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THE PHOSPHAZOTRIHALIDES

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I. Introduction

A great number of compounds containing the phosphazo group -N=PX₃ (X = halogen) is known; their reactions and applications have led to very intensive investigations. In the last 7 years (since 1964) over

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300 new papers dealing with this subject have been published; yet there is no comprehensive and up-to-date review about these compounds.

The present review does not consider the chemistry of the cyclic phosphonitrilic compounds (phosphazenes) $(\text{PNCl}_2)_n$ ($n \geq 3$); many authoritative reviews on this subject have appeared (182, 188b, 220b, 292, 355, 357, 407, 418, 420, 525) as well as shorter ones (3a, 4, 55, 406, 415–417). Linear phosphorus–nitrogen compounds have been reviewed lately (161, 188). Also phosphinimines do not fall within the scope of this survey, unless they can be prepared from phosphazotrihalides or are made available through analogous syntheses. There exists an excellent review about phosphinimines (483) and another one which is related to them (392).

Phosphazotrihalides are, however, sometimes mentioned in reviews (16, 19, 68, 161, 188b, 206a, 342, 350, 389, 408a, 411, 492a). Kirsanov and co-workers have provided an excellent coverage of these compounds up to early 1964 (137), and very recently a Russian review about cyclodiphosphazanes (180b) has been published. Otherwise only very short reviews (224, 227, 427b) from Kirsanov's group have appeared.

The present survey considers the syntheses and reactions, along with physical data, of all compounds containing a $-\text{N}=\text{PX}_3$ group ($\text{X} = \text{halogen}$). The abbreviations used are: Me = methyl, Et = ethyl, Pr = *n*-propyl, Bu = *n*-butyl, Am = *n*-amyl, and Ph = phenyl; if not otherwise stated, R = alkyl group, Ar = aryl group, X = halogen, and Y, Z = other substituents.

Original papers (over 80% of the literature references) were consulted whenever and wherever possible. The literature (primary, secondary, and tertiary) has been surveyed up to the end of November 1971. Names of Russian and Japanese authors are given as listed in *Chemical Abstracts*.

II. Nomenclature

No consistent system is available for naming phosphorus–nitrogen compounds. In the particular case of $-\text{N}=\text{PX}_3$ compounds the presence of the monomeric form $-\text{N}=\text{PX}_3$ (as a derivative of the hypothetical phosphinimine $\text{HN}=\text{PH}_3$) and the dimeric form $(-\text{N}=\text{PX}_3)_2$ (cyclodiphosphazane) gives rise to very different nomenclature systems. Table I summarizes the most commonly used nomenclature; nomenclature preferred by *Chemical Abstracts* is set in italics.

TABLE I
NOMENCLATURE OF PHOSPHORUS COMPOUNDS^a

Compound	Trivial name	Rational or partly rational nomenclature	
$[\text{Cl}_3\text{P} \equiv \text{N} = \text{PCl}_3]^+ \text{PCl}_6^-$	1,1,1,3,3,3-Hexachlorodiphosponitrilium hexachlorophosphate	Iminobis(trichlorophosphazyl)hexachlorophosphate	
	—	<i>Trichloro[(trichlorophosphoranylidene)amino]-phosphorus(V) hexachlorophosphate</i>	
	1,1,1,3,3,3-Hexachloro-2,1,3-azadiphosphopropanium[1]hexachlorophosphamethanate	—	
$\text{Cl}_2\text{OPN} = \text{PCl}_3$	—	Trichlorophosphazophosphorus(V) oxychloride (<i>Trichlorophosphoranylidene</i>)amidophosphoryldichloride	
$\text{ClSO}_2\text{N} = \text{PCl}_3$	—	<i>Trichlorophosphazosulfonyl (or -sulfonyl) chloride</i> <i>Trichlorophosphoranylidenesulfamoyl chloride</i>	
$\text{HN} = \text{PH}_3$	<i>Phosphinimine</i>	Monomeric form:	Dimeric form:
		Phosphazene	<i>Diazadiphosphetidine</i> Diazadiphosphacyclobutane
$\text{RN} = \text{PCl}_3$	<i>Alkylphosphorimidic trichloride</i>	Monomeric form:	Dimeric form:
		<i>N-Alkyltrichlorophosphinimine</i>	Dimeric <i>N-alkyltrichlorophosphinimine</i>

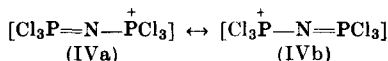
(continued)

TABLE I—continued

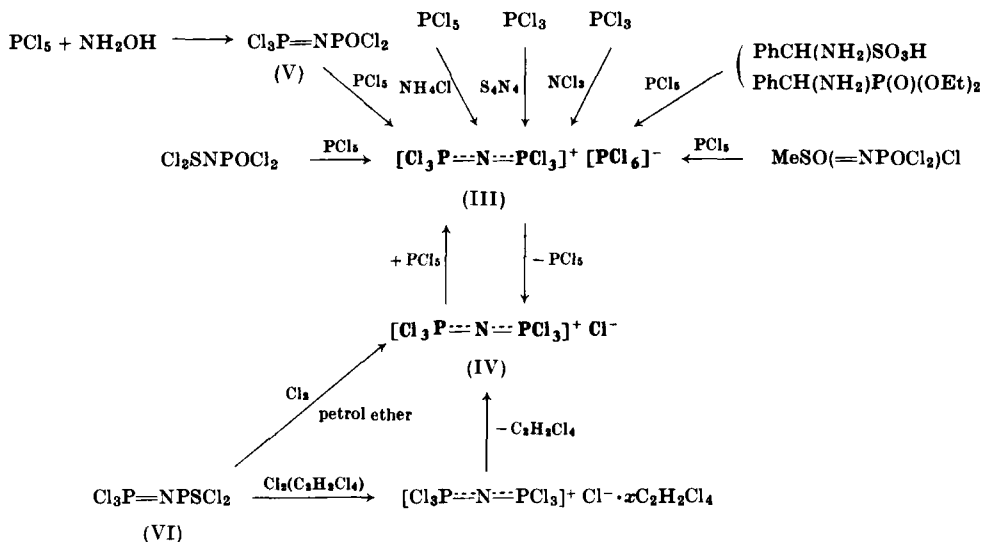
Compound	Trivial name	Rational or partly rational nomenclature	
$RN=PCl_3$	<i>Alkylphosphorimidic trichloride</i>	<i>N</i> -Alkyltrichloro-phosphazene	Dimeric <i>N</i> -alkyltrichlorophosphazene <i>1,3-Dialkyl-2,2,4,4-tetrahydro-2,2,2,4,4,4-hexachloro-1,3,2,4-diazadiphosphetidine</i> <i>2,2,2,4,4,4-Hexachloro-1,3-dialkylcyclo-diphosphazene</i>
		<i>Trichlorophosphazoalkyl</i>	<i>2,2,2,4,4,4-Hexachloro-1,3-dialkyl-1,3-diaza-2,4-diphosphacyclobutane</i>
	—	<i>2,2,2-Trichloro-1,3-dimethyl-2,1,3-phosphazetidinone-4</i> <i>2,2,2-Trichloro-1,3-dimethyl-1,3,2-diazaphosphacyclobutanone-4</i>	

^a Compound names in italics are those preferred by *Chemical Abstracts*.

The chloride corresponding to (III), namely, $[\text{Cl}_3\text{P}=\text{N}=\text{PCl}_3]^+\text{Cl}^-$ (IV), is formed as a $\text{C}_2\text{H}_2\text{Cl}_4$ adduct from P_2NSCl_5 (VI) with chlorine which loses the solvent by heating (29); (IV) is also formed from hydroxylamine hydrochloride and PCl_5 (11, 24). These compounds like all ionic compounds containing at least two $-\text{N}=\text{PX}_3$ groups in the cation, are resonance-stabilized, and are best represented by the formulas (IVa) and (IVb). Other derivatives of (IV), such as the BCl_4^- (346) or SbCl_6^-



compound (15, 29, 395) are known. The former compound may also be prepared from $\text{NH}_3 \cdot \text{BF}_3$ and 3 moles of PCl_5 (51e). The latter can also be prepared directly from NH_4SbCl_6 and PCl_5 (395) or from $\text{PCl}_4^+\text{SbCl}_6^-$ and NH_4Cl (310) or results from the thermolytic degradation of bis(trichlorophosphazo)benzyl hexachloroantimonate, $[\text{PhC}(\text{N}=\text{PCl}_3)_2]^+\text{SbCl}_6^-$ with loss of benzonitrile (402). Similarly, $[\text{Cl}_3\text{P}=\text{N}=\text{PCl}_3]^+\text{X}^-$ ($\text{X}^- = \text{AlCl}_4^-, \text{FeCl}_4^-$) have been isolated (509a).

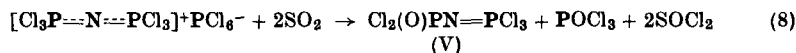


SCHEME 1. Syntheses of P_2NCl_7 (IV) and $\text{P}_3\text{NCl}_{12}$ (III).

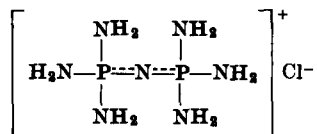
2. Reactions of the Chlorides

Reaction of (III) (15, 28, 315) or (IV) (29) with SO_2 or $\text{NH}_2\text{OH} \cdot \text{HCl}$ (with addition of PCl_3) (24) yields trichlorophosphazophosphorus(V)

oxychloride (V). The same compound can be obtained from (III) with P_4O_{10} (413) or formic acid (192).



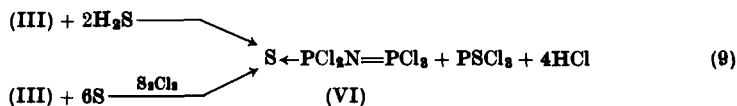
Liquid ammonia and (IV) produce a compound, $P_2N_7H_{12}Cl$, having the following structure:



(36), which can also be obtained by thermal condensation of $[P(NH_2)_4]^+ Cl^-$ (287, 405) or, as the iodide, from $[P(NH_2)_4]^+ I^-$ (404). The reaction of (IV) with NH_4Cl yields higher linear polymers (30) (cf. Section III).

$[Cl_3P \equiv N \equiv PCl_3]^+ BCl_4^-$ and SO_2 react in a rather complex way, whereas with H_2S the compound (VI) is obtained (51e) and with $MeNH_3Cl$ a ring-closure reaction occurs (51d). Excess ammonium thiocyanate gives $[(SCN)_8P \equiv N \equiv P(NCS)_3]^+ [B(NCS)_4]^-$ (51b) and fluorination (AsF_3) affords the cyclic compound $(NPF_2 \cdot PF_5)_3$ (51a).

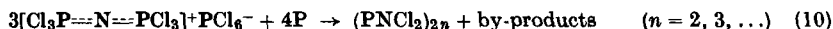
The thio analog of (V) can be prepared according to Eq. (9) (13, 29);



it results also as a by-product from the reaction of S_4N_4 with PCl_3 (29).

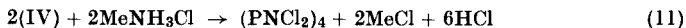
For further details concerning compounds (V) and (VI), cf. Section V, A.

A longer chain polymer $[Cl_3P \equiv NPCL_2 \equiv NPCL_3]^+ PCl_6^-$ is obtained from (III) and NH_4Cl (molar ratios 5:2 to 3:2) (29) (for details, cf. Section IV, B, 1); reaction with H_2NSO_3H gives $NPCL_2(NSOCl)_2$ (70a). Compound (III) and red phosphorus do not yield the expected $Cl_2PN \equiv PCl_3$ (postulated as an intermediate), but give mainly cyclic phosphazenes (158).



The reaction of (IV) with a linear substrate $Ph_4P_2N_3H_4Cl$ gives no characterizable product (78), but with $MeNH_3Cl$ in the presence of BCl_3 a six-membered ring containing P, N, and B atoms can be obtained (16, 34; cf. also 512); an analogous six-membered ring with P, N, and Al

atoms is known (509a). (IV) and MeNH_3Cl react only (169) according to Eq. (11).

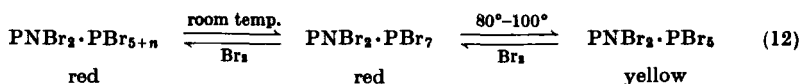


Various amidinium chlorides react with $[\text{Cl}_3\text{P}=\text{N}=\text{PCl}_3]^+\text{SbCl}_6^-$ to give substituted diphospha-1,3,5-triazines (400, 402). Heating $[\text{Cl}_3\text{P}=\text{N}=\text{PCl}_3]^+\text{BCl}_4^-$ with AlCl_3 in sym. $\text{C}_2\text{H}_2\text{Cl}_4$ is said to give a product $(\text{BP}_2\text{N}_3\text{Cl}_4)_n$ to which a borazine-like structure with four fused six-membered rings was assigned (346), but no adequate confirmation was given.

Linear phosphonitrile compounds analogous to (III) and (IV), such as $[\text{Ph}_2\text{P}(\text{Cl})=\text{N}=\text{P}(\text{Cl})\text{Ph}_2]^+\text{Cl}^-$, have been reviewed recently (161) and so are not within the scope of this review.

3. Syntheses and Reactions of the Bromides

John and Moeller (205) obtained only poor yields of $(\text{PNBr}_2)_n$ by reacting PBr_3 , excess bromine, and NH_4Br at temperatures of 115° – 120° , but red crystalline substances of the general formula $\text{PNBr}_2 \cdot \text{PBr}_{5+n}$

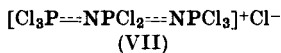


($n \geq 0$) (206) were formed. These substances can be formulated as $[\text{Br}_3\text{P}=\text{N}=\text{PBr}_3]^+\text{Br}_3^-$ and $[\text{Br}_3\text{P}=\text{N}=\text{PBr}_3]^+\text{Br}^-$, respectively. Easy addition of bromine with probable formation of polybromides $\text{PNBr}_2 \cdot \text{PBr}_{5+n}$ ($n \geq 0$) with varying bromine content occurs (206). On raising the temperature to 85° , $[\text{Br}_3\text{P}=\text{N}=\text{PBr}_3]^+\text{Br}_3^-$ slowly loses bromine (75); above 120° polymerization to smaller amounts of $(\text{PNBr}_2)_3$ and $(\text{PNBr}_2)_4$, as well as larger amounts of higher polymers, was observed. A short discussion concerning the ionic structure of these substances is given in the literature (75).

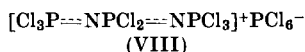
B. HIGHER IONIC P–N COMPOUNDS (MORE THAN TWO P ATOMS IN THE CATION)

1. Syntheses

As already mentioned in Section IV, A, 2 the reaction of $\text{P}_3\text{NCl}_{12}$ (III) with NH_4Cl (ratios 5:2 to 3:2) gives $\text{P}_3\text{N}_2\text{Cl}_9$ (VII) (29); the same



compound had already been described earlier in a patent (51) but was not characterized properly. Compound (VII) is also obtained by heating the corresponding hexachlorophosphate (VIII) (29). Compound (VIII)

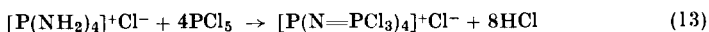


also results from PCl_5 and NH_4Cl (2:1) along with (IV) (16a, 23), as well as from the thermolysis of (IV) at 150° (2 hr) in 82% yield (30). It is also a by-product from the reaction of S_4N_4 with PCl_3 (23, 29) and a major product from that of $(\text{PNCl}_2)_3$ with PCl_5 (156) at elevated temperatures (200° – 220°) (cf. Scheme 3).

A higher homolog of (VIII), $\text{P}_5\text{N}_3\text{Cl}_{16}$, $[\text{Cl}_3\text{P}=\text{NPCl}_2=\text{NPCl}_2=\text{NPCl}_3]^+\text{PCl}_6^-$, is formed in poor yields in the synthesis of (VIII) (30). The same compound is formed in the reaction of $(\text{PNCl}_2)_3$ with PCl_5 (1:2, 250° , 11 hr) (339). The next higher homolog, $[\text{Cl}_3\text{PN}-(\text{PCl}_2\text{N})_3-\text{PCl}_3]^+\text{PCl}_6^-$, is formed from $(\text{PNCl}_2)_4$ and PCl_5 (1:2, 250° , 100 hr) (339). Higher polymers, $[\text{Cl}_3\text{PN}-(\text{PCl}_2\text{N})_n-\text{PCl}_3]^+\text{PCl}_6^-$ ($n = 4$ or 5), have been identified by ^{31}P NMR (339); a cationic mechanism for the formation of these compounds is suggested.

Long-chain polymers of the probable structure $\text{Cl}_3\text{P}=\text{N}-(\text{PCl}_2\text{N})_n-\text{PCl}_2=\text{NH}$ ($n = 8$ – 13) have been reported (27). Related high polymers with terminal $-\text{N}=\text{PCl}_3$ groups were isolated by Paddock (356) and Lund *et al.* (323) from the reaction of $(\text{PNCl}_2)_n$ ($n = 3, 4$) with PCl_5 (molar ratios 100:1).

Recently Schmidpeter and Weingand (405) synthesized the compounds $[\text{P}(\text{N}=\text{PCl}_3)_4]^+\text{X}^-$ ($\text{X}^- = \text{Cl}^-, \text{SbCl}_6^-, \text{Cl}_2\text{I}^-, \text{HgI}_3^-$).



$\text{P}_3\text{N}_3\text{F}_6$ and alkali metal fluorides in the presence of Ph_4AsCl undergo ring cleavage forming the compounds $[\text{F}_3\text{P}=\text{NPF}_2=\text{NPF}_2=\text{N}]^-[\text{AsPh}_4]^+$ (376) and $[\text{F}_3\text{P}=\text{NPF}_2=\text{N}]^-\text{AsPh}_4^+$ (identified spectroscopically) [see also (140a)].

