  
**Fe<sub>2</sub>NO<sub>6</sub>S<sub>2</sub>\*C<sub>8</sub>H<sub>6</sub>B**  
**Fe<sub>2</sub>O<sub>3</sub>**  
   **Fe<sub>2</sub>O<sub>3</sub>**  
     Reaction with  $AlI_3$ : 2.9.4.8  
     Reaction with  $FeF_3-O_2$ : 2.11.2.2  
     Reaction with  $FeCl_3$ : 2.9.12.6  
     Reaction with  $RX$ : 2.9.4.6  
     Reaction with  $HX$ : 2.9.4.2  
**Fe<sub>2</sub>O<sub>12</sub>S<sub>3</sub>**  
   **Fe<sub>2</sub>[SO<sub>4</sub>]<sub>3</sub>**  
     Formation from  $HgCl_2$ ,  $FeSO_4$  and  
      $H_2SO_4$ : 2.8.21.2
- Fe<sub>2</sub>S**  
**Fe<sub>2</sub>S**  
   Reaction with  $Cl_2$ : 2.9.5  
**Fe<sub>3</sub>H<sub>32</sub>O<sub>16</sub>\*Br<sub>8</sub>**  
**Fe<sub>3</sub>O<sub>12</sub>\*C<sub>12</sub>**  
**Fr**  
   **Fr**  
     Reaction with  $X_2$ : 2.7.2  
     Reaction with  $HX$ : 2.7.3.1  
**Fr\*F**  
**Ga**  
   **Ga**  
     Reaction with  $AgBr$ ,  $PbBr_2$ : 2.6.3.3  
     Reaction with  $RX$ : 2.6.3.2  
     Reaction with  $HX$ : 2.6.3.1  
     Reaction with  $X_2$ : 2.6.2.1  
**Ga\*Br<sub>3</sub>**  
**Ga\*C<sub>2</sub>H<sub>7</sub>**  
**Ga\*C<sub>3</sub>H<sub>9</sub>**  
**Ga\*C<sub>6</sub>H<sub>5</sub>Cl<sub>2</sub>**  
**Ga\*C<sub>6</sub>H<sub>15</sub>**  
**Ga\*C<sub>12</sub>H<sub>10</sub>Cl**  
**Ga\*C<sub>18</sub>H<sub>15</sub>**  
**Ga\*Cl**  
**Ga\*Cl<sub>3</sub>**  
**Ga\*F**  
**Ga\*F<sub>3</sub>**  
**GaH<sub>4</sub>Li**  
   **Li[GaH<sub>4</sub>]**  
     Thermal stability: 2.6.5.1  
**Gal**  
   **Gal**  
     Formation: 2.6.3.2  
**Gal\*C<sub>2</sub>H<sub>6</sub>**  
**GalS<sub>2</sub>\*C<sub>4</sub>H<sub>10</sub>**  
**Gal<sub>2</sub>\*CH<sub>3</sub>**  
**Gal<sub>2</sub>S\*CH<sub>3</sub>**  
**Gal<sub>3</sub>**  
   **Gal<sub>3</sub>**  
     Formation: 2.6.2.1, 2.6.10.1, 2.6.10.2  
**Gal<sub>4</sub>S\*C<sub>3</sub>H<sub>9</sub>**  
**GalSi<sub>4</sub>\*C<sub>12</sub>H<sub>36</sub>**  
**GaN\*C<sub>3</sub>H<sub>9</sub>Br<sub>3</sub>**  
**GaN\*C<sub>3</sub>H<sub>9</sub>Cl<sub>3</sub>**  
**GaN\*C<sub>3</sub>H<sub>12</sub>**  
**GaS<sub>2</sub>\*C<sub>10</sub>H<sub>15</sub>**  
**Ga<sub>2</sub>\*Br<sub>2</sub>**  
**Ga<sub>2</sub>\*Br<sub>6</sub>**  
**Ga<sub>2</sub>K<sub>2</sub>\*C<sub>6</sub>H<sub>18</sub>**  
**Ga<sub>2</sub>K<sub>2</sub>\*Cl<sub>6</sub>**  
**Ga<sub>2</sub>O<sub>3</sub>**  
   **Ga<sub>2</sub>O<sub>3</sub>**  
     Reaction with  $BX_3$ : 2.6.6.4

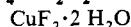
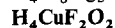
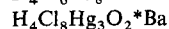
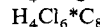
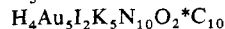
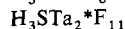
- Reaction with  $\text{MF}_3$ : 2.6.6.4  
 Reaction with  $\text{F}_2$ ,  $\text{Cl}_2$ : 2.6.6.1  
 Reaction with  $\text{CCl}_4$ : 2.6.6.4  
 Reaction with  $\text{CCl}_4\text{-Cl}_2$ : 2.6.6.2  
 Reaction with ag  $\text{HX}$ : 2.6.6.3
- Ga<sub>2</sub>S<sub>3</sub>**  
**Ga<sub>2</sub>S<sub>3</sub>**  
 Reaction with  $\text{X}_2$ : 2.6.7.1
- Gd**  
**Gd**  
 Reaction with  $\text{HX}$ : 2.9.14.1.1
- Gd\*F<sub>3</sub>**  
**GdIS**  
**GdSI**  
 Formation: 2.9.14.1.1
- GdS\*Br**  
**GdSe\*F**  
**Ge\*CH<sub>2</sub>Br**  
**Ge\*CH<sub>7</sub>As**  
**Ge\*C<sub>2</sub>H<sub>8</sub>**  
**Ge\*C<sub>3</sub>H<sub>9</sub>**  
**Ge\*C<sub>3</sub>H<sub>9</sub>Cl**  
**Ge\*C<sub>3</sub>H<sub>11</sub>As**  
**Ge\*C<sub>6</sub>H<sub>15</sub>Br**  
**Ge\*C<sub>12</sub>HCIF<sub>10</sub>**  
**Ge\*C<sub>18</sub>ClF<sub>15</sub>**  
**Ge\*C<sub>18</sub>HF<sub>15</sub>**  
**Ge\*Cl**  
**Ge\*Cl<sub>2</sub>**  
**Ge\*Cl<sub>4</sub>**  
**GeH<sub>3</sub>\*Br**  
**GeH<sub>3</sub>\*Cl**  
**GeH<sub>4</sub>**  
**GeH<sub>4</sub>**  
 Formation: 2.6.9.3
- GeH<sub>5</sub>\*As**  
**GeP\*C<sub>3</sub>H<sub>11</sub>**  
**GePd\*F<sub>6</sub>**  
**GeS\*CH<sub>6</sub>**  
**GeS\*C<sub>4</sub>H<sub>12</sub>**  
**GeTi\*C<sub>14</sub>H<sub>5</sub>F<sub>10</sub>**  
**Ge<sub>2</sub>\*C<sub>2</sub>H<sub>10</sub>**  
**Ge<sub>2</sub>H<sub>5</sub>\*Br**  
**Ge<sub>2</sub>H<sub>6</sub>**  
**Ge<sub>2</sub>H<sub>6</sub>**  
 Formation: 2.6.9.3
- Ge<sub>2</sub>H<sub>7</sub>\*As**  
**Ge<sub>2</sub>Hg\*C<sub>36</sub>F<sub>30</sub>**  
**Ge<sub>3</sub>Tl\*C<sub>18</sub>H<sub>45</sub>**  
**Ge<sub>4</sub>Hg\*C<sub>84</sub>H<sub>12</sub>CrF<sub>60</sub>**  
**Ge<sub>6</sub>Hg<sub>2</sub>\*C<sub>108</sub>CoF<sub>90</sub>**  
**Ge<sub>6</sub>Hg<sub>2</sub>Mn\*C<sub>108</sub>F<sub>90</sub>**
- Ge<sub>6</sub>Hg<sub>2</sub>Ni\*C<sub>108</sub>F<sub>90</sub>**  
**Ge<sub>6</sub>Hg<sub>2</sub>Ti<sub>2</sub>\*C<sub>108</sub>H<sub>20</sub>F<sub>90</sub>**  
**H\*AlBr<sub>2</sub>**  
**H\*AlCl<sub>2</sub>**  
**H\*Br**  
**H\*Cl**  
**HCIF<sub>10</sub>Ge\*C<sub>12</sub>**  
**HCl<sub>3</sub>\*C**  
**H\*F**  
**HF<sub>15</sub>Ge\*C<sub>18</sub>**  
**HHgl<sub>2</sub>\*Br**  
**HHgl<sub>2</sub>\*Cl**  
**HHgO\*F**  
**HI**  
**HI**  
 Metathesis: 2.6.12.1  
 Reaction with B, Al, Ga, In, Tl: 2.6.3.1  
 Reaction with  $[\text{B}_3\text{H}_8]^-$ : 2.6.4.2  
 Reaction with  $\text{CdCO}_3$ : 2.8.17.1  
 Reaction with Cd: 2.8.14.3  
 Reaction with  $\text{CdO}$ : 2.8.15.2  
 Reaction with  $\text{HgCl}_2$ : 2.8.18  
 Reaction with  $\text{Hg}_2\text{I}_2$ : 2.8.20.1  
 Reaction with MO, MOH,  $\text{MCO}_3$ : 2.7.5  
 Reaction with  $\text{R}_3\text{B} \dots \text{R}_3\text{Tl}$ : 2.6.10.2  
 Reaction with Group IIIB–Group IVB bonds: 2.6.11.2  
 Reaction with  $\text{HX}$ : 2.7.3.1  
 Reaction with  $\text{ZnO}$ : 2.8.15.2  
 Reaction with  $\text{Be}_2\text{C}$ : 2.7.8  
 Reaction with transition-metal oxides: 2.9.4.3  
 Reaction with transition-metals: 2.9.3.2, 2.9.3.3, 2.9.14.1.1  
 Use as reducing agent: 2.9.13.2
- HI<sub>2</sub>\*Al**  
**HK\*F<sub>2</sub>**  
**HLi**  
**LiH**  
 Reaction with  $\text{X}_2$ : 2.7.4
- HMgO\*Cl**  
**HMnO<sub>5</sub>\*C<sub>5</sub>**  
**HNO<sub>3</sub>**  
**HNO<sub>3</sub>**  
 Formation from  $\text{Hg}[\text{NO}_3]_2$  and  $\text{Br}_2$ : 2.8.17.3
- HNaO**  
**NaOH**  
 Reaction with  $\text{X}_2$ : 2.7.4
- HO\*Br**  
**HO\*BrCd**  
**HO\*Cl**

- $\text{HO}^*\text{CuF}$   
 $\text{HO}^*\text{Cu}_2\text{F}_3$   
 $\text{HORu}^*\text{Cl}_3$   
 $\text{HOZn}^*\text{Cl}$   
 $\text{HO}_3\text{S}^*\text{Cl}$   
 $\text{HO}_3\text{S}^*\text{F}$   
 $\text{HO}_4^*\text{Cl}$   
 $\text{HO}_8^*\text{Ag}_7\text{F}_2$   
 $\text{H}_2$   
 $\text{H}_2$   
 Reaction with  $\text{HgBr}_2$ : 2.8.21.2  
 $\text{H}_2^*\text{AlBr}$   
 $\text{H}_2^*\text{AlCl}$   
 $\text{H}_2\text{AuCl}_2\text{KN}_2\text{O}^*\text{C}_2$   
 $\text{H}_2^*\text{Ba}$   
 $\text{H}_2\text{Cu}_2\text{O}_5^*\text{C}$   
 $\text{H}_2\text{HgI}_3\text{KO}$   
 $\text{K}[\text{HgI}_3]\cdot\text{H}_2\text{O}$   
 Formation: 2.8.22  
 $\text{H}_2\text{HgI}_4$   
 $\text{H}_2[\text{HgI}_4]$   
 Formation: 2.8.22  
 $\text{H}_2\text{HgKO}^*\text{Br}_3$   
 $\text{H}_2\text{HgKO}^*\text{Cl}_3$   
 $\text{H}_2\text{HgK}_2\text{O}^*\text{Cl}_4$   
 $\text{H}_2\text{HgN}^*\text{Cl}$   
 $\text{H}_2\text{I}^*\text{Al}$   
 $\text{H}_2\text{IO}^*\text{Ag}_2\text{F}$   
 $\text{H}_2\text{I}_3\text{O}^*\text{CdCs}$   
 $\text{H}_2\text{IrO}_3$   
 $\text{IrO}_2\cdot\text{H}_2\text{O}$   
 Reaction with  $\text{HX}$ : 2.9.4.2  
 $\text{H}_2\text{KO}^*\text{Br}_3\text{Cd}$   
 $\text{H}_2\text{KO}^*\text{CdCl}_3$   
 $\text{H}_2\text{MoO}_3^*\text{F}_3$   
 $\text{H}_2\text{MoO}_3^*\text{F}_4$   
 $\text{H}_2\text{MoO}_4^*\text{F}_2$   
 $\text{H}_2\text{MoO}_4^*\text{F}_3$   
 $\text{H}_2\text{NaOZn}^*\text{Br}_3$   
 $\text{H}_2\text{O}^*\text{BaBr}_4\text{Cd}$   
 $\text{H}_2\text{O}^*\text{Br}_2\text{Cd}$   
 $\text{H}_2\text{O}^*\text{CdCl}_2$   
 $\text{H}_2\text{OZn}^*\text{Cl}_2$   
 $\text{H}_2\text{O}_2^*\text{Be}$   
 $\text{H}_2\text{O}_2^*\text{Cu}$   
 $\text{H}_2\text{O}_2\text{Sr}$   
 $\text{Sr}(\text{OH})_2$   
 Reaction with  $\text{X}_2$ : 2.7.4  
 $\text{H}_2\text{O}_2\text{Ti}^*\text{F}_3$   
 $\text{H}_3\text{O}_3\text{W}^*\text{F}_3$   
 $\text{H}_2\text{S}$   
 $\text{H}_2\text{S}$   
 Formation from  $\text{ZnS}$  and  $\text{HCl}$ : 2.8.16.2  
 Reaction with  $\text{HgBr}_2$ : 2.8.21.2  
 $\text{H}_2\text{Se}$   
 $\text{H}_2\text{Se}$   
 Formation: 2.6.7.2  
 $\text{H}_3^*\text{Al}$   
 $\text{H}_3\text{BCl}_2^*\text{C}$   
 $\text{H}_3\text{BeCl}^*\text{C}$   
 $\text{H}_3^*\text{BrGe}$   
 $\text{H}_3\text{BrMg}^*\text{C}_4$   
 $\text{H}_3\text{BrO}^*\text{C}_2$   
 $\text{H}_3\text{Br}_2\text{O}_2\text{Ti}^*\text{C}_2$   
 $\text{H}_3\text{Br}_5\text{NNb}^*\text{C}_2$   
 $\text{H}_3\text{CdCl}^*\text{C}_4$   
 $\text{H}_3^*\text{ClGe}$   
 $\text{H}_3\text{ClHg}^*\text{C}_2$   
 $\text{H}_3\text{ClHgSe}^*\text{C}_4$   
 $\text{H}_3\text{ClO}^*\text{C}_2$   
 $\text{H}_3\text{Cl}_3\text{Si}^*\text{C}$   
 $\text{H}_3\text{Cl}_3\text{Si}^*\text{C}_2$   
 $\text{H}_3\text{Cl}_3\text{Ti}^*\text{C}$   
 $\text{H}_3\text{Cl}_4\text{NNb}^*\text{C}_2$   
 $\text{H}_3\text{GaI}_2^*\text{C}$   
 $\text{H}_3\text{GaI}_2\text{S}^*\text{C}$   
 $\text{H}_3\text{I}^*\text{C}$   
 $\text{H}_3\text{Li}^*\text{AlCl}$   
 $\text{H}_3\text{MnO}_5^*\text{C}_6$   
 $\text{H}_3\text{MnO}_6^*\text{C}_7$   
 $\text{H}_3\text{N}^*\text{AuCl}_3$   
 $\text{H}_3\text{NO}^*\text{F}_4$   
 $\text{H}_3\text{NbO}^*\text{F}_6$   
 $\text{H}_3\text{OPt}^*\text{F}_6$   
 $\text{H}_3\text{ORu}^*\text{F}_6$   
 $\text{H}_3\text{OS}^*\text{Cl}$   
 $\text{H}_3\text{OTa}^*\text{F}_6$   
 $\text{H}_3\text{OTi}^*\text{F}_6$   
 $\text{H}_3\text{O}_2\text{P}$   
 $\text{H}_3\text{PO}_2$   
 Reaction with  $\text{HgCl}_2$ : 2.8.21.2  
 $\text{H}_3\text{O}_2\text{Ti}^*\text{C}_2$   
 $\text{H}_3\text{O}_2\text{W}^*\text{F}_5$   
 $\text{H}_3\text{O}_3^*\text{Ac}$   
 $\text{H}_3\text{O}_3\text{P}$   
 $\text{H}_3\text{PO}_3$   
 Formation from  $\text{HgCl}_2$  and  $\text{H}_3\text{PO}_2$ :  
 2.8.21.2  
 Reaction with  $\text{HgCl}_2$ : 2.8.21.2  
 $\text{H}_3\text{O}_3\text{Sc}$   
 $\text{Sc}(\text{OH})_3$   
 Reaction with  $\text{HF}$ : 2.11.2.1  
 $\text{H}_3\text{O}_3\text{W}_2^*\text{F}_9$   
 $\text{H}_3\text{O}_4\text{P}$   
 $\text{H}_3\text{PO}_4$   
 Formation from  $\text{HgCl}_2$  and  $\text{H}_3\text{PO}_3$ :  
 2.8.21.2

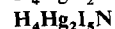
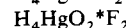
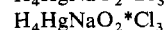
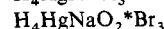
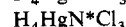
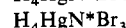
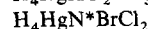
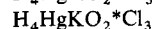
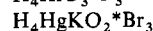
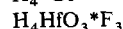


**H<sub>3</sub>P**

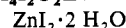
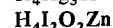
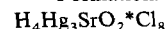
Formation: 2.6.5.3, 2.6.9.3



Formation: 2.8.8.3



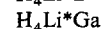
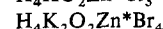
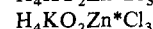
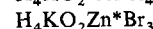
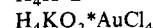
Formation: 2.8.22



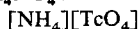
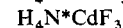
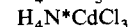
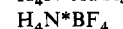
Dehydration: 2.8.19



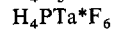
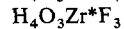
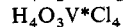
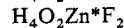
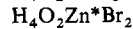
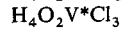
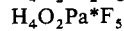
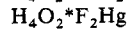
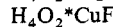
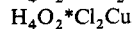
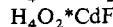
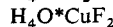
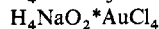
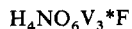
Thermal stability: 2.6.5.1



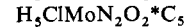
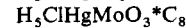
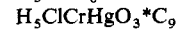
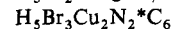
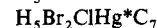
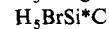
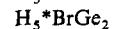
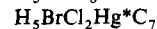
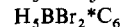
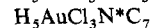
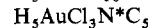
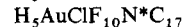
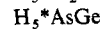
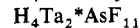
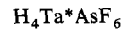
Thermal stability: 2.6.5.1



Reaction with HF: 2.11.3.1



Formation: 2.6.9.3



$\text{H}_5\text{Cl}_2\text{Ga}^*\text{C}_6$   
 $\text{H}_5\text{Cl}_2\text{I}^*\text{C}_6$   
 $\text{H}_5\text{Cl}_2\text{OV}^*\text{C}_6$   
 $\text{H}_5\text{Cl}_2\text{Ti}^*\text{C}_6$   
 $\text{H}_5\text{Cl}_3^*\text{C}_7$   
 $\text{H}_5\text{Cl}_3\text{Hg}^*\text{C}_7$   
 $\text{H}_5\text{Cl}_3\text{V}^*\text{C}_6$   
 $\text{H}_5\text{F}_{10}\text{GeTi}^*\text{C}_{14}$   
 $\text{H}_5\text{I}^*\text{B}_2$   
 $\text{H}_5\text{I}^*\text{C}_2$   
 $\text{H}_5\text{IMoO}_3^*\text{C}_8$   
 $\text{H}_5\text{IO}_3\text{W}^*\text{C}_8$   
 $\text{H}_5\text{I}_2\text{O}_{2.5}^*\text{Ag}_7\text{F}_5$   
 $\text{H}_5\text{MnO}_3^*\text{C}_8$   
 $\text{H}_5\text{MnO}_6^*\text{C}_{12}$   
 $\text{H}_5\text{N}^*\text{F}_2$   
 $\text{H}_5\text{N}_2^*\text{Cl}$   
 $\text{H}_5\text{N}_2^*\text{CoF}_3$   
 $\text{H}_5\text{OZn}^*\text{Cl}_3$   
 $\text{H}_5\text{O}_2\text{Zn}_2^*\text{Cl}_5$   
 $\text{H}_5\text{P}^*\text{C}$   
 **$\text{H}_5\text{PSi}$**   
 $\text{H}_3\text{SiPH}_2$   
 Formation: 2.6.9.3  
 $\text{H}_5\text{Si}^*\text{As}$   
 $\text{H}_5\text{Si}_2^*\text{Br}$   
 $\text{H}_5\text{Si}_2^*\text{Cl}$   
 $\text{H}_6\text{AlCl}_2\text{N}^*\text{C}_2$   
 $\text{H}_6\text{AuBr}_3\text{S}^*\text{C}_2$   
 $\text{H}_6\text{AuCl}_2\text{Cs}^*\text{C}_2$   
 $\text{H}_6\text{AuCl}_4\text{N}^*\text{C}_5$   
 $\text{H}_6\text{Au}_2\text{Br}_4^*\text{C}_2$   
 $\text{H}_6\text{Au}_2\text{Cl}_6^*\text{C}_4$   
 $\text{H}_6\text{Au}_2\text{Cl}_7^*\text{C}_4$   
 $\text{H}_6\text{BCl}^*\text{C}_2$   
 $\text{H}_6\text{BCl}_2\text{N}^*\text{C}_2$   
 $\text{H}_6\text{BF}^*\text{C}_2$   
 $\text{H}_6\text{BFe}_2\text{NO}_6\text{S}_2^*\text{C}_8$   
 $\text{H}_6^*\text{B}_2$   
 $\text{H}_6\text{B}_2\text{Br}_4\text{S}_2^*\text{C}_2$   
 $\text{H}_6\text{B}_2\text{Cl}_4\text{S}_2^*\text{C}_2$   
 $\text{H}_6\text{B}_3\text{Cl}^*\text{C}_2$   
 $\text{H}_6\text{BrCuIN}^*\text{C}_5$   
 $\text{H}_6\text{BrHgIN}^*\text{C}$   
 $\text{H}_6\text{BrTi}^*\text{C}_2$   
 $\text{H}_6\text{Br}_2\text{HgIN}^*\text{C}$   
 $\text{H}_6\text{Cd}^*\text{C}_2$   
 $\text{H}_6\text{CdO}_4^*\text{C}_4$   
 $\text{H}_6\text{ClNO}^*\text{C}_3$   
 $\text{H}_6\text{ClNS}^*\text{C}_3$   
 $\text{H}_6\text{ClTi}^*\text{C}_2$   
 $\text{H}_6\text{Cl}_2\text{Hg}_2^*\text{C}_4$

$\text{H}_6\text{Cl}_3\text{NP}^*\text{C}_2$   
 $\text{H}_6\text{CrO}_3^*\text{C}_9$   
 $\text{H}_6\text{GaI}^*\text{C}_2$   
 $\text{H}_6\text{GeS}^*\text{C}$   
 $\text{H}_6^*\text{Ge}_2$   
 $\text{H}_6\text{HfO}_3^*\text{F}_4$   
 $\text{H}_6\text{Hg}^*\text{C}_4$   
 **$\text{H}_6\text{HgI}_3\text{NO}$**   
 $[\text{NH}_4][\text{HgI}_3]\cdot\text{H}_2\text{O}$   
 Formation: 2.8.22  
 $\text{H}_6\text{HgO}_4^*\text{C}_4$   
 $\text{H}_6\text{ITl}^*\text{C}_2$   
 $\text{H}_6\text{I}_2\text{Si}^*\text{C}_2$   
 **$\text{H}_6\text{I}_3\cdot\text{NaO}_3\text{Zn}$**   
 $\text{Na}[\text{ZnI}_3]\cdot 3\text{H}_2\text{O}$   
 Formation: 2.8.22  
 $\text{H}_6\text{LiO}_3\text{Zn}^*\text{Cl}_3$   
 $\text{H}_6\text{MoO}_3^*\text{C}_8$   
 $\text{H}_6\text{Mo}_4\text{O}_{16}^*\text{F}$   
 $\text{H}_6\text{N}_2\text{Os}_2^*\text{F}_{12}$   
 $\text{H}_6\text{N}_2\text{Ti}^*\text{F}_6$   
 $\text{H}_6\text{N}_4\text{Na}_2\text{NiO}_3^*\text{C}_4$   
 $\text{H}_6\text{Na}_2\text{O}_3\text{Zn}^*\text{Cl}_4$   
 $\text{H}_6\text{O}_2\text{Pt}^*\text{F}_6$   
 $\text{H}_6\text{O}_3\text{V}^*\text{F}_3$   
 $\text{H}_6\text{O}_3\text{Zn}^*\text{Br}_2$   
 $\text{H}_6\text{O}_3\text{Zn}^*\text{Cl}_2$   
 $\text{H}_6\text{O}_4^*\text{C}_2$   
 **$\text{H}_6\text{P}_2\text{Si}$**   
 $\text{H}_2\text{Si}(\text{PH}_2)_2$   
 Formation: 2.6.9.3  
 $\text{H}_6\text{SSi}^*\text{C}$   
 $\text{H}_7\text{AsGe}^*\text{C}$   
 $\text{H}_7^*\text{AsGe}_2$   
 $\text{H}_7\text{AsSi}^*\text{C}$   
 $\text{H}_7\text{B}_5^*\text{C}_2$   
 $\text{H}_7\text{ClSi}^*\text{C}_2$   
 $\text{H}_7\text{CoF}_3\text{O}_{3.5}$   
 $\text{CoF}_3\cdot 3.5\text{H}_2\text{O}$   
 Formation: 2.11.2.2  
 $\text{H}_7\text{Ga}^*\text{C}_2$   
 $\text{H}_7\text{O}_2\text{Ti}^*\text{C}_5$   
 $\text{H}_7\text{P}^*\text{C}_2$   
 $\text{H}_7\text{P}^*\text{C}_6$   
 $\text{H}_7\text{PSi}^*\text{C}$   
 $\text{H}_7\text{Si}_2^*\text{As}$   
 $\text{H}_8\text{AlCl}_4\text{P}^*\text{C}_2$   
 $\text{H}_8\text{AuBr}_2\text{F}_5\text{S}^*\text{C}_{10}$   
 $\text{H}_8\text{AuCl}_2\text{F}_5\text{S}^*\text{C}_{10}$   
 $\text{H}_8\text{AuF}_5\text{S}^*\text{C}_{10}$   
 $\text{H}_8\text{Au}_2\text{Cl}_2\text{F}_{20}\text{N}_2^*\text{C}_{34}$   
 $\text{H}_8\text{Au}_2\text{Cl}_2\text{F}_{20}\text{N}_2^*\text{C}_{36}$

$H_8BClS \cdot C_2$   
 $H_8BaN_4NiO_4 \cdot C_4$   
 $H_8Cl_2FeHg_2 \cdot C_{10}$   
 $H_8Cl_3Cu_2N \cdot C_2$   
 $H_8CuI_2N \cdot C_6$   
 $H_8F_6MnN_2$

$[NH_4]_2[MnF_6]$

Formation: 2.11.2.1

$H_8Ge \cdot C_2$

$H_8HgI_4 \cdot N_2$

$[NH_4]_2[HgI_4]$

Formation: 2.8.22

$H_8HgI_4Na_2O_4$

$Na_2[HgI_4] \cdot 4 H_2O$

Formation: 2.8.22

$H_8HgN_2 \cdot Br_2Cl_2$

$H_8HgN_2 \cdot Br_4$

$H_8HgN_2 \cdot Cl_4$

$H_8I_2O_4Zn$

$ZnI_2 \cdot 4 H_2O$

Dehydration: 2.8.19

$H_8I_4N_2Zn$

$[NH_4]_2[ZnI_4]$

Formation: 2.8.22

$H_8I_6N_2 \cdot Au_2$

$H_8Li \cdot AlAs_4$

$H_8LiN_4 \cdot Al$

$H_8LiP_4 \cdot Al$

$H_8MoO_3 \cdot C_9$

$H_8MoO_3 \cdot C_{10}$

$H_8N_2 \cdot BeF_4$

$H_8N_2 \cdot Be_2F_5$

$H_8N_2 \cdot Br_4Cd$

$H_8N_2 \cdot Cl_4Cu$

$H_8N_2 \cdot CuF_4$

$H_8N_2Os \cdot Br_6$

$H_8N_2Os \cdot Cl_6$

$H_8N_2Zn \cdot Br_4$

$H_8N_2Zn \cdot Cl_4$

$H_8O_4 \cdot Br_2Cd$

$H_8O_4 \cdot Br_2Cu$

$H_8O_4 \cdot CdCl_2$

$H_8O_4 \cdot CdCl_6Cu_2$

$H_8O_4Zn \cdot BaCl_4$

$H_8O_4Zn \cdot Cl_2$

$H_8O_4Zn \cdot F_2$

$H_8SSi_2 \cdot C$

$H_9AsBr_2 \cdot C_3$

$H_9AuBrP \cdot C_3$

$H_9AuBr_3P \cdot C_3$

$H_9AuBr_4O_4$

$H[AuBr_4] \cdot 4 H_2O$

Reaction with RMgBr: 2.8.5

$H_9Au \cdot C_3$

$H_9B \cdot C_3$

$H_9BCl_2O \cdot C_4$

$H_9BO_3 \cdot C_3$

$H_9BS \cdot C_2$

$H_9BS \cdot C_3$

$H_9B_3Br_3N_3 \cdot C_3$

$H_9B_3Cl_3N_3 \cdot C_3$

$H_9B_3F_3N_3 \cdot C_3$

$H_9 \cdot B_4Br$

$H_9 \cdot B_6Br$

$H_9BrSn \cdot C_3$

$H_9Br_3GaN \cdot C_3$

$H_9ClGe \cdot C_3$

$H_9ClSi \cdot C_3$

$H_9ClSn \cdot C_3$

$H_9 \cdot Cl_2$

$H_9Cl_3GaN \cdot C_3$

$H_9Cu_2I_3S \cdot C_3$

$H_9FSi \cdot C_3$

$H_9FSn \cdot C_3$

$H_9Ga \cdot C_3$

$H_9GaI_4S \cdot C_3$

$H_9Ge \cdot C_3$

$H_9I \cdot B_6$

$H_9In \cdot C_3$

$H_9O_4 \cdot AuBr_4$

$H_9O_4 \cdot AuCl_4$

$H_9PSi \cdot C_2$

$H_9Si \cdot C_3$

$H_9Ti \cdot C_3$

$H_{10}Ag_2I_3N \cdot C_4$

$H_{10}AlBr \cdot C_4$

$H_{10}AlCl \cdot C_4$

$H_{10}AlF \cdot C_4$

$H_{10}AlI \cdot C_4$

$H_{10}AuBr_2NS_2 \cdot C_5$

$H_{10}AuNS_2 \cdot C_5$

$H_{10}AuN_3S_2Se_2 \cdot C_7$

$H_{10}AuN_3S_4 \cdot C_7$

$H_{10}Au_2Cl_2N_2 \cdot C_{10}$

$H_{10}Au_2Cl_4 \cdot C_{12}$

$H_{10}Au_2I_2N_2 \cdot C_{10}$

$H_{10}BBr \cdot C_{12}$

$H_{10}BBrFeNO_4 \cdot C_8$

$H_{10}BCl \cdot C_4$

$H_{10}BCl_2N \cdot C_4$

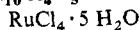
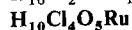
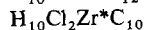
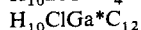
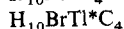
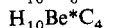
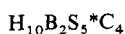
$H_{10}BCl_2P \cdot C_4$

$H_{10}BF_2N \cdot C_4$

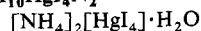
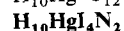
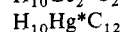
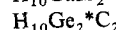
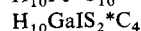
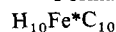
$H_{10}BI_2N \cdot C_4$

$H_{10}B_2FFeIO_3S \cdot C_9$

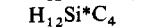
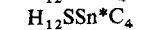
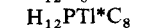
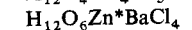
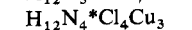
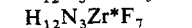
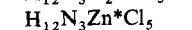
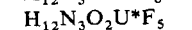
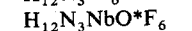
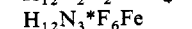
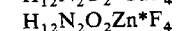
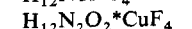
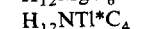
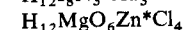
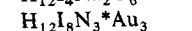
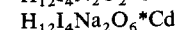
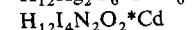
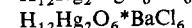
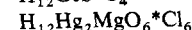
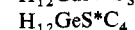
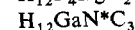
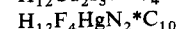
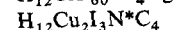
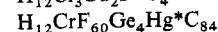
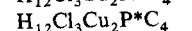
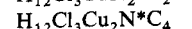
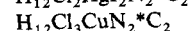
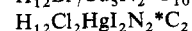
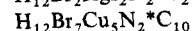
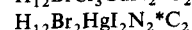
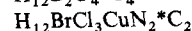
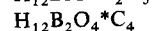
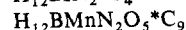
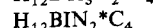
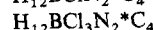
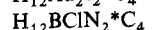
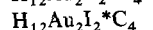
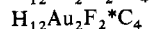
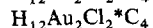
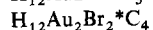
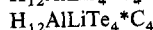
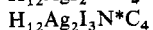
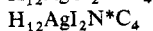
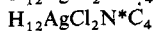
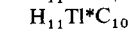
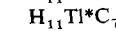
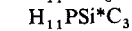
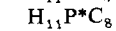
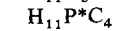
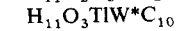
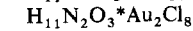
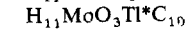
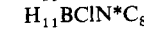
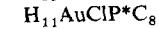
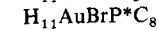
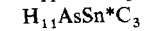
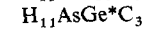
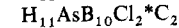
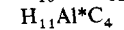
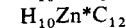
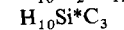
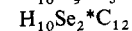
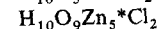
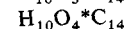
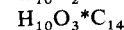
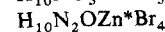
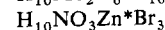
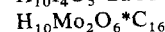
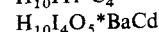
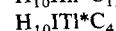
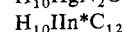
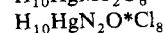
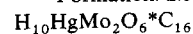
$H_{10}B_2FeI_2O_3S \cdot C_9$