2. Reactions

Compounds (VII) and (VIII) react with SO_2 giving $\text{Cl}_3\text{P}=\text{NPCl}_2=\text{NPOCl}_2$ (23, 28, 29, 524a), the corresponding thio analog is obtained from (VIII) and H_2S (13a, 29). Ammonolysis of (VIII) yields $(\text{PNCl}_2)_3$ (19); with $\text{H}_2\text{NSO}_3\text{H}$ the compound $\text{NPCl}_2(\text{NSOCl})_2$ is obtained (70a). This compound can also be obtained on other ways (cf. Section VI, B).

When $[\text{Cl}_3\text{PN}=(\text{PNCl}_2)_2=\text{PCl}_3]^+\text{PCl}_6^-$ is heated to 300° – 350° , it yields different linear polymers, among them (III) (339). The tetrachloroaluminate and tetrachloroborate of the $[\text{Cl}_3\text{PN}=(\text{PCl}_2\text{N})_2=\text{PCl}_3]^+$ ion are

thermally stable substances up to 700° (339); analogous compounds with other anions have been described [(344, 345), cf. also (407)]. The compounds $[\text{Cl}_3\text{PN}=(\text{PCl}_2\text{N})_n=\text{PCl}_3]^+\text{Cl}^-$ ($n = 2, 3$) react with metal halides such as NbCl_5 , MoCl_5 , TaCl_5 , PtCl_4 , WCl_6 , or RuCl_4 to give viscous oils of probable composition $[\text{Cl}_3\text{PN}=(\text{PCl}_2\text{N})_n\text{PCl}_3]^+\text{M}^m\text{Cl}_{m+1}$ (m = valency state of the metal ion) (341); reactions with NbOCl_3 and WO_2Cl_2 (341) and with phenol (192c, 374), aniline, MeNH_2 , and EtOH (374) have also been reported.

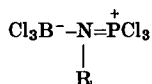
The higher polymers $[\text{Cl}_3\text{P}(=\text{NPCl}_2)_n\text{NPCl}_3]^+\text{Cl}^-$ ($n = 3-15$) lose PCl_5 when heated in an inert atmosphere to 240°–260°, forming longer P–N chains with an average molecular weight of 3000 to 10000 (50c). The ammonolysis product of only one higher linear polymer has been described (509c).

Finally, $[\text{P}(\text{N}=\text{PCl}_3)_4]^+\text{Cl}^-$ reacts with SO_2 to give $\text{Cl}_2\text{OPN}=\text{P}(\text{N}=\text{PCl}_3)_3$ (403).

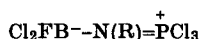
C. IONIC COMPOUNDS CONTAINING $[\text{P}\equiv\text{N}\equiv\text{C}(\text{R})\equiv\text{N}\equiv\text{P}]$ UNITS

1. Syntheses

The first member of this series is $[\text{Me}_2\text{NPCl}_3]^+\text{SbCl}_6^-$, which can be isolated from the reaction of $[\text{Me}_2\text{NH}_2]^+\text{SbCl}_6^-$ and PCl_5 (395). The corresponding hexachlorophosphates $[\text{R}_2\text{NPCl}_3]^+\text{PCl}_6^-$ have previously been described by Michaelis (334), but have been formulated as $\text{R}_2\text{NPCl}_4 \cdot \text{PCl}_5$. The tetrachloroborates result from $\text{R}_2\text{NH} \cdot \text{BF}_3$ and PCl_5 (51g). Reaction of $\text{RNH}_2 \cdot \text{BF}_3$ ($\text{R} = \text{Me}, \text{Ph}$) and 2 moles of PCl_5 gives rise to the compounds

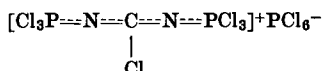


(51f);

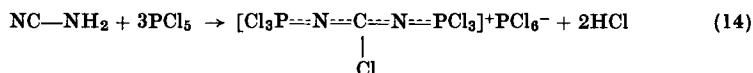


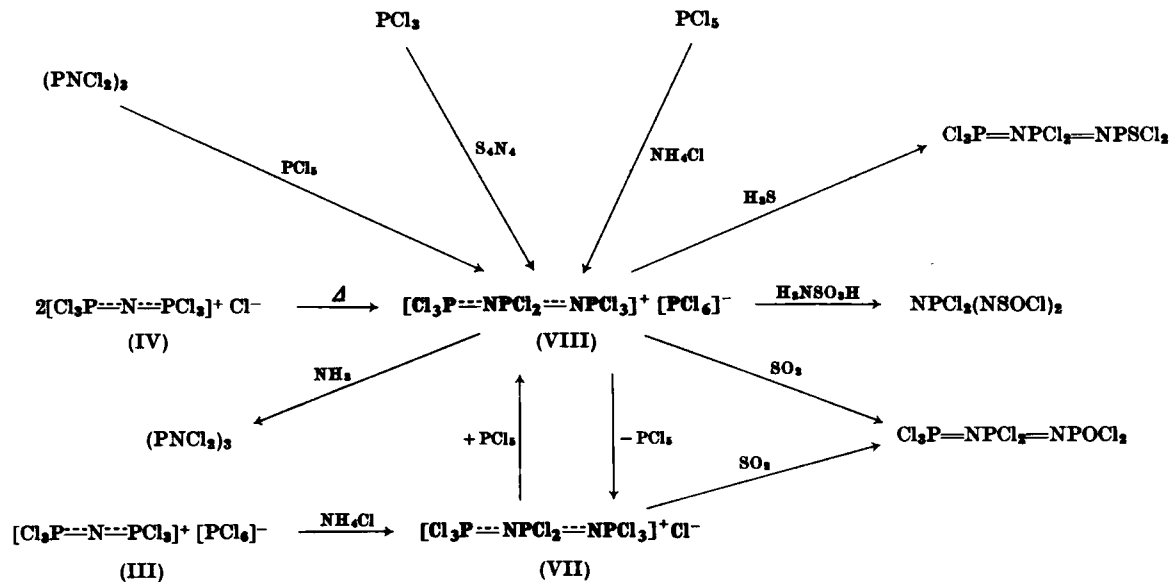
may also be obtained (51f).

Cyanamide and PCl_5 give



(26b, 207); the same compound is isolable in poor yield from the reaction

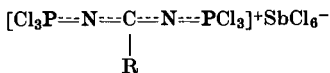




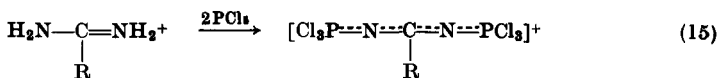
SCHEME 3. Syntheses and reactions of (VII) and (VIII).

of urea and PCl_5 (207). The mechanism involved in the first step is thought to be a Kirsanov reaction on the amino group (introducing a $-\text{N}=\text{PCl}_3$ group), followed by attack of a PCl_5 molecule on the $\text{C}\equiv\text{N}$ triple bond with chlorination and formation of a second trichlorophosphazo group (16).

Similar compounds

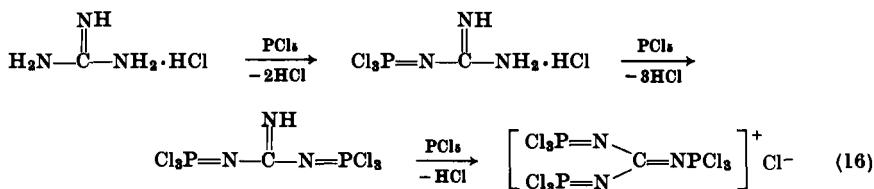


were obtained by Schmidpeter *et al.* (396, 397) as condensation products of amidinium hexachloroantimonates and PCl_5 .



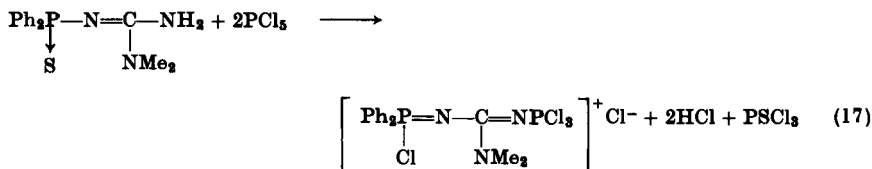
$\text{R} = \text{Me}, \text{Ph}, \text{NMe}_2, \text{CCl}_3$ (the latter by using an excess of PCl_5 during the reaction of the methyl compound)

Stepwise phosphorylation of guanidine with PCl_5 has been accomplished; all intermediates could be isolated (422).



The latter compound has also been described independently (26b); the hexachloroantimonate salt had been described earlier (396, 397).

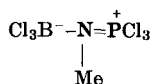
The analogous condensation of Ph_2PSCl with dimethylguanidinium sulfate yields $\text{Ph}_2\text{P}(\text{S})-\text{N}=\text{C}(\text{NMe}_2)\text{NH}_2$ (398) which reacts with PCl_5



(399) as shown in Eq. (17). The corresponding hexachloroantimonates could also be obtained (399).

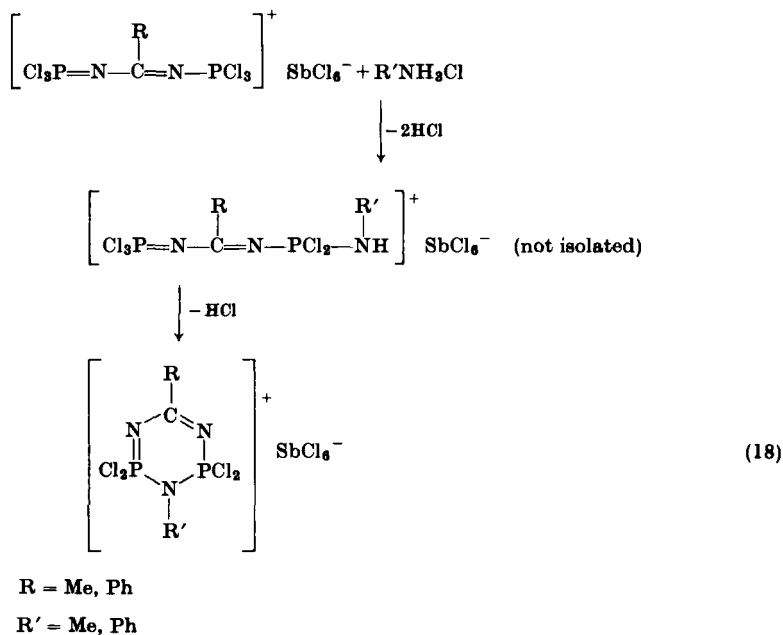
2. Reactions

Arsenic trifluoride fluorinates



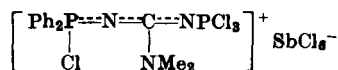
to BF_3 and $(\text{MeN}=\text{PF}_3)_2$ (51h) and $[\text{Me}_2\text{NPCl}_3]^+\text{BCl}_4^-$ to Me_2NPF_4 .

A ring-closure reaction occurs with bis(trichlorophosphazyl)methyl- (393, 402) or -phenylhexachloroantimonates (393, 394, 402) and excess ammonium chloride to give the corresponding diphosphatriazines $\text{RC}(\text{NPCl}_2)_2\text{N}$ in good yields. The same cyclocondensation with MeNH_3Cl or PhNH_3Cl stops at the hexachloroantimonate salt of these triazines (394, 396).

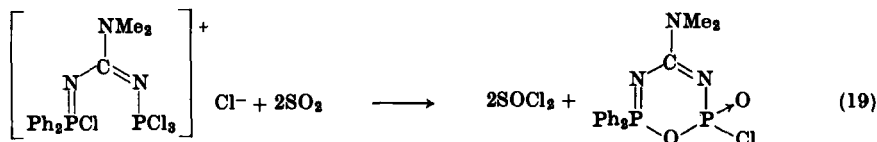


The thermolytic behavior of $[\text{RC}(\text{NPCl}_2)_2]^+\text{SbCl}_6^-$ depends strongly on the nature of R. With $\text{R} = \text{Ph}$, elimination of benzonitrile occurs giving $[\text{N}(\text{PCl}_3)_2]^+\text{SbCl}_6^-$; with $\text{R} = \text{Me}$, only tars are formed and with $\text{R} = \text{Me}_2\text{N}$ no condensation occurs (402).

The reaction of the saltlike compound



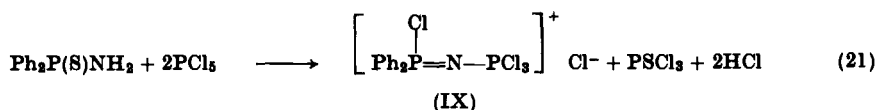
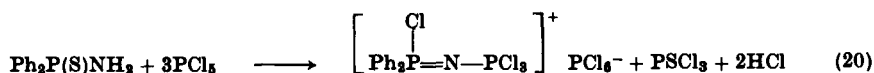
with SO_2 results in the formation of a six-membered ring (393).



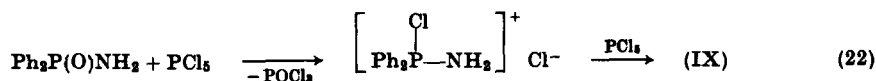
D. UNSYMMETRICAL IONIC P-N COMPOUNDS

1. Syntheses

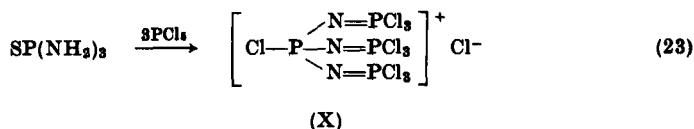
The reaction of $\text{Ph}_2\text{P}(\text{S})\text{NH}_2$ with PCl_5 proceeds in the following manner (26):



Compound (IX) results also (25) as shown in Eq. (22).

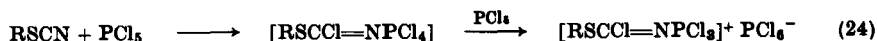


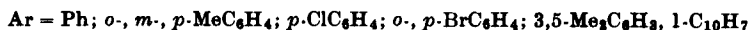
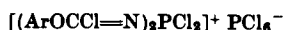
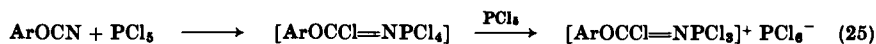
Thiophosphoryl triamide reacts with PCl_5 to give the ionic compound (X) (33, 155) in contrast to the reaction of $\text{OP}(\text{NH}_2)_3$ (cf. Section V, A).



Excess PCl_5 produces the hexachlorophosphate salt of (X), $\text{P}_5\text{N}_3\text{Cl}_{16}$ (XI) (isolated as the $\text{C}_2\text{H}_2\text{Cl}_4$ adduct) (302).

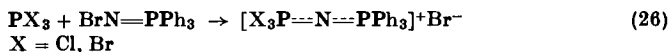
Other $-\text{N}=\text{PCl}_3$ -containing unsymmetrical ionic compounds are formed in the first step of the phosphorylation of aliphatic (297f, 442) or aromatic (443) thiocyanates and of aryl cyanates (443a).



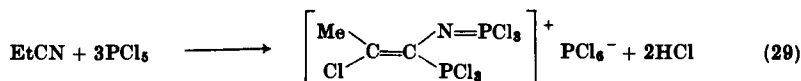
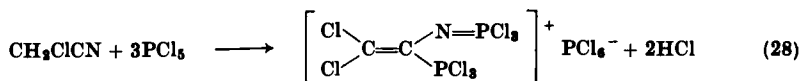
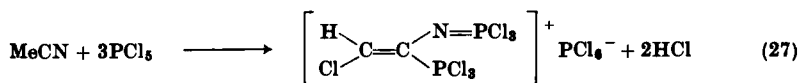


Derkach and co-workers prepared compounds of the type $[\text{RC}(=\text{NPCl}_3)\text{OR}']^+\text{Cl}^-$ ($\text{R} = \text{Ph}$, $p\text{-BrC}_6\text{H}_4$; $\text{R}' = \text{Et}$) by reacting $\text{RC}(=\text{NCl})\text{OR}'$ and PCl_3 (or PCl_5), as well as $[(\text{RO})_2\text{C}=\text{NPCl}_3]^+\text{Cl}^-$ ($\text{R} = \text{Me}$, Et) from $(\text{RO})_2\text{C}=\text{NCl}$ and PCl_3 (127) (see also Section VII, A).

Addition of PX_3 to N -bromotriphenylphosphinimine results in the formation of ionic compounds $[\text{X}_3\text{P}=\text{N}=\text{PPh}_3]^+\text{Br}^-$ (7).

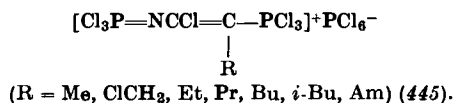


The phosphorylation of various cyanides (for details see Section VIII, B, 1, phosphorylation of nitriles) at room temperature results in the formation of ionic compounds (16, 239, 307, 423, 425, 445). These



compounds were formulated earlier as $\text{H}_2\text{C}=\text{CNPCl}_4 \cdot \text{PCl}_5$ and $\text{ClCH}=\text{CNPCl}_4 \cdot \text{PCl}_5$, respectively (239, 425).

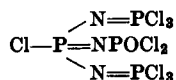
Higher nitriles yield



The compounds $[\text{R}_2\text{C}(\text{CN})\text{CCl}=\text{NPCI}_3]^+\text{PCI}_6^-$ ($\text{R} = \text{Cl}, \text{Me}, \text{Et}, \text{Pr}$) result as intermediates in the phosphorylation of dinitriles (290c) (cf. Section VIII, B, 1).

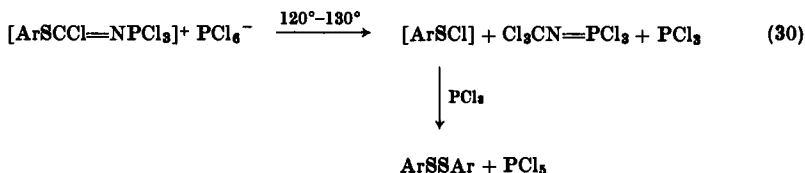
2. Reactions

Reaction of $[\text{Ph}_2\text{P}(\text{Cl})\text{NPCI}_3]^+\text{PCI}_6^-$ with SO_2 (26) or DMSO (192) gives $\text{Ph}_2\text{P}(\text{Cl})\text{NPOCl}_2$. Analogously, (X) reacts with SO_2 giving



(155) and with H_2S to give the corresponding thio compound.