Formation: 2.9.4.3



Formation: 2.8.22



- $H_{13}AlLiP_3 \cdot C_3$   
 $H_{13}AuO_2 \cdot C_7$   
 $H_{14}AlClO_2 \cdot C_6$   
 $H_{14}AlClO_2 \cdot C_{14}$   
 $H_{14}AuBrS \cdot C_{14}$   
 $H_{14}AuBr_3S \cdot C_{14}$   
 $H_{14}Au_2F_{20}O_4 \cdot C_{34}$   
 $H_{14}Au_2O_2 \cdot C_4$   
 $H_{14}BCl \cdot C_6$   
 $H_{14}BCl_3N \cdot C_4$   
 $H_{14} \cdot B_{10}$   
 $H_{14}HgO_2 \cdot C_{16}$   
 $H_{14}MoO_3Sn \cdot C_{11}$   
 $H_{14}N_3OZn \cdot Br_5$   
 $H_{14}O_7 \cdot CaCd_2Cl_6$   
 $H_{14}O_7Sr \cdot Cd_2Cl_6$   
 $H_{14}O_7Zn \cdot Cl_2$   
 $H_{15}Al \cdot C_6$   
 $H_{15}Al \cdot C_{18}$   
 $H_{15}AlSe_3 \cdot C_{18}$   
 $H_{15}Al_2I_3 \cdot C_6$   
 $H_{15}AsAuBr_2F_5 \cdot C_{24}$   
 $H_{15}AsAuBr_2NO \cdot C_{19}$   
 $H_{15}AsAuBr_3 \cdot C_{18}$   
 $H_{15}AsAuCl_5 \cdot C_{24}$   
 $H_{15}AsAuCl_7 \cdot C_{24}$   
 $H_{15}AsAuF_5 \cdot C_{24}$   
 $H_{15}AsAuI \cdot C_{18}$   
 $H_{15}AsAuI_3 \cdot C_{18}$   
 $H_{15}AsAuNO \cdot C_{19}$   
 $H_{15}AuBrCl_2P \cdot C_6$   
 $H_{15}AuBrCl_2P \cdot C_{18}$   
 $H_{15}AuBrP \cdot C_6$   
 $H_{15}AuBrP \cdot C_{18}$   
 $H_{15}AuBr_2ClP \cdot C_6$   
 $H_{15}AuBr_2ClP \cdot C_{18}$   
 $H_{15}AuBr_2F_5P \cdot C_{24}$   
 $H_{15}AuBr_2NOP \cdot C_{19}$   
 $H_{15}AuBr_3P \cdot C_6$   
 $H_{15}AuBr_3P \cdot C_{18}$   
 $H_{15}AuClI_2P \cdot C_6$   
 $H_{15}AuClIP \cdot C_6$   
 $H_{15}AuClIP \cdot C_{18}$   
 $H_{15}AuCl_3P \cdot C_6$   
 $H_{15}AuCl_3P \cdot C_{18}$   
 $H_{15}AuF_5P \cdot C_{24}$   
 $H_{15}AuIP \cdot C_6$   
 $H_{15}AuI_3P \cdot C_6$   
 $H_{15}AuNOP \cdot C_{19}$   
 $H_{15}B \cdot C_6$   
 $H_{15}BCINO \cdot C_6$   
 $H_{15}BMoO_3 \cdot C_{20}$   
 $H_{15}BSe_3 \cdot C_{18}$   
 $H_{15}BrGe \cdot C_6$   
 $H_{15}BrSi \cdot C_{18}$   
 $H_{15}BrSn \cdot C_6$   
 $H_{15}ClSn \cdot C_6$   
 $H_{15}ClSn \cdot C_{18}$   
 $H_{15}Cl_4Cu_2P \cdot C_6$   
 $H_{15}CoO_4Sn \cdot C_{22}$   
 $H_{15}Ga \cdot C_6$   
 $H_{15}Ga \cdot C_{18}$   
 $H_{15}GaS_2 \cdot C_{10}$   
 $H_{15}ISn \cdot C_6$   
 $H_{15}MoO_3Ti \cdot C_{12}$   
 $H_{15}NbO \cdot C_{12}$   
 $H_{16}Ag_2Br_2CuI_2N_4 \cdot C_4$   
 $H_{16}Ag_2Br_4N_4Ni \cdot C_4$   
 $H_{16}As_2AuI_3 \cdot C_{10}$   
 $H_{16}As_4AuI \cdot C_{10}$   
 $H_{16}Br_3Cu_2N_4 \cdot C_4$   
 $H_{16}Cl_2CuN \cdot C_6$   
 $H_{16}CuI_2N_8 \cdot C_{12}$   
 $H_{16}Cu_2O_{10} \cdot C_8$   
 $H_{16}F_2O_4Ti \cdot C_{10}$   
 $H_{16}F_4HgN_2O_2 \cdot C_{10}$   
 $H_{16}HgN_4 \cdot Br_6$   
 $H_{16}HgN_4 \cdot Cl_6$   
 $H_{16}I_4O_8Sr \cdot Ag_2$   
 $H_{16}I_4O_8Sr \cdot Cd$   
 $H_{16}LiP \cdot C_{19}$   
 $H_{16}N_4 \cdot CdCl_6$   
 $H_{16}O_7 \cdot CdCl_4$   
 $H_{16}O_8 \cdot BaCdCl_4$   
 $H_{17}AuBrP \cdot C_{20}$   
 $H_{17}AuBr_3P \cdot C_{20}$   
 $H_{17}BCl_2N_2 \cdot C_5$   
 $H_{17}CoF_4N_4 \cdot C_4$   
 $H_{18}AsBN_2 \cdot C_6$   
 $H_{18}AsBr_2In \cdot C_6$   
 $H_{18}AsCu_3I_4 \cdot C_{19}$   
 $H_{18}AuBr_2NS_2 \cdot C_9$   
 $H_{18}AuNS_2 \cdot C_9$   
 $H_{18}BCl \cdot C_8$   
 $H_{18}BClO_2 \cdot C_8$   
 $H_{18}BF_4N_3S \cdot C_6$   
 $H_{18}BN_2Ti \cdot C_6$   
 $H_{18}BN_3 \cdot C_6$   
 $H_{18}B_{10}Sn \cdot C_2$   
 $H_{18}ClSi_2Ti \cdot C_6$   
 $H_{18}Cu_2I_3P \cdot C_{19}$   
 $H_{18}Ga_2K_2 \cdot C_6$   
 $H_{18}ISi_2Ti \cdot C_6$   
 $H_{18}N_6 \cdot Br_3Cl_2CrCu$

- $H_{18}N_6*Br_5CrCu$   
 $H_{18}N_6*CdCl_5Co$   
 $H_{18}N_6*CoF_3$   
 $H_{19}AuBrFeP*C_{22}$   
 $H_{19}AuBrP*C_{21}$   
 $H_{19}AuBr_3FeP*C_{22}$   
 $H_{19}AuBr_3P*C_{21}$   
 $H_{19}AuCl_4N_2O_2*C_8$   
 $H_{19}N_6O_{0.5}*Co_2F_6$   
 $H_{20}AgBr_2P*C_{24}$   
 $H_{20}Ag_2Br_3N*C_8$   
 $H_{20}Ag_2Cl_3N*C_8$   
 $H_{20}AlLiSe_4*C_{24}$   
 $H_{20}AsAuBr_2N_2O_2*C_{26}$   
 $H_{20}AsAuCl_2N_2O_2*C_{26}$   
 $H_{20}AsAuCl_4*C_{24}$   
 $H_{20}AsAuN_2O_2*C_{26}$   
 $H_{20}AsF_2O_2V*C_{24}$   
 $H_{20}AuBr_2N*C_8$   
 $H_{20}AuBr_4N*C_8$   
 $H_{20}AuCl_2N*C_8$   
 $H_{20}AuCl_2N_3O_4*C_{16}$   
 $H_{20}AuCl_4N*C_8$   
 $H_{20}AuI_2N*C_8$   
 $H_{20}AuI_4N*C_8$   
 $H_{20}AuP*C_{24}$   
 $H_{20}Au_2Br_2*C_8$   
 $H_{20}Au_2Br_2*C_{10}$   
 $H_{20}Au_2Br_2N_2S_4*C_{10}$   
 $H_{20}Au_2Cl_2N_2*C_{14}$   
 $H_{20}Au_2Cl_2N_2*C_{16}$   
 $H_{20}Au_2I_2*C_8$   
 $H_{20}Au_2I_2N_2S_4*C_{10}$   
 $H_{20}Au_2N_4S_4Se_2*C_{12}$   
 $H_{20}Au_2N_4S_6*C_{12}$   
 $H_{20}BClNP*C_8$   
 $H_{20}B_2O_4*C_8$   
 $H_{20}Br_2CuP*C_{20}$   
 $H_{20}Br_2CuP*C_{24}$   
 $H_{20}Br_4FeN*C_8$   
 $H_{20}Br_6NNb*C_8$   
 $H_{20}Br_6NTa*C_8$   
 $H_{20}Cl_2CuP*C_{24}$   
 $H_{20}Cl_3CuP*C_{24}$   
 $H_{20}Cl_3Cu_2N*C_8$   
 $H_{20}Cl_3NTi*C_8$   
 $H_{20}Cl_6NNb*C_8$   
 $H_{20}Cl_6NTa*C_8$   
 $H_{20}Cl_9NTi_2*C_8$   
 $H_{20}Cl_{10}Cu_4N_2*C_6$   
 $H_{20}CuI_2N*C_8$   
 $H_{20}F_2O_2PV*C_{24}$   
 $H_{20}F_{90}Ge_6Hg_2Ti_2*C_{108}$   
 $H_{20}Pb*C_8$   
 $H_{20}Se_4Ti*C_{24}$   
 $H_{20}Se_4Zr*C_{24}$   
 $H_{21}Al*C_9$   
 $H_{21}Au_2Cl_2NP_2*C_{24}$   
 $H_{21}Au_2Cl_6NP_2*C_{24}$   
 $H_{21}BN_2Si*C_7$   
 $H_{22}Au_2Br_4Cl_2P_2*C_{25}$   
 $H_{22}Au_2Cl_2P_2*C_{25}$   
 $H_{22}Au_2Cl_6P_2*C_{25}$   
 $H_{22}BN_2P*C_8$   
 $H_{22}B_2N_2*C_{16}$   
 $H_{22}Be*C_{10}$   
 $H_{22}Br_2CuP*C_{21}$   
 $H_{24}AlLiN_4*C_8$   
 $H_{24}AuCl_2N_3O_4*C_{18}$   
 $H_{24}Br_2CuP*C_{22}$   
 $H_{24}CuI_2KO_6*C_{12}$   
 $H_{24}Cu_2I_6N_4*C_{22}$   
 $H_{24}N_6*Ag_2Au_3Cl_{17}$   
 $H_{25}BIN_2P*C_9$   
 $H_{25}BMnO_4P*C_{34}$   
 $H_{25}Cl_2CuNOP*C_{18}$   
 $H_{25}O_2Sb*C_{22}$   
 $H_{26}AsAuBr_2*C_{26}$   
 $H_{26}AsAuCl_2*C_{26}$   
 $H_{26}AsAuI_2*C_{26}$   
 $H_{26}Au_2Cl_2P_2*C_{27}$   
 $H_{26}Au_2Cl_6P_2*C_{27}$   
 $H_{27}B*C_{12}$   
 $H_{27}BN_2Sn*C_{10}$   
 $H_{27}BO_3*C_{12}$   
 $H_{27}B_3O_6*C_{12}$   
 $H_{27}Si_3Ti*C_9$   
 $H_{28}Au_2Br_2*C_{12}$   
 $H_{28}BrCdCl_2N*C_{12}$   
 $H_{28}BrCdI_2N*C_{12}$   
 $H_{28}Br_2CdIN*C_{12}$   
 $H_{28}CdCl_2N*C_{12}$   
 $H_{28}CdCl_2IN*C_{12}$   
 $H_{28}Cl_2CuN*C_{12}$   
 $H_{28}Cu_3I_4N*C_{12}$   
 $H_{30}BNP_2*C_{12}$   
 $H_{30}BN_3*C_{12}$   
 $H_{30}Br_{10}Cu_4N_2O*C_{10}$   
 $H_{32}As_4Au_2I_2*C_{20}$   
 $H_{32}Cu_4I_6K_2O_8*C_{16}$   
 $H_{32}O_{16}*Br_8Fe_3$   
 $H_{33}BrSi_3Sn*C_{12}$   
 $H_{33}Si_3SnTi*C_{12}$

$H_{36}AgI_3P_2 \cdot C_{38}$   
 $H_{36}Ag_3I_4N \cdot C_{16}$   
 $H_{36}AuBrF_5N \cdot C_{22}$   
 $H_{36}AuBrF_{15}N \cdot C_{34}$   
 $H_{36}AuBr_2F_{10}N \cdot C_{28}$   
 $H_{36}AuBr_2N \cdot C_{16}$   
 $H_{36}AuBr_3F_5N \cdot C_{22}$   
 $H_{36}AuCl_2F_{10}N \cdot C_{28}$   
 $H_{36}AuCl_2N \cdot C_{16}$   
 $H_{36}AuI_2N \cdot C_{16}$   
 $H_{36}BLiSi_4 \cdot C_{12}$   
 $H_{36}Br_2CuN \cdot C_{16}$   
 $H_{36}Br_3CuP_2 \cdot C_{38}$   
 $H_{36}Br_5Cu_2N_3 \cdot C_{12}$   
 $H_{36}Cl_2CuN \cdot C_{16}$   
 $H_{36}CuI_3P_2 \cdot C_{38}$   
 $H_{36}F_6NNb \cdot C_{16}$   
 $H_{36}F_{11}NNb_2 \cdot C_{16}$   
 $H_{36}GaLiSi_4 \cdot C_{12}$   
 $H_{40}Ag_2Br_4P_2 \cdot C_{48}$   
 $H_{40}Ag_2Cl_4P_2 \cdot C_{48}$   
 $H_{40}As_2Cl_6Re_2 \cdot C_{48}$   
 $H_{40}BCIP_2Pt \cdot C_{24}$   
 $H_{40}Br_3CuN_2 \cdot C_{16}$   
 $H_{40}Br_4CoN_2 \cdot C_{16}$   
 $H_{40}Br_4CuN_2 \cdot C_{16}$   
 $H_{40}Br_4Cu_2N_2 \cdot C_{16}$   
 $H_{40}Br_4N_2Ni \cdot C_{16}$   
 $H_{40}Br_6N_2Th \cdot C_{16}$   
 $H_{40}Br_6N_2Ti \cdot C_{16}$   
 $H_{40}Br_6N_2U \cdot C_{16}$   
 $H_{40}Br_6N_2Zr \cdot C_{16}$   
 $H_{40}Cl_3InN_2 \cdot C_{16}$   
 $H_{40}Cl_6N_2Th \cdot C_{16}$   
 $H_{40}Cl_6N_2Ti \cdot C_{16}$   
 $H_{40}Cl_6N_2U \cdot C_{16}$   
 $H_{40}Cl_6N_2Zr \cdot C_{16}$   
 $H_{40}Cu_2I_4N_2 \cdot C_{16}$   
 $H_{40}Cu_4I_6K_2O_{10} \cdot C_{20}$   
 $H_{40}I_6N_2Ti \cdot C_{16}$   
 $H_{41}AuI_3N \cdot C_{22}$   
 $H_{44}Au_2Br_2 \cdot C_{20}$   
 $H_{45}AlClKS_3 \cdot C_{54}$   
 $H_{45}CuFP_3 \cdot C_{54}$   
 $H_{45}Ge_3Ti \cdot C_{18}$   
 $H_{48}Cl_6LnP_3 \cdot C_{54}$   
 $H_{48}Cl_{10}Co_2Cu_2N_{12} \cdot C_{12}$   
 $H_{54}AgBr_4P_3 \cdot C_{57}$   
 $H_{54}AlP_9 \cdot C_{21}$   
 $H_{54}B_3N_3Si_3 \cdot C_{57}$   
 $H_{54}Br_9Cu_6N_3 \cdot C_{21}$   
 $H_{56}Cu_2I_4N_2 \cdot C_{24}$

$H_{56}Cu_5I_7N_2 \cdot C_{24}$   
 $H_{60}Ag_2As_3Cl_5 \cdot C_{72}$   
 $H_{60}Br_5CuN_3 \cdot C_{24}$   
 $H_{60}Cl_5Cu_2N_3 \cdot C_{24}$   
 $H_{60}CuI_4N_3 \cdot C_{24}$   
 $H_{63}AlP_6Si_3 \cdot C_{24}$   
 $H_{64}Cu_4I_6K_2O_{16} \cdot C_{48}$   
 $H_{72}Cl_3Cu_2N_{18}P_6 \cdot C_{24}$   
 $H_{72}Cu_2I_4N_2 \cdot C_{32}$   
 $H_{80}Cl_{12}Cu_4N_4 \cdot C_{32}$   
 $H_{88}Ag_{31}I_{39}N_8 \cdot C_{32}$   
 $H_{99}Si_9Sn_3Ti \cdot C_{36}$   
 $H_{120}Cu_6I_{12}N_6 \cdot C_{48}$   
 $H_{144}Cu_{36}I_{60}N_{24} \cdot C_{120}$   
 $H_9O_4Zn \cdot F_2$

**Hf****Hf**

Fluorination: 2.11.4.1

Reaction with HF: 2.11.4.1

Reaction with  $F_2$ : 2.9.2.1

Reaction with  $Cl_2$ : 2.9.2.2

Reaction with HX: 2.9.3.2

**Hf\*B<sub>2</sub>****Hf\*Br<sub>4</sub>****Hf\*C****Hf\*Cl<sub>4</sub>****Hf\*F<sub>4</sub>****HfI<sub>4</sub>****HfI<sub>4</sub>**

Reaction with CsI: 2.9.10.1

**HfI<sub>6</sub>\*Cs<sub>2</sub>****HfO<sub>2</sub>****HfO<sub>2</sub>**

Reaction with  $S_2Cl_2$ ,  $PCl_5$ : 2.9.4.5

Reaction with  $X_2$  or  $C-X_2$ : 2.9.4.2

**HfO<sub>3</sub>\*F<sub>3</sub>H<sub>4</sub>****HfO<sub>3</sub>\*F<sub>4</sub>H<sub>6</sub>****Hf<sub>2</sub>O\*F<sub>6</sub>****Hf<sub>2</sub>O<sub>2</sub>\*F<sub>8</sub>****Hg****Hg**

Fluorination: 2.11.4.3

Formation from  $Hg_2F_2$ : 2.8.20.2

Formation from  $Hg_2Cl_2$ : 2.8.20.1, 2.8.20.2

Formation from  $Hg_2I_2$ : 2.8.20.2

Formation from  $Br_2$ : 2.8.20.2

Reaction with  $FeCl_3$ : 2.8.21.3

Reaction with  $Hg[SO_4]$  and  $NaCl$ : 2.8.21.3

Reaction with  $HgBr_2$ : 2.8.21.2

Reaction with  $HgCl_2$ : 2.8.21.2

Reaction with  $\text{HgI}_2$ : 2.8.21.2  
 Reaction with  $\text{PBr}_3$ : 2.8.14.4  
 Reaction with  $\text{PCl}_5$ : 2.8.14.4  
 Reaction with  $\text{PI}_3$ : 2.8.14.4  
 Reaction with  $\text{OSBr}_2$ : 2.8.14.4  
 Reaction with  $\text{OSCl}_2$ : 2.8.14.4  
 Reaction with  $\text{O}_2\text{SCl}_2$ : 2.8.14.4  
 Reaction with  $\text{S}_2\text{Cl}_2$ : 2.8.14.4  
 Reaction with  $\text{ONCl}$ : 2.8.14.4  
 Reaction with  $\text{ONF} \cdot 3 \text{ HF}$ : 2.8.14.4  
 Reaction with  $\text{F}_2$ : 2.8.14.1  
 Reaction with  $\text{ClF}_3$ : 2.8.14.4  
 Reaction with  $\text{KI}_3$ : 2.8.21.3  
 Reaction with  $\text{NaCl}$ ,  $\text{MnO}_2$ ,  $\text{H}_2\text{SO}_4$ :  
 2.8.21.3  
 Reaction with  $\text{IBr}$ : 2.8.14.4  
 Reaction with  $\text{HBr}$ : 2.8.14.3  
 Reaction with  $\text{Br}_2$ : 2.8.14.1  
 Reaction with  $\text{CBr}_4$ : 2.8.21.3  
 Reaction with  $\text{HCl}$ : 2.8.14.2, 2.8.14.3  
 Reaction with  $\text{HCl}$  and  $\text{O}_2$ : 2.8.21.3  
 Reaction with  $\text{Cl}_2$ : 2.8.14.1, 2.8.21.3  
 Reaction with  $\text{CCl}_4$ : 2.8.21.3  
 Reaction with  $\text{I}_2$ : 2.8.14.1, 2.8.21.3  
 Reaction with  $\text{Cl}_4$ : 2.8.21.3

$\text{Hg}^*\text{AgF}_4$   
 $\text{Hg}^*\text{BaBr}_4$   
 $\text{Hg}^*\text{BrCl}$   
 $\text{Hg}^*\text{BrF}$   
 $\text{Hg}^*\text{Br}_2$   
 $\text{Hg}^*\text{Br}_2\text{Cl}_3\text{Cs}_3$   
 $\text{Hg}^*\text{Br}_3\text{Cs}$   
 $\text{Hg}^*\text{Br}_4\text{Cs}_2$   
 $\text{Hg}^*\text{Br}_5\text{Cs}_3$   
 $\text{Hg}^*\text{C}_2\text{H}_3\text{Cl}$   
 $\text{Hg}^*\text{C}_4\text{H}_6$   
 $\text{Hg}^*\text{C}_5\text{H}_5\text{Cl}$   
 $\text{Hg}^*\text{C}_6\text{H}_5\text{Br}$   
 $\text{Hg}^*\text{C}_6\text{H}_5\text{Cl}$   
 $\text{Hg}^*\text{C}_7\text{H}_5\text{BrCl}_2$   
 $\text{Hg}^*\text{C}_7\text{H}_5\text{Br}_2\text{Cl}$   
 $\text{Hg}^*\text{C}_7\text{H}_5\text{Cl}_3$   
 $\text{Hg}^*\text{C}_{12}\text{H}_{10}$   
 $\text{Hg}^*\text{C}_{36}\text{F}_{30}\text{Ge}_2$   
 $\text{Hg}^*\text{C}_{84}\text{H}_{12}\text{CrF}_{60}\text{Ge}_4$   
 $\text{Hg}^*\text{Cl}_2$   
 $\text{Hg}^*\text{Cl}_4\text{Cs}_2$   
 $\text{Hg}^*\text{F}_2$   
 $\text{HgH}_4\text{O}_2^*\text{F}_2$   
 $\text{HgI}^*\text{Br}$   
 $\text{HgIN}^*\text{CH}_6\text{Br}$   
 $\text{HgIN}^*\text{CH}_6\text{Br}_2$

**HgI<sub>2</sub>****HgI<sub>2</sub>**

Formation from  $\text{Hg}[\text{OAc}]_2$  and  $\text{I}_2$ :  
 2.8.17.3  
 Formation from  $\text{Hg}[\text{CH}_3\text{C}(\text{O})\text{O}]_2$  and  
 $\text{CH}_3\text{I}$ : 2.8.17.3  
 Formation from  $\text{HgCl}_2$  and  $\text{KI}$ : 2.8.18  
 Formation from  $\text{HgCl}_2$  and  $\text{I}_2$ : 2.8.18  
 Formation from  $\text{HgCl}_2$  and  $\text{HI}$ : 2.8.18  
 Formation from  $\text{Hg}$  and  $\text{AlI}_3$ : 2.8.14.5  
 Formation from  $\text{Hg}$  and  $\text{PI}_3$ : 2.8.14.4  
 Formation from  $\text{Hg}$  and  $\text{I}_2$ : 2.8.14.1  
 Formation from  $\text{HgO}$  and  $\text{I}_2$ : 2.8.15.1,  
 2.8.20.1  
 Formation from  $\text{HgS}$  and  $\text{I}_2$ : 2.8.16.1  
 Formation from  $\text{Hg}_2[\text{NO}_3]_2$  and  $\text{I}_2$ :  
 2.8.20.1  
 Formation from  $\text{Hg}_2\text{Br}_2$  and  $\text{I}_2$ : 2.8.20.1  
 Formation from  $\text{Hg}_2\text{Cl}_2$  and  $\text{I}_2$ : 2.8.20.1  
 Formation from  $\text{Hg}_2\text{I}_2$ : 2.8.20.2  
 Formation from  $\text{Hg}_2\text{I}_2$  and  $\text{HI}$ : 2.8.20.1  
 Formation from  $\text{CH}_3\text{I}$  and  $\text{HgCl}_2$ :  
 2.8.18  
 Reaction with  $\text{Hg}[\text{CH}_2\text{C}(\text{O})\text{C}_6\text{H}_5]_2$ :  
 2.8.23.2  
 Reaction with  $\text{Hg}$ : 2.8.21.2  
 Reaction with  $\text{Mo}(\text{CO})_6$ ,  $\text{W}(\text{CO})_6$ :  
 2.9.15.1.1  
 Reaction with  $\text{R}_2\text{NBX}-\text{NR}'\text{BX}_2$ :  
 2.6.8.3  
 Reaction with  $\text{Zn}$ : 2.8.14.5  
 Reaction with  $\text{Cl}_2$ : 2.8.18

**I<sub>2</sub>Hg**

Formation from  $\text{KI}$  and  $\text{Hg}[\text{ClO}_4]_2$ :  
 2.8.17.2

**HgI<sub>2</sub>\*BrH****HgI<sub>2</sub>\*ClH****HgI<sub>2</sub>N<sub>2</sub>\*C<sub>2</sub>H<sub>12</sub>Br<sub>2</sub>****HgI<sub>2</sub>N<sub>2</sub>\*C<sub>2</sub>H<sub>12</sub>Cl<sub>2</sub>****HgI<sub>2</sub>O<sub>6</sub>****Hg[IO<sub>3</sub>]<sub>2</sub>**

Formation from  $\text{HgO}$  and  $\text{I}_2$ : 2.8.15.1

**HgI<sub>2</sub>Rb<sub>2</sub>\*Br<sub>2</sub>****HgI<sub>3</sub>\*Cs****HgI<sub>3</sub>K****K[HgI<sub>3</sub>]**

Formation: 2.8.22

**HgI<sub>3</sub>KO\*H<sub>2</sub>****HgI<sub>3</sub>NO\*H<sub>6</sub>****HgI<sub>3</sub>Rb****Rb[HgI<sub>3</sub>]**

Formation: 2.8.22



- $\text{HgI}_4 \cdot \text{Ag}_2$   
 $\text{HgI}_4 \cdot \text{Cd}$   
 $\text{HgI}_4 \cdot \text{Cs}_2$   
 $\text{HgI}_4 \cdot \text{Cu}_2$   
 $\text{HgI}_4 \cdot \text{H}_2$   
 $\text{HgI}_4\text{K}_2$   
 $\text{K}_2[\text{HgI}_4]$   
 Formation: 2.8.22  
 $\text{HgI}_4\text{N}_2 \cdot \text{H}_8$   
 $\text{HgI}_4\text{N}_2 \cdot \text{H}_{10}$   
 $\text{HgI}_4\text{Na}_2$   
 $\text{Na}_2[\text{HgI}_4]$   
 Formation from melt and solution:  
 2.8.22  
 $\text{HgI}_4\text{Na}_2\text{O}_4 \cdot \text{H}_8$   
 $\text{HgI}_4\text{Rb}_2$   
 $\text{Rb}_2[\text{HgI}_4]$   
 Formation: 2.8.22  
 $\text{HgI}_4\text{Zn}$   
 $\text{Zn}[\text{HgI}_4]$   
 Formation: 2.8.22  
 $\text{HgI}_5 \cdot \text{Cs}_3$   
 $\text{HgI}_6\text{Rb}_4$   
 $\text{Rb}_4[\text{HgI}_6]$   
 Formation from melt: 2.8.22  
 $\text{HgK} \cdot \text{Br}_3$   
 $\text{HgK} \cdot \text{Cl}_3$   
 $\text{HgK} \cdot \text{F}_3$   
 $\text{HgKO} \cdot \text{Br}_3\text{H}_2$   
 $\text{HgKO} \cdot \text{Cl}_3\text{H}_2$   
 $\text{HgKO}_2 \cdot \text{Br}_3\text{H}_4$   
 $\text{HgKO}_2 \cdot \text{Cl}_3\text{H}_4$   
 $\text{HgK}_2 \cdot \text{Br}_2\text{Cl}_2$   
 $\text{HgK}_2 \cdot \text{Br}_4$   
 $\text{HgK}_2 \cdot \text{Cl}_4$   
 $\text{HgK}_2\text{O} \cdot \text{Cl}_4\text{H}_2$   
 $\text{HgMnO}_3 \cdot \text{C}_8\text{H}_4\text{Cl}$   
 $\text{HgMoO}_3 \cdot \text{C}_8\text{H}_5\text{Cl}$   
 $\text{HgMo}_2\text{O}_6 \cdot \text{C}_{16}\text{H}_{10}$   
 $\text{HgN} \cdot \text{BrCl}_2\text{H}_4$   
 $\text{HgN} \cdot \text{Br}_3\text{H}_4$   
 $\text{HgN} \cdot \text{ClH}_2$   
 $\text{HgN} \cdot \text{Cl}_3\text{H}_4$   
 $\text{HgN}_2 \cdot \text{Br}_2\text{Cl}_2\text{H}_8$   
 $\text{HgN}_2 \cdot \text{Br}_4\text{H}_8$   
 $\text{HgN}_2 \cdot \text{C}_{10}\text{H}_{12}\text{F}_4$   
 $\text{HgN}_2 \cdot \text{Cl}_4\text{H}_9$   
 $\text{HgN}_2\text{O} \cdot \text{Cl}_8\text{H}_{10}$   
 $\text{HgN}_2\text{O}_2 \cdot \text{C}_{10}\text{H}_{16}\text{F}_4$   
 $\text{HgN}_2\text{O}_6$   
 $\text{Hg}[\text{NO}_3]_2$   
 Reaction with  $\text{X}_2$ : 2.8.17.3  
 Reaction with  $\text{CH}_3\text{C}(\text{O})\text{Cl}$ : 2.8.17.3  
 Reaction with  $\text{KBr}$ : 2.8.17.2  
 Reaction with  $\text{HCl}$ : 2.8.17.1  
 $\text{HgN}_4 \cdot \text{Br}_6\text{H}_{16}$   
 $\text{HgN}_4 \cdot \text{Cl}_6\text{H}_{16}$   
 $\text{HgNa} \cdot \text{Br}_3$   
 $\text{HgNaO}_2 \cdot \text{Br}_3\text{H}_4$   
 $\text{HgNaO}_2 \cdot \text{Cl}_3\text{H}_4$   
 $\text{HgNa}_2 \cdot \text{Br}_2\text{Cl}_2$   
 $\text{HgNa}_2 \cdot \text{Br}_4$   
 $\text{HgO}$   
 $\text{HgO}$   
 Formation from  $\text{HgF} \cdot 2 \text{H}_2\text{O}$  and heat:  
 2.8.19  
 Reaction with  $\text{BBr}_3$ : 2.8.15.3, 2.8.20.1  
 Reaction with  $\text{SF}_4$ : 2.11.4.3  
 Reaction with  $\text{TiCl}_4$ : 2.8.15.3  
 Reaction with  $\text{C}_6\text{H}_5\text{C}(\text{O})\text{Cl}$ : 2.8.15.3  
 Reaction with  $\text{NaCl}$ : 2.8.15.3  
 Reaction with  $\text{HF}(\text{g})$ : 2.8.15.2  
 Reaction with  $\text{HBr}$ : 2.8.15.2  
 Reaction with  $\text{Br}_2$ : 2.8.15.1  
 Reaction with  $\text{HCl}$ : 2.8.15.2  
 Reaction with  $\text{Cl}_2$ : 2.8.15.1  
 Reaction with  $\text{I}_2$ : 2.8.15.1, 2.8.20.1  
 Reaction with  $\text{HF}$ : 2.11.4.3  
 Reaction with  $\text{py-HF}$ : 2.11.4.3  
 Reaction with  $\text{aq HF}$ : 2.11.4.3, 2.8.15.2  
 $\text{HgO} \cdot \text{FH}$   
 $\text{HgO}_2 \cdot \text{C}_{16}\text{H}_{14}$   
 $\text{HgO}_2 \cdot \text{F}_2\text{H}_4$   
 $\text{HgO}_3 \cdot \text{C}_9\text{H}_2\text{ClCr}$   
 $\text{HgO}_4 \cdot \text{C}_4\text{H}_6$   
 $\text{HgO}_4\text{S}$   
 $\text{HgSO}_4$   
 Formation from  $\text{Hg}_2\text{Br}_2$  and  $\text{SO}_3$ :  
 2.8.20.1  
 Reaction with  $\text{Hg}[\text{NO}_3]_2$ : 2.8.17.1  
 Reaction with  $\text{Hg}$ , and  $\text{NaCl}$ : 2.8.21.3  
 Reaction with  $\text{NaBr}$ : 2.8.17.2  
 Reaction with  $\text{NaCl}$ : 2.8.17.2  
 $\text{HgO}_6 \cdot \text{Br}_2$   
 $\text{HgO}_6 \cdot \text{Cl}_2$   
 $\text{HgO}_8 \cdot \text{Cl}_2$   
 $\text{HgRb} \cdot \text{Cl}_3$   
 $\text{HgRb}_2 \cdot \text{Cl}_4$   
 $\text{HgS}$   
 $\text{HgS}$   
 Formation from  $\text{HgCl}_2 \cdot 2 \text{HgS}$ : 2.8.21.2  
 Reaction with  $\text{AlCl}_3$ : 2.8.16.2  
 Reaction with  $\text{Br}_2$ : 2.8.16.1  
 Reaction with  $\text{Cl}_2$ : 2.8.16.1

- Reaction with  $I_2$ : 2.8.16.1  
 $HgSe \cdot C_4H_3Cl$   
 $HgSr \cdot Br_4$   
 $Hg_2 \cdot Br_2$   
 $Hg_2 \cdot C_4H_5Cl_2$   
 $Hg_2 \cdot C_{10}H_8Cl_2Fe$   
 $Hg_2 \cdot C_{108}CoF_{90}Ge_6$   
 $Hg_2 \cdot Cl_2$   
 $Hg_2 \cdot F_2$   
 $Hg_2I_2$   
 $Hg_2I_2$   
 Disproportionation: 2.8.20.2  
 Formation from  $HgI_2$  and  $Hg$ : 2.8.21.2  
 Formation from  $Hg$  and  $KI_3$ : 2.8.21.3  
 Formation from  $Hg$  and  $I_2$ : 2.8.21.3  
 Formation from  $Hg$  and  $Cl_4$ : 2.8.21.3  
 Formation from  $Hg_2[NO_3]_2$  and  $KI$ :  
 2.8.21.1  
 Formation from  $Hg_2[NO_3]_2$  and  $EtI$ :  
 2.8.21.1  
 Formation from  $Hg_2Br_2$  and  $KI$ :  
 2.8.21.1  
 Formation from  $Hg_2Cl_2$  and  $KI$ :  
 2.8.21.1  
 Formation from  $Hg_2O$  and  $KI$ : 2.8.21.1  
 Formation from  $SnCl_2$ ,  $HgCl_2$  and  $KI$ :  
 2.8.21.2  
 Reaction with  $SO_3$ : 2.8.20.1  
 Reaction with  $HI$ : 2.8.20.1  
 $Hg_2I_5 \cdot Cs$   
 $Hg_2I_5N \cdot H_4$   
 $Hg_2I_7Rb_3$   
 $Rb_3[Hg_2I_7]$   
 Formation from melt: 2.8.22  
 $Hg_2K \cdot Br_5$   
 $Hg_2MgO_6 \cdot Cl_6H_{12}$   
 $Hg_2Mn \cdot C_{108}F_{90}Ge_6$   
 $Hg_2N_2O_6$   
 $Hg_2[NO_3]_2$   
 Reaction with  $EtI$ : 2.8.21.1  
 Reaction with  $KBr$ : 2.8.21.1  
 Reaction with  $KI$ : 2.8.21.1  
 Reaction with  $NaCl$ : 2.8.21.1  
 Reaction with  $NaF$ : 2.8.21.1  
 Reaction with  $HCl$ : 2.8.20.1  
 Reaction with  $I_2$ : 2.8.20.1  
 $Hg_2Ni \cdot C_{108}F_{90}Ge_6$   
 $Hg_2O$   
 $Hg_2O$   
 Reaction with  $HCl$ : 2.8.21.1  
 Reaction with  $KI$ : 2.8.21.1  
 $Hg_2O \cdot Cl_2$
- $Hg_2O_3 \cdot C$   
 $Hg_2O_6 \cdot BaCl_6H_{12}$   
 $Hg_2Ti_2 \cdot C_{108}H_{20}F_{90}Ge_6$   
 $Hg_3I_8 \cdot Cs_2$   
 $Hg_3O_2 \cdot BaH_4Cl_8$   
 $Hg_3S_2 \cdot Cl_2$   
 $Hg_3SrO_2 \cdot Cl_8H_4$   
**Ho**  
**Ho**  
 Reaction with  $HX$ : 2.9.14.1.1  
 $Ho \cdot Cl_3$   
 $HoS \cdot Br$   
 $HoS \cdot F$   
 $I \cdot Ag$   
 $I \cdot Al$   
 $I \cdot AlH_2$   
 $I \cdot Au$   
 $I \cdot AuF_{12}$   
 $I \cdot B_2H_5$   
 $I \cdot B_6H_9$   
 $I \cdot Br$   
 $I \cdot BrHg$   
 $I \cdot CH_3$   
 $I \cdot C_2H_5$   
 $I \cdot C_2H_6Ga$   
 $I \cdot C_4H_{10}Al$   
 $I \cdot C_6F_5$   
 $I \cdot C_6H_5Cl_2$   
 $I \cdot C_{10}H_{16}As_4Au$   
 $I \cdot C_{18}H_{15}AsAu$   
 $I \cdot Cl$   
 $I \cdot ClCu$   
 $I \cdot Cl_3$   
 $I \cdot Cs$   
 $I \cdot Cu$   
 $I \cdot F_3$   
 $I \cdot F_5$   
 $I \cdot F_7$   
 $I \cdot Ga$   
 $I \cdot H$   
 $IIn \cdot C_{12}H_{10}$   
**IK**  
**KI**  
 Reaction with  $Hg[ClO_4]_2$ : 2.8.17.2  
 Reaction with  $HgCl_2$ : 2.8.18  
 Reaction with  $Hg_2[NO_3]_2$ : 2.8.21.1  
 Reaction with  $Hg_2Cl_2$ : 2.8.21.1  
 Reaction with  $CdSO_4$ : 2.8.17.2  
**ILaS**  
**LaSI**  
 Formation: 2.9.14.1.1  
**ILi**  
**LiI**  
 Formation: 2.7.4

IMnO<sub>5</sub>\*C<sub>5</sub>  
 IMoO<sub>3</sub>\*C<sub>8</sub>H<sub>5</sub>  
 IMoS

MoSI

Formation: 2.9.14.1.2

IN\*CH<sub>6</sub>BrHg  
 IN\*CH<sub>6</sub>Br<sub>2</sub>Hg  
 IN\*C<sub>5</sub>H<sub>6</sub>BrCu  
 IN\*C<sub>12</sub>H<sub>28</sub>Br<sub>2</sub>Cd  
 IN\*C<sub>12</sub>H<sub>28</sub>CdCl<sub>2</sub>  
 IN<sub>2</sub>\*C<sub>4</sub>H<sub>12</sub>B  
 IN<sub>2</sub>P\*C<sub>9</sub>H<sub>25</sub>B  
 INaO<sub>3</sub>

Na[IO<sub>3</sub>]

Formation: 2.7.4

INbO

NbOI

Formation: 2.9.14.1.2

INi\*C<sub>6</sub>F<sub>5</sub>  
 IO\*Ag<sub>2</sub>FH<sub>2</sub>

IO<sub>2</sub>W

WO<sub>2</sub>I

Formation: 2.9.11.3

IO<sub>3</sub>S\*C<sub>9</sub>H<sub>10</sub>B<sub>2</sub>FFe  
 IO<sub>3</sub>W\*C<sub>8</sub>H<sub>5</sub>  
 IO<sub>3</sub>Re\*C<sub>5</sub>  
 IO<sub>5</sub>Tc\*C<sub>5</sub>

IOs

OsI

Formation: 2.9.4.3

IP\*C<sub>6</sub>H<sub>15</sub>Au

IPd\*At

IPt\*F<sub>10</sub>

IS\*Al

IS\*Ce

IS\*Gd

ISSm

SmSI

Formation: 2.9.14.1.1

IS<sub>2</sub>\*C<sub>4</sub>H<sub>10</sub>Ga

ISe\*Al

ISe\*Cr

ISe<sub>3</sub>\*Cu

ISi<sub>2</sub>Tl\*C<sub>6</sub>H<sub>18</sub>

ISn\*C<sub>6</sub>H<sub>15</sub>

ITe\*Al

ITe\*Au

ITe<sub>2</sub>\*Au

ITI

TII

Formation: 2.6.14.2

Reaction with HX: 2.6.11.2

ITl\*C<sub>2</sub>H<sub>6</sub>

ITl\*C<sub>4</sub>H<sub>10</sub>

IXe\*F<sub>7</sub>

I<sub>2</sub>

I<sub>2</sub>

Reaction with LiAlH<sub>4</sub>: 2.6.5.1

Reaction with Al, Ga, In Tl: 2.6.2.1

Reaction with B<sub>10</sub>H<sub>14</sub>: 2.6.5.1

Reaction with [B<sub>12</sub>H<sub>12</sub>]<sup>2-</sup>: 2.6.4.1

Reaction with Cd[CH<sub>3</sub>C(O)O]<sub>2</sub>:

2.8.17.3

Reaction with Cd: 2.8.14.1

Reaction with η<sup>5</sup>-CpMoNO(CO)<sub>2</sub>:

2.9.15.1.2

Reaction with I<sub>2</sub>Fe(CO)<sub>4</sub>: 2.9.6

Reaction with Fe(CO)<sub>5</sub>, Ru(CO)<sub>5</sub>:

2.9.15.1.1

Reaction with Group IIIB-Group IVB  
bonds: 2.6.11.1

Reaction with Hg[OAc]<sub>2</sub>: 2.8.17.3

Reaction with HgCl<sub>2</sub>: 2.8.18

Reaction with Hg: 2.8.14.1, 2.8.21.3

Reaction with HgO: 2.8.15.1, 2.8.20.1

Reaction with HgS: 2.8.16.1

Reaction with Hg<sub>2</sub>[NO<sub>3</sub>]<sub>2</sub>: 2.8.20.1

Reaction with Hg<sub>2</sub>Br<sub>2</sub>: 2.8.20.1

Reaction with Hg<sub>2</sub>Cl<sub>2</sub>: 2.8.20.1

Reaction with Mn<sub>2</sub>(CO)<sub>10</sub>, Tc<sub>2</sub>(CO)<sub>10</sub>,

Re<sub>2</sub>(CO)<sub>10</sub>: 2.9.15.1.1

Reaction with MOH: 2.7.4

Reaction with M(CO)<sub>6</sub>: 2.9.6

Reaction with MH: 2.7.4

Reaction with Nb-Nb<sub>2</sub>O<sub>5</sub>: 2.9.11.3

Reaction with R<sub>2</sub>BSeH: 2.6.7.1

Reaction with RGa(SR)<sub>2</sub>: 2.6.7.1

Reaction with R<sub>3</sub>B...R<sub>3</sub>Tl: 2.6.10.1

Reaction with ZnS: 2.8.16.1

Reaction with TaS<sub>2</sub>: 2.9.5

Reaction with group-IA and -IIA me-  
tals: 2.7.2

Reaction with Zn: 2.8.14.1

Reaction with metal carbonyl anions:  
2.9.15.1.2

Reaction with transition-metal oxides:  
2.9.4.1

Reaction with transition-metals: 2.9.2.4

I<sub>2</sub>\*AlH

I<sub>2</sub>\*Ba

I<sub>2</sub>\*Be

I<sub>2</sub>\*BrHHg

I<sub>2</sub>\*CH<sub>3</sub>Ga

I<sub>2</sub>\*C<sub>2</sub>H<sub>5</sub>Al

- $I_2 \cdot C_4H_{12}Au_2$   
 $I_2 \cdot C_8H_{20}Au_2$   
 $I_2 \cdot C_{20}H_{32}As_4Au_2$   
 $I_2 \cdot C_{26}H_{26}AsAu$   
 $I_2 \cdot Ca$   
 $I_2 \cdot Cd$   
 $I_2 \cdot ClHHg$   
 $I_2 \cdot Cl_3CsCu_4$   
 $I_2 \cdot Co$   
 $I_2 \cdot Cr$   
 $I_2 \cdot Cu$   
 $I_2 \cdot Fe$   
 $I_2 \cdot Hg$   
 $I_2 \cdot Hg_2$   
 $I_2 \cdot K \cdot Cu$   
 $I_2KN_2 \cdot C_2Au$   
 $I_2KO_6 \cdot C_{12}H_{24}Cu$   
 $I_2K_2 \cdot CdCl_2$   
 $I_2K_5N_{10}O_2 \cdot C_{10}H_4Au_5$   
 $I_2Mg$   
 $MgI_2$   
 Formation: 2.7.2, 2.7.3.1  
 $I_2Mn$   
 $MnI_2$   
 Formation: 2.9.2.4, 2.9.4.8, 2.9.7  
 $I_2Mo$   
 $MoI_2$   
 Formation: 2.9.4.8  
 $I_2Mo_2O_8 \cdot C_8$   
 $I_2N \cdot C_4H_{10}B$   
 $I_2N \cdot C_4H_{12}Ag$   
 $I_2N \cdot C_6H_8Cu$   
 $I_2N \cdot C_8H_{20}Au$   
 $I_2N \cdot C_8H_{20}Cu$   
 $I_2N \cdot C_{12}H_{28}BrCd$   
 $I_2N \cdot C_{12}H_{28}CdCl$   
 $I_2N \cdot C_{16}H_{36}Au$   
 $I_2N_2 \cdot C_2H_{12}Br_2Hg$   
 $I_2N_2 \cdot C_2H_{12}Cl_2Hg$   
 $I_2N_2 \cdot C_{10}H_{10}Au_2$   
 $I_2N_2S_4 \cdot C_{10}H_{20}Au_2$   
 $I_2N_4 \cdot C_4H_{16}Ag_2Br_2Cu$   
 $I_2N_8 \cdot C_{12}H_{16}Cu$   
 $I_2NbO$   
 $NbOI_2$   
 Formation: 2.9.11.3  
 $I_2NbS_2$   
 $NbS_2I_2$   
 Formation: 2.9.14.1.2  
 $I_2NbSe_2$   
 $NbSe_2I_2$   
 Formation: 2.9.14.1.2  
 $I_2Ni$   
 $NiI_2$   
 Electrochemical formation: 2.9.3.7  
 Formation: 2.9.3.8, 2.9.4.8, 2.9.7  
 $I_2O_2W$   
 $WO_2I_2$   
 Formation: 2.9.11.3  
 $I_2O_2Zn \cdot H_4$   
 $I_2O_{2.5} \cdot Ag_7F_5H_5$   
 $I_2O_3S \cdot C_9H_{10}B_2Fe$   
 $I_2O_3W \cdot F_{10}$   
 $I_2O_4 \cdot C_4Fe$   
 $I_2O_4W \cdot C_4$   
 $I_2O_4Zn \cdot H_8$   
 $I_2O_6 \cdot Hg$   
 $I_2O_8 \cdot C_8Fe_2$   
 $I_2O_8Tc_2 \cdot C_8$   
 $I_2O_8W_2 \cdot C_8$   
 $I_2Os$   
 $OsI_2$   
 Formation: 2.9.4.3  
 $I_2P \cdot C_6H_{15}AuCl$   
 $I_2Pd$   
 $PdI_2$   
 Formation: 2.9.11.1  
 Reaction with elemental Se: 2.9.14.3  
 $I_2Ra$   
 $RaI_2$   
 Formation: 2.7.2  
 $I_2Rb_2 \cdot Br_2Hg$   
 $I_2Re$   
 $ReI_2$   
 Formation: 2.9.4.2  
 $I_2S \cdot CH_3Ga$   
 $I_2Si \cdot C_2H_6$   
 $I_2Sr$   
 $SrI_2$   
 Formation: 2.7.2  
 $I_2Ti$   
 $TiI_2$   
 Formation: 2.9.2.4  
 $I_2Tl \cdot At$   
 $I_2V$   
 $VI_2$   
 Formation: 2.9.3.7, 2.9.4.8  
 $I_2Zn$   
 $ZnI_2$   
 Formation from ZnO and HI: 2.8.15.2  
 Formation from ZnS and  $I_2$ : 2.8.16.1  
 Formation from Zn and  $AlI_3$ : 2.8.14.5  
 Formation from Zn and  $I_2$ : 2.8.14.1  
 Formation from Zn and HI: 2.8.14.3

- Formation from  $\text{BaI}_2$  and  $\text{Zn}[\text{SO}_4]$ :  
 2.8.17.2  
 Stability: 2.8.19
- $\text{I}_3^* \text{AgCs}_2$   
 $\text{I}_3^* \text{Ag}_2\text{Cs}$   
 $\text{I}_3^* \text{Al}$   
 $\text{I}_3^* \text{As}$   
 $\text{I}_3^* \text{AtCs}$   
 $\text{I}_3^* \text{Au}$   
 $\text{I}_3^* \text{B}$   
 $\text{I}_3^* \text{C}_6\text{H}_{15}\text{Al}_2$   
 $\text{I}_3^* \text{C}_{10}\text{H}_{16}\text{As}_2\text{Au}$   
 $\text{I}_3^* \text{C}_{18}\text{H}_{15}\text{AsAu}$   
 $\text{I}_3^* \text{CdCs}$   
 $\text{I}_3^* \text{Cr}$   
 $\text{I}_3^* \text{Cs}$   
 $\text{I}_3^* \text{CsCu}$   
 $\text{I}_3^* \text{CsHg}$   
 $\text{I}_3^* \text{Ga}$   
 $\text{I}_3\text{In}$   
 $\text{InI}_3$   
 Formation: 2.6.2.1
- $\text{I}_3\text{Ir}$   
 $\text{IrI}_3$   
 Formation: 2.9.4.3
- $\text{I}_3\text{K}$   
 $\text{KI}_3$   
 Reaction with Hg: 2.8.21.3
- $\text{I}_3\text{K}^* \text{Cd}$   
 $\text{I}_3\text{K}^* \text{Hg}$   
 $\text{I}_3\text{KO}^* \text{H}_2\text{Hg}$   
 $\text{I}_3\text{K}_2^* \text{Ag}$   
 $\text{I}_3\text{Mo}$   
 $\text{MoI}_3$   
 Formation: 2.9.2.4, 2.9.6
- $\text{I}_3\text{Mo}_2\text{O}_6^* \text{F}_{15}$   
 $\text{I}_3\text{Mo}_2\text{S}_5$   
 $\text{Mo}_2\text{S}_5\text{I}_3$   
 Formation: 2.9.14.3
- $\text{I}_3\text{N}^* \text{C}_4\text{H}_{10}\text{Ag}_2$   
 $\text{I}_3\text{N}^* \text{C}_4\text{H}_{12}\text{Ag}_2$   
 $\text{I}_3\text{N}^* \text{C}_4\text{H}_{12}\text{Cu}_2$   
 $\text{I}_3\text{N}^* \text{C}_{22}\text{H}_{41}\text{Au}$   
 $\text{I}_3\text{NO}^* \text{H}_6\text{Hg}$   
 $\text{I}_3\text{NaO}_3\text{Zn}^* \text{H}_6$   
 $\text{I}_3\text{Nb}$   
 $\text{NbI}_3$   
 Formation: 2.9.4.8
- $\text{I}_3\text{NbO}$   
 $\text{NbOI}_3$   
 Formation: 2.9.11.3
- $\text{I}_3\text{Nd}$   
 $\text{NdI}_3$   
 Formation: 2.9.7
- $\text{I}_3\text{O}^* \text{CdCsH}_2$   
 $\text{I}_3\text{O}_5\text{V}_2^* \text{F}_{21}$   
 $\text{I}_3\text{P}$   
 $\text{PI}_3$   
 Reaction with Hg: 2.8.14.4
- $\text{I}_3\text{P}^* \text{C}_6\text{H}_{15}\text{Au}$   
 $\text{I}_3\text{P}^* \text{C}_{19}\text{H}_{18}\text{Cu}_2$   
 $\text{I}_3\text{P}_2^* \text{C}_{38}\text{H}_{36}\text{Ag}$   
 $\text{I}_3\text{P}_2^* \text{C}_{38}\text{H}_{36}\text{Cu}$   
 $\text{I}_3\text{Pd}_2\text{Se}$   
 $\text{Pd}_2\text{SeI}_3$   
 Formation: 2.9.14.3
- $\text{I}_3\text{Rb}^* \text{Hg}$   
 $\text{I}_3\text{Re}$   
 $\text{ReI}_3$   
 Formation: 2.9.3.3
- $\text{I}_3\text{S}^* \text{C}_3\text{H}_9\text{Cu}_2$   
 $\text{I}_3\text{Sm}$   
 $\text{SmI}_3$   
 Formation: 2.9.7
- $\text{I}_3\text{Ti}$   
 $\text{TiI}_3$   
 Formation: 2.9.2.4
- $\text{I}_3\text{Tl}$   
 $\text{TlI}_3$   
 Formation: 2.6.2.1, 2.6.14.2
- $\text{I}_3\text{V}$   
 $\text{VI}_3$   
 Formation: 2.9.2.4
- $\text{I}_3\text{W}$   
 $\text{WI}_3$   
 Formation: 2.9.6
- $\text{I}_4^* \text{Ag}_2\text{Hg}$   
 $\text{I}_4^* \text{B}_2$   
 $\text{I}_4^* \text{C}$   
 $\text{I}_4^* \text{C}_{19}\text{H}_{18}\text{AsCu}_3$   
 $\text{I}_4^* \text{CdCs}_2$   
 $\text{I}_4^* \text{CdHg}$   
 $\text{I}_4^* \text{Cs}_2\text{Hg}$   
 $\text{I}_4^* \text{Cu}_2\text{Hg}$   
 $\text{I}_4^* \text{H}_2\text{Hg}$   
 $\text{I}_4^* \text{Hf}$   
 $\text{I}_4\text{K}_2^* \text{Cd}$   
 $\text{I}_4\text{K}_2^* \text{Hg}$   
 $\text{I}_4\text{N}^* \text{C}_8\text{H}_{20}\text{Au}$   
 $\text{I}_4\text{N}^* \text{C}_{12}\text{H}_{28}\text{Cu}_3$   
 $\text{I}_4\text{N}^* \text{C}_{16}\text{H}_{36}\text{Ag}_3$   
 $\text{I}_4\text{N}_2^* \text{C}_{16}\text{H}_{40}\text{Cu}_2$   
 $\text{I}_4\text{N}_2^* \text{C}_{24}\text{H}_{36}\text{Cu}_2$   
 $\text{I}_4\text{N}_2^* \text{C}_{32}\text{H}_{72}\text{Cu}_2$   
 $\text{I}_4\text{N}_2^* \text{H}_8\text{Hg}$   
 $\text{I}_4\text{N}_2^* \text{H}_{10}\text{Hg}$

- $I_4N_2O_2 \cdot CdH_{12}$   
 $I_4N_2Zn \cdot H_8$   
 $I_4N_3 \cdot C_{24}H_{60}Cu$   
 $I_4Na_2 \cdot Hg$   
 $I_4Na_2O_4 \cdot H_8Hg$   
 $I_4Na_2O_6 \cdot CdH_{12}$   
 $I_4O_5 \cdot BaCdH_{10}$   
 $I_4O_8Sr \cdot Ag_2H_{16}$   
 $I_4O_8Sr \cdot CdH_{16}$   
 $I_4Pt$   
 $PtI_4$   
 Formation: 2.9.2.4  
 $I_4Rb_2 \cdot Hg$   
 $I_4Re$   
 $ReI_4$   
 Formation: 2.9.3.3  
 $I_4S \cdot C_3H_9Ga$   
 $I_4SeTi_2$   
 $Ti_2SeI_4$   
 Formation: 2.6.16  
 $I_4Si$   
 $SiI_4$   
 Formation: 2.7.2  
 Reaction with  $Mo(CO)_6$ ,  $W(CO)_6$ :  
 2.9.15.1.1  
 $I_4Ta$   
 $TaI_4$   
 Formation: 2.9.5  
 $I_4Th$   
 $ThI_4$   
 Reaction with MI: 2.9.10.1  
 $I_4Ti$   
 $TiI_4$   
 Formation: 2.9.2.4, 2.9.4.8  
 Reaction with CsI: 2.9.10.1  
 $I_4W$   
 $WI_4$   
 Formation: 2.9.4.8  
 $I_4Zn \cdot Cs_2$   
 $I_4Zn \cdot Hg$   
 $I_4Zr$   
 $ZrI_4$   
 Formation: 2.9.2.4, 2.9.4.8  
 Reaction with CsI: 2.9.10.1  
 $I_5 \cdot CdCs_3$   
 $I_5 \cdot CsHg_2$   
 $I_5 \cdot Cs_3Cu_2$   
 $I_5 \cdot Cs_3Hg$   
 $I_5N \cdot H_4Hg_2$   
 $I_5Nb$   
 $NbI_5$   
 Formation: 2.9.2.4  
 $I_5Rb \cdot Ag_4$   
 $I_5Ta$   
 $TaI_5$   
 Formation: 2.9.2.4, 2.9.4.8  
 $I_5Zn \cdot Cs_3$   
 $I_6 \cdot Au_2Cs_2$   
 $I_6 \cdot Au_2K_6$   
 $I_6 \cdot Cs_2Hf$   
 $I_6KRe$   
 $K[ReI_6]$   
 Formation: 2.9.10.2  
 $I_6K_2 \cdot Au_2$   
 $I_6K_2O_8 \cdot C_{16}H_{32}Cu_4$   
 $I_6K_2O_{10} \cdot C_{20}H_{40}Cu_4$   
 $I_6K_2O_{16} \cdot C_{48}H_{64}Cu_4$   
 $I_6K_2Os$   
 $K_2[OsI_6]$   
 Formation: 2.9.10.2  
 $I_6K_2Th$   
 $K_2[ThI_6]$   
 Formation: 2.9.10.1  
 $I_6K_4 \cdot Cd$   
 $I_6N_2 \cdot Au_2H_8$   
 $I_6N_2Ti \cdot C_{16}H_{40}$   
 $I_6N_4 \cdot C_{22}H_{24}Cu_2$   
 $I_6Nb \cdot Cs_2$   
 $I_6Rb_2 \cdot Au_2$   
 $I_6Rb_4 \cdot Hg$   
 $I_6Ti \cdot Cs_2$   
 $I_6Zr \cdot Cs_2$   
 $I_7Li \cdot Al_2$   
 $I_7N_2 \cdot C_{24}H_{36}Cu_5$   
 $I_7Rb_3 \cdot Hg_2$   
 $I_8 \cdot B_8$   
 $I_8 \cdot Cs_2Hg_3$   
 $I_8K_3 \cdot Au_3$   
 $I_8N_3 \cdot Au_3H_{12}$   
 $I_8P \cdot Al$   
 $I_8Rb_2 \cdot AgAu_3$   
 $I_8Rb_3 \cdot Au_3$   
 $I_9 \cdot B_9$   
 $I_{12}Mo_6$   
 $[Mo_6I_8]I_4$   
 Reaction with elemental S: 2.9.14.3  
 $I_{12}N_6 \cdot C_{48}H_{120}Cu_6$   
 $I_{39}N_9 \cdot C_{32}H_{88}Ag_{31}$   
 $I_{60}N_{24} \cdot C_{120}H_{144}Cu_{36}$   
**In**  
**In**  
 Reaction with RX: 2.6.3.2  
 Reaction with HX: 2.6.3.1  
 Reaction with  $X_2$ : 2.6.2.1

- In\*Br  
 In\*Br<sub>3</sub>  
 In\*C<sub>3</sub>H<sub>9</sub>  
 In\*C<sub>6</sub>H<sub>18</sub>AsBr<sub>2</sub>  
 In\*C<sub>12</sub>H<sub>10</sub>I  
 In\*Cl<sub>2</sub>  
 In\*Cl<sub>3</sub>  
 In\*F  
 In\*F<sub>3</sub>  
 In\*I<sub>3</sub>  
 InLi\*H<sub>4</sub>  
 InMnO<sub>5</sub>\*C<sub>5</sub>Br<sub>2</sub>  
 InMnO<sub>5</sub>\*C<sub>5</sub>Cl<sub>2</sub>  
 InMn<sub>2</sub>O<sub>10</sub>\*C<sub>10</sub>Br  
 InMn<sub>2</sub>O<sub>10</sub>\*C<sub>10</sub>Cl  
 InMn<sub>3</sub>O<sub>15</sub>\*C<sub>15</sub>  
 InN  
   InN  
     Reaction with HX: 2.6.8.2  
 InN<sub>2</sub>\*C<sub>16</sub>H<sub>40</sub>Cl<sub>5</sub>  
 InO\*F  
 In<sub>2</sub>\*Cl<sub>3</sub>  
 In<sub>2</sub>\*Cl<sub>9</sub>Cs<sub>3</sub>  
 In<sub>2</sub>Mn<sub>3</sub>O<sub>15</sub>\*C<sub>15</sub>  
 In<sub>2</sub>O<sub>3</sub>  
   In<sub>2</sub>O<sub>3</sub>  
     Reaction with MF<sub>3</sub>: 2.6.6.4  
     Reaction with C-X<sub>2</sub>: 2.6.6.2  
     Reaction with BX<sub>3</sub>: 2.6.6.4  
     Reaction with F<sub>2</sub>: 2.6.6.1  
     Reaction with ag HX: 2.6.6.3  
 In<sub>3</sub>\*Cl<sub>4</sub>  
 In<sub>4</sub>\*Br<sub>7</sub>  
 In<sub>5</sub>\*Cl<sub>9</sub>  
 In<sub>7</sub>\*Br<sub>3</sub>  
 Ir  
   Ir  
     Fluorination: 2.11.4.2  
     Reaction with F<sub>2</sub>: 2.9.2.1  
 Ir\*Br<sub>2</sub>  
 Ir\*Br<sub>3</sub>  
 Ir\*Br<sub>4</sub>  
 Ir\*F<sub>5</sub>  
 Ir\*F<sub>6</sub>  
 Ir\*I<sub>3</sub>  
 IrK<sub>2</sub>\*Cl<sub>6</sub>  
 IrNO\*F<sub>6</sub>  
 IrN<sub>2</sub>O<sub>2</sub>\*F<sub>6</sub>  
 IrO<sub>2</sub>  
   IrO<sub>2</sub>  
     Reaction with HX: 2.9.10.2  
     Reaction with aq HX: 2.9.4.3  
 IrO<sub>2</sub>\*ClF<sub>6</sub>  
 IrO<sub>3</sub>\*H<sub>2</sub>  
 IrXe\*F<sub>7</sub>  
 IrXe\*F<sub>11</sub>  
 IrXe<sub>2</sub>\*F<sub>9</sub>  
 IrXe<sub>2</sub>\*F<sub>17</sub>  
 Ir<sub>2</sub>Xe\*F<sub>12</sub>  
 K  
   K  
     Reaction with HX: 2.7.3.1  
     Reaction with X<sub>2</sub>: 2.7.2  
 K\*AgCs<sub>2</sub>F<sub>6</sub>  
 K\*AgF<sub>3</sub>  
 K\*AgF<sub>4</sub>  
 K\*At  
 K\*AuBr<sub>4</sub>  
 K\*AuCl<sub>4</sub>  
 K\*AuF<sub>4</sub>  
 K\*AuF<sub>6</sub>  
 K\*BF<sub>4</sub>  
 K\*BH<sub>4</sub>  
 K\*Br  
 K\*Br<sub>2</sub>Cu  
 K\*Br<sub>3</sub>Hg  
 K\*Br<sub>5</sub>Hg<sub>2</sub>  
 K\*CdCl<sub>3</sub>  
 K\*CdF<sub>3</sub>  
 K\*CdI<sub>3</sub>  
 K\*Cl  
 K\*Cl<sub>2</sub>Cu  
 K\*Cl<sub>3</sub>Cu  
 K\*Cl<sub>3</sub>Hg  
 K\*CrF<sub>3</sub>  
 K\*C<sub>u</sub>F<sub>3</sub>  
 K\*C<sub>u</sub>I<sub>2</sub>  
 K\*F  
 K\*F<sub>2</sub>H  
 K\*F<sub>3</sub>Hg  
 K\*HgI<sub>3</sub>  
 K\*I  
 K\*I<sub>3</sub>  
 KMnO<sub>4</sub>  
   K[MnO<sub>4</sub>]  
     Reaction of a KCl mixture with BrF<sub>3</sub>:  
       2.11.2.1  
     Reaction with HSO<sub>3</sub>F: 2.11.2.1  
     Reaction with HF: 2.11.2.1  
     Reaction with H<sub>5</sub>O<sub>3</sub>X: 2.9.12.5  
     Reaction with IF<sub>5</sub>: 2.11.2.1, 2.9.12.3  
     Reduction by Et<sub>2</sub>O or H<sub>2</sub>O in HF:  
       2.11.2.1  
 KNO<sub>3</sub>  
   K[NO<sub>3</sub>]  
     Formation from Hg[NO<sub>3</sub>]<sub>2</sub> and KBr:  
       2.8.17.2

- $\text{KN}_2^*\text{C}_2\text{Au}$   
 $\text{KN}_2^*\text{C}_2\text{AuBr}_2$   
 $\text{KN}_2^*\text{C}_2\text{AuCl}_2$   
 $\text{KN}_2^*\text{C}_2\text{AuI}_2$   
 $\text{KN}_2\text{O}^*\text{C}_2\text{H}_2\text{AuCl}_2$   
 $\text{KN}_3^*\text{C}_3\text{AuBr}$   
 $\text{KN}_3^*\text{C}_3\text{AuCl}$   
 $\text{KN}_4^*\text{C}_4\text{Au}$   
 $\text{KO}^*\text{Br}_3\text{CdH}_2$   
 $\text{KO}^*\text{Br}_3\text{H}_2\text{Hg}$   
 $\text{KO}^*\text{CdCl}_3\text{H}_2$   
 $\text{KO}^*\text{Cl}_3\text{H}_2\text{Hg}$   
 $\text{KO}^*\text{H}_2\text{HgI}_3$   
 $\text{KOW}^*\text{F}_5$   
 $\text{KO}_2^*\text{AuCl}_4\text{H}_4$   
 $\text{KO}_2^*\text{Br}_3\text{H}_4\text{Hg}$   
 $\text{KO}_2^*\text{Cl}_4\text{H}_4\text{Hg}$   
 $\text{KO}_2\text{Re}^*\text{F}_2$   
 $\text{KO}_2\text{Zn}^*\text{Br}_3\text{H}_4$   
 $\text{KO}_2\text{Zn}^*\text{Cl}_3\text{H}_4$   
 $\text{KO}_4^*\text{Cl}$   
 $\text{KO}_4\text{Re}$   
 $\text{K}[\text{ReO}_4]$   
 Fluorination: 2.11.4.1  
 Reaction with  $\text{BrF}_3$ : 2.11.4.1  
 Reaction with  $\text{IF}_5$ : 2.9.12.3, 2.11.4.1  
 Reaction with  $\text{HX}$ : 2.9.10.2  
 $\text{KO}_6^*\text{C}_{12}\text{H}_{24}\text{CuI}_2$   
 $\text{KPt}^*\text{F}_6$   
 $\text{KRe}^*\text{F}_8$   
 $\text{KRe}^*\text{I}_6$   
 $\text{KSi}_3^*\text{C}_{54}\text{H}_{45}\text{AlCl}$   
 $\text{KV}^*\text{F}_6$   
 $\text{KW}^*\text{Cl}_6$   
 $\text{KW}^*\text{F}_6$   
 $\text{KZn}^*\text{F}_3$   
 $\text{K}_2^*\text{AgF}_4$   
 $\text{K}_2^*\text{AgI}_3$   
 $\text{K}_2^*\text{Au}_2\text{I}_6$   
 $\text{K}_2^*\text{Br}_2\text{Cl}_2\text{Hg}$   
 $\text{K}_2^*\text{Br}_4\text{Cd}$   
 $\text{K}_2^*\text{Br}_4\text{Hg}$   
 $\text{K}_2^*\text{C}_6\text{H}_{18}\text{Ga}_2$   
 $\text{K}_2^*\text{CdCl}_2\text{I}_2$   
 $\text{K}_2^*\text{CdF}_4$   
 $\text{K}_2^*\text{CdI}_4$   
 $\text{K}_2^*\text{Cl}_3\text{Cu}$   
 $\text{K}_2^*\text{Cl}_4\text{Hg}$   
 $\text{K}_2^*\text{Cl}_6\text{Ga}_2$   
 $\text{K}_2^*\text{Cl}_6\text{Ir}$   
 $\text{K}_2^*\text{HgI}_4$   
 $\text{K}_2\text{Mn}^*\text{Cl}_6$   
 $\text{K}_2\text{Mn}^*\text{F}_6$   
 $\text{K}_2\text{Mo}^*\text{Cl}_6$   
 $\text{K}_2\text{Mo}^*\text{F}_8$   
 $\text{K}_2\text{MoO}_4$   
 $\text{K}_2[\text{MoO}_4]$   
 Reaction with  $\text{ClF}$ : 2.11.3.1  
 $\text{K}_2\text{Na}^*\text{CuF}_6$   
 $\text{K}_2\text{Ni}^*\text{F}_6$   
 $\text{K}_2\text{O}^*\text{Cl}_4\text{H}_2\text{Hg}$   
 $\text{K}_2\text{OV}^*\text{F}_5$   
 $\text{K}_2\text{O}_2\text{Zn}^*\text{Br}_4\text{H}_4$   
 $\text{K}_2\text{O}_4\text{S}$   
 $\text{K}_2[\text{SO}_4]$   
 Formation from  $\text{KI}$  and  $\text{Cd}[\text{SO}_4]$ :  
 2.8.17.2  
 $\text{K}_2\text{O}_4\text{W}$   
 $\text{K}_2[\text{WO}_4]$   
 Reaction with  $\text{HX}$ : 2.9.10.2  
 $\text{K}_2\text{O}_8^*\text{C}_{16}\text{H}_{32}\text{Cu}_4\text{I}_6$   
 $\text{K}_2\text{O}_{10}^*\text{C}_{20}\text{H}_{40}\text{Cu}_4\text{I}_6$   
 $\text{K}_2\text{O}_{16}^*\text{C}_{48}\text{H}_{64}\text{Cu}_4\text{I}_6$   
 $\text{K}_2\text{Os}^*\text{I}_6$   
 $\text{K}_3\text{Pd}^*\text{Cl}_6$   
 $\text{K}_3\text{Pd}^*\text{F}_6$   
 $\text{K}_3\text{Re}^*\text{Br}_6$   
 $\text{K}_3\text{Re}^*\text{Cl}_6$   
 $\text{K}_3\text{Ru}^*\text{Br}_6$   
 $\text{K}_3\text{Th}^*\text{I}_6$   
 $\text{K}_3\text{Ti}^*\text{F}_6$   
 $\text{K}_3\text{W}^*\text{Cl}_6$   
 $\text{K}_3\text{W}^*\text{F}_8$   
 $\text{K}_3\text{Zn}^*\text{Cl}_4$   
 $\text{K}_3\text{Zn}^*\text{F}_4$   
 $\text{K}_3^*\text{Au}_3\text{I}_8$   
 $\text{K}_3^*\text{CuF}_6$   
 $\text{K}_3^*\text{Cu}_2\text{F}_7$   
 $\text{K}_3\text{Mo}^*\text{Cl}_6$   
 $\text{K}_3\text{Nb}^*\text{F}_8$   
 $\text{K}_3\text{NbO}^*\text{F}_6$   
 $\text{K}_3\text{Ni}^*\text{F}_6$   
 $\text{K}_3\text{OTa}^*\text{F}_6$   
 $\text{K}_3\text{O}_2\text{Ti}^*\text{F}_5$   
 $\text{K}_3\text{O}_2\text{U}^*\text{F}_5$   
 $\text{K}_3\text{O}_4\text{V}_2^*\text{F}_5$   
 $\text{K}_3\text{Ta}^*\text{F}_8$   
 $\text{K}_3\text{Ti}^*\text{F}_6$   
 $\text{K}_3\text{W}_2^*\text{Cl}_9$   
 $\text{K}_3\text{W}_3^*\text{Cl}_9$   
 $\text{K}_4^*\text{Br}_6\text{Cd}$   
 $\text{K}_4^*\text{CdCl}_6$   
 $\text{K}_4^*\text{CdI}_6$   
 $\text{K}_4\text{O}_3\text{V}_2^*\text{F}_8$