Interaction of $[\text{RSCCl}=\text{NPCI}_3]^+\text{PCI}_6^-$ ($\text{R} = \text{Et}, \text{Ph}, p\text{-MeC}_6\text{H}_4, p\text{-O}_2\text{NC}_6\text{H}_4$) (442, 443) with excess PCI_5 yields $\text{CCl}_3\text{N}=\text{PCI}_3$, which can also be obtained on other ways (cf. Section VIII, B, 1). Heating the above-mentioned ionic compounds ($120^\circ\text{--}130^\circ$) results also in formation of $\text{CCl}_3\text{N}=\text{PCI}_3$, as well as HCl , PCI_3 , and MeCHClSCl (in case of $\text{R} = \text{Et}$) (442), whereas with $\text{R} = \text{aryl groups}$, PCI_5 and ArSSAr are obtained as by-products (443).

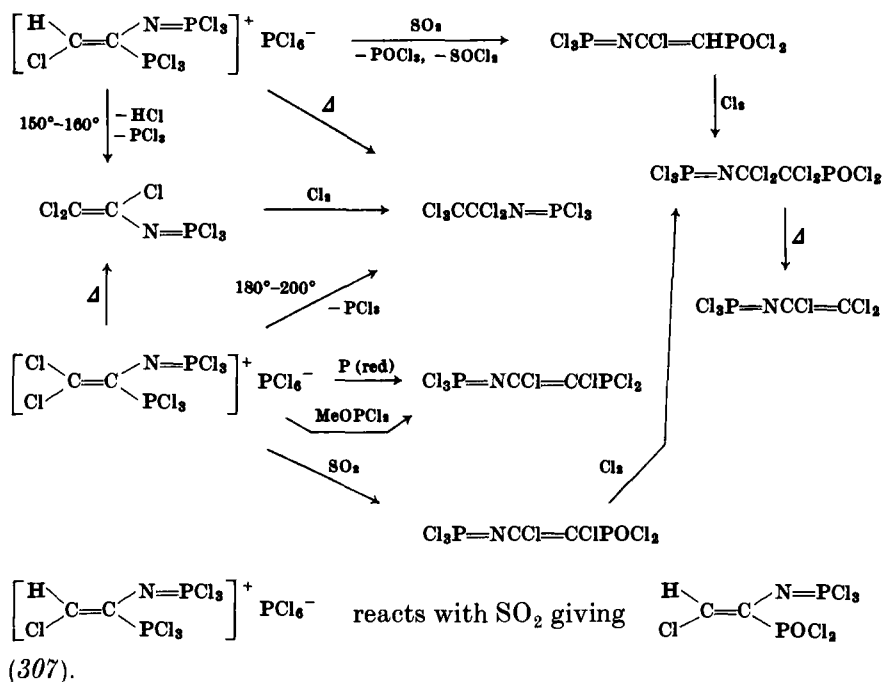


Sulfur dioxide reacts with $[\text{ArXCCl}=\text{NPCI}_3]^+\text{PCI}_6^-$ [$\text{X} = \text{S}$ (443); $\text{X} = \text{O}$ (443a)] to give $\text{ArXCCl}=\text{NPOCl}_2$.

The thermal decomposition of $[\text{Cl}_3\text{P}=\text{NCCl}=\text{CRPCI}_3]^+\text{PCI}_6^-$ ($\text{R} = \text{Me}, \text{CHCl}_2, \text{Et}, \text{Pr}, \text{Bu}, i\text{-Bu}, \text{Am}$) at $150^\circ\text{--}200^\circ$ results in formation of HCl , PCI_5 , PCI_3 , and $\text{RCCl}_2\text{CCl}_2\text{N}=\text{PCI}_3$ (445) (for details cf. Section VIII, B, 1), and compounds with the formula $[\text{RC}(=\text{NPCI}_3)\text{OR}']^+\text{Cl}^-$ ($\text{R} = \text{Ph}, p\text{-BrC}_6\text{H}_4$; $\text{R}' = \text{Et}$) at 130° give $\text{R}'\text{Cl}$ and $\text{RCN}=\text{PCI}_3$ (127) (see also Section VII, A).

The ionic compounds $[\text{Ph}_3\text{P}=\text{N}=\text{PX}_3]^+\text{Br}^-$ ($\text{X} = \text{Cl}, \text{Br}$) hydrolyze with HX elimination to yield $\text{Ph}_3\text{PNP}(\text{O})\text{X}_2$ (5, 7); in the case of $\text{X} = \text{Cl}$ the corresponding product results also from the reaction of Ph_3P , PCI_5 , and hydroxylamine hydrochloride (7).

The reactions of the ionic intermediates obtained by the phosphorylation of nitriles are represented by the following scheme (16, 307, 423).



Compounds $[\text{R}_2\text{C}(\text{CN})\text{CCl}=\text{NPCl}_3]^+\text{PCl}_6^-$ react with SO_2 to give $\text{R}_2\text{C}(\text{CN})\text{CCl}=\text{NPOCl}_2$, SOCl_2 , and POCl_3 (290c).

E. SPECTROSCOPIC INVESTIGATIONS

1. Infrared Spectroscopy

A normal coordinate analysis of $[\text{Cl}_3\text{P}=\text{N}=\text{PCl}_3]^+\text{Cl}^-$ (IV) and $[\text{Cl}_3\text{P}=\text{N}=\text{PCl}_3]^+\text{PCl}_6^-$ (III) has been carried out (12); the most probable value of $\angle \text{PNP}$ is 140° * giving a force constant of 6.97 mdynes/Å and a bond order of $b = 2.0$ (12, 180). As characteristic frequencies of these compounds the following have been assigned (12): $\nu_s \text{NP}_2$ at 833 cm^{-1} , $\nu_{as} \text{NP}_2$ at 1298 cm^{-1} , $\nu_s \text{PCl}_3$ at 468 cm^{-1} and $\nu_{as} \text{PCl}_3$ at 653 cm^{-1} for compound (III) and 778 cm^{-1} for $\nu_s \text{NP}_2$, 1338 cm^{-1} for $\nu_{as} \text{NP}_2$, 421 cm^{-1} for $\nu_s \text{PCl}_3$, and 592 cm^{-1} for $\nu_{as} \text{PCl}_3$ for compound (IV).

Three characteristic bands for compounds of the type $[\text{RC}(\text{NPCl}_3)_2]^+\text{SbCl}_6^-$ are assigned between 700 and 1100 cm^{-1} (397); $\nu_s \text{PN}$ lies between 670 ($\text{R} = \text{CCl}_3$) and 727 cm^{-1} ($\text{R} = \text{Me}$).

* The X-ray structure investigation of the related compound $[\text{Ph}_2\text{P}(\text{NH}_2)=\text{N}=\text{P}(\text{NH}_2)\text{Ph}_2]^+\text{Cl}^-$ gives a value of $\angle \text{PNP}$ of 136° (74).

2. Nuclear Magnetic Resonance

Phosphorus-31 NMR has proved very successful in elucidating the structures of the compounds described in Sections IV,A,1 to IV,D,1. Mention of this subject is made in a few reviews [(159, 160), see also (19)].

a. Symmetrical Cations. The cations of (III) and (IV) show only one peak ($\delta_P = -21.4$ ppm) in the ^{31}P NMR (15, 23, 155), thus showing magnetic equivalence of the two phosphorus atoms. The PCl_6^- anion in (III) gives the peak at ~ 305 ppm (Fig. 1).

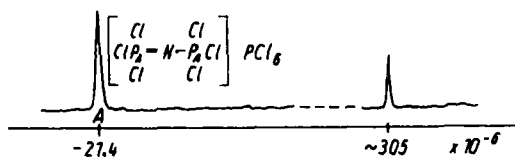


FIG. 1. ^{31}P NMR spectrum of $[\text{Cl}_3\text{P}=\text{N}=\text{PCl}_3]^+[\text{PCl}_6]^-$. From reference (155).

A spin-spin coupling is observed in compound (VIII) with the characteristic AB_2C pattern (153, 155) (Fig. 2).

The compound $[\text{Cl}_3\text{P}=\text{N}(\text{NCl}_2)_x\text{PCl}_3]^+[\text{PCl}_6]^-$ ($x = 2$) has been shown to be linear (30, 157). Higher homologs ($x = 2, 3$) have been synthesized

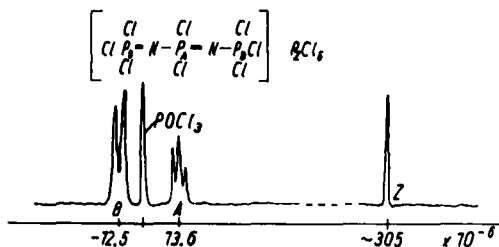


FIG. 2. ^{31}P NMR spectrum of $[\text{Cl}_3\text{P}=\text{NPCl}_2=\text{NPCl}_3]^+[\text{PCl}_6]^-$. From reference (155).

recently (339), but has been postulated earlier on the basis of ^{31}P NMR results (156). Figures 3a-c and 4 give the appropriate spectra. In general, a $\text{Cl}_3\text{P}=\text{N}$ group (terminal group) gives a chemical shift around -12 ppm (39, 156, 310), a $-\text{NPCl}_2$ group (in the chain) is centered around 14 ppm (155, 156), and the PCl_6^- anion at ~ 300 ppm (155, 156, 160). Furthermore, increasing the value of x results in shifting the cationic phosphorus atoms to higher field and, in addition to this, the band width of the most shifted cationic phosphorus atom decreases. It can be concluded that

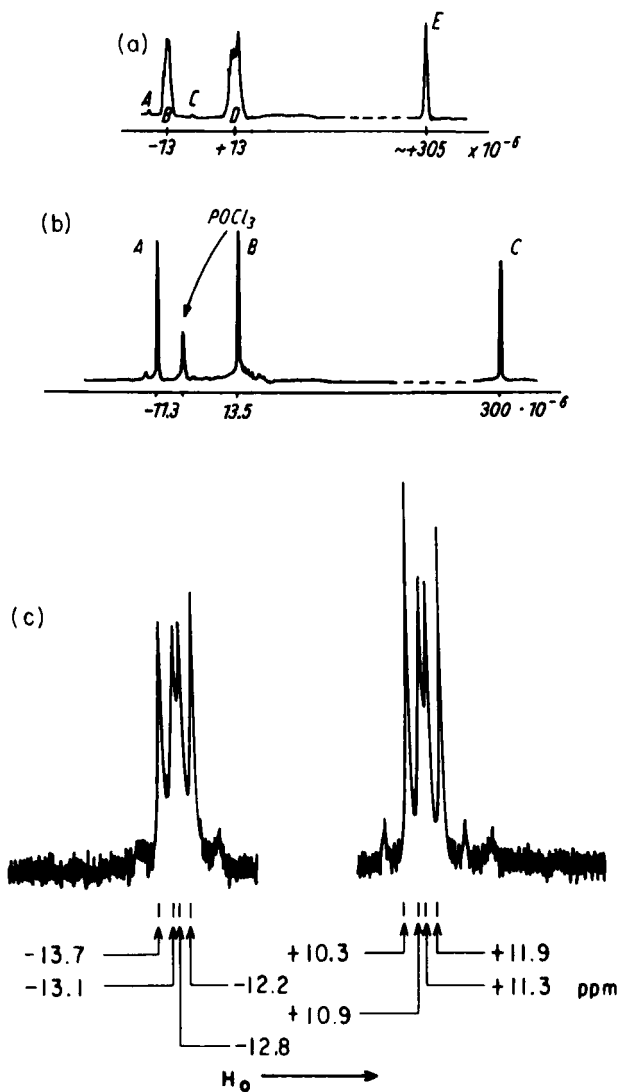


FIG. 3. (a) ^{31}P NMR spectrum of $[\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})_2\text{PCl}_3]^+[\text{PCl}_6]^-$ (from the reaction of $\text{PCl}_5/(\text{PNCl}_2)_3$. From reference (156). (b) ^{31}P NMR spectrum of $[\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})_2\text{PCl}_3]^+[\text{PCl}_6]^-$ neat. From reference (157). (c) ^{31}P NMR spectrum of $[\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})_2\text{PCl}_3]^+[\text{BCl}_4]^-$ (from the reaction of PCl_5 and $(\text{PNCl}_2)_3$. From reference (339).

with higher values of x (4 or 5) the cationic peak shifts to 15 ppm (339) or with $x \sim 10$ to 18 ppm (323).

The compound $[P_A(N=P_BCl_3)_4]^+X^-$ (405) gives a characteristic AB_4 spectrum with $\delta_{P_B} = 38.5\text{--}39.3$ ppm (depending on the nature of X^-) and with $\delta_{P_A} = 3.4\text{--}4.1$ ppm ($J_{PNP} = 28.7\text{--}29.9$ Hz).

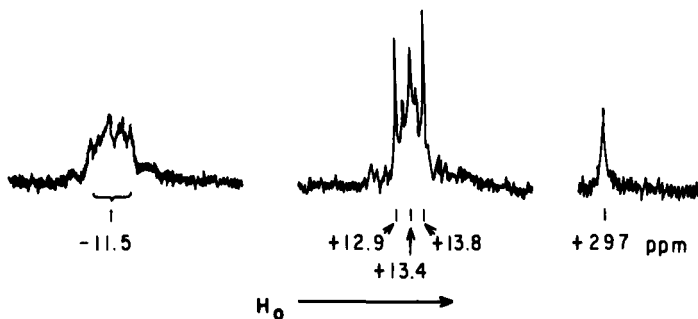
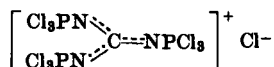


FIG. 4. ^{31}P NMR spectrum of $[Cl_3PN(PCl_2N)_3PCl_3]^+[PCl_6]^-$. From reference (339).

b. Cations with $(P \equiv N \equiv C(R) \equiv N \equiv P)$ Units. The resonance in cations of the type $[Cl_3P \equiv N \equiv C(R) \equiv N \equiv PCl_3]^+X^-$ ($R = Cl$; $X^- = PCl_6^-$) is shown by the fact that only one peak ($\delta_P = -38.5$ ppm) for the cation is obtained (16). Similar results occur with $R = Me, Me_2N, Cl_3P=N-$, and $X^- = SbCl_6^-$, but a strong dependence of the chemical shift of the cationic phosphorus atoms on the nature of R is observed (396, 397). An obviously erroneous result for



with two peaks (-13.2 and -32.9 ppm, ratio 2:1, respectively) was recently reported (422).

The equivalence of the two phosphorus atoms is also shown in the 1H NMR spectrum (396, 397) of $[MeC(NPCl_3)_2]^+SbCl_6^-$ consisting of a triplet. The proton nuclear magnetic resonance spectrum of $[Me_2NC(NPCl_3)_2]^+SbCl_6^-$ (at 40°) shows a quartet of nonequidistant lines (part of an A_2X_2 system) (396, 397), which turns to a triplet (AX_2) at 90° (Fig. 5).

c. Unsymmetrical Cations. The compound $[Ph_2P_A(Cl)=NP_BCl_3]^+Cl^-$ gives two peaks ($\delta_{P_A} = -42.3$ and $\delta_{P_B} = -14.3$ ppm), both showing tetra-coordinate phosphorus (26); $[ClP_A(N=P_BCl_3)_3]^+X^-$ [$X^- = Cl^-$ (X); $X^- = PCl_6^-$ (XI)] similarly show two cationic peaks ($\delta_{P_A} = 26.8$ and $\delta_{P_B} = -6.5$ ppm) (302).

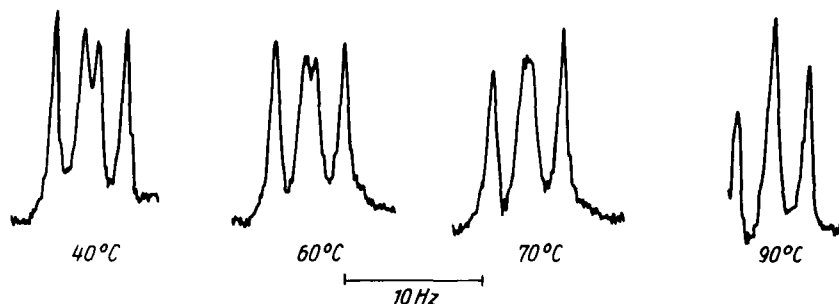
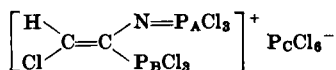
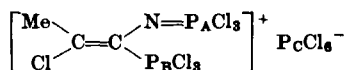


FIG. 5. ^1H NMR spectrum of $[\text{Me}_2\text{NC}(\text{NPCl}_3)_2]^+[\text{SbCl}_6]^-$. From reference (397).

The structures of the ionic compounds resulting from the phosphorylation of nitriles have been elucidated mainly by ^{31}P NMR spectroscopy (16, 307). Cis-trans isomerism was shown for the following substances.

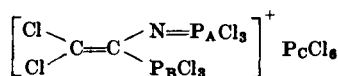


$$\delta_{\text{P}_\text{A}} = -15.9 \text{ ppm} \quad \delta_{\text{P}_\text{B}} = -83.1 \text{ and} \\ -80.7 \text{ ppm} \quad \delta_{\text{P}_\text{C}} = 297 \text{ ppm}$$



$$\delta_{\text{P}_\text{A}} = -7.8 \text{ ppm} \quad \delta_{\text{P}_\text{B}} = -84.0 \text{ and} \\ -86.0 \text{ ppm} \quad \delta_{\text{P}_\text{C}} = 292 \text{ ppm}$$

The compound



gives only the three expected peaks ($\delta_{\text{P}_\text{A}} = -14.2$, $\delta_{\text{P}_\text{B}} = -85.0$, $\delta_{\text{P}_\text{C}} = 296$ ppm) (16, 307).

Finally, the chemical shift of $[(\text{EtO}_2)\text{C}=\text{NPCl}_3]^+\text{Cl}^-$ ($\delta_{\text{P}} = -20.4$ ppm) is reported (475).