- $K_4Ta_6*Cl_{18}$   
 $K_5N_{10}O_2*C_{10}H_4Au_5I_2$   
 $K_5O_3V_3*F_{14}$   
 $K_6I_6*Au_2$   
 $Kr*AuF_7$   
 $Kr*F$   
 $Kr*F_2$   
 $KrPt*F_7$   
 $KrSb*F_7$   
 $KrSb_2*F_{12}$   
**La**  
 La  
 Reaction with HX: 2.9.14.1.1  
 $La*Cl_3$   
 $La*F_3$   
 $LaS*Br$   
 $LaS*Cl$   
 $LaS*F$   
 $LaS*I$   
 $LaSe*F$   
 $La_2S_3$   
 $La_2S_3$   
 Reaction with  $LaF_3$ : 2.9.14.2  
 $La_2Se*F_4$   
 $La_2Se_3$   
 $La_2Se_3$   
 Reaction with  $LaF_3$ : 2.9.14.2  
**Li**  
 Li  
 Reaction with  $X_2$ : 2.7.2  
 Reaction with HX: 2.7.3.1  
 $Li*AlAs_4H_8$   
 $Li*AlClH_3$   
 $Li*AlH_4$   
 $Li*Al_2I_7$   
 $Li*BH_4$   
 $Li*F$   
 $Li*GaH_4$   
 $Li*H$   
 $Li*H_4In$   
 $Li*I$   
 $LiN_4*AlH_8$   
 $LiN_4*C_8H_{24}Al$   
 $LiO_3Zn*Cl_3H_6$   
 $LiP*C_{19}H_{16}$   
 $LiP_3*C_3H_{13}Al$   
 $LiP_4*AlH_8$   
 $LiS_4*C_4H_{12}Al$   
 $LiSe_4*C_{24}H_{20}Al$   
 $LiSi_4*C_{12}H_{36}B$   
 $LiSi_4*C_{12}H_{36}Ga$   
 $LiTe_4*C_4H_{12}Al$   
 $LiTi*H_4$   
 $Li_2O_3S$   
 $Li_2[SO_3]$   
 Reaction with  $HgCl_2$ : 2.8.21.2  
 $LnP_3*C_{54}H_{48}Cl_6$   
 $Ln_2O_3$   
 $Ln_2O_3$   
 Reaction with HX: 2.9.10.2  
**Lu**  
 Lu  
 Reaction with HX: 2.9.14.1.1  
 $Lu*F_3$   
 $LuS*Br$   
 $LuS*F$   
 $LuSe*F$   
 $MO*Cl_3$   
 $MO*F_4$   
**Mg**  
 Mg  
 Reaction with RX: 2.7.3.2.2  
 Reaction with HX: 2.7.3.1  
 Reaction with  $[NH_4]X$ : 2.7.3.2.1  
 Reaction with  $HgX_2$ : 2.7.3.2.1  
 Reaction with  $X(CH_2)_nX$ : 2.7.3.2.1  
 $Mg*Al_2$   
 $Mg*Br_2$   
 $Mg*C_4H_3Br$   
 $Mg*Cl_2$   
 $Mg*F_2$   
 $Mg*I_2$   
**MgO**  
 MgO  
 Reaction with HX: 2.7.5  
 Reaction with  $X_2$ -CO: 2.7.6  
 $MgO*ClH$   
 $MgO_6*Cl_6H_{12}Hg_2$   
 $MgO_6Zn*Cl_4H_{12}$   
**Mn**  
 Mn  
 Catalyst for the fluorination of Cr:  
 2.11.2.1  
 Fluorination: 2.11.2.1  
 Fluorination of alkali metal salt  
 mixtures: 2.11.2.1  
 Reaction with  $F_2$ : 2.9.2.1  
 Reaction with  $Cl_2$ : 2.9.2.2  
 Reaction with  $I_2$ : 2.9.2.4  
 Reaction with HX: 2.9.3.2  
 Reaction with ag HX: 2.9.3.3  
 $Mn*Br_2$   
 $Mn*C_{108}F_{90}Ge_6Hg_2$   
 $Mn*Cl_2$

$\text{Mn}^*\text{Cl}_3$   
 $\text{Mn}^*\text{Cl}_6\text{K}_2$   
 $\text{Mn}^*\text{F}_2$   
 $\text{Mn}^*\text{F}_3$   
 $\text{Mn}^*\text{F}_4$   
 $\text{Mn}^*\text{F}_6\text{K}_2$   
 $\text{Mn}^*\text{I}_2$   
 $\text{MnN}_2^*\text{H}_8\text{F}_6$   
 $\text{MnN}_2\text{O}_5^*\text{C}_9\text{H}_{12}\text{B}$   
**MnO<sub>2</sub>**  
     Reaction with Hg, NaCl, H<sub>2</sub>SO<sub>4</sub>:  
         2.8.21.3  
     Reaction with RCl: 2.9.4.6  
     Reaction with AlI<sub>3</sub>: 2.9.4.8  
     Reaction with X<sub>2</sub> or C-X<sub>2</sub>: 2.9.4.2  
     Reaction with F<sub>2</sub>-O<sub>2</sub>: 2.11.2.1  
     Reaction with HX: 2.9.4.2  
 $\text{MnO}_2^*\text{Cl}_2$   
 $\text{MnO}_3^*\text{C}_3\text{F}_3$   
 $\text{MnO}_3^*\text{C}_8\text{H}_4\text{ClHg}$   
 $\text{MnO}_3^*\text{C}_8\text{H}_5$   
 $\text{MnO}_3^*\text{Cl}$   
 $\text{MnO}_3^*\text{F}$   
 $\text{MnO}_4^*\text{K}$   
 $\text{MnO}_4\text{P}^*\text{C}_{34}\text{H}_{25}\text{B}$   
**MnO<sub>4</sub>S**  
     Mn[SO<sub>4</sub>]  
         Formation from Hg, MnO<sub>2</sub>, NaCl and  
         H<sub>2</sub>SO<sub>4</sub>: 2.8.21.3  
 $\text{MnO}_5^*\text{C}_5\text{BCl}_2$   
 $\text{MnO}_5^*\text{C}_5\text{Br}$   
 $\text{MnO}_5^*\text{C}_5\text{Br}_2\text{In}$   
 $\text{MnO}_5^*\text{C}_5\text{Cl}$   
 $\text{MnO}_5^*\text{C}_5\text{Cl}_2\text{In}$   
 $\text{MnO}_5^*\text{C}_5\text{H}$   
 $\text{MnO}_5^*\text{C}_5\text{I}$   
 $\text{MnO}_5^*\text{C}_6\text{H}_3$   
 $\text{MnO}_5\text{Ti}^*\text{C}_5$   
 $\text{MnO}_6^*\text{C}_7\text{H}_3$   
 $\text{MnO}_6^*\text{C}_{12}\text{H}_5$   
 $\text{MnXe}^*\text{F}_6$   
 $\text{MnXe}^*\text{F}_8$   
 $\text{MnXe}_{0.5}^*\text{F}_5$   
 $\text{MnXe}_{0.5}^*\text{F}_6$   
 $\text{MnXe}_2^*\text{F}_{12}$   
 $\text{MnXe}_4^*\text{F}_{20}$   
 $\text{Mn}_2\text{O}_2^*\text{F}_9$   
 $\text{Mn}_2\text{O}_8^*\text{C}_8\text{F}_2$   
 $\text{Mn}_2\text{O}_{10}^*\text{C}_{10}$   
 $\text{Mn}_2\text{O}_{10}^*\text{C}_{10}\text{BrIn}$   
 $\text{Mn}_2\text{O}_{10}^*\text{C}_{10}\text{ClIn}$

$\text{Mn}_3\text{O}_{15}^*\text{C}_{15}\text{In}$   
 $\text{Mn}_3\text{O}_{15}^*\text{C}_{15}\text{In}_2$   
 $\text{Mn}_3\text{O}_{15}\text{Ti}^*\text{C}_{15}$

**Mo****Mo**

    Electrical explosion in SF<sub>6</sub>: 2.11.3.1  
     Flourination: 2.11.3.1  
     Reaction with MF in BrF<sub>3</sub>: 2.11.3.1  
     Reaction with HX: 2.9.3.2  
     Reaction with S<sub>2</sub>X<sub>2</sub>, S: 2.9.14.1.2  
     Reaction with X<sub>2</sub>-O<sub>2</sub>: 2.9.11.2  
     Reaction with O<sub>2</sub>-F<sub>2</sub>: 2.11.3.1  
     Reaction with Cl<sub>2</sub>: 2.9.2.2  
     Reaction with F<sub>2</sub>: 2.9.2.1  
     Reaction with ClF<sub>3</sub>, BrF<sub>3</sub>: 2.9.3.4  
     Reaction with Br<sub>2</sub>: 2.9.2.3  
     Reaction with ClF: 2.11.3.1  
     Reaction with Cl<sub>2</sub>: 2.9.11.1  
     Reaction with I<sub>2</sub>: 2.9.2.4

$\text{Mo}^*\text{Br}_2$   
 $\text{Mo}^*\text{Br}_3$   
 $\text{Mo}^*\text{Br}_4$   
 $\text{Mo}^*\text{Cl}_2$   
 $\text{Mo}^*\text{Cl}_3$   
 $\text{Mo}^*\text{Cl}_4$   
 $\text{Mo}^*\text{Cl}_5$   
 $\text{Mo}^*\text{Cl}_6\text{K}_2$   
 $\text{Mo}^*\text{Cl}_6\text{K}_3$   
 $\text{Mo}^*\text{F}_3$   
 $\text{Mo}^*\text{F}_4$   
 $\text{Mo}^*\text{F}_5$   
 $\text{Mo}^*\text{F}_6$   
 $\text{Mo}^*\text{F}_8\text{K}_2$   
 $\text{Mo}^*\text{I}_2$   
 $\text{Mo}^*\text{I}_3$   
 $\text{MoNO}^*\text{F}_7$   
 $\text{MoNO}_2^*\text{F}_7$   
 $\text{MoNO}_3^*\text{F}_3$   
 $\text{MoN}_2\text{O}_2^*\text{C}_5\text{H}_5\text{Cl}$   
 $\text{MoNa}_2^*\text{F}_8$   
**MoNa<sub>2</sub>O<sub>4</sub>**  
     Na<sub>2</sub>[MoO<sub>4</sub>]  
         Reaction with ClF: 2.11.3.1

$\text{MoO}^*\text{BrCl}_4$   
 $\text{MoO}^*\text{Br}_4$   
 $\text{MoO}^*\text{Br}_5$   
 $\text{MoO}^*\text{Cl}_2$   
 $\text{MoO}^*\text{Cl}_3$   
 $\text{MoO}^*\text{Cl}_4$   
 $\text{MoO}^*\text{Cl}_5$   
 $\text{MoO}^*\text{F}_4$   
 $\text{MoO}^*\text{F}_5$

- MoOSb\*F<sub>9</sub>  
**MoO<sub>2</sub>**  
   MoO<sub>2</sub>  
     Reaction with RCl: 2.9.4.6  
     Reaction with X<sub>2</sub>: 2.9.12.1  
 MoO<sub>2</sub>\*Br<sub>2</sub>  
 MoO<sub>2</sub>\*Cl<sub>2</sub>  
 MoO<sub>2</sub>\*Cl<sub>4</sub>  
 MoO<sub>2</sub>\*F<sub>2</sub>  
 MoO<sub>2</sub>\*F<sub>3</sub>  
 MoO<sub>2</sub>Se\*F<sub>6</sub>  
**MoO<sub>3</sub>**  
   MoO<sub>3</sub>  
     Reaction with AlI<sub>3</sub>: 2.9.4.8  
     Reaction with MoCl<sub>3</sub>: 2.9.12.6  
     Reaction with RCl: 2.9.4.6  
     Reaction with SOX<sub>2</sub>, S<sub>2</sub>X<sub>2</sub>, BX<sub>3</sub>:  
       2.9.12.5  
     Reaction with SF<sub>4</sub>: 2.9.4.4, 2.9.4.5,  
       2.11.3.1  
     Reaction with XeF<sub>2</sub>: 2.11.3.1  
     Reaction with CX<sub>4</sub>: 2.9.12.4  
     Reaction with NF<sub>3</sub>: 2.11.3.1  
     Reaction with BrF<sub>3</sub>: 2.11.3.1  
     Reaction with BrF<sub>3</sub>, ClF<sub>3</sub>, IF<sub>5</sub>: 2.9.4.4  
     Reaction with ClF<sub>3</sub>: 2.11.3.1  
     Reaction with IF<sub>5</sub>: 2.9.12.3, 2.11.3.1  
     Reaction with Cl<sub>2</sub>: 2.9.11.2  
     Reaction with aq Hf: 2.9.13.1.1  
 MoO<sub>3</sub>\*C<sub>8</sub>H<sub>5</sub>ClHg  
 MoO<sub>3</sub>\*C<sub>8</sub>H<sub>5</sub>I  
 MoO<sub>3</sub>\*C<sub>8</sub>H<sub>6</sub>  
 MoO<sub>3</sub>\*C<sub>9</sub>H<sub>8</sub>  
 MoO<sub>3</sub>\*C<sub>10</sub>H<sub>8</sub>  
 MoO<sub>3</sub>\*C<sub>20</sub>H<sub>15</sub>B  
 MoO<sub>3</sub>\*Cl  
 MoO<sub>3</sub>\*F<sub>2</sub>  
 MoO<sub>3</sub>\*F<sub>3</sub>H<sub>2</sub>  
 MoO<sub>3</sub>\*F<sub>4</sub>H<sub>2</sub>  
 MoO<sub>3</sub>Sn\*C<sub>11</sub>H<sub>14</sub>  
 MoO<sub>3</sub>Ti\*C<sub>10</sub>H<sub>11</sub>  
 MoO<sub>3</sub>Ti\*C<sub>12</sub>H<sub>15</sub>  
 MoO<sub>4</sub>\*C<sub>4</sub>Br<sub>2</sub>  
 MoO<sub>4</sub>\*C<sub>4</sub>Cl<sub>2</sub>  
 MoO<sub>4</sub>\*C<sub>4</sub>F<sub>2</sub>  
 MoO<sub>4</sub>\*F<sub>2</sub>H<sub>2</sub>  
 MoO<sub>4</sub>\*F<sub>3</sub>H<sub>2</sub>  
 MoO<sub>4</sub>\*K<sub>2</sub>  
 MoO<sub>6</sub>\*C<sub>6</sub>  
 MoRb<sub>3</sub>\*Cl<sub>6</sub>  
 MoS\*Br  
 MoS\*Cl  
 MoS\*Cl<sub>2</sub>  
 MoS\*Cl<sub>3</sub>  
 MoS\*F<sub>4</sub>  
 MoS\*I  
**MoS<sub>2</sub>**  
   MoS<sub>2</sub>  
     Reaction with SF<sub>4</sub>: 2.9.5  
     Reaction with Cl<sub>2</sub>: 2.9.5  
     Reaction with ClF: 2.11.3.1  
     Reaction with Cl<sub>2</sub>: 2.9.14.2  
 MoS<sub>2</sub>\*Br<sub>2</sub>  
 MoS<sub>2</sub>\*Cl<sub>2</sub>  
**MoS<sub>3</sub>**  
   MoS<sub>3</sub>  
     Reaction with S<sub>2</sub>X<sub>3</sub>: 2.9.14.2  
     Reaction with CCl<sub>4</sub>: 2.9.5  
 MoSe\*Cl<sub>3</sub>  
 MoSe\*F<sub>4</sub>  
**MoTe<sub>2</sub>**  
   MoTe<sub>2</sub>  
     Reaction with Br<sub>2</sub>: 2.9.14.2  
 MoTe<sub>2</sub>\*Br<sub>10</sub>  
 Mo<sub>2</sub>\*Br<sub>9</sub>Cs<sub>2</sub>  
 Mo<sub>2</sub>\*Cl<sub>9</sub>Cs<sub>3</sub>  
 Mo<sub>2</sub>O<sub>4</sub>\*F<sub>4</sub>  
 Mo<sub>2</sub>O<sub>4</sub>\*F<sub>6</sub>  
 Mo<sub>2</sub>O<sub>6</sub>\*C<sub>16</sub>H<sub>10</sub>  
 Mo<sub>2</sub>O<sub>6</sub>\*C<sub>16</sub>H<sub>10</sub>Hg  
 Mo<sub>2</sub>O<sub>6</sub>\*F<sub>15</sub>I<sub>3</sub>  
 Mo<sub>2</sub>O<sub>8</sub>\*C<sub>8</sub>I<sub>2</sub>  
 Mo<sub>2</sub>S<sub>4</sub>\*Cl<sub>5</sub>  
 Mo<sub>2</sub>S<sub>5</sub>\*Br<sub>3</sub>  
 Mo<sub>2</sub>S<sub>5</sub>\*Cl<sub>3</sub>  
 Mo<sub>2</sub>S<sub>5</sub>\*I<sub>3</sub>  
 Mo<sub>3</sub>S<sub>7</sub>\*Br<sub>4</sub>  
 Mo<sub>3</sub>Se<sub>7</sub>\*Br<sub>4</sub>  
 Mo<sub>3</sub>Y<sub>7</sub>\*Cl<sub>4</sub>  
 Mo<sub>4</sub>O<sub>16</sub>\*FH<sub>6</sub>  
 Mo<sub>6</sub>\*Br<sub>12</sub>  
 Mo<sub>6</sub>\*Cl<sub>12</sub>  
 Mo<sub>6</sub>\*I<sub>12</sub>  
 Mo<sub>6</sub>S<sub>6</sub>\*Cl<sub>2</sub>  
 N\*Al  
 N\*AuCl<sub>3</sub>H<sub>3</sub>  
 N\*AuCl<sub>4</sub>H<sub>4</sub>  
 N\*B  
 N\*BF<sub>4</sub>H<sub>4</sub>  
 N\*BeF<sub>3</sub>H<sub>4</sub>  
 N\*BrCl<sub>2</sub>H<sub>4</sub>Hg  
 N\*BrH<sub>4</sub>  
 N\*Br<sub>3</sub>CdH<sub>4</sub>  
 N\*Br<sub>3</sub>H<sub>4</sub>Hg

$N^*C_{16}Ag$   
 $N^*CAu$   
 $N^*CH_3BrHgI$   
 $N^*CH_3Br_2HgI$   
 $N^*C_2H_6AlCl_2$   
 $N^*C_3H_6BCl_2$   
 $N^*C_2H_8Cl_3Cu_2$   
 $N^*C_3H_9Br_3Ga$   
 $N^*C_3H_9Cl_3Ga$   
 $N^*C_3H_{12}Ga$   
 $N^*C_4H_{10}Ag_2I_3$   
 $N^*C_4H_{10}BCl_2$   
 $N^*C_4H_{10}BF_2$   
 $N^*C_4H_{10}BI_2$   
 $N^*C_4H_{11}BCl_3$   
 $N^*C_4H_{12}AgBr_2$   
 $N^*C_4H_{12}AgCl_2$   
 $N^*C_4H_{12}AgI_2$   
 $N^*C_4H_{12}Ag_2I_3$   
 $N^*C_4H_{12}Cl_3Cu_2$   
 $N^*C_4H_{12}Cu_2I_3$   
 $N^*C_4H_{14}BCl_3$   
 $N^*C_5H_5AuCl_3$   
 $N^*C_5H_6AuCl_4$   
 $N^*C_5H_6BrCuI$   
 $N^*C_6H_8CuI_2$   
 $N^*C_6H_{16}Cl_2Cu$   
 $N^*C_7H_5AuCl_3$   
 $N^*C_8H_{11}BCl$   
 $N^*C_8H_{20}Ag_2Br_3$   
 $N^*C_8H_{20}Ag_2Cl_3$   
 $N^*C_8H_{20}AuBr_2$   
 $N^*C_8H_{20}AuBr_4$   
 $N^*C_8H_{20}AuCl_2$   
 $N^*C_8H_{20}AuCl_4$   
 $N^*C_8H_{20}AuI_2$   
 $N^*C_8H_{20}AuI_4$   
 $N^*C_8H_{20}Br_4Fe$   
 $N^*C_8H_{20}Cl_3Cu_2$   
 $N^*C_8H_{20}CuI_2$   
 $N^*C_9H_{11}BCl_3$   
 $N^*C_{12}H_{28}BrCdCl_2$   
 $N^*C_{12}H_{28}BrCdI_2$   
 $N^*C_{12}H_{28}Br_2CdCl$   
 $N^*C_{12}H_{28}Br_2CdI$   
 $N^*C_{12}H_{28}CdClI_2$   
 $N^*C_{12}H_{28}CdCl_2I$   
 $N^*C_{12}H_{28}Cl_2Cu$   
 $N^*C_{12}H_{28}Cu_3I_4$   
 $N^*C_{16}H_{36}Ag_3I_4$   
 $N^*C_{16}H_{36}AuBr_2$   
 $N^*C_{16}H_{36}AuCl_2$

$N^*C_{16}H_{36}AuI_2$   
 $N^*C_{16}H_{36}Br_2Cu$   
 $N^*C_{16}H_{36}Cl_2Cu$   
 $N^*C_{17}H_5AuClF_{10}$   
 $N^*C_{22}H_{36}AuBrF_5$   
 $N^*C_{22}H_{36}AuBr_3F_5$   
 $N^*C_{22}H_{41}AuI_3$   
 $N^*C_{28}H_{36}AuBr_2F_{10}$   
 $N^*C_{28}H_{36}AuCl_2F_{10}$   
 $N^*C_{34}H_{36}AuBrF_{15}$   
 $N^*CdCl_3H_4$   
 $N^*CdF_3H_4$   
 $N^*Cd_2Cl_5H_4$   
 $N^*ClH_2Hg$   
 $N^*ClH_4$   
 $N^*Cl_3CuH_4$   
 $N^*Cl_3H_4Hg$   
 $N^*CuF_3H_4$   
 $N^*FH_4$   
 $N^*F_2H_5$   
 $N^*H_4Hg_2I_5$   
 $N^*In$   
 $NNaO_3$   
 $Na[NO_3]$   
 Formation from  $Hg_2[NO_3]_2$  and NaF:  
 2.8.21.1  
 $NNb^*C_2H_3Br_5$   
 $NNb^*C_2H_3Cl_5$   
 $NNb^*C_8H_{20}Br_6$   
 $NNb^*C_8H_{20}Cl_6$   
 $NNb^*C_{16}H_{36}F_6$   
 $NNb_2^*C_{16}H_{36}F_{11}$   
**NO**  
 Reaction with  $M(CO)_xL_y$ : 2.9.15.1.2  
 $NO^*AgF_3$   
 $NO^*AlCl_4$   
 $NO^*AuF_4$   
 $NO^*AuF_6$   
 $NO^*BF_4$   
 $NO^*Br$   
 $NO^*C_{16}Ag$   
 $NO^*C_3H_6Cl$   
 $NO^*C_6H_{15}BCl$   
 $NO^*C_{19}H_{15}AsAu$   
 $NO^*C_{19}H_{15}AsAuBr_2$   
 $NO^*Cl$   
 $NO^*F$   
 $NO^*F_4H_3$   
 $NO^*F_6Ir$   
 $NO^*F_7Mo$   
 $NO^*H_6HgI_3$

NOO <sub>8</sub> *F <sub>7</sub>	N <sub>2</sub> *C <sub>2</sub> AuCl <sub>2</sub> K
NOP*C <sub>18</sub> H <sub>25</sub> Cl <sub>2</sub> Cu	N <sub>2</sub> *C <sub>2</sub> AuI <sub>3</sub> K
NOP*C <sub>19</sub> H <sub>15</sub> Au	N <sub>2</sub> *C <sub>2</sub> AuK
NOP*C <sub>19</sub> H <sub>15</sub> AuBr <sub>2</sub>	N <sub>2</sub> *C <sub>2</sub> H <sub>12</sub> BrCl <sub>3</sub> Cu
NOPt*F <sub>6</sub>	N <sub>2</sub> *C <sub>2</sub> H <sub>12</sub> Br <sub>2</sub> HgI <sub>2</sub>
NORe*F <sub>7</sub>	N <sub>2</sub> *C <sub>2</sub> H <sub>12</sub> Cl <sub>2</sub> HgI <sub>2</sub>
NORu*F <sub>6</sub>	N <sub>2</sub> *C <sub>2</sub> H <sub>12</sub> Cl <sub>3</sub> Cu
NOW*F <sub>7</sub>	N <sub>2</sub> *C <sub>4</sub> H <sub>12</sub> BCl
NOW*F <sub>9</sub>	N <sub>2</sub> *C <sub>4</sub> H <sub>12</sub> BCl <sub>3</sub>
NO <sub>2</sub> *AuF <sub>4</sub>	N <sub>2</sub> *C <sub>4</sub> H <sub>12</sub> BI
NO <sub>2</sub> *F <sub>7</sub> Mo	N <sub>2</sub> *C <sub>5</sub> H <sub>17</sub> BCl <sub>2</sub>
NO <sub>2</sub> Pt*F <sub>6</sub>	N <sub>2</sub> *C <sub>6</sub> H <sub>5</sub> Br <sub>3</sub> Cu <sub>2</sub>
NO <sub>2</sub> Tc*F <sub>7</sub>	N <sub>2</sub> *C <sub>6</sub> H <sub>18</sub> AsB
NO <sub>2</sub> V*F <sub>4</sub>	N <sub>2</sub> *C <sub>6</sub> H <sub>20</sub> Cl <sub>10</sub> Cu <sub>4</sub>
NO <sub>2</sub> W*F <sub>5</sub>	N <sub>2</sub> *C <sub>10</sub> H <sub>10</sub> Au <sub>2</sub> Cl <sub>2</sub>
NO <sub>2</sub> W*F <sub>7</sub>	N <sub>2</sub> *C <sub>10</sub> H <sub>10</sub> Au <sub>2</sub> I <sub>2</sub>
NO <sub>2</sub> W <sub>2</sub> *F <sub>13</sub>	N <sub>2</sub> *C <sub>10</sub> H <sub>12</sub> Br <sub>7</sub> Cu <sub>5</sub>
NO <sub>3</sub> *Ag	N <sub>2</sub> *C <sub>10</sub> H <sub>12</sub> F <sub>4</sub> Hg
NO <sub>3</sub> *F <sub>3</sub> Mo	N <sub>2</sub> *C <sub>14</sub> H <sub>20</sub> Au <sub>2</sub> Cl <sub>2</sub>
NO <sub>3</sub> *H	N <sub>2</sub> *C <sub>16</sub> H <sub>20</sub> Au <sub>2</sub> Cl <sub>2</sub>
NO <sub>3</sub> *K	N <sub>2</sub> *C <sub>16</sub> H <sub>22</sub> B <sub>2</sub>
NO <sub>3</sub> Zn*Br <sub>3</sub> H <sub>10</sub>	N <sub>2</sub> *C <sub>16</sub> H <sub>40</sub> Br <sub>3</sub> Cu
NO <sub>4</sub> *C <sub>3</sub> Co	N <sub>2</sub> *C <sub>16</sub> H <sub>40</sub> Br <sub>4</sub> Co
NO <sub>4</sub> *C <sub>8</sub> H <sub>10</sub> BBrFe	N <sub>2</sub> *C <sub>16</sub> H <sub>40</sub> Br <sub>4</sub> Cu
NO <sub>4</sub> Tc*H <sub>4</sub>	N <sub>2</sub> *C <sub>16</sub> H <sub>40</sub> Br <sub>4</sub> Cu <sub>2</sub>
NO <sub>6</sub> S <sub>2</sub> *C <sub>8</sub> H <sub>6</sub> BF <sub>2</sub>	N <sub>2</sub> *C <sub>16</sub> H <sub>40</sub> Cl <sub>5</sub> In
NO <sub>6</sub> V <sub>3</sub> *FH <sub>4</sub>	N <sub>2</sub> *C <sub>16</sub> H <sub>40</sub> Cu <sub>2</sub> I <sub>4</sub>
NP*C <sub>2</sub> H <sub>6</sub> Cl <sub>3</sub>	N <sub>2</sub> *C <sub>24</sub> H <sub>56</sub> Cu <sub>2</sub> I <sub>4</sub>
NP*C <sub>8</sub> H <sub>20</sub> BCl	N <sub>2</sub> *C <sub>24</sub> H <sub>56</sub> Cu <sub>5</sub> I <sub>7</sub>
NP <sub>2</sub> *C <sub>12</sub> H <sub>30</sub> B	N <sub>2</sub> *C <sub>32</sub> H <sub>72</sub> Cu <sub>2</sub> I <sub>4</sub>
NP <sub>2</sub> *C <sub>24</sub> H <sub>21</sub> Au <sub>2</sub> Cl <sub>2</sub>	N <sub>2</sub> *C <sub>34</sub> H <sub>8</sub> Au <sub>2</sub> Cl <sub>2</sub> F <sub>20</sub>
NP <sub>2</sub> *C <sub>24</sub> H <sub>21</sub> Au <sub>2</sub> Cl <sub>6</sub>	N <sub>2</sub> *C <sub>36</sub> H <sub>8</sub> Au <sub>2</sub> Cl <sub>2</sub> F <sub>20</sub>
NRe*ClF <sub>5</sub>	N <sub>2</sub> *ClH <sub>5</sub>
NRe*F <sub>6</sub>	N <sub>2</sub> *Cl <sub>4</sub> CuH <sub>8</sub>
NS*C <sub>3</sub> H <sub>6</sub> Cl	N <sub>2</sub> *Cl <sub>4</sub> H <sub>8</sub> Hg
NS <sub>2</sub> *C <sub>5</sub> H <sub>10</sub> Au	N <sub>2</sub> *CoF <sub>3</sub> H <sub>5</sub>
NS <sub>2</sub> *C <sub>5</sub> H <sub>10</sub> AuBr <sub>2</sub>	N <sub>2</sub> *CuF <sub>4</sub> H <sub>8</sub>
NS <sub>2</sub> *C <sub>9</sub> H <sub>18</sub> Au	N <sub>2</sub> *H <sub>8</sub> F <sub>6</sub> Mn
NS <sub>2</sub> *C <sub>9</sub> H <sub>18</sub> AuBr <sub>2</sub>	N <sub>2</sub> *H <sub>8</sub> HgI <sub>4</sub>
NTa*C <sub>8</sub> H <sub>20</sub> Br <sub>6</sub>	N <sub>2</sub> *H <sub>10</sub> HgI <sub>4</sub>
NTa*C <sub>8</sub> H <sub>20</sub> Cl <sub>6</sub>	N <sub>2</sub> Ni*C <sub>16</sub> H <sub>40</sub> Br <sub>4</sub>
NTi*C <sub>8</sub> H <sub>20</sub> Cl <sub>5</sub>	N <sub>2</sub> Ni*F <sub>14</sub>
NTi <sub>2</sub> *C <sub>8</sub> H <sub>20</sub> Cl <sub>9</sub>	N <sub>2</sub> NiO <sub>2</sub> *F <sub>6</sub>
NTi*C <sub>4</sub> H <sub>12</sub>	N <sub>2</sub> O*C <sub>2</sub> H <sub>2</sub> AuCl <sub>2</sub> K
NZn*F <sub>3</sub> H <sub>4</sub>	N <sub>2</sub> O*C <sub>10</sub> H <sub>30</sub> Br <sub>10</sub> Cu <sub>4</sub>
N <sub>2</sub> *Au <sub>2</sub> H <sub>8</sub> I <sub>6</sub>	N <sub>2</sub> O*Cl <sub>6</sub> H <sub>10</sub> Hg
N <sub>2</sub> *BeF <sub>4</sub> H <sub>8</sub>	N <sub>2</sub> OZn*Br <sub>4</sub> H <sub>10</sub>
N <sub>2</sub> *Be <sub>2</sub> F <sub>5</sub> H <sub>8</sub>	N <sub>2</sub> O <sub>2</sub> *C <sub>5</sub> H <sub>5</sub> ClMo
N <sub>2</sub> *Br <sub>2</sub> Cl <sub>2</sub> H <sub>8</sub> Hg	N <sub>2</sub> O <sub>2</sub> *C <sub>8</sub> H <sub>19</sub> AuCl <sub>4</sub>
N <sub>2</sub> *Br <sub>4</sub> CdH <sub>8</sub>	N <sub>2</sub> O <sub>2</sub> *C <sub>10</sub> H <sub>16</sub> F <sub>4</sub> Hg
N <sub>2</sub> *Br <sub>4</sub> H <sub>8</sub> Hg	N <sub>2</sub> O <sub>2</sub> *C <sub>26</sub> H <sub>20</sub> AsAu
N <sub>2</sub> *C <sub>2</sub> AuBr <sub>2</sub> K	N <sub>2</sub> O <sub>2</sub> *C <sub>26</sub> H <sub>20</sub> AsAuBr <sub>2</sub>

- $N_2O_2 \cdot C_{26}H_{20}AsAuCl_2$   
 $N_2O_2 \cdot CdH_{12}I_4$   
 $N_2O_2 \cdot CuF_4H_{12}$   
 $N_2O_2 \cdot F_6Ir$   
 $N_2O_2Os \cdot F_8$   
 $N_2O_2Re \cdot F_8$   
 $N_2O_2Tc \cdot F_8$   
 $N_2O_2Ti \cdot F_6$   
 $N_2O_2W \cdot Br_2$   
 $N_2O_2W \cdot Cl_2$   
 $N_2O_2W \cdot F_8$   
 $N_2O_2Zn \cdot F_4H_{12}$   
 $N_2O_3 \cdot Au_2Cl_8H_{11}$   
 $N_2O_3 \cdot C_9H_{12}BMn$   
 $N_2O_6 \cdot Cd$   
 $N_2O_6 \cdot Hg$   
 $N_2O_6 \cdot Hg_2$   
 $N_2Os \cdot Br_6H_8$   
 $N_2Os \cdot Cl_6H_8$   
 $N_2Os_2 \cdot F_{12}H_6$   
 $N_2P \cdot C_8H_{22}B$   
 $N_2P \cdot C_9H_{25}BI$   
 $N_2S_2 \cdot C_{26}Au_2F_{20}$   
 $N_2S_4 \cdot C_{10}H_{20}Au_2Br_2$   
 $N_2S_4 \cdot C_{10}H_{20}Au_2I_2$   
 $N_2Si \cdot C_7H_{21}B$   
 $N_2Sn \cdot C_{10}H_{27}B$   
 $N_2Th \cdot C_{16}H_{40}Br_6$   
 $N_2Th \cdot C_{16}H_{40}Cl_6$   
 $N_2Ti \cdot C_{16}H_{40}Br_6$   
 $N_2Ti \cdot C_{16}H_{40}Cl_6$   
 $N_2Ti \cdot C_{16}H_{40}I_6$   
 $N_2Ti \cdot F_6H_6$   
 $N_2Ti \cdot C_6H_{18}B$   
 $N_2U \cdot C_{16}H_{40}Br_6$   
 $N_2U \cdot C_{16}H_{40}Cl_6$   
 $N_2Zn \cdot Br_4H_8$   
 $N_2Zn \cdot Cl_4H_8$   
 $N_2Zn \cdot H_8I_4$   
 $N_2Zr \cdot C_{16}H_{40}Br_6$   
 $N_2Zr \cdot C_{16}H_{40}Cl_6$   
 $N_3 \cdot Au_3H_{12}I_8$   
 $N_3 \cdot C_3AuBrK$   
 $N_3 \cdot C_3AuClK$   
 $N_3 \cdot C_3H_9B_3Br_3$   
 $N_3 \cdot C_3H_9B_3Cl_3$   
 $N_3 \cdot C_3H_9B_3F_3$   
 $N_3 \cdot C_6H_{12}AuBrCl$   
 $N_3 \cdot C_6H_{18}B$   
 $N_3 \cdot C_{12}H_{30}B$   
 $N_3 \cdot C_{12}H_{36}Br_3Cu_2$   
 $N_3 \cdot C_{21}H_{54}Br_9Cu_6$   
 $N_3 \cdot C_{24}H_{60}Br_5Cu$   
 $N_3 \cdot C_{24}H_{60}Cl_5Cu_2$   
 $N_3 \cdot C_{24}H_{60}CuI_4$   
 $N_3 \cdot F_6FeH_{12}$   
 $N_3NbO \cdot F_5H_{12}$   
 $N_3OTa \cdot F_6H_{12}$   
 $N_3OZn \cdot Br_5H_{14}$   
 $N_3O_2U \cdot F_5H_{12}$   
 $N_3O_4 \cdot C_{16}H_{20}AuCl_2$   
 $N_3O_4 \cdot C_{18}H_{24}AuCl_2$   
 $N_3S \cdot C_6H_{18}BF_4$   
 $N_3S_2Se_2 \cdot C_7H_{10}Au$   
 $N_3S_4 \cdot C_7H_{10}Au$   
 $N_3Si_3 \cdot C_5H_{54}B_3$   
 $N_3W \cdot F_5$   
 $N_3Zn \cdot Cl_5H_{12}$   
 $N_3Zr \cdot F_7H_{12}$   
 $N_4 \cdot AlH_8Li$   
 $N_4 \cdot Br_6H_{16}Hg$   
 $N_4 \cdot C_4AuK$   
 $N_4 \cdot C_4H_{16}Ag_2Br_2CuI_2$   
 $N_4 \cdot C_4H_{16}Br_3Cu_2$   
 $N_4 \cdot C_4H_{17}CoF_4$   
 $N_4 \cdot C_8H_{24}AlLi$   
 $N_4 \cdot C_{22}H_{24}Cu_2I_6$   
 $N_4 \cdot C_{32}H_{80}Cl_{12}Cu_4$   
 $N_4 \cdot CdCl_6H_{16}$   
 $N_4 \cdot Cl_4Cu_3H_{12}$   
 $N_4 \cdot Cl_6H_{16}Hg$   
 $N_4Na_2NiO_3 \cdot C_4H_6$   
 $N_4Ni \cdot C_4Ba$   
 $N_4Ni \cdot C_4H_{16}Ag_2Br_4$   
 $N_4NiO_4 \cdot C_4H_8Ba$   
 $N_4S_4Se_2 \cdot C_{12}H_{20}Au_2$   
 $N_4S_6 \cdot C_{12}H_{20}Au_2$   
 $N_6 \cdot Ag_2Au_3Cl_{17}H_{24}$   
 $N_6 \cdot Br_3Cl_2CrCuH_{18}$   
 $N_6 \cdot Br_5CrCuH_{18}$   
 $N_6 \cdot C_{24}Au_2F_{20}$   
 $N_6 \cdot C_{48}H_{120}Cu_6I_{12}$   
 $N_6 \cdot CdCl_5CoH_{18}$   
 $N_6 \cdot CoF_3H_{18}$   
 $N_6O_{0.5} \cdot Co_2F_6H_{19}$   
 $N_8 \cdot C_{12}H_{16}CuI_2$   
 $N_8 \cdot C_{32}H_{88}Ag_{31}I_{39}$   
 $N_{10}O_2 \cdot C_{10}H_4Au_5I_2K_5$   
 $N_{12} \cdot C_{12}H_{48}Cl_{10}Co_2Cu_2$   
 $N_{18}P_6 \cdot C_{24}H_{72}Cl_3Cu_2$   
 $N_{24} \cdot C_{120}H_{144}Cu_{36}I_{60}$   
Na  
Reaction with  $X_2$ : 2.7.2

- Reaction with HX: 2.7.3.1
- Na\*AgF<sub>4</sub>
- Na\*AuCl<sub>4</sub>
- Na\*Br
- Na\*Br<sub>3</sub>Hg
- Na\*Cl
- Na\*CuF<sub>6</sub>K<sub>2</sub>
- Na\*F
- NaO\*H
- NaOZn\*Br<sub>3</sub>H<sub>2</sub>
- NaO<sub>2</sub>\*AuCl<sub>4</sub>H<sub>4</sub>
- NaO<sub>2</sub>\*Br<sub>3</sub>H<sub>4</sub>Hg
- NaO<sub>2</sub>\*Cl<sub>3</sub>H<sub>4</sub>Hg
- NaO<sub>2</sub>Re\*F<sub>2</sub>
- NaO<sub>3</sub>\*I
- NaO<sub>3</sub>\*N
- NaO<sub>3</sub>V
- Na[VO<sub>3</sub>]
- Reaction with HF: 2.11.2.1
- NaO<sub>3</sub>Zn\*H<sub>6</sub>I<sub>3</sub>
- NaO<sub>4</sub>Re
- Na[ReO<sub>4</sub>]
- Reaction with BrF<sub>3</sub>: 2.11.4.1
- NaPr\*F<sub>5</sub>
- NaSc\*F<sub>4</sub>
- NaU\*F<sub>7</sub>
- NaY\*F<sub>4</sub>
- NaZn\*F<sub>3</sub>
- Na<sub>2</sub>\*Br<sub>2</sub>Cl<sub>2</sub>Hg
- Na<sub>2</sub>\*Br<sub>4</sub>Cd
- Na<sub>2</sub>\*Br<sub>4</sub>Hg
- Na<sub>2</sub>\*CdCl<sub>4</sub>
- Na<sub>2</sub>\*F<sub>8</sub>Mo
- Na<sub>2</sub>\*HgI<sub>4</sub>
- Na<sub>2</sub>Ni\*F<sub>6</sub>
- Na<sub>2</sub>NiO<sub>3</sub>\*C<sub>4</sub>H<sub>6</sub>N<sub>4</sub>
- Na<sub>2</sub>O\*B<sub>4</sub>F<sub>12</sub>
- Na<sub>2</sub>O<sub>3</sub>\*C
- Na<sub>2</sub>O<sub>3</sub>Zn\*Cl<sub>4</sub>H<sub>6</sub>
- Na<sub>2</sub>O<sub>4</sub>\*H<sub>8</sub>HgI<sub>4</sub>
- Na<sub>2</sub>O<sub>4</sub>\*Mo
- Na<sub>2</sub>O<sub>4</sub>S
- Na<sub>2</sub>[SO<sub>4</sub>]
- Formation from Hg, HgSO<sub>4</sub>, and NaCl: 2.8.21.3
- Formation from Hg, MnO<sub>2</sub>, NaCl and H<sub>2</sub>SO<sub>4</sub>: 2.8.21.3
- Na<sub>2</sub>O<sub>4</sub>W
- Na<sub>2</sub>[WO<sub>4</sub>]
- Reaction with ClF: 2.11.4.1
- Na<sub>2</sub>O<sub>6</sub>\*CdH<sub>12</sub>I<sub>4</sub>
- Na<sub>2</sub>O<sub>7</sub>\*B<sub>4</sub>
- Na<sub>2</sub>Pr\*F<sub>6</sub>
- Na<sub>2</sub>U\*F<sub>8</sub>
- Na<sub>2</sub>W\*F<sub>8</sub>
- Na<sub>3</sub>\*CuF<sub>6</sub>
- Na<sub>3</sub>Sc\*F<sub>6</sub>
- Nb
- Nb
- Bromination followed by the addition of KF or NH<sub>4</sub>F: 2.11.3.1
- Fluorination: 2.11.3.1
- Reaction with Nb<sub>2</sub>O<sub>5</sub>-X<sub>2</sub>: 2.9.11.3
- Reaction with Nb<sub>2</sub>O<sub>5</sub>-NbCl<sub>5</sub>: 2.9.11.4
- Reaction with Se-NbCl<sub>4</sub>, Se-I<sub>2</sub>: 2.9.14.1.2
- Reaction with SnF<sub>2</sub>: 2.11.3.1
- Reaction with S-NbCl<sub>5</sub>, S<sub>2</sub>Cl<sub>2</sub>, S-I<sub>2</sub>: 2.9.14.1.2
- Reaction with F<sub>2</sub>-O<sub>2</sub>: 2.11.3.1
- Reaction with ClF<sub>3</sub>, BrF<sub>3</sub>: 2.9.3.4
- Reaction with F<sub>2</sub>: 2.9.2.1
- Reaction with Br<sub>2</sub>: 2.9.2.3
- Reaction with Cl<sub>2</sub>: 2.9.2.2
- Reaction with I<sub>2</sub>: 2.9.2.4
- Reaction with HF: 2.11.3.1
- Reaction with HX: 2.9.3.2
- Nb\*Br<sub>5</sub>
- Nb\*C<sub>2</sub>H<sub>3</sub>Br<sub>5</sub>N
- Nb\*C<sub>2</sub>H<sub>3</sub>Cl<sub>5</sub>N
- Nb\*C<sub>8</sub>H<sub>20</sub>Br<sub>6</sub>N
- Nb\*C<sub>8</sub>H<sub>20</sub>Cl<sub>6</sub>N
- Nb\*C<sub>16</sub>H<sub>36</sub>F<sub>6</sub>N
- Nb\*Cl<sub>5</sub>
- Nb\*Cl<sub>6</sub>Cs
- Nb\*Cs<sub>2</sub>I<sub>6</sub>
- Nb\*F<sub>3</sub>
- Nb\*F<sub>5</sub>
- Nb\*F<sub>8</sub>K<sub>3</sub>
- Nb\*I<sub>3</sub>
- Nb\*I<sub>5</sub>
- NbO\*Br<sub>3</sub>
- NbO\*Br<sub>5</sub>
- NbO\*C<sub>12</sub>H<sub>15</sub>
- NbO\*Cl<sub>2</sub>
- NbO\*Cl<sub>3</sub>
- NbO\*Cl<sub>4</sub>
- NbO\*Cl<sub>5</sub>
- NbO\*F<sub>6</sub>
- NbO\*F<sub>6</sub>H<sub>3</sub>
- NbO\*F<sub>6</sub>H<sub>12</sub>N<sub>3</sub>
- NbO\*F<sub>6</sub>K<sub>3</sub>
- NbO\*I
- NbO\*I<sub>2</sub>

- NbO\*I<sub>3</sub>  
 NbO<sub>2</sub>\*F  
 NbO<sub>2</sub>\*F<sub>2</sub>  
 NbO<sub>2</sub>\*F<sub>6</sub>  
 NbS\*Br<sub>3</sub>  
 NbS\*Cl<sub>2</sub>  
 NbS\*Cl<sub>3</sub>  
 NbS<sub>2</sub>\*Br<sub>2</sub>  
 NbS<sub>2</sub>\*Cl<sub>2</sub>  
 NbS<sub>2</sub>\*I<sub>2</sub>  
 NbSb\*F<sub>10</sub>  
 NbSe\*Br<sub>3</sub>  
 NbSe<sub>2</sub>\*Br<sub>2</sub>  
 NbSe<sub>2</sub>\*Cl<sub>2</sub>  
 NbSe<sub>2</sub>\*I<sub>2</sub>  
 Nb<sub>2</sub>\*C<sub>16</sub>H<sub>36</sub>F<sub>11</sub>N  
 Nb<sub>2</sub>O<sub>2</sub>\*F<sub>11</sub>  
 Nb<sub>2</sub>O<sub>5</sub>  
     Nb<sub>2</sub>O<sub>5</sub>  
         Reaction with AlX<sub>3</sub>: 2.9.4.8  
         Reaction with NbCl<sub>5</sub>: 2.9.12.6  
         Reaction with RCl: 2.9.4.6  
         Reaction with SOX<sub>2</sub>, BX<sub>3</sub>: 2.9.12.5  
         Reaction with SOCl<sub>2</sub>: 2.9.4.5  
         Reaction with C-X<sub>2</sub>: 2.9.12.1  
         Reaction with X<sub>2</sub> or C-X<sub>2</sub>: 2.9.4.2  
         Reaction with CX<sub>4</sub>: 2.9.12.4  
         Reaction with HF: 2.11.3.1, 2.9.12.2  
         Reaction with ag H<sub>2</sub>O<sub>2</sub>: 2.9.13.1.1  
 Nb<sub>2</sub>S<sub>3</sub>\*Br<sub>4</sub>  
 Nb<sub>2</sub>S<sub>3</sub>\*Cl<sub>4</sub>  
 Nb<sub>2</sub>Se\*F<sub>14</sub>  
 Nb<sub>3</sub>\*Br<sub>6</sub>  
 Nb<sub>3</sub>\*Br<sub>8</sub>  
 Nb<sub>3</sub>Se<sub>5</sub>\*Cl<sub>7</sub>  
 Nb<sub>4</sub>\*Br<sub>11</sub>Cs  
 Nb<sub>6</sub>Rb<sub>4</sub>\*Br<sub>18</sub>  
 Nd  
     Nd  
         Reaction with HX: 2.9.14.1.1  
 Nd\*Br<sub>3</sub>  
 Nd\*Cl<sub>2</sub>  
 Nd\*Cl<sub>3</sub>  
 Nd\*I<sub>3</sub>  
 NdS\*Br  
 NdSe\*F  
 Nd<sub>2</sub>Se\*F<sub>4</sub>  
 Ni  
     Ni  
         Reaction with F<sub>2</sub>: 2.9.2.1  
         Reaction with Br<sub>2</sub>: 2.9.2.3  
         Reaction with Cl<sub>2</sub>: 2.9.2.2  
 Ni\*BaF<sub>5</sub>  
 Ni\*BaF<sub>6</sub>  
 Ni\*Br<sub>2</sub>  
 Ni\*C<sub>4</sub>BaN<sub>4</sub>  
 Ni\*C<sub>2</sub>H<sub>16</sub>Ag<sub>2</sub>Br<sub>4</sub>N<sub>4</sub>  
 Ni\*C<sub>6</sub>F<sub>5</sub>I  
 Ni\*C<sub>12</sub>F<sub>10</sub>  
 Ni\*C<sub>16</sub>H<sub>40</sub>Br<sub>4</sub>N<sub>2</sub>  
 Ni\*C<sub>108</sub>F<sub>90</sub>Ge<sub>6</sub>Hg<sub>2</sub>  
 Ni\*Cl<sub>2</sub>  
 Ni\*Cs<sub>2</sub>F<sub>6</sub>  
 Ni\*F<sub>2</sub>  
 Ni\*F<sub>3</sub>  
 Ni\*F<sub>6</sub>K<sub>2</sub>  
 Ni\*F<sub>6</sub>K<sub>3</sub>  
 Ni\*F<sub>6</sub>Na<sub>2</sub>  
 Ni\*F<sub>14</sub>N<sub>2</sub>  
 Ni\*I<sub>2</sub>  
 NiO  
     NiO  
         Reaction with X<sub>2</sub>: 2.9.4.1  
 NiO<sub>2</sub>  
     NiO<sub>2</sub>  
         Reaction with ClF<sub>3</sub>: 2.9.4.4  
 NiO<sub>2</sub>\*F<sub>6</sub>N<sub>2</sub>  
 NiO<sub>3</sub>\*C<sub>4</sub>H<sub>6</sub>N<sub>4</sub>Na<sub>2</sub>  
 NiO<sub>4</sub>\*C<sub>4</sub>  
 NiO<sub>4</sub>\*C<sub>4</sub>H<sub>8</sub>BaN<sub>4</sub>  
 NiO<sub>4</sub>S  
     Ni[SO<sub>4</sub>]  
         Fluorination: 2.11.2.2  
 NiXe<sub>2</sub>\*F<sub>16</sub>  
 NiXe<sub>4</sub>\*F<sub>28</sub>  
 Ni<sub>2</sub>O<sub>3</sub>  
     Ni<sub>2</sub>O<sub>3</sub>  
         Reaction with AlI<sub>3</sub>: 2.9.4.8  
 No\*AuF<sub>6</sub>  
 Np\*CsF<sub>6</sub>  
 Np\*F<sub>6</sub>  
 NpO\*F<sub>4</sub>  
 NpO<sub>2</sub>\*F<sub>2</sub>  
 NpO<sub>3</sub>  
     NpO<sub>3</sub>  
         Fluorination: 2.11.5.2  
         Reaction with HF: 2.11.5.2  
 O\*AcF  
 O\*AgF<sub>3</sub>N  
 O\*Ag<sub>2</sub>  
 O\*Ag<sub>2</sub>FH<sub>2</sub>I  
 O\*AlCl  
 O\*AlCl<sub>4</sub>N  
 O\*AuCl



O*AuF <sub>4</sub> N	O*Cl <sub>3</sub> Nb
O*AuF <sub>6</sub> N	O*Cl <sub>4</sub> Cr
O*B	O*Cl <sub>4</sub> H <sub>2</sub> HgK <sub>2</sub>
O*BF <sub>4</sub> N	O*Cl <sub>4</sub> Mo
O*B <sub>4</sub> F <sub>12</sub> Na <sub>2</sub>	O*Cl <sub>4</sub> Nb
O*Ba	O*Cl <sub>5</sub> Cr
O*BaBr <sub>4</sub> CdH <sub>2</sub>	O*Cl <sub>5</sub> M
O*Be	O*Cl <sub>5</sub> Mo
O*BrCdH	O*Cl <sub>5</sub> Nb
O*BrCl <sub>4</sub> Mo	O*Cl <sub>8</sub> H <sub>10</sub> HgN <sub>2</sub>
O*BrH	O*CrF <sub>3</sub>
O*BrN	O*CrF <sub>4</sub>
O*Br <sub>2</sub> CdH <sub>2</sub>	O*Cu
O*Br <sub>3</sub> CdH <sub>2</sub> K	O*CuFH
O*Br <sub>3</sub> H <sub>2</sub> HgK	O*CuF <sub>2</sub> H <sub>4</sub>
O*Br <sub>3</sub> Nb	O*Cu <sub>2</sub>
O*Br <sub>4</sub> Mo	O*Cu <sub>2</sub> F <sub>3</sub> H
O*Br <sub>5</sub> Cr	O*FFe
O*Br <sub>5</sub> Mo	O*FHHg
O*Br <sub>5</sub> Nb	O*FI <sub>n</sub>
O*CAgN	O*FN
O*CAuCl	O*F <sub>4</sub> H <sub>3</sub> N
O*CCl <sub>2</sub>	O*F <sub>4</sub> M
O*CF	O*F <sub>4</sub> Mo
O*C <sub>2</sub> H <sub>2</sub> AuCl <sub>2</sub> KN <sub>2</sub>	O*F <sub>4</sub> Np
O*C <sub>2</sub> H <sub>3</sub> Br	O*F <sub>5</sub> Mo
O*C <sub>2</sub> H <sub>3</sub> Cl	O*F <sub>6</sub> H <sub>3</sub> Nb
O*C <sub>3</sub> H <sub>6</sub> ClN	O*F <sub>6</sub> H <sub>12</sub> N <sub>3</sub> Nb
O*C <sub>4</sub> H <sub>9</sub> BCl <sub>2</sub>	O*F <sub>6</sub> Hf <sub>2</sub>
O*C <sub>6</sub> H <sub>15</sub> BClN	O*F <sub>6</sub> IrN
O*C <sub>7</sub> H <sub>5</sub> Cl	O*F <sub>6</sub> K <sub>3</sub> Nb
O*C <sub>10</sub> H <sub>30</sub> Br <sub>10</sub> Cu <sub>4</sub> N <sub>2</sub>	O*F <sub>6</sub> Nb
O*C <sub>12</sub> H <sub>15</sub> Nb	O*F <sub>7</sub> MoN
O*C <sub>19</sub> H <sub>15</sub> AsAuBr <sub>2</sub> N	O*HNa
O*C <sub>19</sub> H <sub>15</sub> AsAuN	O*H <sub>2</sub> HgI <sub>3</sub> K
O*Ca	O*H <sub>6</sub> HgI <sub>3</sub> N
O*Cd	O*Hg
O*CdCl <sub>2</sub> H <sub>2</sub>	O*Hg <sub>2</sub>
O*CdCl <sub>3</sub> H <sub>2</sub> K	O*INb
O*CdCsH <sub>2</sub> I <sub>3</sub>	O*I <sub>2</sub> Nb
O*ClCr	O*I <sub>3</sub> Nb
O*ClFe	O*Mg
O*ClH	O*N
O*ClHMg	O*Ni
O*ClN	OOs*Cl <sub>4</sub>
O*Cl <sub>x</sub> CrF <sub>5+x</sub>	OOs*F <sub>4</sub>
O*Cl <sub>2</sub> Hg <sub>2</sub>	OOs*F <sub>5</sub>
O*Cl <sub>2</sub> Mo	OOs*F <sub>7</sub> N
O*Cl <sub>2</sub> Nb	OP*C <sub>18</sub> H <sub>25</sub> Cl <sub>2</sub> CuN
O*Cl <sub>3</sub> Cr	OP*C <sub>19</sub> H <sub>15</sub> AuBr <sub>2</sub> N
O*Cl <sub>3</sub> H <sub>2</sub> HgK	OP*C <sub>19</sub> H <sub>15</sub> AuN
O*Cl <sub>3</sub> Mo	OP*Cl <sub>3</sub>

OPa<sub>2</sub>\*F<sub>8</sub>  
 OPt\*ClF<sub>8</sub>  
 OPt\*F<sub>3</sub>  
 OPt\*F<sub>6</sub>H<sub>3</sub>  
 OPt\*F<sub>6</sub>N  
 OPu\*F<sub>4</sub>

**ORa**

RaO

Reaction with HX: 2.7.5

ORe\*Br<sub>4</sub>  
 ORe\*Cl<sub>2</sub>  
 ORe\*Cl<sub>4</sub>  
 ORe\*Cl<sub>5</sub>  
 ORe\*F<sub>4</sub>  
 ORe\*F<sub>5</sub>  
 ORe\*F<sub>7</sub>N  
 OReSb\*F<sub>9</sub>  
 ORu\*Cl<sub>3</sub>H  
 ORu\*Cl<sub>10</sub>  
 ORu\*F<sub>4</sub>  
 ORu\*F<sub>6</sub>H<sub>3</sub>  
 ORu\*F<sub>6</sub>N  
 ORu<sub>2</sub>\*Cl<sub>10</sub>  
 OS\*Br<sub>2</sub>  
 OS\*C  
 OS\*ClH<sub>3</sub>  
 OS\*Cl<sub>2</sub>  
 OSW\*Cl<sub>2</sub>  
 OSW\*F<sub>2</sub>  
 OSb\*F<sub>9</sub>Mo  
 OSbW\*F<sub>9</sub>  
 OSc\*F  
 OSeW\*F<sub>8</sub>

**OSr**

SrO

Reaction with HX: 2.7.5

OTa\*Br<sub>3</sub>  
 OTa\*Cl<sub>2</sub>  
 OTa\*Cl<sub>3</sub>  
 OTa\*Cl<sub>4</sub>  
 OTa\*F<sub>3</sub>  
 OTa\*F<sub>6</sub>  
 OTa\*F<sub>6</sub>H<sub>3</sub>  
 OTa\*F<sub>6</sub>H<sub>12</sub>N<sub>3</sub>  
 OTa\*F<sub>6</sub>K<sub>3</sub>  
 OTc\*Br<sub>3</sub>  
 OTc\*Cl<sub>3</sub>  
 OTc\*F<sub>4</sub>  
 OTh\*F<sub>2</sub>  
 OTi\*Cl  
 OTi\*Cl<sub>2</sub>  
 OTi\*Cl<sub>4</sub>

OTi\*F<sub>2</sub>  
 OTi\*F<sub>4</sub>  
 OTi\*F<sub>5</sub>  
 OTi\*F<sub>6</sub>H<sub>3</sub>  
 OTi\*F  
 OU\*F<sub>4</sub>  
 OV\*Br<sub>2</sub>  
 OV\*Br<sub>3</sub>  
 OV\*Br<sub>4</sub>  
 OV\*C<sub>6</sub>H<sub>5</sub>Cl<sub>2</sub>  
 OV\*Cl  
 OV\*Cl<sub>2</sub>  
 OV\*Cl<sub>3</sub>  
 OV\*Cl<sub>4</sub>  
 OV\*Cl<sub>5</sub>  
 OV\*CsF<sub>4</sub>  
 OV\*F<sub>3</sub>  
 OV\*F<sub>4</sub>  
 OV\*F<sub>5</sub>  
 OV\*F<sub>5</sub>K<sub>2</sub>  
 OW\*Br<sub>2</sub>  
 OW\*Br<sub>3</sub>  
 OW\*Br<sub>4</sub>  
 OW\*Br<sub>5</sub>  
 OW\*Cl<sub>2</sub>  
 OW\*Cl<sub>3</sub>  
 OW\*Cl<sub>4</sub>  
 OW\*Cl<sub>5</sub>  
 OW\*CsF<sub>5</sub>  
 OW\*F<sub>2</sub>  
 OW\*F<sub>4</sub>  
 OW\*F<sub>5</sub>  
 OW\*F<sub>5</sub>K  
 OW\*F<sub>7</sub>N  
 OW\*F<sub>9</sub>N  
 OXe\*F<sub>4</sub>  
 OY\*F

**OZn**

ZnO

Fluorination: 2.11.2.3

Formation from Zn(OH)Cl: 2.8.19

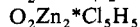
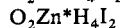
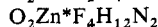
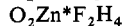
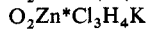
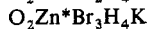
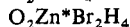
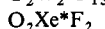
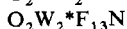
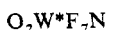
Formation from ZnCl<sub>2</sub>·4 Zn(OH)<sub>2</sub>·-H<sub>2</sub>O: 2.8.19Formation in ZnF<sub>2</sub> dehydration: 2.8.19Reaction with BCl<sub>3</sub>: 2.8.15.3Reaction with PF<sub>3</sub>: 2.8.15.3Reaction with S<sub>2</sub>Cl<sub>2</sub>: 2.8.15.3Reaction with [NH<sub>4</sub>]Cl: 2.8.15.3Reaction with CH<sub>3</sub>C(O)Cl: 2.8.15.3Reaction with OCl<sub>2</sub>: 2.8.15.3

Reaction with HF: 2.11.2.3

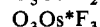
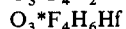
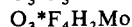
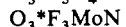
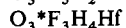
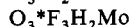
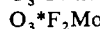
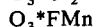
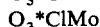
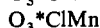
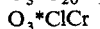
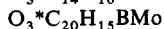
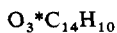
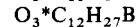
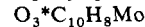
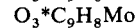
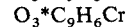
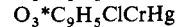
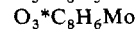
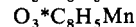
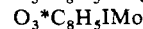
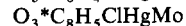
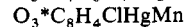
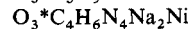
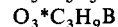
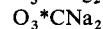
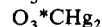
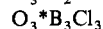
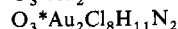
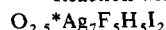
Reaction with HI: 2.8.15.2

- Reaction with  $\text{CF}_2\text{BrCl}$ : 2.8.15.3  
 Reaction with  $\text{F}_2$ : 2.8.15.1  
 Reaction with  $\text{HBr}$ : 2.8.15.2  
 Reaction with  $\text{HCl}$ : 2.8.15.2  
 Reaction with  $\text{Cl}_2$ : 2.8.15.1  
 Reaction with  $\text{CCl}_4$ : 2.8.15.3  
 Reaction with  $\text{HF}$ : 2.8.15.2  
 $\text{OZn}^*\text{Br}_3\text{H}_2\text{Na}$   
 $\text{OZn}^*\text{Br}_4\text{H}_{10}\text{N}_2$   
 $\text{OZn}^*\text{Br}_5\text{H}_{14}\text{N}_3$   
 $\text{OZn}^*\text{C}_8\text{H}_{11}\text{Cl}$   
 $\text{OZn}^*\text{ClH}$   
 $\text{OZn}^*\text{Cl}_2\text{H}_2$   
 $\text{OZn}^*\text{Cl}_3\text{H}_5$   
 $\text{OZr}^*\text{Cl}_4$   
 $\text{OZr}_2^*\text{Cl}_{10}$   
 $\text{O}_{0.5}^*\text{Co}_2\text{F}_6\text{H}_{19}\text{N}_6$   
 $\text{O}_2^*\text{AgF}_4$   
 $\text{O}_2^*\text{AmF}_2$   
 $\text{O}_2^*\text{AuCl}_4\text{H}_4\text{K}$   
 $\text{O}_2^*\text{AuCl}_4\text{H}_4\text{Na}$   
 $\text{O}_2^*\text{AuF}_4\text{N}$   
 $\text{O}_2^*\text{AuF}_6$   
 $\text{O}_2^*\text{BaH}_4\text{Cl}_8\text{Hg}_3$   
 $\text{O}_2^*\text{BeH}_2$   
 $\text{O}_2^*\text{Br}_2\text{Cr}$   
 $\text{O}_2^*\text{Br}_2\text{Mo}$   
 $\text{O}_2^*\text{Br}_3\text{H}_4\text{HgK}$   
 $\text{O}_2^*\text{Br}_3\text{H}_4\text{HgNa}$   
 $\text{O}_2^*\text{C}_4\text{H}_{14}\text{Au}_2$   
 $\text{O}_2^*\text{C}_5\text{H}_5\text{ClMoN}_2$   
 $\text{O}_2^*\text{C}_6\text{H}_{14}\text{AlCl}$   
 $\text{O}_2^*\text{C}_7\text{H}_{13}\text{Au}$   
 $\text{O}_2^*\text{C}_8\text{H}_{18}\text{BCl}$   
 $\text{O}_2^*\text{C}_8\text{H}_{19}\text{AuCl}_4\text{N}_2$   
 $\text{O}_2^*\text{C}_{10}\text{H}_4\text{Au}_5\text{I}_2\text{K}_5\text{N}_{10}$   
 $\text{O}_2^*\text{C}_{10}\text{H}_{16}\text{F}_4\text{HgN}_2$   
 $\text{O}_2^*\text{C}_{14}\text{H}_{14}\text{AlCl}$   
 $\text{O}_2^*\text{C}_{16}\text{H}_{14}\text{Hg}$   
 $\text{O}_2^*\text{C}_{26}\text{H}_{20}\text{AsAuBr}_2\text{N}_2$   
 $\text{O}_2^*\text{C}_{26}\text{H}_{20}\text{AsAuCl}_2\text{N}_2$   
 $\text{O}_2^*\text{C}_{26}\text{H}_{20}\text{AsAuN}_2$   
 $\text{O}_2^*\text{CdF}_2\text{H}_4$   
 $\text{O}_2^*\text{CdH}_{12}\text{I}_4\text{N}_2$   
 $\text{O}_2^*\text{Ce}$   
 $\text{O}_2^*\text{ClF}_6\text{Ir}$   
 $\text{O}_2^*\text{Cl}_2\text{Cr}$   
 $\text{O}_2^*\text{Cl}_2\text{CuH}_4$   
 $\text{O}_2^*\text{Cl}_2\text{Mn}$   
 $\text{O}_2^*\text{Cl}_2\text{Mo}$   
 $\text{O}_2^*\text{Cl}_3\text{H}_4\text{HgK}$   
 $\text{O}_2^*\text{Cl}_3\text{H}_4\text{HgNa}$   
 $\text{O}_2^*\text{Cl}_4\text{Mo}$   
 $\text{O}_2^*\text{Cl}_8\text{H}_4\text{Hg}_3\text{Sr}$   
 $\text{O}_2^*\text{CrF}_2$   
 $\text{O}_2^*\text{CrF}_4$   
 $\text{O}_2^*\text{CuF}_2\text{H}_4$   
 $\text{O}_2^*\text{CuF}_4\text{H}_{12}\text{N}_2$   
 $\text{O}_2^*\text{CuH}_2$   
 $\text{O}_2^*\text{FNB}$   
 $\text{O}_2^*\text{F}_2\text{H}_4\text{Hg}$   
 $\text{O}_2^*\text{F}_2\text{HgH}_4$   
 $\text{O}_2^*\text{F}_2\text{Mo}$   
 $\text{O}_2^*\text{F}_2\text{Nb}$   
 $\text{O}_2^*\text{F}_2\text{Np}$   
 $\text{O}_2^*\text{F}_3\text{Mo}$   
 $\text{O}_2^*\text{F}_6\text{IrN}_2$   
 $\text{O}_2^*\text{F}_6\text{N}_2\text{Ni}$   
 $\text{O}_2^*\text{F}_6\text{Nb}$   
 $\text{O}_2^*\text{F}_7\text{MoN}$   
 $\text{O}_2^*\text{F}_8\text{Hf}_3$   
 $\text{O}_2^*\text{F}_9\text{Mn}_2$   
 $\text{O}_2^*\text{F}_{11}\text{Nb}_2$   
 $\text{O}_2^*\text{H}_4\text{CuF}_2$   
 $\text{O}_2^*\text{Hf}$   
 $\text{O}_2^*\text{Ir}$   
 $\text{O}_2^*\text{Mn}$   
 $\text{O}_2^*\text{Mo}$   
 $\text{O}_2^*\text{Ni}$   
 $\text{O}_2\text{Os}$   
 $\text{OsO}_2$   
 Fluorination: 2.11.4.2  
 $\text{O}_2\text{Os}^*\text{Br}_4$   
 $\text{O}_2\text{Os}^*\text{Cl}_4$   
 $\text{O}_2\text{Os}^*\text{F}_3$   
 $\text{O}_2\text{Os}^*\text{F}_8\text{N}_2$   
 $\text{O}_2\text{P}^*\text{H}_3$   
 $\text{O}_2\text{PV}^*\text{C}_{24}\text{H}_{20}\text{F}_2$   
 $\text{O}_2\text{Pa}^*\text{F}_5\text{H}_4$   
 $\text{O}_2\text{Pd}^*\text{F}_6$   
 $\text{O}_2\text{Pt}$   
 $\text{PtO}_2$   
 Fluorination: 2.11.4.2  
 Reaction with  $\text{X}_2$ : 2.9.4.1  
 $\text{O}_2\text{Pt}^*\text{F}_6$   
 $\text{O}_2\text{Pt}^*\text{F}_6\text{H}_6$   
 $\text{O}_2\text{Pt}^*\text{F}_6\text{N}$   
 $\text{O}_2\text{Pu}^*\text{F}_2$   
 $\text{O}_2\text{Rb}^*\text{AmF}_2$   
 $\text{O}_2\text{Re}$   
 $\text{ReO}_2$   
 Fluorination: 2.11.4.1  
 Reaction with  $\text{SOCl}_2$ : 2.9.4.5  
 Reaction with  $\text{X}_2$ : 2.9.12.1