3. Other Physical Investigations

X-Ray powder patterns of compounds (III), (IV), (VII), and (VIII) are reported in the literature (29) and discussed in detail, especially in view of the earlier published data for (III) and (VIII) (183). Powder diagrams of $[\text{Br}_3\text{P}=\text{N}=\text{PBr}_3]^+\text{Br}^-$ and $[\text{Br}_3\text{P}=\text{N}=\text{PBr}_3]^+\text{Br}_3^-$ are also available (206).

Electric conductance studies of (III) (28), (IV) (34), (VIII) (23, 29), and (IX) (26), as well as (X) and (XI) (302) show these substances to be 1:1 electrolytes in the specified solvents.

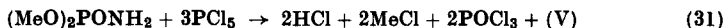
Chlorine-35 NQR work on (III)* and (VIII) was recently published (215), but no positive results could be obtained.

V. *N*-Phosphorylated Phosphazotrihalides

A. SYNTHESSES

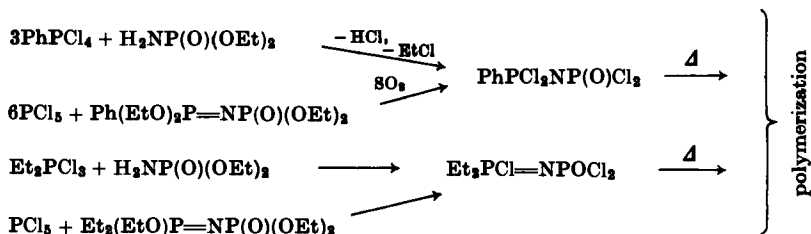
The synthesis of the simplest *N*-phosphorylated phosphazotri-chloride, $\text{Cl}_2\text{PNP}\text{Cl}_3$, was attempted (158) by reaction of $[\text{Cl}_3\text{P}=\text{N}=\text{PCl}_3]^+\text{PCl}_6^-$ (III) with red phosphorus, but the compound could not be isolated. Recently, a derivative $(\text{C}_3\text{F}_7)_2\text{PN}=\text{PCl}_3$ has been described (366a). Trifluorophosphazodifluorophosphine is also known (180c).

The corresponding oxygen-containing substance (V), $\text{Cl}_2(\text{O})\text{PNP}\text{Cl}_3$, is formed (cf. Scheme 2) in the reaction of PCl_5 and hydroxylamine hydrochloride (24, 214) or with phosphoric acid amides (33, 214) or ammonium diamidophosphate (33) or other ammonium salts (146a). The same compound is synthesized from SO_2 and (III) (15, 20, 28, 315, 543) or (IV) (29), by acidolysis (HCOOH) of (III) (192), or from PCl_3 and N_2O_4 (15, 18). The last synthesis had already been carried out earlier [(286), see also (11)], but the compound was characterized erroneously. Interaction of hexamethyldisilazane and POCl_3 results first in a white material having the approximate composition $(\text{HNO}\text{P}\text{Cl})_n$ [(173), see also (42)], which with PCl_5 at 120° gives compound (V) (173). The compound $\text{Cl}_2\text{P}(\text{O})\text{NP}\text{Cl}_3$ is also (548) formed by reaction (31).

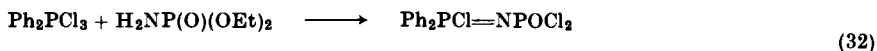


The same compound is formed from PCl_5 and NH_4Cl in POCl_3 -solvent using P_4O_{10} as oxidizing agent [with (III) as intermediate] (413).

Compounds similar to (V) are obtained in the following ways [(524), see also (366a)].

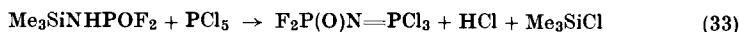


* However, a recent ^{35}Cl NQR paper (191a) of the same authors reports affirmative results on compound (III).

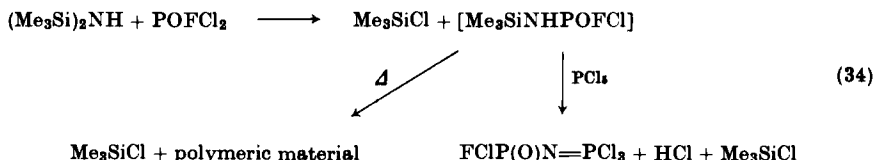


Compounds $\text{Ph}_3\text{P=NP(O)X}_2$ ($\text{X} = \text{Cl}, \text{Br}$) result by hydrolysis of $[\text{Ph}_3\text{P=NPX}_3]^+\text{Br}^-$ (5).

The series $\text{F}_n\text{Cl}_{2-n}\text{P(O)NPCl}_3$ ($n = 0, 1, 2$) are obtained from $\text{F}_n\text{Cl}_{2-n}\text{P(O)NH}_2$ and PCl_5 (387) [for $n = 2$, cf. also (176, 290)]; $\text{F}_2\text{P(O)N=PCl}_3$ is formed also from the Si-N cleavage of $\text{Me}_3\text{SiNHPOF}_2$ with PCl_5 (173).



Hexamethyldisilazane and POFCl_2 react in two ways (347):

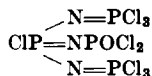


The compound $\text{Cl}_2\text{P(S)N=PCl}_3$ (VI), representing the thio analog of (V), is formed from (III) and H_2S or sulfur (requiring S_2Cl_2 addition) (13, 29), as well as from S_4N_4 and PCl_3 in poor yield (29). The syntheses of (V) and (VI) are summarized in Scheme 2.

The analogous compounds $(\text{PhO})_2\text{P(X)N=PCl}_3$ ($\text{X} = \text{O}, \text{S}$) are formed by the Kirsanov reaction of $(\text{PhO})_2\text{P(X)NH}_2$ (283); $\text{Ph}_2\text{P(O)N=PCl}_3$, which should be formed from $\text{Ph}_2\text{P(O)NH}_2$ and PCl_5 , could not be isolated. Only $[\text{Ph}_2\text{P(Cl)NH}_2]^+\text{Cl}^-$ (25) is formed in the first step (cf. Sections IV, D, 1 and 2); the corresponding tautomer $\text{Ph}_2\text{PClNPOCl}_2$ is described (Section IV, D, 2).*

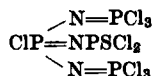
Derkach and co-workers described compounds* such as $\text{RR'P(O)N=PCl}_3(?)$ ($\text{R} = \text{Me}, \text{R}' = \text{Cl}, \text{OPh}, p\text{-ClC}_6\text{H}_4\text{O}, p\text{-MeC}_6\text{H}_4\text{O}$; $\text{R} = \text{CH}_2\text{Cl}, \text{R}' = \text{Cl}, \text{OPh}, p\text{-O}_2\text{NC}_6\text{H}_4\text{O}, p\text{-MeC}_6\text{H}_4\text{O}$) (473). Recently EtP(S)FN=PCl_3 was isolated (385), but the analogous reaction of PhP(S)FNH_2 did not give concrete results.

The compound $\text{Cl}_3\text{P=NPCl}_2=\text{NPOCl}_2$ is obtained from (VII) or (VIII) with SO_2 (23, 28, 29), the thio analog by treating (VIII) with H_2S (23, 29). Similarly, (X) with SO_2 yields



* $\text{Et}_2\text{P(O)N=PCl}_3$ cannot be isolated from $\text{Et}_2\text{P(O)NCl}_2$ and PCl_3 nor from $\text{Et}_2\text{P(O)NH}_2$ and PCl_5 , but its tautomer $\text{Et}_2\text{PCl=NPOCl}_2$ can (523a); the same applies to MeP(O)ClN=PCl_3 which should rather be considered as $\text{MePCl}_2=\text{NPOCl}_2$ (473a).

(155), and with H_2S

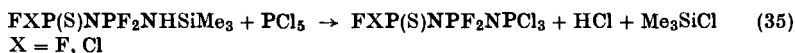


The compound $\text{F}_2\text{P}(\text{O})\text{N}=\text{PF}_3$ results from $\text{F}_2\text{P}(\text{O})\text{NH}_2$ and PF_3Cl_2 (324), analogous compounds $\text{FX}(\text{S})\text{PN}=\text{PF}_3$ ($\text{X} = \text{Cl}, \text{F}$) from the corresponding amine and PF_3Cl_2 (324, 383).

Compounds OPX_2NH_2 and SPX_2NH_2 ($\text{X} = \text{F}, \text{Cl}$) with MePCl_4 or CCl_3PCl_4 give the corresponding phosphazo compounds (378a); $\text{SP}(\text{X}, \text{Y})\text{NH}_2$ ($\text{X} = \text{Cl}, \text{F}$) and PhPF_4 react similarly to $\text{SP}(\text{X}, \text{Y})\text{N}=\text{PF}_2\text{Ph}$ (379a).

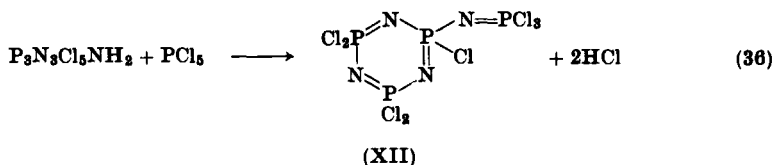
The series $\text{F}_n\text{Cl}_{2-n}\text{P}(\text{S})\text{N}=\text{PF}_{3-m}\text{Cl}_m$ ($n = 0, 1, 2$; $m = 0, 1$) has been described recently (382); $\text{F}_2\text{P}(\text{S})\text{N}=\text{PCl}_3$ and $\text{FCIP}(\text{S})\text{N}=\text{PCl}_3$ are also formed from $\text{Me}_3\text{SiNHPSF}_2$ or $\text{Me}_3\text{SiNHPSFCl}$ and PCl_5 (174), as well as from $\text{Cl}_n\text{F}_{2-n}\text{P}(\text{S})\text{NH}_2$ ($n = 0, 1, 2$) and PCl_5 (378). A higher *N*-phosphorylated phosphazotrichloride $\text{Cl}_2(\text{O})\text{PN}=\text{P}(\text{N}=\text{PCl}_3)_3$ results from $[\text{P}(\text{N}=\text{PCl}_3)_4]^+\text{Cl}^-$ and sulfur dioxide (403).

Longer chains are also obtained (381d) according to Eq. (35).

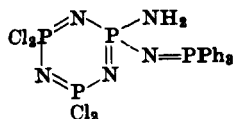


Compounds $\text{SPX}_2\text{NPF}_2\text{Br}$ ($\text{X} = \text{Cl}, \text{F}$) have also been prepared (382a).

The reaction of the monoamide of $(\text{PNCl}_2)_3$, namely, $\text{P}_3\text{N}_3\text{Cl}_5\text{NH}_2$, with PCl_5 (149) proceeds in a normal Kirsanov reaction to give (XII).

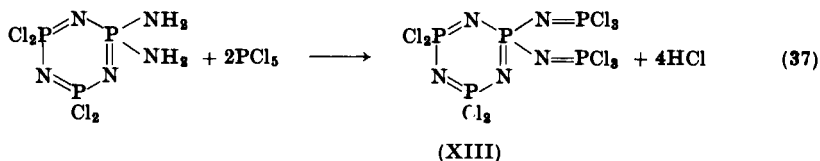


The compound

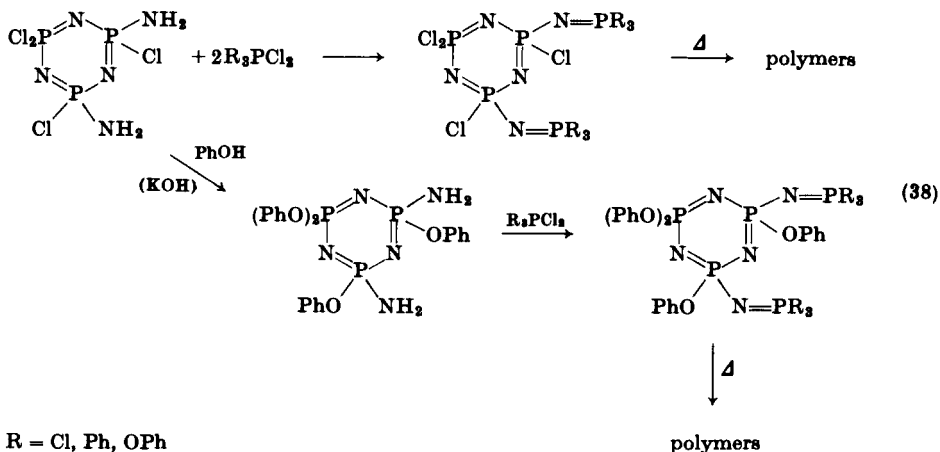


(218), also obtained by other ways [(150), Section V, B] on phosphorylation with PCl_5 probably gives the trichlorophosphazo compound (309).

The geminal diamide of hexachlorophosphazatriene, $\text{P}_3\text{N}_3\text{Cl}_4(\text{NH}_2)_2$, and PCl_5 give (XIII) (149, 308, 309). For the similar reaction with Ph_3PBr_2 , Ph_3PCl_2 , and Ph_2PCl_3 cf. (217, 218).



The reactions of a nongeminal diamide of $(\text{PNCl}_2)_3$ [the existence of which is questioned by other authors (309)] with PCl_5 and Ph_3PCl_2 were recently described (204).

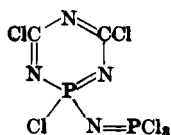


Interaction of $\text{P}_3\text{N}_3\text{F}_5\text{NH}_2$ and PCl_5 (386) gives $\text{P}_3\text{N}_3\text{F}_5\text{N}=\text{PCl}_3$, with PF_3Cl_2 $\text{P}_3\text{N}_3\text{F}_5\text{N}=\text{PF}_3$ (385, 385d), and with PhPF_4 the compound $\text{P}_3\text{N}_3\text{F}_5\text{N}=\text{PPhF}_2$ (379a) is obtained. $\text{P}_4\text{N}_4\text{F}_7\text{N}=\text{PX}_3$ ($\text{X} = \text{Cl}, \text{F}$) are obtained similarly from $\text{P}_4\text{N}_4\text{F}_7\text{NH}_2$ and PCl_5 or PF_3Cl_2 , respectively (385d). Analogous compounds $\text{P}_3\text{N}_3\text{F}_5\text{N}=\text{PPh}_n\text{Cl}_{3-n}$ ($n = 0, 1, 2$) result from $\text{P}_3\text{N}_3\text{F}_5\text{NH}_2$ and $\text{Ph}_n\text{PCl}_{5-n}$ (347a).

The reactions of some geminal and nongeminal amido derivatives of $(\text{PNCl}_2)_4$ has been investigated (309a).

$\text{P}_3\text{N}_3\text{F}_5\text{NPX}_2\text{N}=\text{PCl}_3$ and $\text{P}_3\text{N}_3\text{F}_5\text{NPX}_2\text{NPCl}_2\text{N}=\text{PCl}_3$ ($\text{X} = \text{F}, \text{Cl}$) as well as $\text{P}_5\text{N}_5\text{F}_9\text{N}=\text{PCl}_3$ and $\text{P}_6\text{N}_6\text{F}_{11}\text{N}=\text{PCl}_3$ were recently prepared (385a).

Finally, dicyandiamide and excess PCl_5 give



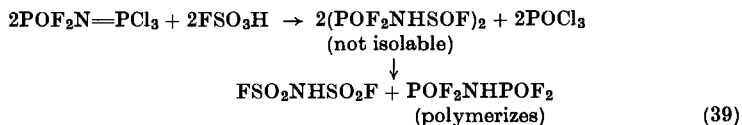
(26b, 110, 207) (cf. also Section VIII, B, 1).

B. REACTIONS

Heating (V) to $\sim 200^\circ$ results in decomposition to POCl_3 and (PNCl_2) units (164, 524) [see also the thermal degradation of $\text{RPCl}_2\text{N}=\text{POCl}_2$ ($\text{R} = \text{Me}, \text{Ph}$) and $\text{Et}_2\text{PCl}=\text{NPOCl}_2$ to long-chain phosphazene units (524)]. Acidolysis yields amidophosphoric acid; at lower pH values $(\text{NH}_4)_3\text{PO}_4$ and H_3PO_4 (33) results. The hydrolysis with DMSO does not give the expected $\text{Cl}_2\text{P}(\text{O})\text{NHPOCl}_2$, but white solids ($\text{P}:\text{N} = 2:1$) with no definite structure (192). Interaction with chlorosulfonic acid leads to POCl_3 , SO_2Cl_2 , and uncharacterized products (192). However, careful hydrolysis of (V) with HCOOH gives $\text{Cl}_2\text{OP}-\text{NH}-\text{POCl}_2$ (374a).

The reaction of $\text{Cl}_2(\text{O})\text{PNPCl}_3$ (V) with aniline (33) or dimethylamine (13, 18) results in replacement of the chlorine atoms; the product of the latter reaction has also been obtained by a phosphine-azide reaction (509). The reaction of (V) with BuONa and various alcohols is described (220c). Compound (V) and $p\text{-O}_2\text{NC}_6\text{H}_4\text{ONa}$ give $(p\text{-O}_2\text{NC}_6\text{H}_4\text{O})_3\text{PNP}(\text{O})(\text{OC}_6\text{H}_4\text{NO}_2\text{-}p)_2$ (315). Analogous compounds such as $(\text{RO})_2\text{P}(\text{O})\text{N}=\text{P}(\text{OR}')_3$ ($\text{R} = \text{Me}, \text{Et}, i\text{-Pr}$; $\text{R}' = \text{Me}, \text{Et}, i\text{-Pr}, \text{Ph}, p\text{-MeC}_6\text{H}_4$) (476), as well as $(\text{MeO})_2\text{PON}=\text{P}(\text{NC}_2\text{H}_4)_3$ (234), have been prepared in other ways [cf. also (10, 209, 211)]. With TiCl_4 (V) gives the compound $\text{TiCl}_4 \cdot 2\text{P}_2\text{NOCl}_5$ (35, 203) [erroneously reported in (164)]; the coordination is by the oxygen atoms. Other crystalline adducts of this type are $2\text{P}_2\text{NCl}_5\text{O} \cdot \text{SnCl}_4$, $\text{P}_2\text{NCl}_5\text{O} \cdot \text{SbCl}_5$, and the liquid 1:1 adduct $\text{P}_2\text{NCl}_5\text{O} \cdot \text{AlCl}_3$ (203). Finally (V) with 2 moles of PCl_5 gives $[\text{Cl}_3\text{P}=\text{N}=\text{PCl}_3]^+\text{PCl}_6^-$ (315).