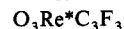
- Reaction with HX: 2.9.10.2
- $O_2Re^*F_2K$
- $O_2Re^*F_2Na$
- $O_2Re^*F_3$
- $O_2Re^*F_8N_2$
- $O_2Rh^*F_6$
- $O_2Ru$
- $RuO_2$
- Fluorination: 2.11.3.2
- $O_2Ru^*Br_4$
- $O_2Ru^*Cl_4$
- $O_2Ru^*F_6$
- $O_2S$
- $SO_2$
- Formation from Hg and  $O_2SCl_2$ : 2.8.14.4
- Formation from ZnO and  $S_2Cl_2$ : 2.8.15.3
- Reaction with  $HgCl_2$ : 2.8.21.2
- Reaction with  $Hg_2Cl_2$  and HCl: 2.8.20.1
- Use as reducing agent: 2.9.13.2
- $O_2S^*Cl_2$
- $O_2S_4U_3$
- $U_3O_2S_4$
- Reaction with  $Br_2$ : 2.9.5
- $O_2Sb^*C_{22}H_{25}$
- $O_2Sb_2^*CrF_{15}$
- $O_2Se$
- $SeO_2$
- Reaction with  $Hg_2Cl_2$  and HCl: 2.8.20.1
- $O_2Se^*F_6Mo$
- $O_2SeW^*F_6$
- $O_2Si$
- $SiO_2$
- Reaction with Ta- $TaCl_4$ : 2.9.11.4
- Reaction with  $BeI_2$ : 2.7.2
- $O_2Sr^*H_2$
- $O_2Ta^*Cl$
- $O_2Ta^*Cl_2$
- $O_2Ta^*F$
- $O_2Ta_2^*F_{11}$
- $O_2Tc$
- $TcO_2$
- Fluorination: 2.11.3.1
- Reaction with  $X_2$ : 2.9.12.1
- $O_2Tc^*F_3$
- $O_2Tc^*F_7N$
- $O_2Tc^*F_8N_2$
- $O_2Te_2W^*F_{14}$
- $O_2Th$
- $ThO_2$
- Reaction with  $ThF_4$ : 2.11.5.2
- Reaction with HF: 2.11.5.2
- $O_2Ti$
- $TiO_2$
- Fluorination: 2.11.2.1
- Formation from HgO and  $TiCl_4$ : 2.8.15.3
- Reaction with  $AlI_3$ : 2.9.4.8
- Reaction with MF-HF: 2.11.2.1
- Reaction with RCl: 2.9.4.6
- Reaction with  $SF_4$ : 2.11.2.1
- Reaction with  $TiCl_3$ : 2.9.12.6
- Reaction with  $X_2$  or C- $X_2$ : 2.9.4.2
- Reaction with  $F_2-O_2$ : 2.11.2.1
- Reaction with ag HF: 2.9.13.1.1
- $O_2Ti^*F_3H_2$
- $O_2Ti^*F_5K_3$
- $O_2Ti^*F_6N_2$
- $O_2Ti_7^*F_{30}$
- $O_2Ti^*C_2H_3$
- $O_2Ti^*C_2H_3Br_2$
- $O_2Ti^*C_5H_7$
- $O_2U^*F_2$
- $O_2U^*F_5H_{12}N_3$
- $O_2U^*F_5K_3$
- $O_2V$
- $VO_2$
- Reaction with  $SOCl_2$ : 2.9.4.5
- Reaction with ag HF: 2.9.13.1.1
- $O_2V^*BaF_3$
- $O_2V^*C_{24}H_{20}AsF_2$
- $O_2V^*Cl$
- $O_2V^*Cl_2$
- $O_2V^*Cl_3H_4$
- $O_2V^*F$
- $O_2V^*F_2$
- $O_2V^*F_4$
- $O_2V^*F_4N$
- $O_2V_2^*F_7$
- $O_2V_2^*F_{11}$
- $O_2W$
- $WO_2$
- Reaction with  $X_2$ : 2.9.12.1
- Reaction with  $CF_2Cl_2$ : 2.11.4.1
- Reaction with HF: 2.9.12.2
- $O_2W^*Br_2$
- $O_2W^*Br_2N_2$
- $O_2W^*Cl_2$
- $O_2W^*Cl_2N_2$
- $O_2W^*Cl_4$
- $O_2W^*F_2$
- $O_2W^*F_5H_3$
- $O_2W^*F_5N$



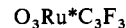
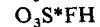
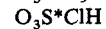
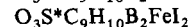
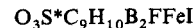
Fluorination: 2.11.3.1

Reaction with  $AlI_3$ : 2.9.4.8Reaction with  $MF-HF$ : 2.11.3.1Reaction with  $S_2Cl_2$ ,  $PCl_5$ : 2.9.4.5Reaction with  $X_2$  or  $C-X_2$ : 2.9.4.2Reaction with  $COCl_2$ : 2.9.4.7

Fluorination: 2.11.4.1

Reaction with  $ReCl_5$ : 2.9.12.6Reaction with  $X_2$ : 2.9.12.1

Formation: 2.10.2.2.2

Reaction with  $Hg_2Br_2$ : 2.8.20.1

- $O_3SXe*F_2$   
 $O_3Sb_2$   
 $Sb_2O_3$   
 Reaction with  $ReF_6$ : 2.9.14.4  
 Reaction with  $TiCl_4$ ,  $VOCl_3$ : 2.9.12.7  
 $O_3Sc*H_3$   
 $O_3Sc_2$   
 $Sc_2O_3$   
 Reaction with  $[NH_4][HF_4]$ : 2.11.2.1  
 $O_3Sn*C_{11}H_{14}Mo$   
 $O_3Tc*F$   
 $O_3Ti*F_{16}$   
 $O_3Ti*C_{10}H_{11}Mo$   
 $O_3Ti*C_{12}H_{15}Mo$   
 $O_3TiW*C_{10}H_{11}$   
 $O_3Ti_2$   
 $Ti_2O_3$   
 Reaction with  $BX_3$ : 2.6.6.4  
 Reaction with  $F_2$ : 2.6.6.1  
 Reaction with  $BrF_3$ : 2.6.6.4  
 Reaction with  $ag\ HX$ : 2.6.6.3  
 $O_3U$   
 $UO_3$   
 Fluorination: 2.11.5.2  
 Reaction with  $XeF_2$ : 2.11.5.2  
 Reaction with  $SF_4$ : 2.11.5.2  
 Reaction with  $HF$ : 2.11.5.2  
 $O_3V*BaF$   
 $O_3V*Cl_4H_4$   
 $O_3V*F_3H_6$   
 $O_3V*Na$   
 $O_3V_2$   
 $V_2O_3$   
 Reaction with  $AlI_3$ : 2.9.4.8  
 Reaction with  $SOCl_2$ : 2.9.4.5  
 Reaction with  $VCl_3$ : 2.9.12.6  
 $O_3V_2*F_8K_4$   
 $O_3V_3*F_{14}$   
 $O_3V_3*F_{14}K_5$   
 $O_3W$   
 $WO_3$   
 Reaction with  $AlI_3$ : 2.9.4.8  
 Reaction with  $RCI$ : 2.9.4.6  
 Reaction with  $SOX_2$ ,  $BX_3$ : 2.9.12.5  
 Reaction with  $SF_4$ : 2.9.4.4, 2.11.4.1  
 Reaction with  $NaF-SF_4$ : 2.11.4.1  
 Reaction with  $W-Br_2$ : 2.9.11.3  
 Reaction with  $WCl_6$ : 2.9.12.6  
 Reaction with  $W-WCl_6$ : 2.9.11.4  
 Reaction with  $CX_4$ : 2.9.12.4  
 Reaction with  $NF_3$ : 2.11.4.1  
 Reaction with  $Cl_2$ : 2.9.11.2  
 Reaction with  $BrF_3$ : 2.11.4.1  
 Reaction with  $BrF_3$ ,  $ClF_3$ ,  $IF_5$ : 2.9.4.4  
 Reaction with  $ClF_3$ : 2.11.4.1  
 Reaction with  $IF_5$ : 2.9.12.3, 2.11.4.1  
 Reaction with  $KF$  and  $SeF_4$ : 2.11.4.1  
 Reaction with  $ClF$ : 2.11.4.1  
 Reaction with  $CCl_4$ : 2.9.12.1  
 $O_3W*C_8H_4I$   
 $O_3W*F_3H_2$   
 $O_3W*F_{10}I_2$   
 $O_3W_2*F_9H_3$   
 $O_3X*Cr$   
 $O_3Xe$   
 $XeO_3$   
 Formation: 2.10.2.2.1  
 $O_3Y_2$   
 $Y_2O_3$   
 Reaction with  $YF_3$ : 2.11.3.1  
 Reaction with  $[NH_4][HF_2]$ : 2.11.3.1  
 Reaction with  $HF$  in  $HCl$ : 2.11.3.1  
 Reaction with  $HF$ : 2.11.3.1  
 $O_3Zn*Br_2H_6$   
 $O_3Zn*Br_3H_{10}N$   
 $O_3Zn*C$   
 $O_3Zn*Cl_2H_6$   
 $O_3Zn*Cl_3H_6Li$   
 $O_3Zn*Cl_4H_6Na_2$   
 $O_3Zn*H_6I_3Na$   
 $O_3Zr*F_3H_4$   
 $O_{3.5}*H_7CoF_3$   
 $O_4*AuBr_4H_9$   
 $O_4*AuCl_4H_9$   
 $O_4*Br_2CdH_8$   
 $O_4*Br_2CuH_8$   
 $O_4*C_2H_6$   
 $O_4*C_3CoN$   
 $O_4*C_4Br_2Fe$   
 $O_4*C_4Br_2Mo$   
 $O_4*C_4Cl_2Fe$   
 $O_4*C_4Cl_2Mo$   
 $O_4*C_4F_2Mo$   
 $O_4*C_4FeI_2$   
 $O_4*C_4H_6Cd$   
 $O_4*C_4H_6Hg$   
 $O_4*C_4H_8BaN_4Ni$   
 $O_4*C_4H_{12}B_2$   
 $O_4*C_4Ni$   
 $O_4*C_8H_{10}BBFeN$   
 $O_4*C_8H_{20}B_2$   
 $O_4*C_{14}H_{10}$   
 $O_4*C_{16}H_{20}AuCl_2N_3$   
 $O_4*C_{18}H_{24}AuCl_2N_3$

- $O_4^*C_{28}Au_2F_{26}$   
 $O_4^*C_{34}H_{14}Au_2F_{20}$   
 $O_4^*CdCl_2H_8$   
 $O_4^*CdCl_6Cu_2H_8$   
 $O_4^*ClH$   
 $O_4^*ClK$   
 $O_4^*Co_3$   
 $O_4^*F_2H_2Mo$   
 $O_4^*F_3H_2Mo$   
 $O_4^*F_4Mo_2$   
 $O_4^*F_6Mo_2$   
 $O_4^*H_8HgI_4Na_2$   
 $O_4^*H_9AuBr_4$   
 $O_4^*KMn$   
 $O_4^*K_2Mo$   
 $O_4^*MoNa_2$   
 $O_4Os$   
 $OsO_4$   
 Fluorination: 2.11.4.2  
 Reaction with  $AgIO_3-BrF_3$ : 2.11.4.2  
 Reaction with  $BF_3$ : 2.9.13.1.1  
 Reaction with  $MBr-BrF_3$ : 2.11.4.2  
 Reaction with  $MF$ : 2.11.4.2  
 Reaction with  $OsF_6$ : 2.11.4.2  
 Reaction with  $SCl_2$ : 2.9.4.5  
 Reaction with  $BrF_3$ : 2.9.12.3, 2.11.4.2  
 Reaction with  $CsF$ : 2.9.13.1.1  
 Reaction with  $HX$ : 2.9.10.2  
 Reaction with  $ag\ HX$ : 2.9.4.3  
 $O_4Os^*C_4Cl_2$   
 $O_4Os^*F_2$   
 $O_4P^*C_{34}H_{25}BMn$   
 $O_4P^*H_3$   
 $O_4Pr_6$   
 $Pr_6O_4$   
 Fluorination of  $MCl$  mixture: 2.11.5.1  
 $O_4Re$   
 $ReO_4$   
 Reaction with  $X_2$  or  $C-X_2$ : 2.9.4.2  
 $O_4Re^*K$   
 $O_4Re^*Na$   
 $O_4Ru$   
 $RuO_4$   
 Reaction with  $BrF_3, BrF_5$ : 2.9.12.3  
 Reaction with  $HX$ : 2.9.10.2  
 Reaction with  $aq\ HX$ : 2.9.4.3  
 $O_4Ru^*C_4Br_2$   
 $O_4Ru^*C_4Cl_2$   
 $O_4S^*Ba$   
 $O_4S^*Cd$   
 $O_4S^*CsF$   
 $O_4S^*Cs_2$   
 $O_4S^*Cu$   
 $O_4S^*Fe$   
 $O_4S^*Hg$   
 $O_4S^*K_2$   
 $O_4S^*Mn$   
 $O_4S^*Na_2$   
 $O_4S^*Ni$   
 $O_4SZn$   
 $Zn[SO_4]$   
 Reaction with  $BaI_2$ : 2.8.17.2  
 Reaction with  $CaCl_2$ : 2.8.17.2  
 Reaction with  $HCl$ : 2.8.17.1  
 $O_4S_2Zn$   
 $Zn[S_2O_4]$   
 Formation from  $Zn$  and  $SO_2Cl_2$ :  
 2.8.14.4  
 $O_4Sn^*C_{22}H_{15}Co$   
 $O_4Tc^*H_4N$   
 $O_4Tc_2^*C_8Cl_2$   
 $O_4Te_4W^*F_{22}$   
 $O_4Ti^*C_{10}H_{16}F_2$   
 $O_4Ti^*C_4Co$   
 $O_4V_2^*F_5$   
 $O_4V_2^*F_5K_3$   
 $O_4W^*C_4Br_2$   
 $O_4W^*C_4Cl_2$   
 $O_4W^*C_4I_2$   
 $O_4W^*K_2$   
 $O_4W^*Na_2$   
 $O_4Xe^*Ba$   
 $O_4Zn^*BaCl_4H_8$   
 $O_4Zn^*Cl_2H_8$   
 $O_4Zn^*F_2H_8$   
 $O_4Zn^*H_8I_2$   
 $O_5^*BaCdH_{10}I_4$   
 $O_5^*BaCd_2Cl_6H_{10}$   
 $O_5^*CH_2Cu_2$   
 $O_5^*C_5BCl_2Mn$   
 $O_5^*C_5BrMn$   
 $O_5^*C_5Br_2InMn$   
 $O_5^*C_5ClMn$   
 $O_5^*C_5Cl_2InMn$   
 $O_5^*C_5Fe$   
 $O_5^*C_5HMn$   
 $O_5^*C_5IMn$   
 $O_5^*C_6H_3Mn$   
 $O_5^*C_9H_{12}BMnN_2$   
 $O_5^*ClCr$   
 $O_5^*Cl_2$   
 $O_5^*Nb_2$   
 $O_5Rb^*CAm$   
 $O_5Re^*C_5Br$

- $O_5Re^*C_5Cl$   
 $O_5Re^*C_5F$   
 $O_5Re^*C_5I$   
 $O_5Re_2^*C_5F_6$   
 $O_5Ru^*H_{10}Cl_4$   
 $O_5Ta_2$   
 $Ta_2O_5$   
 Reaction with  $AlX_3$ : 2.9.4.8  
 Reaction with  $RCl$ : 2.9.4.6  
 Reaction with  $SOCl_2$ : 2.9.4.5  
 Reaction with  $TaCl_5$ : 2.9.12.6  
 Reaction with  $TaCl_5$ -Ta: 2.9.11.4  
 Reaction with  $X_2$  or  $C-X_2$ : 2.9.4.2  
 Reaction with  $HF$ : 2.11.4.1, 2.9.12.2  
 Reaction with aq  $HF$ : 2.9.13.1.1  
 $O_5Tc^*C_5Br$   
 $O_5Tc^*C_5Cl$   
 $O_5Tc^*C_5I$   
 $O_5Tc_2^*F_4$   
 $O_5Tl^*C_5Mn$   
 $O_5V_2$   
 $V_2O_5$   
 Fluorination: 2.11.2.1  
 Reaction with  $RCl$ : 2.9.4.6  
 Reaction with  $SOX_2$ ,  $AlX_3$ ,  $BX_3$ : 2.9.12.5  
 Reaction with  $S_2Cl_2$ : 2.9.4.5  
 Reaction with  $VCl_3$ ,  $VOCl_3$ : 2.9.12.6  
 Reaction with  $X_2$  or  $C-X_2$ : 2.9.4.2  
 Reaction with  $NF_3$ : 2.11.2.1  
 Reaction with  $KF$ - $HF$ : 2.11.2.1  
 Reaction with  $CsF$ - $HF$ : 2.11.2.1  
 Reaction with  $IF_5$ : 2.9.12.3  
 Reaction with  $C_5Cl_8$ ,  $C_5Cl_6$ : 2.9.12.4  
 Reaction with ag  $HX$ : 2.9.4.3  
 Reaction with ag  $HF$ : 2.9.13.1.1  
 $O_5V_2^*F_{21}I_3$   
 $O_6^*BaCl_6H_{12}Hg_2$   
 $O_6^*Br_2Hg$   
 $O_6^*C_6Cr$   
 $O_6^*C_6Mo$   
 $O_6^*C_7H_3Mn$   
 $O_6^*C_{12}H_5Mn$   
 $O_6^*C_{12}H_{24}CuI_2K$   
 $O_6^*C_{12}H_{27}B_3$   
 $O_6^*C_{16}H_{10}HgMo_2$   
 $O_6^*C_{16}H_{10}Mo_2$   
 $O_6^*CdH_{12}I_4Na_2$   
 $O_6^*CdN_2$   
 $O_6^*Cl_2Hg$   
 $O_6^*Cl_6H_{12}Hg_2Mg$   
 $O_6^*F_{15}I_3Mo_2$   
 $O_6^*HgI_2$   
 $O_6^*HgN_2$   
 $O_6^*Hg_2N_2$   
 $O_6Os_2^*C_6Cl_4$   
 $O_6P_2Zn_3$   
 $Zn_3[PO_3]_2$   
 Formation from  $ZnO$  and  $PF_3$ : 2.8.15.3  
 $O_6P_6^*Al_4Cl_{30}$   
 $O_6Re_3^*C_6F_{11}$   
 $O_6S_2^*C_8H_6BFe_2N$   
 $O_6Sr^*Br_2$   
 $O_6V_3^*F$   
 $O_6V_3^*FH_4N$   
 $O_6W^*C_6$   
 $O_6Zn^*BaCl_4H_{12}$   
 $O_6Zn^*Cl_2$   
 $O_6Zn^*Cl_4H_{12}Mg$   
 $O_7^*B_4Na_2$   
 $O_7^*CaCd_2Cl_6H_{14}$   
 $O_7^*CdCl_4H_{16}$   
 $O_7Re_2$   
 $Re_2O_7$   
 Fluorination: 2.11.4.1  
 Reaction with  $ReF_7$ : 2.11.4.1  
 Reaction with  $ReCl_5$ : 2.9.12.6  
 Reaction with  $RCl$ : 2.9.4.6  
 Reaction with  $HF$ : 2.9.12.2  
 $O_7Sr^*Cd_2Cl_6H_{14}$   
 $O_7Ta_3^*F$   
 $O_7Tb_4$   
 $Tb_4O_7$   
 Fluorination of  $MCl$  mixture: 2.11.5.1  
 Reaction with  $ClF_3$ - $HF$ : 2.11.5.1  
 $O_7Zn^*Cl_2H_{14}$   
 $O_8^*Ag_7F_2H$   
 $O_8^*BaCdCl_4H_{16}$   
 $O_8^*C_8F_2Mn_2$   
 $O_8^*C_8Fe_2I_2$   
 $O_8^*C_8I_2Mo_2$   
 $O_8^*C_{16}H_{32}Cu_4I_6K_2$   
 $O_8^*Cl_2Hg$   
 $O_8Re_2^*C_8Cl_2$   
 $O_8S_2^*CoCs_2$   
 $O_8Sr^*Ag_2H_{16}I_4$   
 $O_8Sr^*CdH_{16}I_4$   
 $O_8Tc_2^*C_8Br_2$   
 $O_8Tc_2^*C_8I_2$   
 $O_8U_3$   
 $U_3O_8$   
 Fluorination: 2.11.5.2  
 Reaction with  $SF_4$ : 2.11.5.2  
 Reaction with  $XeF_2$ : 2.11.5.2



- $\text{O}_8\text{W}_2*\text{C}_8\text{I}_2$   
 $\text{O}_9\text{Ta}_4*\text{F}_4$   
 $\text{O}_9\text{Zn}_5*\text{Cl}_2\text{H}_{10}$   
 $\text{O}_{10}*\text{C}_8\text{H}_{16}\text{Cu}_2$   
 $\text{O}_{10}*\text{C}_{10}\text{BrInMn}_2$   
 $\text{O}_{10}*\text{C}_{10}\text{ClInMn}_2$   
 $\text{O}_{10}*\text{C}_{10}\text{Mn}_2$   
 $\text{O}_{10}*\text{C}_{20}\text{H}_{40}\text{Cu}_4\text{I}_6\text{K}_2$   
 $\text{O}_{10}\text{Pa}_2$   
 $\text{Pa}_2\text{O}_{10}$   
 Reaction with  $\text{HF}-\text{O}_2$ : 2.11.5.2  
 Reaction with  $\text{F}_2$ : 2.11.5.2  
 $\text{O}_{10}\text{Re}_2*\text{C}_{10}$   
 $\text{O}_{10}\text{Tc}_2*\text{C}_{10}$   
 $\text{O}_{11}\text{Pr}_6$   
 $\text{Pr}_6\text{O}_{11}$   
 Reaction with  $\text{ClF}_3$  and  $\text{NaCl}-\text{HF}$ :  
 2.11.5.1  
 $\text{O}_{12}*\text{C}_{12}\text{Co}_4$   
 $\text{O}_{12}*\text{C}_{12}\text{Fe}_3$   
 $\text{O}_{12}\text{Os}_3*\text{C}_{12}$   
 $\text{O}_{12}\text{Ru}_3*\text{C}_{12}$   
 $\text{O}_{12}\text{Ru}_4*\text{C}_{12}\text{F}_8$   
 $\text{O}_{12}\text{S}_3*\text{Fe}_2$   
 $\text{O}_{15}*\text{C}_{15}\text{InMn}_3$   
 $\text{O}_{15}*\text{C}_{15}\text{In}_2\text{Mn}_3$   
 $\text{O}_{15}\text{Ti}*\text{C}_{15}\text{Mn}_3$   
 $\text{O}_{16}*\text{Br}_8\text{Fe}_3\text{H}_{32}$   
 $\text{O}_{16}*\text{C}_{48}\text{H}_{64}\text{Cu}_4\text{I}_6\text{K}_2$   
 $\text{O}_{16}*\text{FH}_6\text{Mo}_4$   
**Os**  
 Os  
 Fluorination: 2.11.4.2  
 Reaction with  $\text{X}_2-\text{O}_2$ : 2.9.11.2  
 Reaction with  $\text{O}_2-\text{F}_2$ : 2.11.4.2  
 Reaction with  $\text{F}_2$ : 2.9.2.1, 2.9.11.1  
 Reaction with  $\text{Br}_2$ : 2.9.2.3  
 Reaction with  $\text{Cl}_2$ : 2.9.2.2  
 $\text{Os}*\text{Br}_2\text{F}_6$   
 $\text{Os}*\text{Br}_4$   
 $\text{Os}*\text{Br}_4\text{O}_2$   
 $\text{Os}*\text{Br}_6\text{H}_8\text{N}_2$   
 $\text{Os}*\text{C}_4\text{Cl}_2\text{O}_4$   
 $\text{Os}*\text{Cl}_4$   
 $\text{Os}*\text{Cl}_4\text{O}$   
 $\text{Os}*\text{Cl}_4\text{O}_2$   
 $\text{Os}*\text{Cl}_5$   
 $\text{Os}*\text{Cl}_6\text{H}_8\text{N}_2$   
 $\text{Os}*\text{FO}_3$   
 $\text{Os}*\text{F}_2\text{O}_3$   
 $\text{Os}*\text{F}_2\text{O}_4$   
 $\text{Os}*\text{F}_3\text{O}_2$   
 $\text{Os}*\text{F}_3\text{O}_3$   
 $\text{Os}*\text{F}_4\text{O}$   
 $\text{Os}*\text{F}_5\text{O}$   
 $\text{Os}*\text{F}_6$   
 $\text{Os}*\text{F}_7$   
 $\text{Os}*\text{F}_7\text{NO}$   
 $\text{Os}*\text{F}_8\text{N}_2\text{O}_2$   
 $\text{Os}*\text{I}$   
 $\text{Os}*\text{I}_2$   
 $\text{Os}*\text{I}_6\text{K}_2$   
 $\text{Os}*\text{O}_2$   
 $\text{Os}*\text{O}_4$   
 $\text{Os}_2*\text{C}_6\text{Cl}_4\text{O}_6$   
 $\text{Os}_2*\text{F}_{12}\text{H}_6\text{N}_2$   
 $\text{Os}_3*\text{C}_{12}\text{O}_{12}$   
 $\text{P}*\text{AlCl}_8$   
 $\text{P}*\text{AlI}_8$   
 $\text{P}*\text{AuCl}_8$   
 $\text{P}*\text{B}$   
 $\text{P}*\text{BCl}_8$   
 $\text{P}*\text{Br}_3$   
 $\text{P}*\text{Br}_5$   
 $\text{P}*\text{CH}_5$   
 $\text{P}*\text{C}_2\text{H}_6\text{Cl}_3\text{N}$   
 $\text{P}*\text{C}_2\text{H}_7$   
 $\text{P}*\text{C}_3\text{H}_8\text{AlCl}_4$   
 $\text{P}*\text{C}_3\text{H}_9\text{AuBr}$   
 $\text{P}*\text{C}_3\text{H}_9\text{AuBr}_3$   
 $\text{P}*\text{C}_3\text{H}_{11}\text{Ge}$   
 $\text{P}*\text{C}_4\text{H}_{10}\text{BCl}_2$   
 $\text{P}*\text{C}_4\text{H}_{11}$   
 $\text{P}*\text{C}_4\text{H}_{12}\text{Al}$   
 $\text{P}*\text{C}_4\text{H}_{12}\text{Cl}_3\text{Cu}_2$   
 $\text{P}*\text{C}_6\text{H}_7$   
 $\text{P}*\text{C}_6\text{H}_{15}\text{AuBr}$   
 $\text{P}*\text{C}_6\text{H}_{15}\text{AuBrCl}_2$   
 $\text{P}*\text{C}_6\text{H}_{15}\text{AuBr}_2\text{Cl}$   
 $\text{P}*\text{C}_6\text{H}_{15}\text{AuBr}_3$   
 $\text{P}*\text{C}_6\text{H}_{15}\text{AuCl}$   
 $\text{P}*\text{C}_6\text{H}_{15}\text{AuClI}_2$   
 $\text{P}*\text{C}_6\text{H}_{15}\text{AuCl}_3$   
 $\text{P}*\text{C}_6\text{H}_{15}\text{AuI}$   
 $\text{P}*\text{C}_6\text{H}_{15}\text{AuI}_3$   
 $\text{P}*\text{C}_6\text{H}_{15}\text{Cl}_4\text{Cu}_2$   
 $\text{P}*\text{C}_8\text{H}_{11}$   
 $\text{P}*\text{C}_8\text{H}_{11}\text{AuBr}$   
 $\text{P}*\text{C}_8\text{H}_{11}\text{AuCl}$   
 $\text{P}*\text{C}_8\text{H}_{20}\text{BCIN}$   
 $\text{P}*\text{C}_8\text{H}_{22}\text{BN}_2$   
 $\text{P}*\text{C}_9\text{H}_{25}\text{BIN}_2$   
 $\text{P}*\text{C}_{18}\text{H}_{15}\text{AuBr}$   
 $\text{P}*\text{C}_{18}\text{H}_{15}\text{AuBrCl}_2$

$P^*C_{18}H_{15}AuBr_2Cl$   
 $P^*C_{18}H_{15}AuBr_3$   
 $P^*C_{18}H_{15}AuCl$   
 $P^*C_{18}H_{15}AuCl_3$   
 $P^*C_{18}H_{25}Cl_2CuNO$   
 $P^*C_{19}H_{15}AuBr_2NO$   
 $P^*C_{19}H_{15}AuNO$   
 $P^*C_{19}H_{16}Li$   
 $P^*C_{19}H_{18}Cu_2I_3$   
 $P^*C_{20}H_{17}AuBr$   
 $P^*C_{20}H_{17}AuBr_3$   
 $P^*C_{20}H_{20}Br_2Cu$   
 $P^*C_{21}H_{19}AuBr$   
 $P^*C_{21}H_{19}AuBr_3$   
 $P^*C_{21}H_{22}Br_2Cu$   
 $P^*C_{22}H_{19}AuBrFe$   
 $P^*C_{22}H_{19}AuBr_3Fe$   
 $P^*C_{22}H_{24}Br_2Cu$   
 $P^*C_{24}H_{15}AuBr_2F_5$   
 $P^*C_{24}H_{15}AuF_5$   
 $P^*C_{24}H_{20}AgBr_2$   
 $P^*C_{24}H_{20}Au$   
 $P^*C_{24}H_{20}Br_2Cu$   
 $P^*C_{24}H_{20}Cl_2Cu$   
 $P^*C_{24}H_{20}Cl_3Cu$   
 $P^*C_{34}H_{25}BMnO_4$   
 $P^*Cl_3$   
 $P^*Cl_3O$   
 $P^*Cl_5$   
 $P^*F_3$   
 $P^*H_3$   
 $P^*H_3O_2$   
 $P^*H_3O_3$   
 $P^*H_3O_4$   
 $P^*I_3$   
 $PS^*Cl_3$   
 $PSi^*CH_7$   
 $PSi^*C_2H_9$   
 $PSi^*C_3H_{11}$   
 $PSi^*H_5$   
 $PTa^*F_6H_4$   
**PTI**  
**TIP**  
 Reaction with  $X_2$ : 2.6.9.1

$PTI^*C_8H_{12}$   
 $PV^*C_{24}H_{20}F_2O_2$   
 $P_2^*C_{12}H_{30}BN$   
 $P_2^*C_{24}H_{21}Au_2Cl_2N$   
 $P_2^*C_{24}H_{21}Au_2Cl_6N$   
 $P_2^*C_{25}H_{22}Au_2Br_4Cl_2$   
 $P_2^*C_{25}H_{22}Au_2Cl_2$   
 $P_2^*C_{25}H_{22}Au_2Cl_6$

$P_2^*C_{27}H_{26}Au_2Cl_2$   
 $P_2^*C_{27}H_{26}Au_2Cl_6$   
 $P_2^*C_{38}H_{36}AgI_3$   
 $P_2^*C_{38}H_{36}Br_3Cu$   
 $P_2^*C_{38}H_{36}CuI_3$   
 $P_2^*C_{48}H_{40}Ag_2Br_4$   
 $P_2^*C_{48}H_{40}Ag_2Cl_4$   
 $P_2^*Cl_4$   
 $P_2Pt^*C_{24}H_{40}BCl$   
 $P_2Si^*H_6$   
 $P_2Zn_3$   
 $Zn_3P_2$   
 Formation from  $ZnO$  and  $PF_3$ : 2.8.15.3

$P_2Zn_3^*O_6$   
 $P_3^*C_3H_{11}AlLi$   
 $P_3^*C_{54}H_{45}CuF$   
 $P_3^*C_{54}H_{48}Cl_6Ln$   
 $P_3^*C_{57}H_{54}AgBr_4$   
 $P_4^*AlH_8Li$   
 $P_6^*Al_4Cl_{30}O_6$   
 $P_6^*C_{24}H_{72}Cl_3Cu_2N_{18}$   
 $P_6Si_3^*C_{24}H_{63}Al$   
 $P_9^*C_{21}H_{54}Al$   
**Pa**