The compound $\text{F}_2(\text{O})\text{PN}=\text{PCl}_3$ decomposes analogously to (V) at 200° with elimination of POF_2Cl and POCl_3 to give a mixture of $(\text{PNCl}_2)_n$ and $(\text{PNF}_2)_n$ (290). No reaction occurs with difluorophosphoric acid at room temperature. $\text{POF}_2\text{NHPOCl}_2$ and POF_2Cl result at 65° and polymerization takes place at 130° (176); $\text{POF}_2\text{NHPOCl}_2$ is also formed by reaction of $\text{F}_2(\text{O})\text{PN}=\text{PCl}_3$ with formic acid. The reaction with FSO_3H is complex and is thought to proceed (176) as outlined in Eq. (39).



Compound (VI) and NaOPh give the corresponding pentaphenoxy compound (29), also obtained in other ways (283).

Aminolysis of $(\text{PhO})_2\text{PON}=\text{PCl}_3$ with aniline gives $(\text{PhO})_2\text{PON}=\text{P}(\text{NHPh})_3$ (283); $(\text{PhO})_2\text{PXN}=\text{PCl}_3$ ($\text{X} = \text{O}, \text{S}$) react with NaOAr

(Ar = Ph, *p*-ClC₆H₄, *p*-O₂NC₆H₄) giving the appropriate esters (283, 534), which can also be obtained from (PhO)₅P and (PhO)₂PONH₂ or (PhO)₂PSNH₂. Attempts to prepare Ph₂PSN=PPh₃ by an azide-phosphine reaction failed (9), only polymerization products being obtained.

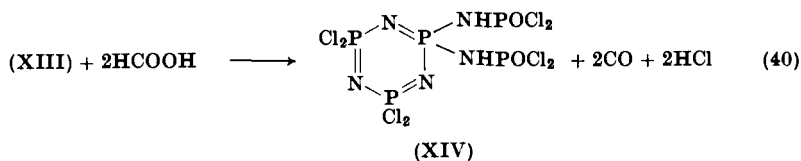
Hydrolysis (HCOOH) of (PhO)₂P(X)N=PCl₃ (X = O, S) gives rise to (PhO)₂P(X)NHPOCl₂ (283). Other (RO)₂PON=P(OR')₃ compounds (R = R' = Et, Bu) are formed from (RO)₂PONSO and P(OR')₃ (518); RP(O)(OAr)N=PCl₃ (R = Me, ClCH₂, Ar = *p*-MeC₆H₄, *p*-ClC₆H₄; R = ClCH₂, Ar = Ph) and ethylenimine give the triamides (369).

Compounds X₂P(S)N=PF₃ (X = Cl, F) and Me₃SiNMe₂ form X₂P(S)NPF₂NMe₂ (382a); with HCOOH or NH₃, SX₂PNHPOF₂ and SPX₂NPF₂NH₂ are obtained (382b). The compounds SPX₂N=PF₂Cl (X = F, Cl) and methanol react to the *S*-methyl derivatives MeSPX₂=NP(O)F₂ (382c). The reaction of the compounds SPF_{*n*}Cl_{2-*n*}N=PF_{*m*}Cl_{3-*m*} (*n* = 0, 1, 2; *m* = 0, 1) with hexamethyldisilazane and subsequent chain elongation is described (383a).

Alcoholysis of Cl₃P=NPCl₂=NPOCl₂ gives the corresponding esters (509b).

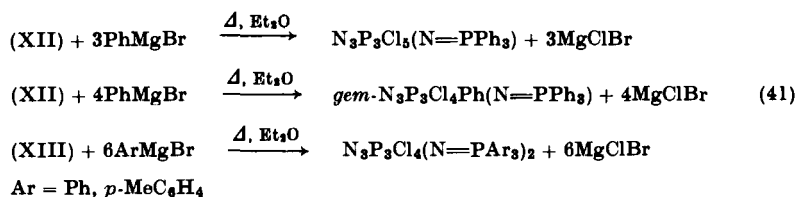
The interaction of 2,2,6,6-tetrakis(trichlorophosphazo)-4,4,8,8-tetrachlorophosphazetetraene with VOCl₃ is reported (483a).

Partial hydrolysis of (XIII) with formic acid (309) leads to (XIV).



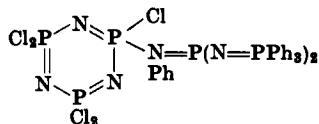
A ring-closure reaction of (XIII) with heptamethyldisilazane yields a spiro compound (308).

Arylation of (XII) and (XIII) has been described (150). Geminal N₃P₃Cl₄Ph(N=PPh₃) could also be obtained in other ways (48, 140, 217).



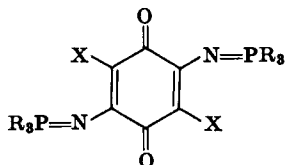
Geminal N₃P₃Cl₄(NH₂)(N=PPh₃) results from geminal N₃P₃Cl₄(NH₂)₂ and Ph₃PBr₂ (150).

Another compound belonging to this group results from $(\text{PNCl}_2)_3$ and diphenylmagnesium (49). This is



A chain elongation results by the reaction of heptamethyldisilazane on $\text{P}_3\text{N}_3\text{F}_5\text{N}=\text{PX}_3$ ($\text{X} = \text{Cl}, \text{F}$) (385a); with $\text{Me}_3\text{SiNMe}_2$ or Me_3SiNCS step-wise replacement of the halogens occurs (383c).

Analogous compounds



$\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{R} = \text{Ph}, p\text{-ClC}_6\text{H}_4, o\text{-BrC}_6\text{H}_4, p\text{-MeC}_6\text{H}_4, p\text{-BuC}_6\text{H}_4, p\text{-BuOC}_6\text{H}_4, 2,4\text{-F}_2\text{C}_6\text{H}_3$, substituted naphthalenes

(340) are also described. Finally, the $-\text{N}=\text{PCl}_3$ group of 2-(trichlorophosphazo)-2,4,6-trichloro-2-phospha-1,3,5-triazine is converted by SO_2 or HCOOH into the $-\text{NHPOCl}_2$ group (26b).

C. SPECTROSCOPIC INVESTIGATIONS

The IR spectrum of (V) is reported (18, 35); Glemser and co-workers assigned the $\nu_{\text{P}=\text{N}}$ at 1320 (173) or 1332 cm^{-1} (387) and $\nu_{\text{P}-\text{N}}$ at 776 cm^{-1} . The $\text{P}=\text{N}$ vibration in $\text{F}_2(\text{O})\text{PN}=\text{PCl}_3$ is found at 1350 (290), 1355 (173) or 1360 cm^{-1} (387) and $\nu_{\text{P}-\text{N}}$ at 768 cm^{-1} (173, 387). For $\text{FCl}(\text{O})\text{PN}=\text{PCl}_3$ $\nu_{\text{P}=\text{N}}$ is at $1347\text{--}1350 \text{ cm}^{-1}$ and $\nu_{\text{P}-\text{N}}$ at 780 cm^{-1} (173, 387). The infrared spectrum of $\text{FCl}(\text{S})\text{PN}=\text{PCl}_3$ is given in the literature (378); the $\nu_{\text{P}=\text{N}}$ in the series $\text{F}_n\text{Cl}_{2-n}(\text{S})\text{PN}=\text{PCl}_3$ decreases from 1340 cm^{-1} ($n = 2$) to 1328 ($n = 1$) and 1305 cm^{-1} ($n = 0$) (378). Recently, the compounds $\text{F}_n\text{Cl}_{2-n}(\text{S})\text{PN}=\text{PF}_{3-m}\text{Cl}_m$ ($n = 0, 1, 2$; $m = 0, 1$) were investigated (382), showing absorption for $\nu_{\text{P}=\text{N}}$ between 1365 and 1430 cm^{-1} .

The IR spectra of $\text{FX}(\text{S})\text{PN}=\text{PF}_3$, reported for $\text{X} = \text{F}$ (324), show the $\text{P}=\text{N}$ vibration at 1415 ($\text{X} = \text{Cl}$) and 1430 cm^{-1} ($\text{X} = \text{F}$) (383).

The compounds (XII) and (XIII) also show (149) the $\text{P}=\text{N}$ vibration in the usual range ($1190\text{--}1335 \text{ cm}^{-1}$).

More attention was given to the nuclear magnetic resonance investigations of the compounds listed in Section V, A. The compound $\text{F}_2\text{P}_\text{B}\text{N}=\text{P}_\text{A}\text{F}_3$ shows $\delta_{\text{P}_\text{B}}$ at -129 ppm and $\delta_{\text{P}_\text{A}}$ at 43.6 ppm , thus proving the

structure (180c). The compound $\text{Cl}_2\text{P}_\text{B}(\text{O})\text{N}=\text{P}_\text{A}\text{Cl}_3$ (V) (AB type) shows coupling of the phosphorus nuclei ($\delta_{\text{P}_\text{A}} = 0.1 \pm 0.5$ ppm; $\delta_{\text{P}_\text{B}} = 14.2 \pm 0.5$ ppm; $J_{\text{P}_\text{A}\text{P}_\text{B}} = 15.4 \pm 0.3$ Hz) (154) (see also (153, 371)). Other authors (2) reported $\delta_{\text{P}_\text{A}} = 1.1$ ppm, $\delta_{\text{P}_\text{B}} = 12.7$ ppm, and $J_{\text{P}_\text{A}\text{P}_\text{B}} = 19.5$ Hz.

The analogous compound $\text{F}_{\text{X}_2}(\text{O})\text{P}_\text{B}\text{N}=\text{P}_\text{A}\text{Cl}_3$ represents a simple ABX₂ spectrum [$\delta_{\text{P}_\text{A}} = -8$ ppm, $\delta_{\text{P}_\text{B}} = 26$ ppm, $\delta_{\text{F}_\text{X}} = 70$ ppm (176); $\delta_{\text{P}_\text{A}} = -6.5$ ppm, $\delta_{\text{P}_\text{B}} = 25$ ppm, and $\delta_{\text{F}_\text{X}} = 70.3$ ppm, $J_{\text{F}-\text{P}_\text{B}} = 973.5$ Hz, $J_{\text{P}_\text{A}\text{P}_\text{B}} = 70$ Hz, and $J_{\text{F}-\text{P}_\text{A}} = 21.5$ Hz (173)]; $\text{FCl}(\text{O})\text{PN}=\text{PCl}_3$ is of an ABX type (173).

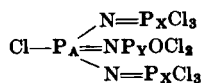
Compound (VI), like (V), is of an AB type, but no coupling of the two phosphorus nuclei could be observed (2, 157). $(\text{PhO})_2\text{P}(\text{O})\text{N}=\text{PCl}_3$ gives only one peak in the ^{31}P NMR spectrum [with a half-band width of 3 Hz (349)], the chemical shift is $\delta_\text{P} = 11.2$ ppm (349a).

Phosphorus-31 NMR results of $(\text{R}'\text{O})_3\text{P}=\text{N}=\text{P}(\text{O})\text{R}_2$ were recently reported (421).

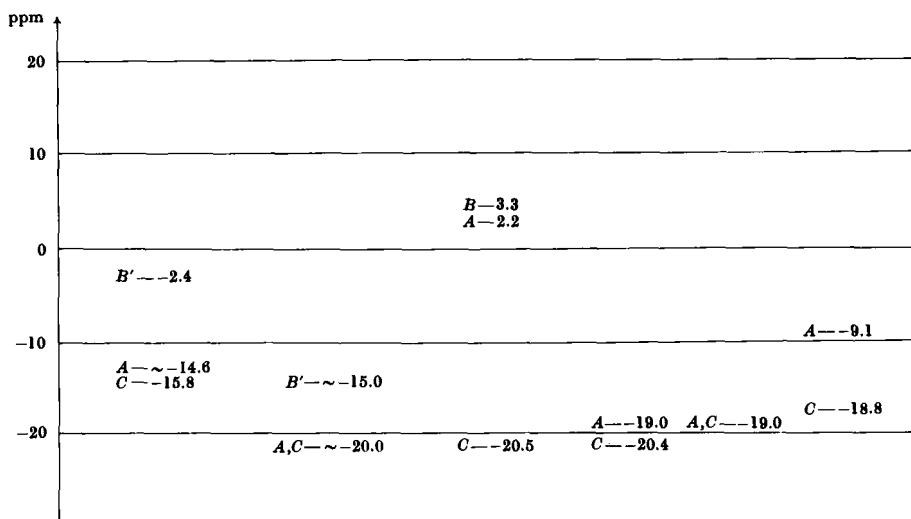
Fluorine-19 spectra of the series $\text{F}_n\text{Cl}_{2-n}(\text{S})\text{PN}=\text{PF}_{3-m}\text{Cl}_m$ ($n = 0, 1, 2$; $m = 0, 1$) have been recorded [(382), see also (383)]; the two compounds $\text{F}_2(\text{S})\text{P}_\text{B}\text{N}=\text{P}_\text{A}\text{Cl}_3$ ($\delta_{\text{P}_\text{A}} = -4.4$ ppm, $\delta_{\text{P}_\text{B}} = -40.7$ ppm, $\delta_\text{F} = +33.7$ ppm, $J_{\text{P}_\text{A}\text{P}_\text{B}} = 70$ Hz, $J_{\text{P}_\text{A}\text{F}} = \pm 22$ Hz, $J_{\text{P}_\text{B}\text{F}} = \pm 1085$ Hz) and $\text{FCl}(\text{S})\text{P}_\text{B}\text{N}=\text{P}_\text{A}\text{Cl}_3$ ($\delta_{\text{P}_\text{A}} = -0.8$ ppm, $\delta_{\text{P}_\text{B}} = -42.3$ ppm, $\delta_\text{F} = 33.5$ ppm, $|J_{\text{P}_\text{A}\text{P}_\text{B}}| = 40$ Hz, $J_{\text{P}_\text{A}\text{F}} = \pm 21.5$ Hz, $J_{\text{P}_\text{B}\text{F}} = +1115$ Hz) have been examined in detail (378).

Fluorine and phosphorus spectra of $\text{Cl}_2(\text{S})\text{PN}=\text{PF}_2\text{Cl}$ and $\text{F}_n\text{Cl}_{2-n}(\text{S})\text{PN}=\text{PF}_3$ ($n = 0, 1, 2$) are reported (163); only data from the ^{19}F NMR spectrum are given for $\text{EtP}(\text{S})\text{FN}=\text{PCl}_3$ (385). The compound $\text{Cl}_3\text{P}_\text{B}=\text{NP}_\text{A}\text{Cl}_2=\text{NP}_\text{X}\text{OCl}_2$ gives a spectrum of the ABX type (155) with $\delta_{\text{P}_\text{A}} = 20.0 \pm 0.5$ ppm, $\delta_{\text{P}_\text{B}} = 13.4 \pm 0.5$ ppm, and $\delta_{\text{P}_\text{X}} = -7.1 \pm 0.5$ ppm, spin-spin coupling occurs ($J_{\text{P}_\text{X}\text{P}_\text{A}} = 29.5 \pm 1$ Hz, $J_{\text{P}_\text{A}\text{P}_\text{B}} = 26.7 \pm 1$ Hz) analogously to (V). $\text{Cl}_3\text{P}=\text{NPCL}_2=\text{NPSCl}_2$ (ABX-type) has also linear structure according to NMR results (157), and a more detailed investigation of this compound has been carried out (2). NMR work (^{19}F , ^{31}P) on higher linear diphosphazenes is available (383a).

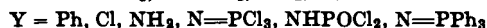
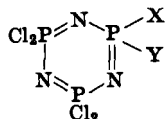
The compound



gives a spectrum of the type AX₂Y with $\delta_{\text{P}_\text{X}} = 1.9 \pm 0.5$ ppm, $\delta_{\text{P}_\text{Y}} = 13.6 \pm 0.5$ ppm, and $\delta_{\text{P}_\text{A}} = 29.6 \pm 0.5$ ppm (155); the corresponding thio compound has the same structure, but no spin-spin coupling between $\text{P}_\text{A}-\text{P}_\text{Y}$ could be observed (157). Some discussion (159, 160) of the ^{31}P NMR spectra of the above-mentioned compounds has been given. An



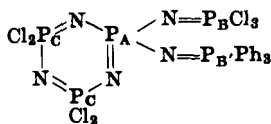
SCHEME 4. Graphical plot of the chemical shifts of the phosphorus nuclei in compounds of the structure



* Ref. (49) gives for $A = -8.6 \pm 0.2$ ppm and for $C = -17.5 \pm 0.2$ ppm.

† Ref. (150) lists the following values: -17.0 ppm (C), -12.1 ppm (B') and 1.8 – 4.1 ppm (A).

The phosphorus nuclei mentioned in the text and in this scheme are denoted as outlined on the following example:



Compilation with values of the refs. (49, 149, 150, 309).

ABC_3 spectrum (403) is observed for $\text{Cl}_2(\text{O})\text{PN}=\text{P}(\text{N}=\text{PCl}_3)_3$; $\text{P}_3\text{N}_3\text{Cl}_5(\text{N}=\text{PCl}_3)$ (XII) has an ABC_2 spectrum (in fact, an approximate ABX_2 spectrum) (149); $\text{P}_3\text{N}_3\text{Cl}_4(\text{N}=\text{PCl}_3)_2$ (XIV), an AB_2C_2 (approximate AB_2X_2) spectrum (149, 309). A more detailed interpretation of the ^{31}P NMR spectra of these two compounds is given in detail [(149), see also (140)].

A—20.3		A—20.4	
		B—13.5	A—13.1
B'—11.8		A—11.6	
A—1.2		B—-0.7	
		B'—-5.5	
B'—-10.6			
C—-15.6		C—-13.4	
C—-18.5		C—-17.5	
B—-19.0			
		C—-21.4	

$P_3N_3Cl_4NH_2(N=PPh_3)^\dagger$ $P_3N_3Cl_4(N=PCl_2)(N=PPh_3)$ $P_3N_3Cl_4(N=PCl_2)_2$ $P_3N_3Cl_4(NHPOCl_2)_2$ $P_3N_3Cl_4(N=PPh_3)_2$

For $P_3N_3F_5N=PF_3$ only ^{19}F NMR data have been reported so far (385).

Scheme 4 gives the variation of the chemical shifts of the phosphorus nuclei of these cyclic phosphazatriene derivatives.

Only a few other physical data of compounds listed in Section V, A have been reported: P_2NOCl_5 (V) is diamagnetic, with a molecular susceptibility of -115.7×10^{-6} (18). The ^{35}Cl NQR spectrum of (V) shows two nonequivalent groups of chlorines (215), whereas no results were obtained on the thio analog. The molecular refractivity of (V) is $M_D^{38} = 46.02$ (214).

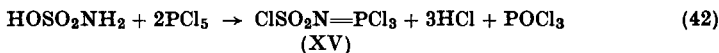
Mass spectra of $F_2(O)PN=PF_3$ (324) and $F_2(S)PN=PF_3$ (324, 382), as well as of $FCl(S)PN=PF_3$, $Cl_2(S)PN=PF_3$, $F_2(S)PN=PF_2Cl$, $FCl(S)PN=PF_2Cl$, $Cl_2(S)PN=PF_2Cl$ (382), and $P_3N_3F_5N=PF_3$ (385), are reported.

VI. Sulfonylphosphazotrihalides


A. SYNTHESSES

Fittig (151), in 1858, and later Gerhardt (170) investigated the reaction of arylsulfonamides with PCl_5 and formulated the products erroneously as imidochlorides $-SO(=NH)Cl$. Wichelhaus (517) gave the formulation $ArSO_2NHPCl_2$ and so did later workers in the field (514).

The simplest species of a sulfonylphosphazotrichloride is $ClSO_2N=PCl_3$ (XV); erroneously reported earlier (148), it can be obtained by phosphorylation of amidosulfuric acid (22, 221, 225a, 229, 508).

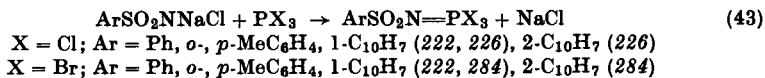


The fluoro analog $\text{FSO}_2\text{N}=\text{PCl}_3$ is obtained from $\text{H}_2\text{NSO}_2\text{F}$ and PCl_5 (289) and in ways listed in Section VI, B; $\text{ClSO}_2\text{N}=\text{PF}_3$ (384) and $\text{FSO}_2\text{N}=\text{PF}_3$ (324) result from ClSO_2NH_2 or FSO_2NH_2 with PCl_5 , respectively. Similarly, fluorosulfonylamide and PhPF_4 yield $\text{FSO}_2\text{N}=\text{PF}_2\text{Ph}$ (379a).

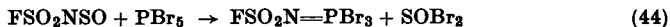
Other sulfonylphosphazotrichlorides, $\text{RSO}_2\text{N}=\text{PCl}_3$, obtained analogously to Eq. (42) are known having the following R: ClCH_2 (317); Me, Et (248); CF_3 (385c); Pr (317); *i*-Pr, Bu (248); C_4F_9 (378c); *i*-Bu, Am, *i*-Am, $n\text{-C}_6\text{H}_{13}$ (317); cyclohexyl, PhCH_2 (248); PhCH_2CH_2 (317); Ph (221, 225b, 230, 354); *o*- MeC_6H_4 (221, 225b, 230); *p*- MeC_6H_4 (221, 225b, 230, 354); *o*-, *m*-, *p*- $\text{O}_2\text{NC}_6\text{H}_4$ (252); *p*- FC_6H_4 , *m*- $\text{CF}_3\text{C}_6\text{H}_4$ (522); *o*- ClC_6H_4 (225b, 316); *p*- ClC_6H_4 (312, 354); *p*- BrC_6H_4 (225b, 316); *p*- MeOC_6H_4 (225b, 316, 354); Me_2N , Et_2N (272, 506); Pr_2N , Bu_2N (337, 506);  (310a, 337, 506); $(\text{CH}_2)_5\text{N}$ (310a); *p*- ClOC_6H_4 (72, 372, 375); *p*- $\text{Me}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4$ (255); $1\text{-C}_{10}\text{H}_7$, $2\text{-C}_{10}\text{H}_7$ (275); *p*-(PhO) $_2\text{SC}_6\text{H}_4$ (320); PhNH (510); and other substituents (71).

Analogously $\text{ArSO}_2\text{N}=\text{PPhCl}_2$ compounds (444) are obtained with $\text{Ar} = \text{Ph}$, *p*- ClC_6H_4 , *o*-, *m*-, *p*- $\text{O}_2\text{NC}_6\text{H}_4$, *o*-, *p*- MeC_6H_4 , $1\text{-C}_{10}\text{H}_7$, $2\text{-C}_{10}\text{H}_7$; interaction with Ph_2PCl_3 yields $\text{RSO}_2\text{N}=\text{PPh}_2\text{Cl}$ ($\text{R} = \text{Cl}$ (192a), Ph, *p*- ClC_6H_4 , *o*-, *m*-, *p*- $\text{O}_2\text{NC}_6\text{H}_4$, *o*- MeC_6H_4 , $1\text{-C}_{10}\text{H}_7$, $2\text{-C}_{10}\text{H}_7$ (456), *p*- MeC_6H_4 (56, 456)); with *p*- $\text{MeC}_6\text{H}_4\text{PPhCl}_3$ the compounds $\text{ArSO}_2\text{N}=\text{PPh}(\text{C}_6\text{H}_4\text{Me-}p)\text{Cl}$ ($\text{Ar} = \text{Ph}$, *o*-, *p*- MeC_6H_4 , *m*- $\text{O}_2\text{NC}_6\text{H}_4$, $2\text{-C}_{10}\text{H}_7$) are obtained [(458), see also (446)]. Ph_3PCl_2 gives $\text{ArSO}_2\text{N}=\text{PPh}_3$ ($\text{Ar} = \text{Ph}$, *o*-, *p*- MeC_6H_4 , *o*- $\text{O}_2\text{NC}_6\text{H}_4$, $1\text{-C}_{10}\text{H}_7$) (457), $(\text{PhO})_3\text{PCl}_2$ yields $\text{ArSO}_2\text{N}=\text{P}(\text{OPh})_3$ (487); $\text{CF}_3\text{SO}_2\text{N}=\text{PPhCl}_2$ has been described (385b).

Another way to sulfonylphosphazotrichlorides (and bromides) is a variation of the chloramine-T method; the use of carefully dried reagents and solvents is essential, otherwise the reaction may be explosive.



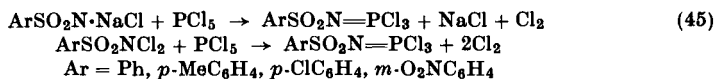
The compound $\text{FSO}_2\text{N}=\text{PBr}_3$ has recently been prepared (379) according to Eq. (44), as well as some homologs $\text{RSO}_2\text{N}=\text{PBr}_3$ [$\text{R} = \text{Me}$, CF_3 , *p*- ClC_6H_4 (387a)].



Variation of the method used in Eq. (43) is described. Thus, ROPCl_2 ($\text{R} = \text{Ph}$, Me, Et) instead of PX_3 gives $\text{PhSO}_2\text{N}=\text{P}(\text{OR})\text{Cl}_2$ (279); with

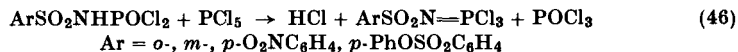
(RO)(R'O)PCl (R = Ph; R' = Ph, *o*-, *m*-, *p*-MeC₆H₄) and PhSO₂N·NaCl the products PhSO₂N=P(OR)(OR')Cl are obtained (279). Phosphorous esters P(OR)(OR')(OR'') give ArSO₂N=P(OR)(OR')(OR'') (R = Ph; R' = Ph, *o*-, *m*-, *p*-MeC₆H₄; R, R', R'' = Ph, *o*-, *m*-, *p*-MeC₆H₄; Ar = Ph or 2-C₁₀H₇) (67, 278). ArSO₂N·NaCl and PhPCl₂ give ArSO₂N=PPhCl₂ (Ar = Ph, *o*-, *p*-MeC₆H₄, *p*-ClC₆H₄, *o*-, *m*-, *p*-O₂NC₆H₄, 1-C₁₀H₇, 2-C₁₀H₇) (444); with PR₃, sulfonylphosphinimines ArSO₂N=PR₃ result (329, 487).

The sodium salts of *N*-chloroarylsulfonamides or the *N,N*-dichloroarylsulfonamides (dichloroamines)* and PCl₅ react with elimination of elemental chlorine and give nearly quantitative yields of arylsulfonylphosphazotrichlorides (313).

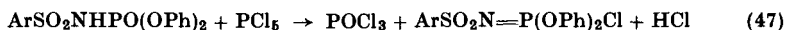


Compounds ArSO₂N=PAR₂'Cl can be obtained from ArSO₂NCl₂ and Ar₂'PCl (446); compounds like ArSO₂N=P(Et)(Ph)CH₂Ph (Ar = Ph, *o*-, *p*-MeC₆H₄, 1-C₁₀H₇) from ArSO₂N·NaCl and PhCH₂PPhEt (459). Further variation of this method is described (202, 412, 447, 478).

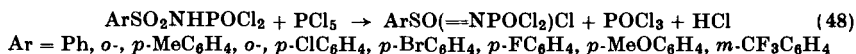
The action of PCl₅ on arylsulfonyldichlorophosphoramidates, ArSO₂NHPOCl₂, also yields sulfonylphosphazotrichlorides (320).



Analogous derivatives may be synthesized (320).

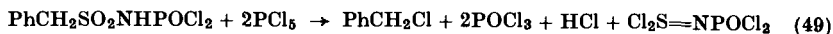


The reaction outlined in Eq. (46) is strongly dependent on the nature of Ar. Only if electronegative groups are present in Ar does this reaction occur; thus, no reaction occurs with Ar = Ph, MeC₆H₄, or ClC₆H₄ (320), but the tautomers of the formula ArSO(=NPOCl₂)Cl are obtained (310a, 314).



The same results are obtained with aliphatic substituents (317).

The compound PhCH₂SO₂NHPOCl₂ and PCl₅ (1:2) react in a different way (315).

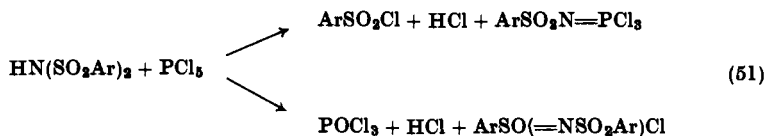


* ArSO₂NCl₂ (Ar = Ph, *p*-MeC₆H₄, *p*-ClC₆H₄, *p*-BrC₆H₄, *p*-O₂NC₆H₄) and elemental selenium give ArSO₂N=SeCl₂ (60).

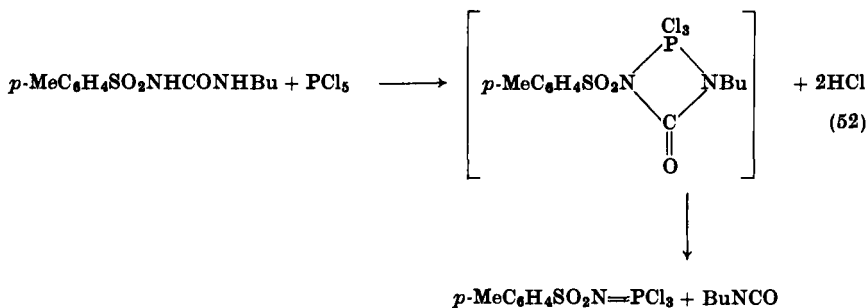
$\text{PhSO}_2\text{N}=\text{SCl}_2$ and PCl_3 give $\text{PhSO}_2\text{N}=\text{PCl}_3$ in quantitative yield (315).



Iminobis(sulfonaryls) and PCl_5 react in two ways, the product depending on the electronegativity of Ar (311).

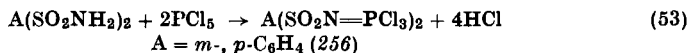


The compound $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{N}=\text{PCl}_3$ results also from the decomposition of a 1,3,2-diazaphosphetidinone (see also Sections VIII, B, 1 and IX), formed by interaction of 1-*p*-toluenesulfonyl-3-butylurea and PCl_5 (498).



In contrast to hexachlorodialkyldiazadiphosphetidines, $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{N}=\text{PCl}_3$ gives no further reaction with isocyanates (see also Section VIII, A, 2).

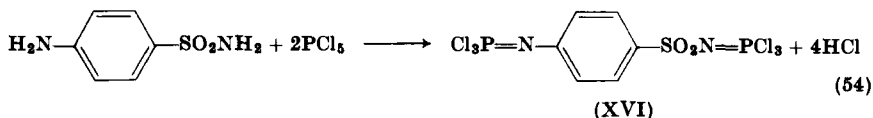
Only few compounds with two $-\text{SO}_2\text{N}=\text{PCl}_3$ groups in the molecule are known. Sulfamide reacts with 2 moles of PCl_5 forming bis(trichlorophosphazo)sulfone $\text{Cl}_3\text{P}=\text{NSO}_2\text{N}=\text{PCl}_3$ (232, 507). Extension of this reaction to disubstituted benzenes has been described (256).



Correspondingly, $(\text{PhCl}_2\text{P}=\text{N})_2\text{SO}_2$ has been prepared from sulfamide and PhPCl_4 (50a).

The compounds $(\text{Cl}_3\text{P}=\text{NSO}_2)_2\text{NMe}$ and $(\text{Cl}_3\text{P}=\text{NSO}_2\text{NMe})_2\text{SO}_2$ have also been prepared (343).

Compounds with one $-\text{SO}_2\text{N}=\text{PCl}_3$ and one $-\text{N}=\text{PCl}_3$ group such as compound (XVI) result from *p*-sulfonamidoaniline and PCl_5 (354, 458, 488). Similarly, $\text{Cl}_3\text{P}=\text{N}(\text{CH}_2)_2\text{SO}_2\text{N}=\text{PCl}_3$ (542) is known. These compounds can also be considered as aryl- or alkylphosphazotrichlorides (Sections VIII, A and B).



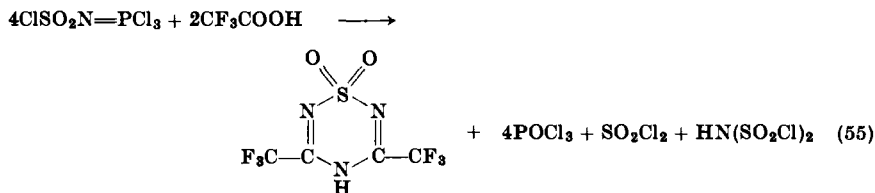
The dimeric ortho and meta isomers of (XVI) are also described (549).

The compound *p*- $\text{Cl}_3\text{P}=\text{NSO}_2\text{C}_6\text{H}_4\text{CON}=\text{PCl}_3$ (367) represents a type with one $-\text{SO}_2\text{N}=\text{PCl}_3$ group and one carbonylphosphazo group (cf. also Section VII, A).

Finally, 4,5-bis(trichlorophosphazosulfone)-1,8-naphthalene has been claimed without any preparative details being given (71).

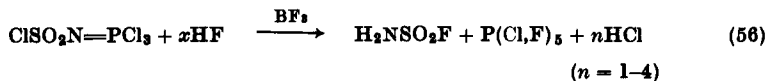
B. REACTIONS

Thermolysis ($118^\circ\text{--}120^\circ/2.5\text{--}5$ Torr) of $\text{ClSO}_2\text{N}=\text{PCl}_3$ (XV) gives mainly POCl_3 and a mixture of α - and β -sulfanuric chlorides (228, 508), as well as minor amounts of $\text{NPCl}_2(\text{NSOCl})_2$ (70a, 180a). Hydrolysis with water leads to phosphoric and amidosulfonic acids; with formic acid an undefined substance is obtained (192). Ammonia or NH_4Cl gives $(\text{H}_2\text{N})_3\text{P}=\text{NSO}_2\text{NH}_2$ (293), and amines yield $(\text{RNH})_3\text{P}=\text{NSO}_2\text{NHR}$; whereas with diamines such as diethylenediamine cross-linked polymers are formed; silylation with heptamethyldisilazane affords $\text{Me}_3\text{SiN}(\text{Me})\text{PCl}_2=\text{NSO}_2\text{Cl}$ (50b). Compound (XV) and chlorosulfonic acid yield $\text{HN}(\text{SO}_2\text{Cl})_2$, also obtained from chlorosulfonic acid and urea (6, 22). Trifluoroacetic acid and $\text{ClSO}_2\text{N}=\text{PCl}_3$ react in a rather complex manner (377):



Reaction of (XV) with SO_2 eliminates POCl_3 and minor quantities of OSNSO_2Cl (388). Fission of the $\text{P}=\text{N}$ bond occurs on the reaction of $\text{ClSO}_2\text{N}=\text{PCl}_3$ with anhydrous hydrogen fluoride in presence of BF_3 (200),

whereas fluorination of (XV) with AsF_3 gives $\text{FSO}_2\text{N}=\text{PCl}_3$ (388), also obtained in other ways (289). The halogen atoms may be successively



replaced in the reaction of $\text{ClSO}_2\text{N}=\text{PX}_3$ or $\text{FSO}_2\text{N}=\text{PX}_3$ ($\text{X} = \text{Cl}, \text{F}$) with $\text{Me}_3\text{SiNMe}_2$ or Me_3SiNCS , respectively (383c).