**Pa**

Fluorination: 2.11.5.2

$Pa^*C$   
 $Pa^*Cl_5$   
 $Pa^*F_4$   
 $Pa^*F_5$   
 $Pa^*F_4H_4O_2$   
 $Pa_2^*F_8O$   
 $Pa_2^*O_{10}$   
 $Pb^*Br_2$   
 $Pb^*C_8H_{20}$   
 $Pb^*Cl_2$   
 $Pb^*F_2$

**Pd**

**Pd**

Oxyfluorination: 2.11.3.2  
 Reaction with F atoms: 2.11.3.2  
 Reaction with  $F_2$ : 2.9.2.1  
 Reaction with  $Br_2$ : 2.9.2.3  
 Reaction with  $Cl_2$ : 2.9.2.2

$Pd^*AtI$   
 $Pd^*Cl_2$   
 $Pd^*Cl_6Cs_2$   
 $Pd^*Cl_6K_2$   
 $Pd^*F_4$   
 $Pd^*F_6$   
 $Pd^*F_6Ge$   
 $Pd^*F_6K_2$

$\text{Pd}^*\text{F}_6\text{O}_2$   
 $\text{Pd}^*\text{I}_2$   
 $\text{PdRb}_2^*\text{Cl}_6$   
 $\text{PdSe}_2^*\text{F}_{12}$   
 $\text{PdXe}^*\text{F}_6$   
 $\text{PdXe}_2^*\text{F}_{16}$   
 $\text{Pd}_2^*\text{F}_6$   
 $\text{Pd}_2\text{Se}^*\text{I}_3$   
 $\text{Pd}_2\text{Xe}^*\text{F}_{10}$

**Pr**

Pr

Reaction with HX: 2.9.14.1.1

$\text{Pr}^*\text{BaCl}_5$   
 $\text{Pr}^*\text{BaF}_6$   
 $\text{Pr}^*\text{Cl}_3$   
 $\text{Pr}^*\text{F}_3$   
 $\text{Pr}^*\text{F}_4$   
 $\text{Pr}^*\text{F}_5\text{Na}$   
 $\text{Pr}^*\text{F}_6\text{Na}_2$   
 $\text{PrS}^*\text{Br}$   
 $\text{PrSe}^*\text{F}$   
 $\text{PrSr}^*\text{F}_6$   
 $\text{Pr}_2\text{Se}^*\text{F}_4$   
 $\text{Pr}_6^*\text{O}_4$   
 $\text{Pr}_6^*\text{O}_{11}$

**Pt**

Pt

Adsorbs At: 2.9.11.1

Catalyst for the reaction of  $\text{UF}_4$  with  $\text{O}_2$ : 2.11.5.2

FluorinationL: 2.11.4.2

Ignition in  $\text{F}_2$  with an electrical current: 2.11.4.2

Reaction with  $\text{F}_2$ : 2.9.2.1

Reaction with  $\text{Br}_2$ : 2.9.2.3

Reaction with  $\text{Cl}_2$ : 2.9.2.2

Reaction with  $\text{I}_2$ : 2.9.2.4

$\text{Pt}^*\text{Br}_2$   
 $\text{Pt}^*\text{Br}_4$   
 $\text{Pt}^*\text{C}_{24}\text{H}_{40}\text{BClP}_2$   
 $\text{Pt}^*\text{ClF}_8\text{O}$   
 $\text{Pt}^*\text{Cl}_2$   
 $\text{Pt}^*\text{Cl}_4$   
 $\text{Pt}^*\text{CsF}_6$   
 $\text{Pt}^*\text{F}_3\text{O}$   
 $\text{Pt}^*\text{F}_5$   
 $\text{Pt}^*\text{F}_6$   
 $\text{Pt}^*\text{F}_6\text{H}_3\text{O}$   
 $\text{Pt}^*\text{F}_6\text{H}_6\text{O}_2$   
 $\text{Pt}^*\text{F}_6\text{K}$   
 $\text{Pt}^*\text{F}_6\text{NO}$   
 $\text{Pt}^*\text{F}_6\text{NO}_2$

$\text{Pt}^*\text{F}_6\text{O}_2$   
 $\text{Pt}^*\text{F}_7\text{Kr}$   
 $\text{Pt}^*\text{F}_{10}\text{I}$   
 $\text{Pt}^*\text{I}_4$   
 $\text{Pt}^*\text{O}_2$   
 $\text{PtRb}^*\text{F}_6$   
 $\text{PtXe}^*\text{F}_6$   
 $\text{PtXe}^*\text{F}_7$   
 $\text{PtXe}^*\text{F}_{11}$   
 $\text{Pt}_2\text{Xe}^*\text{F}_{12}$   
 $\text{Pu}^*\text{F}_2\text{O}_2$   
 $\text{Pu}^*\text{F}_3$   
 $\text{Pu}^*\text{F}_4$   
 $\text{Pu}^*\text{F}_4\text{O}$   
 $\text{Pu}^*\text{F}_6$

**Ra**

Ra

Reaction with  $\text{X}_2$ : 2.7.2

Reaction with HX: 2.7.3.1

$\text{Ra}^*\text{Br}_2$   
 $\text{Ra}^*\text{Cl}_2$   
 $\text{Ra}^*\text{F}_2$   
 $\text{Ra}^*\text{I}_2$   
 $\text{Ra}^*\text{O}$

**Rb**

Rb

Reaction with  $\text{X}_2$ : 2.7.2

Reaction with HX: 2.7.3.1

$\text{Rb}^*\text{AgF}_3$   
 $\text{Rb}^*\text{AgF}_4$   
 $\text{Rb}^*\text{Ag}_4\text{I}_5$   
 $\text{Rb}^*\text{AmF}_2\text{O}_2$   
 $\text{Rb}^*\text{AuBr}_4$   
 $\text{Rb}^*\text{Br}_3\text{Cd}$   
 $\text{Rb}^*\text{CAmO}_5$   
 $\text{Rb}^*\text{CdCl}_3$   
 $\text{Rb}^*\text{CdF}_3$   
 $\text{Rb}^*\text{Cl}_3\text{Hg}$   
 $\text{Rb}^*\text{Cl}_4\text{Cu}_3$   
 $\text{Rb}^*\text{CuF}_3$   
 $\text{Rb}^*\text{F}$   
 $\text{Rb}^*\text{F}_6\text{Pt}$   
 $\text{Rb}^*\text{HgI}_3$   
 $\text{Rb}_2^*\text{AgAu}_3\text{I}_8$   
 $\text{Rb}_2^*\text{AgF}_4$   
 $\text{Rb}_2^*\text{AmF}_6$   
 $\text{Rb}_2^*\text{Au}_2\text{Br}_6$   
 $\text{Rb}_2^*\text{Au}_2\text{I}_6$   
 $\text{Rb}_2^*\text{Br}_2\text{HgI}_2$   
 $\text{Rb}_2^*\text{CdF}_4$   
 $\text{Rb}_2^*\text{Cl}_3\text{Cu}$   
 $\text{Rb}_2^*\text{Cl}_4\text{Hg}$

Rb<sub>2</sub>\*Cl<sub>6</sub>Pd  
 Rb<sub>2</sub>\*HgI<sub>4</sub>  
 Rb<sub>2</sub>Zn\*Cl<sub>4</sub>  
 Rb<sub>3</sub>\*Au<sub>3</sub>Br<sub>8</sub>  
 Rb<sub>3</sub>\*Au<sub>3</sub>I<sub>8</sub>  
 Rb<sub>3</sub>\*Cd<sub>2</sub>F<sub>7</sub>  
 Rb<sub>3</sub>\*Cl<sub>6</sub>Mo  
 Rb<sub>3</sub>\*Cl<sub>7</sub>Cu<sub>2</sub>  
 Rb<sub>3</sub>\*Hg<sub>2</sub>I<sub>7</sub>  
 Rb<sub>4</sub>\*Br<sub>6</sub>Cd  
 Rb<sub>4</sub>\*Br<sub>18</sub>Nb<sub>6</sub>  
 Rb<sub>4</sub>\*CdCl<sub>6</sub>  
 Rb<sub>4</sub>\*HgI<sub>6</sub>

**Re****Re**

Fluorination: 2.11.4.1  
 Oxyfluorination: 2.11.4.1  
 Reaction with ReF<sub>7</sub>: 2.11.4.1  
 Reaction with S<sub>2</sub>Cl<sub>2</sub>: 2.9.3.5  
 Reaction with X<sub>2</sub>-O<sub>2</sub>: 2.9.11.2  
 Reaction with F<sub>2</sub>: 2.9.2.1  
 Reaction with ClF<sub>3</sub>: 2.9.3.4  
 Reaction with Br<sub>2</sub>: 2.9.2.3  
 Reaction with Cl<sub>2</sub>: 2.9.2.2  
 Reaction with HX: 2.9.3.2  
 Reaction with aq HX: 2.9.3.3

Re\*Br<sub>4</sub>O  
 Re\*Br<sub>5</sub>  
 Re\*Br<sub>6</sub>K<sub>2</sub>  
 Re\*C<sub>3</sub>F<sub>3</sub>O<sub>3</sub>  
 Re\*C<sub>5</sub>BrO<sub>5</sub>  
 Re\*C<sub>5</sub>ClO<sub>5</sub>  
 Re\*C<sub>5</sub>FO<sub>5</sub>  
 Re\*C<sub>5</sub>IO<sub>5</sub>  
 Re\*ClF<sub>5</sub>N  
 Re\*ClO<sub>3</sub>  
 Re\*Cl<sub>2</sub>O  
 Re\*Cl<sub>3</sub>  
 Re\*Cl<sub>3</sub>O<sub>3</sub>  
 Re\*Cl<sub>4</sub>  
 Re\*Cl<sub>4</sub>O  
 Re\*Cl<sub>5</sub>  
 Re\*Cl<sub>5</sub>O  
 Re\*Cl<sub>6</sub>  
 Re\*Cl<sub>6</sub>K<sub>2</sub>  
 Re\*FO<sub>3</sub>  
 Re\*F<sub>2</sub>KO<sub>2</sub>  
 Re\*F<sub>2</sub>NaO<sub>2</sub>  
 Re\*F<sub>3</sub>O<sub>2</sub>  
 Re\*F<sub>4</sub>O  
 Re\*F<sub>5</sub>  
 Re\*F<sub>5</sub>O

Re\*F<sub>6</sub>  
 Re\*F<sub>6</sub>N  
 Re\*F<sub>7</sub>  
 Re\*F<sub>7</sub>NO  
 Re\*F<sub>8</sub>K  
 Re\*F<sub>8</sub>N<sub>2</sub>O<sub>2</sub>  
 Re\*I<sub>2</sub>  
 Re\*I<sub>3</sub>  
 Re\*I<sub>4</sub>  
 Re\*I<sub>6</sub>K  
 Re\*KO<sub>4</sub>  
 Re\*NaO<sub>4</sub>  
 Re\*O<sub>2</sub>  
 Re\*O<sub>3</sub>  
 Re\*O<sub>4</sub>  
 ReS\*Br<sub>2</sub>  
 ReS\*Cl<sub>2</sub>  
 ReS\*F<sub>3</sub>  
 ReS\*F<sub>4</sub>  
 ReS\*F<sub>5</sub>  
 ReS<sub>2</sub>  
 ReS<sub>2</sub>  
 Reaction with X<sub>2</sub>: 2.9.14.2  
 Reaction with Cl<sub>2</sub>: 2.9.5  
 ReSb\*F<sub>9</sub>O  
 ReSb\*F<sub>12</sub>  
 ReSb<sub>2</sub>\*F<sub>17</sub>  
 ReSe\*Br<sub>2</sub>  
 ReSe\*Cl<sub>2</sub>  
 ReSe<sub>2</sub>  
 ReSe<sub>2</sub>  
 Reaction with X<sub>2</sub>: 2.9.14.2  
 Re<sub>2</sub>\*C<sub>5</sub>F<sub>6</sub>O<sub>5</sub>  
 Re<sub>2</sub>\*C<sub>8</sub>Cl<sub>2</sub>O<sub>8</sub>  
 Re<sub>2</sub>\*C<sub>10</sub>O<sub>10</sub>  
 Re<sub>2</sub>\*C<sub>48</sub>H<sub>40</sub>As<sub>2</sub>Cl<sub>8</sub>  
 Re<sub>2</sub>\*O<sub>7</sub>  
 Re<sub>2</sub>S<sub>3</sub>\*Cl<sub>4</sub>  
 Re<sub>2</sub>S<sub>7</sub>  
 Re<sub>2</sub>S<sub>7</sub>  
 Reaction with X<sub>2</sub>: 2.9.14.2  
 Reaction with Cl<sub>2</sub>: 2.9.5  
 Reaction with CCl<sub>4</sub>: 2.9.5  
 Re<sub>3</sub>\*Br<sub>9</sub>  
 Re<sub>3</sub>\*C<sub>6</sub>F<sub>11</sub>O<sub>6</sub>  
 Re<sub>3</sub>\*Cl<sub>9</sub>  
 Rh  
 Rh  
 Fluorination: 2.11.3.2  
 Reaction with F<sub>2</sub>: 2.9.2.1  
 Reaction with Cl<sub>2</sub>: 2.9.2.2  
 Rh\*Cl<sub>3</sub>

Rh\*CsF<sub>6</sub>Rh\*F<sub>3</sub>Rh\*F<sub>5</sub>Rh\*F<sub>6</sub>Rh\*F<sub>6</sub>O<sub>2</sub>RhXe\*F<sub>6</sub>**Rn**

Rn

Reaction with F<sub>2</sub>: 2.10.2.2.2

Reaction with interhalogens: 2.10.2.2.2

Rn\*F

Rn\*F<sub>2</sub>Rn\*F<sub>4</sub>Rn\*F<sub>6</sub>Rn\*O<sub>3</sub>**Ru**

Ru

Fluorination: 2.11.3.2

Fluorination in a flow system: 2.11.3.2

Reaction with AgBr-BrF<sub>5</sub>: 2.11.3.2Reaction with F<sub>2</sub>-O<sub>2</sub>: 2.11.3.2Reaction with F<sub>2</sub>: 2.9.2.1Reaction with BrF<sub>3</sub>: 2.9.3.4Reaction with BrF<sub>3</sub>-Br<sub>2</sub>: 2.11.3.2Reaction with CsCl-BrF<sub>5</sub>: 2.11.3.2Reaction with KBr-BrF<sub>5</sub>: 2.11.3.2Reaction with Br<sub>2</sub>: 2.9.2.3Reaction with Cl<sub>2</sub>: 2.9.2.2Ru\*BrF<sub>10</sub>Ru\*Br<sub>3</sub>Ru\*Br<sub>4</sub>O<sub>2</sub>Ru\*Br<sub>6</sub>K<sub>2</sub>Ru\*C<sub>3</sub>F<sub>3</sub>O<sub>3</sub>Ru\*C<sub>4</sub>Br<sub>2</sub>O<sub>4</sub>Ru\*C<sub>4</sub>Cl<sub>2</sub>O<sub>4</sub>Ru\*Cl<sub>3</sub>Ru\*Cl<sub>3</sub>HORu\*Cl<sub>4</sub>O<sub>2</sub>Ru\*Cl<sub>10</sub>ORu\*F<sub>4</sub>ORu\*F<sub>5</sub>Ru\*F<sub>6</sub>Ru\*F<sub>6</sub>H<sub>3</sub>ORu\*F<sub>6</sub>NORu\*F<sub>6</sub>O<sub>2</sub>Ru\*F<sub>8</sub>Ru\*H<sub>10</sub>Cl<sub>4</sub>O<sub>5</sub>Ru\*O<sub>2</sub>Ru\*O<sub>4</sub>RuXe\*F<sub>11</sub>Ru<sub>2</sub>\*Cl<sub>10</sub>ORu<sub>3</sub>\*C<sub>12</sub>O<sub>12</sub>Ru<sub>4</sub>\*C<sub>12</sub>F<sub>8</sub>O<sub>12</sub>**S****S**Reaction with [Mo<sub>6</sub>X<sub>8</sub>]X<sub>4</sub>, MoX<sub>3</sub>:

2.9.14.3

Reaction with NbCl<sub>5</sub>, TaCl<sub>5</sub>: 2.9.14.3Reaction with ReX<sub>5</sub>: 2.9.14.3Reaction with Re<sub>3</sub>X<sub>9</sub>: 2.9.14.3Reaction with WX<sub>6</sub>: 2.9.14.3

Reaction with transition-metals:

2.9.14.1.2

S\*Ag<sub>2</sub>

S\*AlBr

S\*AlCl

S\*AlCl<sub>7</sub>

S\*AlI

S\*AuBr

S\*AuCl<sub>7</sub>S\*BaO<sub>4</sub>

S\*BrCe

S\*BrCr

S\*BrDy

S\*BrEr

S\*BrGd

S\*BrHo

S\*BrLa

S\*BrLu

S\*BrMo

S\*BrNd

S\*BrPr

S\*Br<sub>2</sub>OS\*Br<sub>2</sub>ReS\*Br<sub>3</sub>NbS\*CCl<sub>2</sub>S\*CH<sub>3</sub>GaI<sub>2</sub>S\*CH<sub>6</sub>Ge

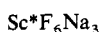
S\*CO

S\*C<sub>2</sub>H<sub>6</sub>AuBr<sub>3</sub>S\*C<sub>2</sub>H<sub>8</sub>BClS\*C<sub>2</sub>H<sub>9</sub>BS\*C<sub>3</sub>H<sub>6</sub>CINS\*C<sub>3</sub>H<sub>9</sub>BS\*C<sub>3</sub>H<sub>9</sub>Cu<sub>2</sub>I<sub>3</sub>S\*C<sub>3</sub>H<sub>9</sub>GaI<sub>4</sub>S\*C<sub>4</sub>H<sub>12</sub>GeS\*C<sub>6</sub>H<sub>18</sub>BF<sub>4</sub>N<sub>3</sub>S\*C<sub>9</sub>H<sub>10</sub>B<sub>2</sub>FFeIO<sub>3</sub>S\*C<sub>9</sub>H<sub>10</sub>B<sub>2</sub>FeI<sub>2</sub>O<sub>3</sub>S\*C<sub>10</sub>H<sub>8</sub>AuBr<sub>2</sub>F<sub>5</sub>S\*C<sub>10</sub>H<sub>8</sub>AuCl<sub>2</sub>F<sub>5</sub>S\*C<sub>10</sub>H<sub>8</sub>AuF<sub>5</sub>S\*C<sub>14</sub>H<sub>14</sub>AuBr

$S^*C_{14}H_{14}AuBr_3$   
 $S^*Cd$   
 $S^*CdO_4$   
 $S^*CeCl$   
 $S^*CeF$   
 $S^*CeI$   
 $S^*ClHO_3$   
 $S^*ClH_3O$   
 $S^*ClLa$   
 $S^*ClMo$   
 $S^*Cl_2$   
 $S^*Cl_2Mo$   
 $S^*Cl_2Nb$   
 $S^*Cl_2O$   
 $S^*Cl_2O_2$   
 $S^*Cl_2Re$   
 $S^*Cl_3Mo$   
 $S^*Cl_3Nb$   
 $S^*Cl_3P$   
 $S^*Cr$   
 $S^*CsFO_4$   
 $S^*Cs_2O_4$   
 $S^*Cu$   
 $S^*CuO_4$   
 $S^*Cu_2$   
 $S^*ErF$   
 $S^*EuF$   
 $S^*FHO_3$   
 $S^*FHo$   
 $S^*FLa$   
 $S^*FLu$   
 $S^*F_3Re$   
 $S^*F_4$   
 $S^*F_4Mo$   
 $S^*F_4Re$   
 $S^*F_5Re$   
 $S^*F_6$   
 $S^*Fe$   
 $S^*FeO_4$   
 $S^*Fe_2$   
 $S^*GdI$   
 $S^*H_2$   
 $S^*Hg$   
 $S^*HgO_4$   
 $S^*ILa$   
 $S^*IMo$   
 $S^*K_2O_4$   
 $S^*Li_2O_3$   
 $S^*MnO_4$   
 $S^*Na_2O_4$   
 $S^*NiO_4$   
 $S^*O_2$

$S^*O_3$   
 $SSeW^*Cl_2$   
 $SSi^*CH_6$   
 $SSi^*C_4H_{12}$   
 $SSI_2^*CH_8$   
 $SSm^*Br$   
 $SSm^*I$   
 $SSn^*C_4H_{12}$   
 $STa^*Cl_3$   
 $STa^*F_6H_3$   
 $STa_2^*F_{11}H_3$   
 $STb^*Br$   
 $SV^*Cl$   
 $SW^*Br_4$   
 $SW^*Cl_2O$   
 $SW^*Cl_3$   
 $SW^*Cl_4$   
 $SW^*F_2$   
 $SW^*F_2O$   
 $SW^*F_3$   
 $SW^*F_4$   
 $SXe^*F_2O_3$   
 $SY^*Br$   
 $SY^*F$   
 $SYb^*Br$   
 $SYb^*F$   
 $SZn$   
 $ZnS$   
 Fluorination: 2.11.2.3  
 Formation from Zn and  $S_2Cl_2$ : 2.8.14.4  
 Reaction with  $AlCl_3$ : 2.8.16.2  
 Reaction with  $CuCl_2$ : 2.8.16.2  
 Reaction with  $FeCl_3$ : 2.8.16.2  
 Reaction with  $SF_4$ : 2.11.2.3  
 Reaction with  $S_2Cl_2$ : 2.8.16.2  
 Reaction with  $F_2$ : 2.8.16.1  
 Reaction with  $NaCl$ : 2.8.16.2  
 Reaction with  $HCl$ : 2.8.16.2  
 Reaction with  $Cl_2$ : 2.8.16.1  
 Reaction with  $I_2$ : 2.8.16.1  
 $SZn^*O_4$   
 $S_2^*AlCl_5$   
 $S_2^*Br_2$   
 $S_2^*Br_2Mo$   
 $S_2^*Br_2Nb$   
 $S_2^*C_2H_6B_2Br_4$   
 $S_2^*C_2H_6B_2Cl_4$   
 $S_2^*C_4H_{10}GaI$   
 $S_2^*C_5H_{10}AuBr_2N$   
 $S_2^*C_5H_{10}AuN$   
 $S_2^*C_8H_6BF_2NO_6$   
 $S_2^*C_9H_{18}AuBr_2N$

- $S_2^*C_9H_{18}AuN$   
 $S_2^*C_{10}H_{15}Ga$   
 $S_2^*C_{26}Au_2F_{20}N_2$   
 $S_2^*Cl_2$   
 $S_2^*Cl_2Hg_3$   
 $S_2^*Cl_2Mo$   
 $S_2^*Cl_2Nb$   
 $S_2^*CoCs_2O_8$   
 $S_2^*Fe$   
 $S_2^*I_2Nb$   
 $S_2^*Mo$   
 $S_2^*Re$   
 $S_2Se_2^*C_7H_{10}AuN_3$   
 $S_2Ta$   
 $TaS_2$   
 Reaction with  $I_2$ : 2.9.5  
 $S_2Ta^*Cl_2$   
 $S_2W$   
 $WS_2$   
 Reaction with  $CX_4$ : 2.9.5  
 $S_2W^*Cl_2$   
 $S_2Zn^*O_4$   
 $S_3^*Al_2$   
 $S_3^*B_2$   
 $S_3^*B_2F_2$   
 $S_3^*B_3Br_3$   
 $S_3^*B_3Cl_3$   
 $S_3^*Br_4Nb_2$   
 $S_3^*C_3BF_9$   
 $S_3^*Cl_4Nb_2$   
 $S_3^*Cl_4Re_2$   
 $S_3^*Cr_2$   
 $S_3^*Fe_2O_{12}$   
 $S_3^*Ga_2$   
 $S_3^*La_2$   
 $S_3^*Mo$   
 $S_3Sb_2$   
 $Sb_2S_3$   
 Reaction with  $NbX_5$ ,  $TaX_5$ ,  $MoCl_5$ :  
 2.9.14.4  
 Reaction with  $WSeCl_4$ ,  $ReF_6$ ,  $ReF_5$ :  
 2.9.14.4  
 Reaction with  $WX_6$ ,  $WX_5$ ,  $WSeCl_4$ :  
 2.9.14.4  
 $S_3W$   
 $WS_3$   
 Reaction with  $Cl_2$ : 2.9.5  
 $S_3W_2^*Cl_4$   
 $S_3Y_1$   
 $Y_2S_3$   
 Reaction with  $YF_3$ : 2.9.14.2  
 $S_4^*C_4H_{12}AlLi$   
 $S_4^*C_7H_{10}AuN_3$   
 $S_4^*C_{10}H_{20}Au_2Br_2N_2$   
 $S_4^*C_{10}H_{20}Au_2I_2N_2$   
 $S_4^*Cl_5Mo_2$   
 $S_4Se_2^*C_{12}H_{20}Au_2N_4$   
 $S_4U_3^*O_2$   
 $S_5^*Br_3Mo_2$   
 $S_5^*C_4H_{10}B_2$   
 $S_5^*Cl_3Mo_2$   
 $S_5^*I_3Mo_2$   
 $S_6^*B_3H_3$   
 $S_6^*C_{12}H_{20}Au_2N_4$   
 $S_6^*Cl_2Mo_6$   
 $S_7^*Br_4Mo_3$   
 $S_7^*Re_2$   
 $Sb^*Br_3$   
 $Sb^*C_{22}H_{25}O_2$   
 $Sb^*Cl_3$   
 $Sb^*Cl_5$   
 $Sb^*F_3$   
 $Sb^*F_3Kr$   
 $Sb^*F_9MoO$   
 $Sb^*F_9ORe$   
 $Sb^*F_{10}Nb$   
 $Sb^*F_{12}Re$   
 $SbW^*F_9O$   
 $SbXe^*F_7$   
 $SbXe^*F_9$   
 $SbXe^*F_{11}$   
 $SbXe_2^*F_{17}$   
 $Sb_2^*C_6CrF_{21}$   
 $Sb_2^*CrF_{15}$   
 $Sb_2^*CrF_{15}O_2$   
 $Sb_2^*F_{12}Kr$   
 $Sb_2^*F_{17}Re$   
 $Sb_2^*O_3$   
 $Sb_2^*S_3$   
 $Sb_2Se_3$   
 $Sb_2Se_3$   
 Reaction with  $NbX_5$ ,  $MoCl_5$ ,  $WX_6$ :  
 2.9.14.4  
 Reaction with  $WSeCl_4$ : 2.9.14.4  
 Reaction with  $WX_5$ ,  $WSeCl_4$ ,  $WSeCl_4$ :  
 2.9.14.4  
 $Sb_2Xe^*F_{16}$   
 $Sb_4Xe^*Cr_2F_{30}$   
 $Sc$   
 $Sc$   
 Fluorination: 2.11.2.1  
 $Sc^*FO$   
 $Sc^*F_3$   
 $Sc^*F_4Na$



Reaction with CuX: 2.9.14.3

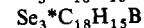
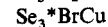
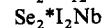
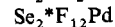
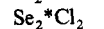
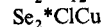
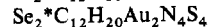
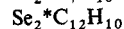
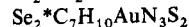
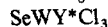
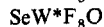
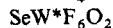
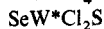
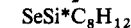
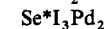
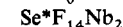
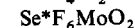
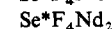
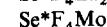
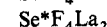
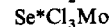
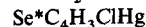
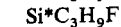
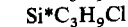
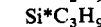
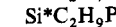
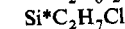
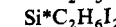
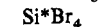
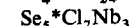
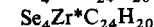
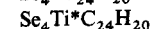
Reaction with [Mo<sub>6</sub>X<sub>8</sub>]X<sub>4</sub>, MoX<sub>3</sub>:

2.9.14.3

Reaction with PdX<sub>2</sub>: 2.9.14.3Reaction with Re<sub>3</sub>X<sub>9</sub>: 2.9.14.3Reaction with WX<sub>6</sub>: 2.9.14.3

Reaction with transition-metals:

2.9.14.1.2

Reaction with YF<sub>3</sub>: 2.9.14.2



$\text{Si}^*\text{C}_3\text{H}_{10}$   
 $\text{Si}^*\text{C}_3\text{H}_{11}\text{As}$   
 $\text{Si}^*\text{C}_3\text{H}_{11}\text{P}$   
 $\text{Si}^*\text{C}_4\text{H}_{12}$   
 $\text{Si}^*\text{C}_4\text{H}_{12}\text{S}$   
 $\text{Si}^*\text{C}_7\text{H}_{21}\text{BN}_2$   
 $\text{Si}^*\text{C}_8\text{H}_{12}\text{Se}$   
 $\text{Si}^*\text{C}_{18}\text{H}_{15}\text{Br}$   
 $\text{Si}^*\text{Cl}_4$   
 $\text{Si}^*\text{F}_4$   
 $\text{Si}^*\text{H}_4$   
 $\text{Si}^*\text{H}_5\text{P}$   
 $\text{Si}^*\text{H}_6\text{P}_2$   
 $\text{Si}^*\text{I}_4$   
 $\text{Si}^*\text{O}_2$   
 $\text{Si}_2^*\text{AsH}_7$   
 $\text{Si}_2^*\text{BrH}_5$   
 $\text{Si}_2^*\text{CH}_8\text{S}$   
 $\text{Si}_2^*\text{ClH}_5$   
 $\text{Si}_2\text{Ti}^*\text{C}_6\text{H}_{18}\text{Cl}$   
 $\text{Si}_2\text{Ti}^*\text{C}_6\text{H}_{18}\text{I}$   
 $\text{Si}_3^*\text{C}_{24}\text{H}_{63}\text{AlP}_6$   
 $\text{Si}_3^*\text{C}_{54}\text{H}_{45}\text{AlClK}$   
 $\text{Si}_3^*\text{C}_{57}\text{H}_{54}\text{B}_3\text{N}_3$   
 $\text{Si}_3\text{Sn}^*\text{C}_{12}\text{H}_{33}\text{Br}$   
 $\text{Si}_3\text{SnTi}^*\text{C}_{12}\text{H}_{33}$   
 $\text{Si}_3\text{Ti}^*\text{C}_9\text{H}_{27}$   
 $\text{Si}_4^*\text{C}_{12}\text{H}_{36}\text{BLi}$   
 $\text{Si}_4^*\text{C}_{12}\text{H}_{36}\text{GaLi}$   
 $\text{Si}_9\text{Sn}_3\text{Ti}^*\text{C}_{36}\text{H}_{99}$

**Sm****Sm**

Reaction with HX: 2.9.14.1.1

$\text{Sm}^*\text{BrS}$   
 $\text{Sm}^*\text{Br}_3$   
 $\text{Sm}^*\text{Cl}_3$   
 $\text{Sm}^*\text{FSe}$   
 $\text{Sm}^*\text{F}_3$   
 $\text{Sm}^*\text{IS}$   
 $\text{Sm}^*\text{I}_3$

**Sn****Sn**

Use as reducing agent: 2.9.13.2

$\text{Sn}^*\text{C}_2\text{H}_{18}\text{B}_{10}$   
 $\text{Sn}^*\text{C}_3\text{H}_9\text{Br}$   
 $\text{Sn}^*\text{C}_3\text{H}_9\text{Cl}$   
 $\text{Sn}^*\text{C}_3\text{H}_9\text{F}$   
 $\text{Sn}^*\text{C}_3\text{H}_{11}\text{As}$   
 $\text{Sn}^*\text{C}_4\text{H}_{12}\text{S}$   
 $\text{Sn}^*\text{C}_6\text{H}_{15}\text{Br}$   
 $\text{Sn}^*\text{C}_6\text{H}_{15}\text{Cl}$   
 $\text{Sn}^*\text{C}_6\text{H}_{15}\text{I}$

$\text{Sn}^*\text{C}_{10}\text{H}_{27}\text{BN}_2$   
 $\text{Sn}^*\text{C}_{11}\text{H}_{14}\text{MoO}_3$   
 $\text{Sn}^*\text{C}_{12}\text{H}_{33}\text{BrSi}_3$   
 $\text{Sn}^*\text{C}_{18}\text{H}_{15}\text{Cl}$   
 $\text{Sn}^*\text{C}_{22}\text{H}_{15}\text{CoO}_4$   
 $\text{Sn}^*\text{Cl}_2$   
 $\text{Sn}^*\text{Cl}_4$   
 $\text{Sn}^*\text{F}_2$   
 $\text{SnTi}^*\text{C}_{12}\text{H}_{33}\text{Si}_3$   
 $\text{Sn}_3\text{Ti}^*\text{C}_{36}\text{H}_{99}\text{Si}_9$

**Sr****Sr**

Reaction with HX: 2.7.3.1

Reaction with  $\text{X}_2$ : 2.7.2

$\text{Sr}^*\text{AgF}_4$   
 $\text{Sr}^*\text{Ag}_2\text{H}_{16}\text{I}_4\text{O}_8$   
 $\text{Sr}^*\text{Au}_2\text{F}_{12}$   
 $\text{Sr}^*\text{Br}_2$   
 $\text{Sr}^*\text{Br}_2\text{O}_6$   
 $\text{Sr}^*\text{Br}_4\text{Hg}$   
 $\text{Sr}^*\text{CdH}_{16}\text{I}_4\text{O}_8$   
 $\text{Sr}^*\text{Cd}_2\text{Cl}_6\text{H}_{14}\text{O}_7$   
 $\text{Sr}^*\text{Cl}_2$   
 $\text{Sr}^*\text{F}_2$   
 $\text{Sr}^*\text{F}_6\text{Pr}$   
 $\text{Sr}^*\text{H}_2\text{O}_2$   
 $\text{Sr}^*\text{I}_2$   
 $\text{Sr}^*\text{O}$   
 $\text{SrO}_2^*\text{Cl}_8\text{H}_4\text{Hg}_3$   
 $\text{T}^*\text{AlCl}$

**Ta****Ta**

Bromination: 2.11.4.1

Dissolution in HF: 2.11.4.1

Fluorination: 2.11.4.1

Reaction with  $\text{SnF}_2$ : 2.11.4.1

Reaction with  $\text{TaCl}_5\text{-SiO}_2$ : 2.9.11.4

Reaction with  $\text{TaCl}_5\text{-Ta}_2\text{O}_5$ : 2.9.11.4

Reaction with  $\text{F}_2\text{-O}_2$ : 2.11.4.1

Reaction with  $\text{BrF}_3$ : 2.9.3.4, 2.11.4.1

Reaction with  $\text{ClF}_3$ : 2.11.4.1

Reaction with  $\text{F}_2$ : 2.9.2.1

Reaction with  $\text{Br}_2$ : 2.9.2.3

Reaction with  $\text{Cl}_2$ : 2.9.2.2

Reaction with  $\text{I}_2$ : 2.9.2.4

Reaction with HF: 2.11.4.1

Reaction with HX: 2.9.3.2

$\text{Ta}^*\text{AsF}_6\text{H}_4$

$\text{Ta}^*\text{Br}_3\text{O}$

$\text{Ta}^*\text{Br}_5$

$\text{Ta}^*\text{C}_8\text{H}_{20}\text{Br}_6\text{N}$

$\text{Ta}^*\text{C}_8\text{H}_{20}\text{Cl}_6\text{N}$

$\text{Ta}^*\text{ClO}_2$   
 $\text{Ta}^*\text{Cl}_2\text{O}$   
 $\text{Ta}^*\text{Cl}_2\text{O}_2$   
 $\text{Ta}^*\text{Cl}_2\text{S}_2$   
 $\text{Ta}^*\text{Cl}_3\text{O}$   
 $\text{Ta}^*\text{Cl}_3\text{S}$   
 $\text{Ta}^*\text{Cl}_4\text{O}$   
 $\text{Ta}^*\text{Cl}_5$   
 $\text{Ta}^*\text{Cl}_6\text{Cs}$   
 $\text{Ta}^*\text{Cl}_6\text{Cs}_2$   
 $\text{Ta}^*\text{FO}_2$   
 $\text{Ta}^*\text{F}_3$   
 $\text{Ta}^*\text{F}_3\text{O}$   
 $\text{Ta}^*\text{F}_5$   
 $\text{Ta}^*\text{F}_6\text{H}_3\text{O}$   
 $\text{Ta}^*\text{F}_6\text{H}_3\text{S}$   
 $\text{Ta}^*\text{F}_6\text{H}_4\text{P}$   
 $\text{Ta}^*\text{F}_6\text{H}_{12}\text{N}_3\text{O}$   
 $\text{Ta}^*\text{F}_6\text{K}_3\text{O}$   
 $\text{Ta}^*\text{F}_6\text{O}$   
 $\text{Ta}^*\text{F}_8\text{K}_3$   
 $\text{Ta}^*\text{I}_4$   
 $\text{Ta}^*\text{I}_5$   
 $\text{Ta}^*\text{S}_2$   
 $\text{Ta}_2^*\text{AsF}_{11}\text{H}_4$   
 $\text{Ta}_2^*\text{F}_{11}\text{H}_3\text{S}$   
 $\text{Ta}_2^*\text{F}_{11}\text{O}_2$   
 $\text{Ta}_2^*\text{O}_5$   
 $\text{Ta}_3^*\text{FO}_7$   
 $\text{Ta}_4^*\text{F}_4\text{O}_9$   
 $\text{Ta}_6^*\text{Cl}_{18}\text{K}_4$

**Tb**

Tb

Reaction with HX: 2.9.14.1.1

$\text{Tb}^*\text{BrS}$   
 $\text{Tb}^*\text{Cl}_3$   
 $\text{Tb}^*\text{F}_3$   
 $\text{Tb}^*\text{F}_4$   
 $\text{Tb}_4^*\text{O}_7$

**Tc**

Tc

Fluorination: 2.11.3.1

Fluorination in a flow system: 2.11.3.1

Reaction with  $\text{F}_2$ : 2.9.2.1

Reaction with HX: 2.9.3.2

Reaction with  $\text{Cl}_2$ : 2.9.2.2

$\text{Tc}^*\text{Br}_3\text{O}$   
 $\text{Tc}^*\text{C}_5\text{BrO}_5$   
 $\text{Tc}^*\text{C}_5\text{ClO}_5$   
 $\text{Tc}^*\text{C}_5\text{IO}_5$   
 $\text{Tc}^*\text{Cl}_3\text{O}$   
 $\text{Tc}^*\text{Cl}_4$

$\text{Tc}^*\text{Cl}_6$   
 $\text{Tc}^*\text{FO}_3$   
 $\text{Tc}^*\text{F}_3\text{O}_2$   
 $\text{Tc}^*\text{F}_4\text{O}$   
 $\text{Tc}^*\text{F}_5$   
 $\text{Tc}^*\text{F}_6$   
 $\text{Tc}^*\text{F}_7\text{NO}_2$   
 $\text{Tc}^*\text{F}_8\text{N}_2\text{O}_2$   
 $\text{Tc}^*\text{H}_4\text{NO}_4$   
 $\text{Tc}^*\text{O}_2$   
 $\text{Tc}_2^*\text{C}_8\text{Br}_2\text{O}_8$   
 $\text{Tc}_2^*\text{C}_8\text{Cl}_2\text{O}_4$   
 $\text{Tc}_2^*\text{C}_8\text{I}_2\text{O}_8$   
 $\text{Tc}_2^*\text{C}_{10}\text{O}_{10}$   
 $\text{Tc}_2^*\text{F}_4\text{O}_5$

**Te**

Te

Reaction with  $\text{CuX}$ : 2.9.14.3

Reaction with transition-metals:

2.9.14.1.2

$\text{Te}^*\text{Ag}_2$   
 $\text{Te}^*\text{AlBr}$   
 $\text{Te}^*\text{AlCl}$   
 $\text{Te}^*\text{AlI}$   
 $\text{Te}^*\text{AuCl}_7$   
 $\text{Te}^*\text{AuI}$   
 $\text{Te}^*\text{ClCu}$   
 $\text{Te}^*\text{Cl}_2$   
 $\text{Te}^*\text{Cl}_4$   
 $\text{Te}^*\text{Cr}$   
 $\text{Te}_2^*\text{AuBr}$   
 $\text{Te}_2^*\text{AuCl}$   
 $\text{Te}_2^*\text{AuI}$   
 $\text{Te}_2^*\text{Br}_{10}\text{Mo}$   
 $\text{Te}_2^*\text{ClCu}$   
 $\text{Te}_2^*\text{Mo}$   
 $\text{Te}_2\text{W}^*\text{F}_{14}\text{O}_2$   
 $\text{Te}_3^*\text{Al}_2$   
 $\text{Te}_4^*\text{C}_4\text{H}_{12}\text{AlLi}$   
 $\text{Te}_4\text{W}^*\text{F}_{22}\text{O}_4$

**Th**

Th

Fluorination: 2.11.5.2

$\text{Th}^*\text{C}_{16}\text{H}_{40}\text{Br}_6\text{N}_2$   
 $\text{Th}^*\text{C}_{16}\text{H}_{40}\text{Cl}_6\text{N}_2$   
 $\text{Th}^*\text{Cl}_4$   
 $\text{Th}^*\text{F}_2\text{O}$   
 $\text{Th}^*\text{F}_4$   
 $\text{Th}^*\text{I}_4$   
 $\text{Th}^*\text{I}_6\text{K}_2$   
 $\text{Th}^*\text{O}_2$

**Ti**

Ti

Fluorination: 2.11.2.1

Reaction with : 2.9.2.3

Reaction with  $\text{ClF}_3$ : 2.9.3.4Reaction with  $\text{BrF}_3\text{-NOCl}$ : 2.11.2.1Reaction with  $\text{F}_2$ : 2.9.2.1Reaction with  $\text{ClF}_3$ : 2.11.2.1Reaction with  $\text{Cl}_2$ : 2.9.2.2Reaction with  $\text{I}_2$ : 2.9.2.4Reaction with  $\text{HX}$ : 2.9.3.2 $\text{Ti}^*\text{Br}_4$  $\text{Ti}^*\text{CH}_3\text{Cl}_3$  $\text{Ti}^*\text{C}_8\text{H}_{20}\text{Cl}_5\text{N}$  $\text{Ti}^*\text{C}_{10}\text{H}_{16}\text{F}_2\text{O}_4$  $\text{Ti}^*\text{C}_{16}\text{H}_{40}\text{Br}_6\text{N}_2$  $\text{Ti}^*\text{C}_{16}\text{H}_{40}\text{Cl}_6\text{N}_2$  $\text{Ti}^*\text{C}_{16}\text{H}_{40}\text{I}_6\text{N}_2$  $\text{Ti}^*\text{C}_{24}\text{H}_{20}\text{Se}_4$  $\text{Ti}^*\text{ClO}$  $\text{Ti}^*\text{Cl}_2\text{F}_2$  $\text{Ti}^*\text{Cl}_2\text{O}$  $\text{Ti}^*\text{Cl}_3$  $\text{Ti}^*\text{Cl}_4$  $\text{Ti}^*\text{Cl}_4\text{O}$  $\text{Ti}^*\text{Cs}_2\text{I}_6$  $\text{Ti}^*\text{F}_2\text{O}$  $\text{Ti}^*\text{F}_3$  $\text{Ti}^*\text{F}_3\text{H}_2\text{O}_2$  $\text{Ti}^*\text{F}_4$  $\text{Ti}^*\text{F}_4\text{O}$  $\text{Ti}^*\text{F}_5\text{K}_3\text{O}_2$  $\text{Ti}^*\text{F}_5\text{O}$  $\text{Ti}^*\text{F}_6\text{H}_3\text{O}$  $\text{Ti}^*\text{F}_6\text{H}_6\text{N}_2$  $\text{Ti}^*\text{F}_6\text{K}_2$  $\text{Ti}^*\text{F}_6\text{K}_3$  $\text{Ti}^*\text{F}_6\text{N}_2\text{O}_2$  $\text{Ti}^*\text{F}_{16}\text{O}_3$  $\text{Ti}^*\text{I}_2$  $\text{Ti}^*\text{I}_3$  $\text{Ti}^*\text{I}_4$  $\text{Ti}^*\text{O}_2$  $\text{TiXe}^*\text{F}_6$  $\text{TiXe}^*\text{F}_{10}$  $\text{TiXe}_4^*\text{F}_{28}$  $\text{Ti}_2^*\text{C}_8\text{H}_{20}\text{Cl}_9\text{N}$  $\text{Ti}_2^*\text{C}_{108}\text{H}_{20}\text{F}_{90}\text{Ge}_6\text{Hg}_2$  $\text{Ti}_2^*\text{Cl}_9\text{Cs}$  $\text{Ti}_2\text{Xe}^*\text{F}_{10}$  $\text{Ti}_2\text{Xe}^*\text{F}_{14}$  $\text{Ti}_2\text{Xe}_3^*\text{F}_{14}$  $\text{Ti}_7^*\text{F}_{30}\text{O}_2$ **Tl****Tl**Reaction with  $\text{HX}$ : 2.6.3.1Reaction with  $\text{X}_2$ : 2.6.2.1 $\text{Tl}^*\text{At}$  $\text{Tl}^*\text{AtI}_2$  $\text{Tl}^*\text{Br}$  $\text{Tl}^*\text{Br}_3$  $\text{Tl}^*\text{C}_2\text{H}_3\text{Br}_2\text{O}_2$  $\text{Tl}^*\text{C}_2\text{H}_3\text{O}_2$  $\text{Tl}^*\text{C}_2\text{H}_6\text{Br}$  $\text{Tl}^*\text{C}_2\text{H}_6\text{Cl}$  $\text{Tl}^*\text{C}_2\text{H}_6\text{I}$  $\text{Tl}^*\text{C}_3\text{H}_9$  $\text{Tl}^*\text{C}_4\text{CoO}_4$  $\text{Tl}^*\text{C}_4\text{H}_{10}\text{Br}$  $\text{Tl}^*\text{C}_4\text{H}_{10}\text{I}$  $\text{Tl}^*\text{C}_4\text{H}_{12}\text{N}$  $\text{Tl}^*\text{C}_5\text{H}_7\text{O}_2$  $\text{Tl}^*\text{C}_5\text{MnO}_3$  $\text{Tl}^*\text{C}_6\text{H}_2\text{Cl}_2$  $\text{Tl}^*\text{C}_6\text{H}_{18}\text{BN}_2$  $\text{Tl}^*\text{C}_6\text{H}_{18}\text{ClSi}_2$  $\text{Tl}^*\text{C}_6\text{H}_{18}\text{ISi}_2$  $\text{Tl}^*\text{C}_7\text{H}_{11}$  $\text{Tl}^*\text{C}_8\text{H}_{12}\text{P}$  $\text{Tl}^*\text{C}_9\text{H}_{27}\text{Si}_3$  $\text{Tl}^*\text{C}_{10}\text{H}_{11}$  $\text{Tl}^*\text{C}_{10}\text{H}_{11}\text{MoO}_3$  $\text{Tl}^*\text{C}_{12}\text{BrF}_{10}$  $\text{Tl}^*\text{C}_{12}\text{ClF}_{10}$  $\text{Tl}^*\text{C}_{12}\text{H}_{15}\text{MoO}_3$  $\text{Tl}^*\text{C}_{12}\text{H}_{33}\text{Si}_3\text{Sn}$  $\text{Tl}^*\text{C}_{14}\text{H}_5\text{F}_{10}\text{Ge}$  $\text{Tl}^*\text{C}_{15}\text{Mn}_3\text{O}_{15}$  $\text{Tl}^*\text{C}_{18}\text{H}_{45}\text{Ge}_3$  $\text{Tl}^*\text{C}_{36}\text{H}_{99}\text{Si}_9\text{Sn}_3$  $\text{Tl}^*\text{CdF}_3$  $\text{Tl}^*\text{Cl}$  $\text{Tl}^*\text{Cl}_2$  $\text{Tl}^*\text{Cl}_3$  $\text{Tl}^*\text{F}$  $\text{Tl}^*\text{FO}$  $\text{Tl}^*\text{F}_3$  $\text{Tl}^*\text{H}_4\text{Li}$  $\text{Tl}^*\text{I}$  $\text{Tl}^*\text{I}_3$  $\text{Tl}^*\text{P}$  $\text{TlW}^*\text{C}_{10}\text{H}_{11}\text{O}_3$  $\text{Tl}_2^*\text{Br}_2\text{Cl}_2$  $\text{Tl}_2^*\text{Br}_4$  $\text{Tl}_2^*\text{I}_4\text{Se}$  $\text{Tl}_2^*\text{O}_3$  $\text{Tm}^*\text{Cl}_3$  $\text{Tm}^*\text{FSe}$

Tm\*F<sub>3</sub>

U

U

Bromination followed by the addition  
of NH<sub>4</sub>F: 2.11.5.2Bromination followed by the addition  
of KF: 2.11.5.2

Fluorination: 2.11.5.2

Reaction with XeF<sub>2</sub>: 2.11.5.2U\*Br<sub>4</sub>U\*C<sub>16</sub>H<sub>40</sub>Br<sub>6</sub>N<sub>2</sub>U\*C<sub>16</sub>H<sub>40</sub>Cl<sub>6</sub>N<sub>2</sub>U\*F<sub>2</sub>O<sub>2</sub>U\*F<sub>4</sub>U\*F<sub>4</sub>OU\*F<sub>5</sub>H<sub>12</sub>N<sub>3</sub>O<sub>2</sub>U\*F<sub>5</sub>K<sub>3</sub>O<sub>2</sub>U\*F<sub>6</sub>U\*F<sub>7</sub>NaU\*F<sub>8</sub>Na<sub>2</sub>U\*O<sub>3</sub>U<sub>3</sub>\*O<sub>2</sub>S<sub>4</sub>U<sub>3</sub>\*O<sub>8</sub>

V

V

Fluorination: 2.11.2.1

Reaction with : 2.9.2.3

Reaction with F<sub>2</sub>: 2.9.2.1Reaction with Cl<sub>2</sub>: 2.9.2.2Reaction with I<sub>2</sub>: 2.9.2.4

Reaction with HX: 2.9.3.2

V\*BaFO<sub>3</sub>V\*BaF<sub>3</sub>O<sub>2</sub>V\*Br<sub>2</sub>V\*Br<sub>2</sub>OV\*Br<sub>3</sub>V\*Br<sub>3</sub>OV\*Br<sub>4</sub>OV\*C<sub>6</sub>H<sub>5</sub>Cl<sub>2</sub>OV\*C<sub>6</sub>H<sub>5</sub>Cl<sub>3</sub>V\*C<sub>24</sub>H<sub>20</sub>AsF<sub>2</sub>O<sub>2</sub>V\*C<sub>24</sub>H<sub>20</sub>F<sub>2</sub>O<sub>2</sub>P

V\*ClO

V\*ClO<sub>2</sub>

V\*ClS

V\*Cl<sub>2</sub>V\*Cl<sub>2</sub>OV\*Cl<sub>2</sub>O<sub>2</sub>V\*Cl<sub>3</sub>V\*Cl<sub>3</sub>H<sub>4</sub>O<sub>2</sub>V\*Cl<sub>3</sub>OV\*Cl<sub>4</sub>V\*Cl<sub>4</sub>H<sub>4</sub>O<sub>3</sub>V\*Cl<sub>4</sub>OV\*Cl<sub>5</sub>V\*Cl<sub>5</sub>OV\*CsF<sub>4</sub>OV\*FO<sub>2</sub>V\*F<sub>2</sub>V\*F<sub>2</sub>O<sub>2</sub>V\*F<sub>3</sub>V\*F<sub>3</sub>H<sub>6</sub>O<sub>3</sub>V\*F<sub>3</sub>OV\*F<sub>4</sub>V\*F<sub>4</sub>NO<sub>2</sub>V\*F<sub>4</sub>OV\*F<sub>4</sub>O<sub>2</sub>V\*F<sub>5</sub>V\*F<sub>5</sub>K<sub>2</sub>OV\*F<sub>5</sub>OV\*F<sub>6</sub>KV\*I<sub>2</sub>V\*I<sub>3</sub>V\*NaO<sub>3</sub>V\*O<sub>2</sub>V<sub>2</sub>\*Cl<sub>9</sub>CsV<sub>2</sub>\*F<sub>5</sub>K<sub>3</sub>O<sub>4</sub>V<sub>2</sub>\*F<sub>5</sub>O<sub>4</sub>V<sub>2</sub>\*F<sub>7</sub>O<sub>2</sub>V<sub>2</sub>\*F<sub>8</sub>K<sub>4</sub>O<sub>3</sub>V<sub>2</sub>\*F<sub>11</sub>O<sub>2</sub>V<sub>2</sub>\*F<sub>21</sub>I<sub>3</sub>O<sub>5</sub>V<sub>2</sub>\*O<sub>3</sub>V<sub>2</sub>\*O<sub>5</sub>V<sub>3</sub>\*FH<sub>4</sub>NO<sub>6</sub>V<sub>3</sub>\*FO<sub>6</sub>V<sub>3</sub>\*F<sub>14</sub>K<sub>5</sub>O<sub>3</sub>V<sub>3</sub>\*F<sub>14</sub>O<sub>3</sub>

W

W

Electrical explosion in SF<sub>6</sub> or CF<sub>4</sub>:  
2.11.4.1

Fluorination: 2.11.4.1

Reaction with SF<sub>6</sub>, S<sub>2</sub>X<sub>2</sub>: 2.9.14.1.2Reaction with WO<sub>3</sub>-X<sub>2</sub>: 2.9.11.3Reaction with WO<sub>3</sub>-WCl<sub>6</sub>: 2.9.11.4Reaction with X<sub>2</sub>-O<sub>2</sub>: 2.9.11.2Reaction with O<sub>2</sub>-F<sub>2</sub>: 2.11.4.1Reaction with Cl<sub>2</sub>: 2.9.2.2Reaction with BrF<sub>3</sub>: 2.9.3.4Reaction with F<sub>2</sub>: 2.9.2.1Reaction with Br<sub>2</sub>: 2.9.2.3

Reaction with ClF: 2.11.4.1

Reaction with Cl<sub>2</sub>-HF: 2.11.4.1

## Reaction with HX: 2.9.3.2

W*Br <sub>2</sub>	W*F <sub>5</sub> KO
W*Br <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	W*F <sub>5</sub> NO <sub>2</sub>
W*Br <sub>2</sub> O	W*F <sub>5</sub> N <sub>3</sub>
W*Br <sub>2</sub> O <sub>2</sub>	W*F <sub>5</sub> O
W*Br <sub>3</sub> O	W*F <sub>6</sub>
W*Br <sub>3</sub> Se	W*F <sub>6</sub> K
W*Br <sub>4</sub>	W*F <sub>6</sub> O <sub>2</sub> Se
W*Br <sub>4</sub> O	W*F <sub>7</sub> NO
W*Br <sub>4</sub> S	W*F <sub>7</sub> NO <sub>2</sub>
W*Br <sub>4</sub> Se	W*F <sub>8</sub> K <sub>2</sub>
W*Br <sub>5</sub>	W*F <sub>8</sub> N <sub>2</sub> O <sub>2</sub>
W*Br <sub>5</sub> O	W*F <sub>8</sub> Na <sub>2</sub>
W*Br <sub>6</sub>	W*F <sub>8</sub> OSe
W*C <sub>4</sub> Br <sub>2</sub> O <sub>4</sub>	W*F <sub>9</sub> NO
W*C <sub>4</sub> Cl <sub>2</sub> O <sub>4</sub>	W*F <sub>9</sub> OSb
W*C <sub>4</sub> I <sub>2</sub> O <sub>4</sub>	W*F <sub>10</sub> I <sub>2</sub> O <sub>3</sub>
W*C <sub>6</sub> O <sub>6</sub>	W*F <sub>14</sub> O <sub>2</sub> Te <sub>2</sub>
W*C <sub>8</sub> H <sub>5</sub> IO <sub>3</sub>	W*F <sub>22</sub> O <sub>4</sub> Te <sub>4</sub>
W*C <sub>10</sub> H <sub>11</sub> O <sub>3</sub> Tl	W*IO <sub>2</sub>
W*ClF <sub>5</sub>	W*I <sub>2</sub> O <sub>2</sub>
W*Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	W*I <sub>3</sub>
W*Cl <sub>2</sub> O	W*I <sub>4</sub>
W*Cl <sub>2</sub> OS	W*K <sub>2</sub> O <sub>4</sub>
W*Cl <sub>2</sub> O <sub>2</sub>	W*Na <sub>2</sub> O <sub>4</sub>
W*Cl <sub>2</sub> SSe	W*O <sub>2</sub>
W*Cl <sub>2</sub> S <sub>2</sub>	W*O <sub>3</sub>
W*Cl <sub>3</sub> O	W*S <sub>2</sub>
W*Cl <sub>3</sub> S	W*S <sub>3</sub>
W*Cl <sub>4</sub>	WY*Cl <sub>3</sub> Se
W*Cl <sub>4</sub> O	WY*F <sub>4</sub> Se
W*Cl <sub>4</sub> O <sub>2</sub>	W <sub>2</sub> *C <sub>8</sub> I <sub>2</sub> O <sub>8</sub>
W*Cl <sub>4</sub> S	W <sub>2</sub> *Cl <sub>4</sub> S <sub>3</sub>
W*Cl <sub>4</sub> Se	W <sub>2</sub> *Cl <sub>9</sub> K <sub>3</sub>
W*Cl <sub>5</sub>	W <sub>2</sub> *F <sub>9</sub> H <sub>3</sub> O <sub>3</sub>
W*Cl <sub>5</sub> O	W <sub>2</sub> *F <sub>13</sub> NO <sub>2</sub>
W*Cl <sub>6</sub>	W <sub>3</sub> *Cl <sub>9</sub> K <sub>3</sub>
W*Cl <sub>6</sub> Cs <sub>2</sub>	XCrF <sub>5+x</sub> O*Cl
W*Cl <sub>6</sub> K	X*CrO <sub>3</sub>
W*Cl <sub>6</sub> K <sub>2</sub>	XO*Cl <sub>X</sub> CrF <sub>5</sub> +
W*C <sub>8</sub> F <sub>5</sub> O	X <sup>e</sup>
W*F <sub>2</sub> O	Xe
W*F <sub>2</sub> OS	Reaction with PtF <sub>6</sub> : 2.10.2.2.1
W*F <sub>2</sub> O <sub>2</sub>	Reaction with OF <sub>2</sub> , O <sub>2</sub> F <sub>2</sub> : 2.10.2.2.1
W*F <sub>3</sub> S	Reaction with F <sub>2</sub> : 2.10.2.2
W*F <sub>3</sub> H <sub>2</sub> O <sub>3</sub>	Reaction with IF <sub>7</sub> : 2.10.2.2.1
W*F <sub>3</sub> S	Reaction with c-C <sub>4</sub> F <sub>8</sub> : 2.10.2.2.1
W*F <sub>4</sub> O	Reaction with Cl <sub>2</sub> : 2.10.2.2.2
W*F <sub>4</sub> S	Xe*AsF <sub>11</sub>
W*F <sub>4</sub> Se	Xe*AuF <sub>11</sub>
W*F <sub>5</sub>	Xe*BaO <sub>4</sub>
W*F <sub>5</sub> H <sub>3</sub> O <sub>2</sub>	Xe*Br <sub>4</sub>
	Xe*Cl <sub>2</sub>

Xe\*Cl<sub>4</sub>  
 Xe\*CoF<sub>9</sub>  
 Xe\*Cr<sub>2</sub>F<sub>30</sub>Sb<sub>4</sub>  
 Xe\*F<sub>2</sub>  
 Xe\*F<sub>2</sub>O<sub>2</sub>  
 Xe\*F<sub>2</sub>O<sub>3</sub>S  
 Xe\*F<sub>4</sub>  
 Xe\*F<sub>4</sub>O  
 Xe\*F<sub>4</sub>O<sub>2</sub>  
 Xe\*F<sub>6</sub>  
 Xe\*F<sub>6</sub>Mn  
 Xe\*F<sub>6</sub>Pd  
 Xe\*F<sub>6</sub>Pt  
 Xe\*F<sub>6</sub>Rh  
 Xe\*F<sub>6</sub>Ti  
 Xe\*F<sub>7</sub>I  
 Xe\*F<sub>7</sub>Ir  
 Xe\*F<sub>7</sub>Pt  
 Xe\*F<sub>7</sub>Sb  
 Xe\*F<sub>8</sub>Mn  
 Xe\*F<sub>9</sub>Fe  
 Xe\*F<sub>9</sub>Sb  
 Xe\*F<sub>10</sub>Pd<sub>2</sub>  
 Xe\*F<sub>10</sub>Ti  
 Xe\*F<sub>10</sub>Ti<sub>2</sub>  
 Xe\*F<sub>11</sub>Ir  
 Xe\*F<sub>11</sub>Pt  
 Xe\*F<sub>11</sub>Ru  
 Xe\*F<sub>11</sub>Sb  
 Xe\*F<sub>12</sub>Ir<sub>2</sub>  
 Xe\*F<sub>12</sub>Pt<sub>2</sub>  
 Xe\*F<sub>14</sub>Ti<sub>2</sub>  
 Xe\*F<sub>16</sub>Sb<sub>2</sub>  
 Xe\*O<sub>3</sub>  
 Xe<sub>0.5</sub>\*F<sub>5</sub>Mn  
 Xe<sub>0.5</sub>\*F<sub>6</sub>Mn  
 Xe<sub>2</sub>\*AuF<sub>9</sub>  
 Xe<sub>2</sub>\*AuF<sub>17</sub>  
 Xe<sub>2</sub>\*F<sub>9</sub>Ir  
 Xe<sub>2</sub>\*F<sub>12</sub>Mn  
 Xe<sub>2</sub>\*F<sub>16</sub>Ni  
 Xe<sub>2</sub>\*F<sub>16</sub>Pd  
 Xe<sub>2</sub>\*F<sub>17</sub>Ir  
 Xe<sub>2</sub>\*F<sub>17</sub>Sb  
 Xe<sub>3</sub>\*F<sub>14</sub>Ti<sub>2</sub>  
 Xe<sub>4</sub>\*F<sub>20</sub>Mn  
 Xe<sub>4</sub>\*F<sub>28</sub>Ni  
 Xe<sub>4</sub>\*F<sub>28</sub>Ti  
 Y  
 Y

Reaction with HX: 2.9.14.1.1

Reaction with transition-metals:  
2.9.14.1.2

Y\*BrS  
 Y\*Cl<sub>3</sub>SeW  
 Y\*FO  
 Y\*FS  
 Y\*FSe  
 Y\*F<sub>3</sub>  
 Y\*F<sub>4</sub>Na  
 Y\*F<sub>4</sub>SeW  
 Y<sub>2</sub>\*O<sub>3</sub>  
 Y<sub>2</sub>\*S<sub>3</sub>  
 Y<sub>2</sub>\*Se<sub>3</sub>  
 Y<sub>7</sub>\*Cl<sub>4</sub>Mo<sub>3</sub>  
 Yb  
 Yb

Reaction with HX: 2.9.14.1.1

Yb\*BrS  
 Yb\*Cl<sub>3</sub>  
 Yb\*FS  
 Yb\*FSe  
 Yb\*F<sub>3</sub>  
 Zn  
 Zn

Fluorination: 2.11.2.3

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Reaction with O<sub>2</sub>SCl<sub>2</sub>: 2.8.14.4

Reaction with SF<sub>6</sub>: 2.8.14.4

Reaction with S<sub>2</sub>Cl<sub>2</sub>: 2.8.14.4

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Reaction with Cl<sub>2</sub>: 2.8.14.1

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Zn\*AgF<sub>3</sub>

Zn\*BaCl<sub>4</sub>

Zn\*BaCl<sub>4</sub>H<sub>8</sub>O<sub>4</sub>

Zn\*BaCl<sub>4</sub>H<sub>12</sub>O<sub>6</sub>

Zn\*Br<sub>2</sub>

Zn\*Br<sub>2</sub>H<sub>4</sub>O<sub>2</sub>

Zn\*Br<sub>2</sub>H<sub>6</sub>O<sub>3</sub>

$\text{Zn}^*\text{Br}_3\text{H}_2\text{NaO}$   
 $\text{Zn}^*\text{Br}_3\text{H}_4\text{KO}_2$   
 $\text{Zn}^*\text{Br}_3\text{H}_{10}\text{NO}_3$   
 $\text{Zn}^*\text{Br}_4\text{Cs}_2$   
 $\text{Zn}^*\text{Br}_4\text{H}_4\text{K}_2\text{O}_2$   
 $\text{Zn}^*\text{Br}_4\text{H}_8\text{N}_2$   
 $\text{Zn}^*\text{Br}_4\text{H}_{10}\text{N}_2\text{O}$   
 $\text{Zn}^*\text{Br}_5\text{Cs}_3$   
 $\text{Zn}^*\text{Br}_5\text{H}_{14}\text{N}_3\text{O}$   
 $\text{Zn}^*\text{CO}_3$   
 $\text{Zn}^*\text{C}_8\text{H}_{11}\text{ClO}$   
 $\text{Zn}^*\text{C}_{12}\text{H}_{10}$   
 $\text{Zn}^*\text{ClHO}$   
 $\text{Zn}^*\text{Cl}_2$   
 $\text{Zn}^*\text{Cl}_2\text{H}_2\text{O}$   
 $\text{Zn}^*\text{Cl}_2\text{H}_6\text{O}_3$   
 $\text{Zn}^*\text{Cl}_2\text{H}_8\text{O}_4$   
 $\text{Zn}^*\text{Cl}_2\text{H}_{14}\text{O}_7$   
 $\text{Zn}^*\text{Cl}_2\text{O}_6$   
 $\text{Zn}^*\text{Cl}_3\text{H}_4\text{KO}_2$   
 $\text{Zn}^*\text{Cl}_3\text{H}_5\text{O}$   
 $\text{Zn}^*\text{Cl}_3\text{H}_6\text{LiO}_3$   
 $\text{Zn}^*\text{Cl}_4\text{Cs}_2$   
 $\text{Zn}^*\text{Cl}_4\text{H}_6\text{Na}_2\text{O}_3$   
 $\text{Zn}^*\text{Cl}_4\text{H}_8\text{N}_2$   
 $\text{Zn}^*\text{Cl}_4\text{H}_{12}\text{MgO}_6$   
 $\text{Zn}^*\text{Cl}_4\text{K}_2$   
 $\text{Zn}^*\text{Cl}_4\text{Rb}_2$   
 $\text{Zn}^*\text{Cl}_5\text{Cs}_3$   
 $\text{Zn}^*\text{Cl}_5\text{H}_{12}\text{N}_3$   
 $\text{Zn}^*\text{Cs}_2\text{I}_4$   
 $\text{Zn}^*\text{Cs}_3\text{I}_5$   
 $\text{Zn}^*\text{F}_2$   
 $\text{Zn}^*\text{F}_2\text{H}_4\text{O}_2$   
 $\text{Zn}^*\text{F}_2\text{H}_8\text{O}_4$   
 $\text{Zn}^*\text{F}_2\text{H}_8\text{O}_4$   
 $\text{Zn}^*\text{F}_3\text{H}_4\text{N}$   
 $\text{Zn}^*\text{F}_3\text{K}$   
 $\text{Zn}^*\text{F}_3\text{Na}$   
 $\text{Zn}^*\text{F}_4\text{H}_{12}\text{N}_2\text{O}_2$

$\text{Zn}^*\text{F}_4\text{K}_2$   
 $\text{Zn}^*\text{H}_4\text{I}_2\text{O}_2$   
 $\text{Zn}^*\text{H}_6\text{I}_3\text{NaO}_3$   
 $\text{Zn}^*\text{H}_8\text{I}_2\text{O}_4$   
 $\text{Zn}^*\text{H}_8\text{I}_4\text{N}_2$   
 $\text{Zn}^*\text{Hgl}_4$   
 $\text{Zn}^*\text{I}_2$   
 $\text{Zn}^*\text{O}$   
 $\text{Zn}^*\text{O}_4\text{S}$   
 $\text{Zn}^*\text{O}_4\text{S}_2$   
 $\text{Zn}^*\text{S}$   
 $\text{Zn}_2^*\text{Cl}_5\text{H}_5\text{O}_2$   
 $\text{Zn}_3^*\text{O}_6\text{P}_2$   
 $\text{Zn}_3^*\text{P}_2$   
 $\text{Zn}_5^*\text{Cl}_2\text{H}_{10}\text{O}_9$   
 $\text{Zr}$

Zr

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$\text{Zr}^*\text{Br}_4$   
 $\text{Zr}^*\text{C}_{10}\text{H}_{10}\text{Cl}_2$   
 $\text{Zr}^*\text{C}_{16}\text{H}_{40}\text{Br}_6\text{N}_2$   
 $\text{Zr}^*\text{C}_{16}\text{H}_{40}\text{Cl}_6\text{N}_2$   
 $\text{Zr}^*\text{C}_{24}\text{H}_{20}\text{Se}_4$   
 $\text{Zr}^*\text{Cl}_4$   
 $\text{Zr}^*\text{Cl}_4\text{O}$   
 $\text{Zr}^*\text{CsF}_5$   
 $\text{Zr}^*\text{Cs}_3\text{F}_6$   
 $\text{Zr}^*\text{Cs}_2\text{I}_6$   
 $\text{Zr}^*\text{Cs}_3\text{F}_7$   
 $\text{Zr}^*\text{F}_3\text{H}_4\text{O}_3$   
 $\text{Zr}^*\text{F}_4$   
 $\text{Zr}^*\text{F}_7\text{H}_{12}\text{N}_3$   
 $\text{Zr}^*\text{I}_4$   
 $\text{Zr}^*\text{O}_2$   
 $\text{Zr}_2^*\text{Cl}_{10}\text{O}$

## Subject Index

This index supplements the compound index and the table of contents by providing access to the text by way of methods, techniques, reaction conditions, properties, effects and other phenomena. Reactions of specific bonds and compound classes are noted when they are not accessed by the heading of the section in which they appear.

For multiple entries, additional keywords indicate contexts and thereby avoid the retrieval of information that is irrelevant to the user's need.

Section numbers are used to direct the reader to those positions in the volume where substantial information is to be found.

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