Fluorosulfonylphosphazotrichloride, $\text{FSO}_2\text{N}=\text{PCl}_3$, which on hydrolysis gives FSO_2NH_2 (388), reacts with fluorosulfonic acid (388) and difluorophosphoric acid (176) to form $(\text{FSO}_2)_2\text{NH}$ and POCl_3 ; with CF_3COOH (381c) and $\text{C}_2\text{F}_5\text{COOH}$ (381b) compounds $\text{FSO}_2\text{NHCOR}_f$ are obtained, whereas with $\text{CF}_3\text{SO}_3\text{H}$ the compound $\text{FSO}_2\text{NHPOCl}_2$ is formed (381a). In the reaction between $\text{ClSO}_2\text{N}=\text{PF}_3$ and PF_3Cl_2 phosphorus(V) fluoride is eliminated and $\text{ClSO}_2\text{N}=\text{PF}_2\text{Cl}$ formed (384); $\text{FSO}_2\text{N}=\text{PF}_3$ reacts similarly with PF_3Cl_2 to form $\text{FSO}_2\text{N}=\text{PF}_2\text{Cl}$ (385). Formic acid hydrolyzes $\text{CF}_3\text{SO}_2\text{N}=\text{PCl}_3$ to $\text{CF}_3\text{SO}_2\text{NHPOCl}_2$, whereas XSO_3H ($\text{X} = \text{F}, \text{Cl}$) yields $\text{CF}_3\text{SO}_2\text{NHSO}_2\text{X}$ (381a).

The reaction of $\text{ArSO}_2\text{N}=\text{PCl}_3$ [$\text{Ar} = \text{Ph}$ (222, 225c, 236); *o*-, *p*- MeC_6H_4 , 1- C_{10}H_7 (222, 236); *p*- MeC_6H_4 , *p*- MeOC_6H_4 , *p*- ClC_6H_4 (354); *o*-, *m*-, *p*- $\text{O}_2\text{NC}_6\text{H}_4$ (252); PhNH (510)] with HCOOH gives all possible intermediates, i.e., $\text{ArSO}_2\text{NHPOCl}_2$, $\text{ArSO}_2\text{NHP}(\text{O})(\text{OH})\text{Cl}$, $\text{ArSO}_2\text{NHP}(\text{O})(\text{OH})_2$, and ArSO_2NH_2 (222, 236). Hydrolysis with water [early work (170, 517)], benzoic acid, or other carboxylic acids leads only to the isolation of the first step (222, 236). Complex mixtures are obtained with acetone, ether, or esters (222). No definite product could be isolated from $\text{PhSO}_2\text{N}=\text{PCl}_3$ and ClSO_3H ; with DMSO, $\text{PhSO}_2\text{NHPOCl}_2$ is formed (192). In contrast, this latter reaction ($\text{ArSO}_2\text{N}=\text{PCl}_3 + \text{DMSO}$) has been described as giving sulphydimines in 44% yield (353).



Alkylsulfonylphosphazotrichlorides, $\text{RSO}_2\text{N}=\text{PCl}_3$ ($\text{R} = \text{Me}, \text{Et}, i\text{-Pr}, \text{Bu}, \text{PhCH}_2, n\text{-C}_6\text{H}_{13}$), and HCOOH yield the dichlorides (249). $\text{R}_2\text{NSO}_2\text{N}=\text{PCl}_3$ ($\text{R} = \text{Me}, \text{Et}$) and formic acid give all three hydrolysis steps (272), whereas their reaction with CF_3COOH proceeds with elimination of CF_3COCl and formation of $\text{R}_2\text{NSO}_2\text{NHPOCl}_2$ (378b).

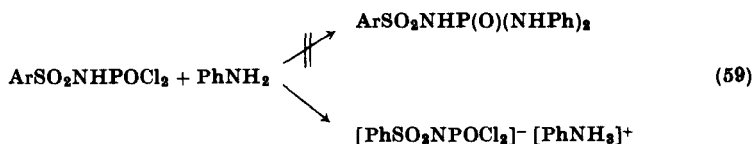
The interaction of $\text{ArSO}_2\text{N}=\text{PCl}_3$ ($\text{Ar} = \text{Ph}, p\text{-MeC}_6\text{H}_4, p\text{-ClC}_6\text{H}_4, m\text{-O}_2\text{NC}_6\text{H}_4$) with Cl_2O is interesting owing to the formation of $\text{ArSO}(\text{OCl})=\text{NPOCl}_2$ (290b).



Several sulfonylphosphazotrichlorides, $\text{ArSO}_2\text{N}=\text{PCl}_3$ ($\text{Ar} = \text{Ph}$, $p\text{-ClC}_6\text{H}_4$, $p\text{-MeC}_6\text{H}_4$, $p\text{-O}_2\text{NC}_6\text{H}_4$) form stable adducts with DMF; these decompose upon heating (297d).

Ammonolysis of arylsulfonylphosphazotrichlorides gives $\text{ArSO}_2\text{N}=\text{P}(\text{NH}_2)_3$ (222, 237); aqueous ammonia yields $\text{ArSO}_2\text{NHPO}(\text{NH}_2)\text{OH}$ (237). Reaction with aniline or p -toluidine gives first the monochlorides $\text{ArSO}_2\text{N}=\text{P}(\text{NHAr}')_2\text{Cl}$ (238, 426), the triamides being obtained only with excess of amine (238). Alkylsulfonylphosphazotrichlorides ($\text{R} = \text{Et}$, Bu) give analogous results (251).

Hydrolysis of the dianilides gives $\text{ArSO}_2\text{NHPO}(\text{NHPh})_2$ which cannot be obtained by the simple action of $\text{ArSO}_2\text{NHPOCl}_2$ and aniline; in the latter case saltlike compounds result (312).



Aminolysis of $\text{ArSO}_2\text{N}=\text{PCl}_3$ with secondary amines such as Me_2NH (254), ethylenimine (296, 354, 489), or methylaziridine (373) gives the corresponding triamides.



With ethylenimine: $\text{Ar} = \text{Ph}$, $p\text{-MeC}_6\text{H}_4$, $p\text{-ClC}_6\text{H}_4$ (296, 354, 489); $p\text{-O}_2\text{NC}_6\text{H}_4$ (296); $p\text{-MeOC}_6\text{H}_4$ (354, 489)

With dimethylamine: $\text{Ar} = o\text{-}$, $m\text{-}$, $p\text{-O}_2\text{NC}_6\text{H}_4$ (254)

With methylaziridine: $\text{Ar} = \text{Ph}$, Me , MeC_6H_4 , $3,4\text{-(O}_2\text{N)(PhNH)C}_6\text{H}_3$ (373)

The reaction with diethylamine stops at the diamides, $o\text{-}$, $m\text{-}$, $p\text{-O}_2\text{NC}_6\text{H}_4\text{SO}_2\text{N}=\text{P}(\text{NEt}_2)_2\text{Cl}$ (254).

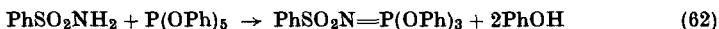
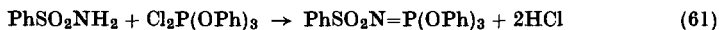
The analogous ammonolysis of $\text{ArSO}_2\text{N}=\text{PPhCl}_2$ gives $\text{ArSO}_2\text{N}=\text{PPh}(\text{NH}_2)_2$ ($\text{Ar} = \text{Ph}$, $o\text{-}$, $p\text{-MeC}_6\text{H}_4$, $p\text{-ClC}_6\text{H}_4$, $1\text{-C}_{10}\text{H}_7$) (453), the reaction with aniline yields $\text{ArSO}_2\text{N}=\text{PPh}(\text{NHPh})_2$ ($\text{Ar} = \text{Ph}$, $o\text{-}$, $m\text{-}$, $p\text{-O}_2\text{NC}_6\text{H}_4$, $1\text{-C}_{10}\text{H}_7$, $2\text{-C}_{10}\text{H}_7$) (452). The compound $\text{PhNHSO}_2\text{N}=\text{PCl}_3$ reacts with PCl_5 at 80° to form $p\text{-ClC}_6\text{H}_4\text{NHSO}_2\text{N}=\text{PCl}_3$, as well as $\text{ClSO}_2\text{N}=\text{PCl}_3$ (XV) and $p\text{-ClC}_6\text{H}_4\text{N}=\text{PCl}_3$ (510).

Compounds of the type $\text{XSO}_2\text{NRPOCl}_2$ ($\text{X} = \text{F}$, Cl) are formed by the alcoholysis ($\text{R} = \text{Me}$, Et , Pr , Bu) of $\text{XSO}_2\text{N}=\text{PCl}_3$ (383b). The compounds $\text{MeSO}_2\text{N}=\text{PCl}_3$ and $\text{ClSO}_2\text{N}=\text{PF}_3$ react with alcohols to give the monoesters which rearrange with catalytic amounts of ether to $\text{MeSO}_2\text{N}(\text{Me})\text{POCl}_2$ and $\text{ClSO}_2\text{N}(\text{Et})\text{POF}_2$, respectively (384a). Reaction

of $\text{ArSO}_2\text{N}=\text{PCl}_3$ with anhydrous* alcohols, ROH ($\text{R} = \text{Me}, \text{Et}, \text{Bu}$), yields $\text{ArSO}_2\text{N}=\text{P}(\text{OR})_3$ ($\text{Ar} = \text{Ph}, o-, p\text{-MeC}_6\text{H}_4, 1\text{-C}_{10}\text{H}_7, 2\text{-C}_{10}\text{H}_7$) as relatively stable substances,† which give on hydrolysis the diesters $\text{ArSO}_2\text{NHPO}(\text{OR})_2$ (275), also obtainable from $\text{ArSO}_2\text{NHPOCl}_2$ and sodium alcoholates (276). The interaction of $o-, m-, p\text{-O}_2\text{NC}_6\text{H}_4\text{SO}_2\text{N}=\text{PCl}_3$ with various alcohols ($\text{R} = \text{Me}, \text{Ph}, p\text{-ClC}_6\text{H}_4, o-, p\text{-O}_2\text{NC}_6\text{H}_4$) is described in detail (253). Isolation of the monoesters ($\text{Ar} = \text{Ph}, o\text{-MeC}_6\text{H}_4, 1\text{-C}_{10}\text{H}_7, 2\text{-C}_{10}\text{H}_7$) is only possible at low temperatures ($2^\circ\text{--}5^\circ$) (280). Some esters may also be obtained by the chloramine-T method (278). The substances $\text{ArSO}_2\text{N}=\text{PPhCl}_2$ ($\text{Ar} = \text{Ph}, o-, p\text{-MeC}_6\text{H}_4, o-, m\text{-O}_2\text{NC}_6\text{H}_4, p\text{-ClC}_6\text{H}_4, 1\text{-C}_{10}\text{H}_7, 2\text{-C}_{10}\text{H}_7$) (454) and $\text{ArSO}_2\text{N}=\text{PPh}_2\text{Cl}$ ($\text{Ar} = \text{Ph}, o-, p\text{-MeC}_6\text{H}_4, p\text{-O}_2\text{NC}_6\text{H}_4, 2\text{-C}_{10}\text{H}_7$) (455) show analogous behavior with RONa ($\text{R} = \text{Me}, \text{Et}, \text{Ph}$). Bis-*t*-butyl peroxides of $\text{ArSO}_2\text{N}=\text{PPhCl}_2$ (524b) as well as the compounds $\text{ArSO}_2\text{N}=\text{PPh}_2(\text{OOtert. Bu})$ (524c) have been described recently.

Unsaturated esters such as $\text{ArSO}_2\text{N}=\text{P}(\text{OCH}_2\text{CH}=\text{CH}_2)_3$ ($\text{Ar} = \text{Ph}, p\text{-MeC}_6\text{H}_4, p\text{-ClC}_6\text{H}_4, o-, m-, p\text{-O}_2\text{NC}_6\text{H}_4, 1\text{-C}_{10}\text{H}_7, 2\text{-C}_{10}\text{H}_7$) (460) and $\text{ArSO}_2\text{N}=\text{PPh}(\text{OCH}_2\text{CH}=\text{CH}_2)_2$ ($\text{Ar} = \text{Ph}, p\text{-MeC}_6\text{H}_4, p\text{-ClC}_6\text{H}_4, p\text{-O}_2\text{NC}_6\text{H}_4$) (461) are described; they may also be prepared from $\text{ArSO}_2\text{N}\cdot\text{NaCl}$ and phosphorous triallyl ester (460).

Esterification of $\text{ArSO}_2\text{N}=\text{PCl}_3$ ($\text{Ar} = \text{Ph}, o\text{-MeC}_6\text{H}_4, o-, p\text{-ClC}_6\text{H}_4, o-, p\text{-O}_2\text{NC}_6\text{H}_4, p\text{-FC}_6\text{H}_4, p\text{-CF}_3\text{C}_6\text{H}_4, 1\text{-C}_{10}\text{H}_7, 2\text{-C}_{10}\text{H}_7$) with aromatic alcohols ($\text{Ar}' = \text{Ph}, o-, m-, p\text{-MeC}_6\text{H}_4, p\text{-FC}_6\text{H}_4, p\text{-ClC}_6\text{H}_4, p\text{-O}_2\text{NC}_6\text{H}_4$) yields the triesters $\text{ArSO}_2\text{N}=\text{P}(\text{OAr}')_3$ (261, 277, 320, 522), which on alkaline hydrolysis give $\text{ArSO}_2\text{NHPO}(\text{OAr}')_2$. The above triesters can also be obtained from the corresponding sulfamide and $(\text{PhO})_3\text{PCl}_2$ or pentaphenoxyporphorus(V) (534).



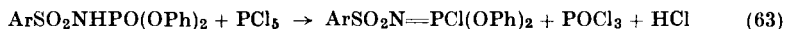
The aliphatic sulfonylphosphazotrichlorides, $\text{R}_2\text{NSO}_2\text{N}=\text{PCl}_3$ ($\text{R} = \text{Me}, \text{Et}$), and $\text{Ar}'\text{ONa}$ ($\text{Ar}' = \text{Ph}, o-, p\text{-ClC}_6\text{H}_4, o-, p\text{-O}_2\text{NC}_6\text{H}_4, 1\text{-C}_{10}\text{H}_7$) (273), as well as $\text{RSO}_2\text{N}=\text{PCl}_3$ ($\text{R} = \text{Me}, \text{Et}, i\text{-Pr}, \text{Bu}, \text{PhCH}_2$; $\text{Ar} = \text{Ph}, p\text{-ClC}_6\text{H}_4, p\text{-O}_2\text{NC}_6\text{H}_4$) (250) give the triesters.

Dieters $\text{ArSO}_2\text{N}=\text{P}(\text{Cl}(\text{OPh}))_2$ may not be obtained in this way. They

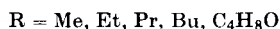
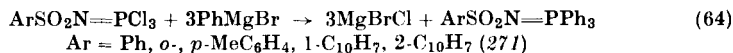
* $\text{ArSO}_2\text{N}=\text{PCl}_3$ and alcohols in the presence of NaOH give water-soluble compounds $\text{ArSO}_2\text{NNaPO}(\text{OR})_2$ ($\text{Ar} = \text{Ph}, p\text{-MeC}_6\text{H}_4$; $\text{R} = \text{Bu}, n\text{-C}_6\text{H}_{13}$ to $n\text{-C}_{10}\text{H}_{21}$) (468) (see also Section X).

† The triesters $\text{ArSO}_2\text{N}=\text{P}(\text{OR})_3$ isomerize on heating at $200^\circ\text{--}210^\circ$ to give $\text{ArSO}_2\text{NRPO}(\text{OR})_2$ (462), in contrast to the results of other authors (178) (see also Section VI, C).

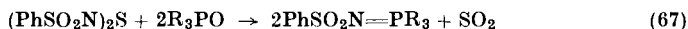
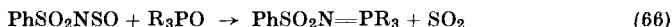
are synthesized (320) following Eq. (63) or from $\text{PhSO}_2\text{N}\cdot\text{NaCl}$ and $(\text{PhO})_2\text{PCl}$ (279) (Section VI, A).



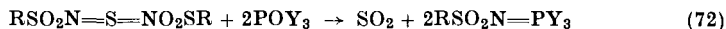
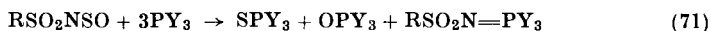
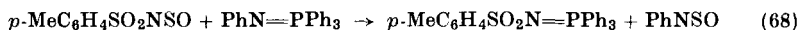
Arylation of sulfonylphosphazotrichlorides with Grignard reagents leads to phosphinimines.



The compound $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{N}=\text{PPh}_3$ was obtained earlier in another way (329); $\text{PhSO}_2\text{N}=\text{PR}_3$ ($\text{R} = \text{Me}, \text{Et}, \text{Bu}, \text{PhCH}_2, \text{Ph}$) compounds are also prepared (318) by the following procedures; see also (139):

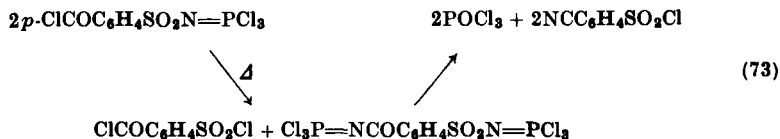


Analogous compounds $\text{RSO}_2\text{N}=\text{PY}_3$ ($\text{Y} = \text{R}, \text{Ar}, \text{OAr}$) were isolated from the reactions of RSO_2NSO with PY_3 , POY_3 or PSY_3 (224, 319, 414).

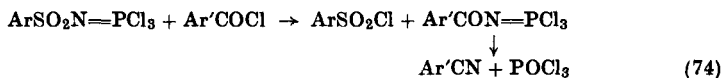


Fluorination (KF) of $\text{ArSO}_2\text{N}=\text{PCl}_3$ in aqueous solution gives the salts $\text{K}^+(\text{ArSO}_2\text{NPOCl}_2)^-$ and $\text{K}^+(\text{ArSO}_2\text{NPOF}_2)^-$ ($\text{Ar} = \text{Ph}, p\text{-MeC}_6\text{H}_4, p\text{-ClC}_6\text{H}_4, p\text{-FC}_6\text{H}_4, o-, m-, p\text{-O}_2\text{NC}_6\text{H}_4$), also obtained from $\text{ArSO}_2\text{NHPOCl}_2$ and $\text{KF}\cdot 2\text{H}_2\text{O}$ (258). The salts $\text{K}_2^+(\text{ArSO}_2\text{NPOF}_2)^{2-}$ have also been described (258).

Formation of nitriles occurs on the attempted distillation of $p\text{-ClCOC}_6\text{H}_4\text{SO}_2\text{N}=\text{PCl}_3$ (221, 231, 372, 375), sometimes with the use of catalysts (71, 72).

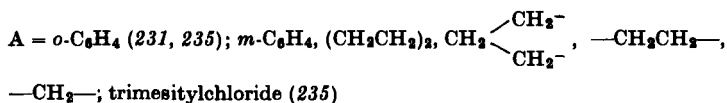


Extension of this method, i.e., the reaction of sulfonylphosphazotrichlorides with acyl chlorides, is described in detail [(221, 231), see also (222)].

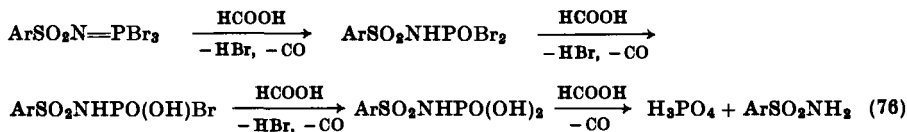


The production of the nitriles is thought to proceed through the intermediate formation of carbonylphosphazotrichlorides (cf. Section VII, B).

Dinitriles are formed in a similar way using dicarbonyl dichlorides.



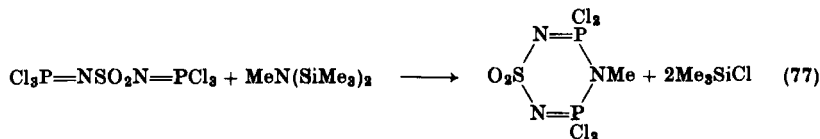
The hydrolytic behavior (HCOOH) of some sulfonylphosphazotribromides $\text{ArSO}_2\text{N}=\text{PBr}_3$ ($\text{Ar} = \text{Ph}, o-, p\text{-MeC}_6\text{H}_4, 1\text{-C}_{10}\text{H}_7, 2\text{-C}_{10}\text{H}_7$) is described; all possible intermediates can be isolated (285).



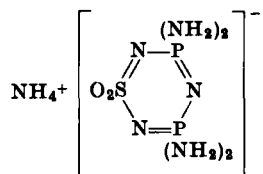
Sulfonylphosphazotribromides $\text{RSO}_2\text{N}=\text{PBr}_3$ ($\text{R} = \text{Me}, \text{CF}_3, \text{Ph}, p\text{-MeC}_6\text{H}_4$) react readily with $\text{Me}_3\text{SiNMe}_2$ or $(\text{Me}_3\text{Si})_2\text{NH}$ to give $\text{RSO}_2\text{N}=\text{PBr}_2\text{NMe}_2$ or $\text{RSO}_2\text{N}=\text{PBr}_2\text{NH}(\text{SiMe}_3)_2$, respectively (378a).

The compound $\text{SO}_2(\text{N}=\text{PCl}_3)_2$ reacts violently with water, amines, NH_3 , ROH , PhOH , and organometallics (232), but no details are given. Excess water gives HCl , phosphoric acid, and sulfamide (192). Molar quantities of HCOOH yields $\text{Cl}_3\text{P}=\text{NSO}_2\text{NHPOCl}_2$; excess of formic acid results in the formation of minor quantities of $\text{Cl}_2\text{OPNHSO}_2\text{NHPOCl}_2$ and large amounts of uncharacterized compounds (192). ArONa gives bis(triesters) $\text{SO}_2[\text{N}=\text{P}(\text{OAr})_3]_2$ ($\text{Ar} = \text{Ph}, o-, m-, p\text{-MeC}_6\text{H}_4, p\text{-ClC}_6\text{H}_4, p\text{-O}_2\text{NC}_6\text{H}_4, 1\text{-C}_{10}\text{H}_7, 2\text{-C}_{10}\text{H}_7$) (267); the bis(triphenylester) can also be prepared on another way (534). Interaction of $\text{SO}_2(\text{N}=\text{PCl}_3)_2$ with ArMgBr [$\text{Ar} = \text{Ph}$ (337, 505), $m-, p\text{-MeC}_6\text{H}_4$ (337)] gives $\text{SO}_2(\text{N}=\text{PAR}_3)_2$. With o -tolylmagnesium bromide no reaction occurs, probably owing to steric factors.

A ring-closure reaction [(17), see also (286a)] between heptamethyldisilazane and $\text{SO}_2(\text{N}=\text{PCl}_3)_2$ proceeds according to Eq. (77). With



ammonia instead of the silazane an ionic compound



is formed, whereas amines such as dimethylamine, aniline (17), or ethylenimine (367) only give the hexamides. With silylamines Me_3SiNR_2 ($\text{R} = \text{Me}, \text{Et}$) (286a) a partial replacement of the chlorine atoms occurs.

Arylation (PhMgBr) of $(\text{Cl}_3\text{P}=\text{NSO}_2)_2\text{NMe}$ leads to $(\text{Ph}_3\text{P}=\text{NSO}_2)_2\text{NMe}$, and the bis(triesters) of $(\text{Cl}_3\text{P}=\text{NSO}_2)_2\text{NMe}$ or $(\text{Cl}_3\text{P}=\text{NSO}_2\text{NMe})_2\text{SO}_2$ are obtained with PhONa (343).

The acidolysis (HCOOH) of *m*- and *p*- $\text{C}_6\text{H}_4(\text{SO}_2\text{N}=\text{PCl}_3)_2$ results in *m*- and *p*- $\text{C}_6\text{H}_4(\text{SO}_2\text{NHPOCl}_2)_2$; the reaction with RONa ($\text{R} = \text{Me}, \text{Et}, \text{Ph}$) gives *m*- or *p*- $\text{C}_6\text{H}_4[\text{SO}_2\text{NHPO}(\text{OR})_2]_2$ (256). Analogous esters $(\text{CH}_2)_n[\text{SO}_2\text{N}=\text{P}(\text{XR})_3]_2$ ($n = 3, 4$; $\text{R} = \text{Et}, \text{Ph}$; $\text{X} = \text{O}, \text{S}$) may be obtained by a Staudinger reaction (178).

The interaction of 1,4- $\text{Cl}_3\text{P}=\text{NC}_6\text{H}_4\text{SO}_2\text{N}=\text{PCl}_3$ (XVI) (354, 488) and *m*- and *p*- $\text{C}_6\text{H}_4(\text{SO}_2\text{N}=\text{PCl}_3)_2$ (367) with ethylenimine giving the hexamides is described. Both $-\text{N}=\text{PCl}_3$ groups are hydrolyzed in the reaction of $\text{Cl}_3\text{P}=\text{NC}_6\text{H}_4\text{SO}_2\text{N}=\text{PCl}_3$ (*o*-, *m*-, *p*-) with HCOOH giving $\text{Cl}_2\text{P}(\text{O})\text{NHC}_6\text{H}_4\text{SO}_2\text{NHP}(\text{O})\text{Cl}_2$ and subsequently $(\text{OH})_2\text{P}(\text{O})\text{NHC}_6\text{H}_4\text{SO}_2\text{NHP}(\text{O})(\text{OH})_2$ (549), in sharp contrast to the difficult hydrolysis of $\text{SO}_2(\text{N}=\text{PCl}_3)_2$.

C. SPECTROSCOPIC INVESTIGATIONS

In general, only a few spectroscopic data of sulfonylphosphazotrihalides are available.

Goerdeler and Ullmann (178) assign the $\text{P}=\text{N}$ vibration at 1260–1290 cm^{-1} in compounds of the type $\text{RSO}_2\text{N}=\text{P}(\text{OR}')_3$; other authors (337,

343) give 1255–1300 cm^{-1} , mentioning that the asymmetric SO_2 stretching vibration is also involved and that coupling cannot be ruled out. Kirsanov and co-workers (462) point out that distillation (in the course of isolation) of the above esters leads to a rearrangement to $\text{RSO}_2\text{NR}'\text{P}(\text{O})(\text{OR}')_2$, and that therefore the assignments cannot be sustained. A detailed investigation concerning the $\text{P}=\text{N}$ vibration in such compounds is available (520).

The $\nu_{\text{P}=\text{N}}$ of $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{N}=\text{PCl}_3$ is given at 1199 cm^{-1} (521). A band at 1357 cm^{-1} is assigned (324) to the $\text{P}=\text{N}$ vibration in $\text{FSO}_2\text{N}=\text{PF}_3$, and at 1190 cm^{-1} a band is tentatively assigned for $\text{FSO}_2\text{N}=\text{PBr}_3$ (379). Infrared tables for $\text{ClSO}_2\text{N}=\text{PF}_3$ and $\text{ClSO}_2\text{N}=\text{PF}_2\text{Cl}$ are given (384).

Only a few chemical shifts (^{31}P) from sulfonylphosphazotrichlorides have been measured so far: $\text{ClSO}_2\text{N}=\text{PCl}_3$ ($\delta_{\text{P}} = -20.5 \pm 0.5$ ppm) (510), $\text{PhSO}_2\text{N}=\text{PCl}_3$ ($\delta_{\text{P}} = -4$ ppm) (192), $\text{PhNHSO}_2\text{N}=\text{PCl}_3$ ($\delta_{\text{P}} = -3.5 \pm 0.3$ ppm) and $p\text{-ClC}_6\text{H}_4\text{NHSO}_2\text{N}=\text{PCl}_3$ ($\delta_{\text{P}} = -4.2 \pm 0.3$ ppm) (510), showing tetracoordinate phosphorus and thus proving their structure. It is interesting to note that the compounds $\text{RSO}_2\text{N}=\text{PBr}_3$ show ^{31}P NMR chemical shifts as follows: $\text{R} = \text{Me}$ ($\delta_{\text{P}} = 105.1$ ppm), $\text{R} = \text{CF}_3$ ($\delta_{\text{P}} = 85.1$ ppm), $\text{R} = \text{Ph}$ ($\delta_{\text{P}} = 101.4$ ppm), $\text{R} = p\text{-MeC}_6\text{H}_4$ ($\delta_{\text{P}} = 108.9$ ppm), and $\text{R} = p\text{-ClC}_6\text{H}_4$ ($\delta_{\text{P}} = 99.5$ ppm), thus showing the great influence of R (387a).

Fluorine-19 NMR measurements have been made on $\text{FSO}_2\text{N}=\text{PF}_3$ ($\delta_{\text{F}} = -59.6$ ppm, $J_{\text{PF}} = 4$ Hz) (388), $\text{ClSO}_2\text{N}=\text{PF}_3$ ($\delta_{\text{F}} = 84.6$ ppm, $J_{\text{PF}} = 1078$ Hz), $\text{ClSO}_2\text{N}=\text{PF}_2\text{Cl}$ ($\delta_{\text{F}} = 50.4$ ppm, $J_{\text{PF}} = 1120$ Hz) (384), and $\text{FSO}_2\text{N}=\text{PBr}_3$ ($\delta_{\text{F}} = -61.4$ ppm, $J_{\text{PF}} = 2$ Hz) (379).

Mass spectral data of $\text{ClSO}_2\text{N}=\text{PF}_3$, $\text{ClSO}_2\text{N}=\text{PF}_2\text{Cl}$ (384), and $\text{FSO}_2\text{N}=\text{PF}_3$ (385) are mentioned in the literature.

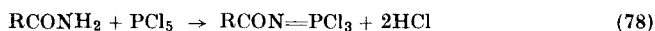
A ^{35}Cl NQR study of $\text{ClSO}_2\text{N}=\text{PCl}_3$ (XV) has been reported recently (191b).

VII. Carbonylphosphazotrichlorides

A. SYNTHESSES

As for the reaction of sulfamides with phosphorus(V) chloride, the interaction of amides of carboxylic acids with PCl_5 attracted attention more than 110 years ago (170). Wallach (511–513) described reaction products RCCl_2NH_2 (imidochlorides) resulting from various oxamides and PCl_5 ; later workers (61, 70, 165, 321, 360, 485, 491), including quite recent ones (361), still assigned the formula RCCINPOCl_2 to the reaction products.

Kirsanov, in 1954, showed in the first of a series of outstanding papers that in this reaction carbonylphosphazotrichlorides $\text{RCON}=\text{PCl}_3$, and not the isomers $\text{RCCl}=\text{NPOCl}_2$, are formed (233).



Compounds following Eq. (78) are known with $\text{R} = \text{Ph}$ (223, 260); *o*-, *m*-, *p*- $\text{O}_2\text{NC}_6\text{H}_4$, *o*-, *p*- ClC_6H_4 , *p*- BrC_6H_4 , 2,4-(O_2N) $_2\text{C}_6\text{H}_3$, 3,5-(O_2N) $_2\text{C}_6\text{H}_3$, 2,4- $\text{Cl}_2\text{C}_6\text{H}_3$ (260); 2,4- $\text{Cl}(\text{O}_2\text{N})\text{C}_6\text{H}_3$ (244, 260); *o*-, *m*-, *p*- FC_6H_4 (136); Ph_2CCl , Ph_3C (243); CCl_3 (240); CF_3 (210, 370); *o*- BrC_6H_4 (246); *o*- MeC_6H_4 (244); *p*- MeOC_6H_4 (133); PhO (265); EtO (223, 233, 264); MeO , PrO , *i*- PrO , BuO , *i*- BuO (264); 2,3,6- $\text{Cl}_3\text{C}_6\text{H}_2$ (484); 1- C_{10}H_7 , 2- C_{10}H_7 (244); CHF_2CF_2 (147); MeCHCl (387*h*); $\text{ClCH}_2\text{CCl}_2$, ClCH_2CHCl (117); MeCCl_2 (119); CBr_3 (295); NCCH_2 (450); Ph_2N (274); $\text{Me}_2\text{C}(\text{CN})$, $\text{Et}_2\text{C}(\text{CN})$, $\text{Pr}_2\text{C}(\text{CN})$, $\text{Bu}_2\text{C}(\text{CN})$, $\text{Am}_2\text{C}(\text{CN})$, $(\text{Me}_2\text{CHCH}_2\text{CH}_2)_2\text{C}(\text{CN})$ (427); $(\text{EtO})_2\text{P}(\text{O})\text{CCl}_2$ (59); see also (225, 234). These carbonylphosphazotrichlorides are also obtained from acylamides and PCl_3 plus Cl_2 (135).

Not mentioned above are earlier papers (61, 170, 485, 512, 513) which assign to these products the formulas of imidochlorides $\text{RCCl}=\text{NPOCl}_2$.

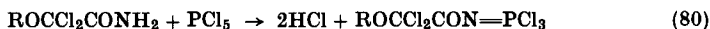
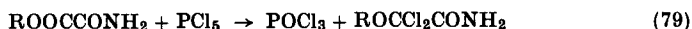
Analogous compounds, $\text{RCON}=\text{PR}'\text{Cl}_2$ ($\text{R} = \text{CHCl}_2$, CCl_3 , CF_3 ; $\text{R}' = \text{CH}_2\text{Cl}$, CHCl_2), result from RCONH_2 and $\text{R}'\text{PCl}_4$ (471*b*). The use of PhPCl_4 gives $\text{RCON}=\text{PPhCl}_2$ ($\text{R} = \text{CCl}_3$) (466), with CCl_3PCl_4 is obtained $\text{RCON}=\text{P}(\text{CCl}_3)\text{Cl}_2$ ($\text{R} = \text{CHCl}_2$, CCl_3 , CF_3 , *p*- ClC_6H_4 , *p*- $\text{O}_2\text{NC}_6\text{H}_4$) (469). MePCl_4 yields $\text{RCON}=\text{PMeCl}_2$ ($\text{R} = \text{CCl}_3$, CF_3 , *p*- $\text{O}_2\text{NC}_6\text{H}_4$, Ph) (471). The interaction of carboxylic amides and Ph_2PCl_3 in a fairly smooth reaction gives $\text{RCON}=\text{PPh}_2\text{Cl}$ with elimination of the HCl formed. Ph_3PCl_2 gives only phosphonium salts, except if electro-negative substituents ($\text{R} = \text{CCl}_3$) are present [(466), see also (137)]. Interaction of $\text{R}_2\text{C}(\text{CN})\text{CONH}_2$ and PhPCl_4 yield $\text{R}_2\text{C}(\text{CN})\text{CON}=\text{PPhCl}_2$ ($\text{R} = \text{Me}$, Et , Pr , Bu , Am) (427*a*).

The similar reaction of ArCSNH_2 and PCl_5 does not give $\text{ArCSN}=\text{PCl}_3$, but, as stated in the example with PhCSNH_2 , a rather complex reaction producing HCl , PSCl_3 , PCl_3 , PhCN , and 3,5-diphenyl-1,2,4-thiadiazole and other products (282).

The distinction between $\text{RCON}=\text{PCl}_3$ and $\text{RCCl}=\text{NPOCl}_2$ was effected by the characterization of the reaction products and by synthesis of ^{18}O -labeled $\text{PhC}^{18}\text{ON}=\text{PCl}_3$ (298) and $\text{Et}^{18}\text{OC}^{18}\text{ON}=\text{PCl}_3$ (3) (see Section VII, B).

Excess PCl_5 partially chlorinates 2-cyanacetamide to give $\text{NCCl}_2\text{-CON}=\text{PCl}_3$ (450), not attacking the CO group (cf. in the following) nor the nitrile group (see Section VIII, B).

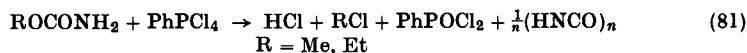
Oxalic ester amides ROOCCONH_2 react with PCl_5 in an initial step to form $\text{ROCCl}_2\text{CONH}_2^*$ and then with excess PCl_5 to form $\text{ROCCl}_2\text{CON}=\text{PCl}_3$.



$\text{R} = \text{Et}$ (223, 268); Me , Bu , $i\text{-Bu}$, C_6H_{11} (268); Ph (270); $p\text{-ClC}_6\text{H}_4$,

$o\text{-}$, $m\text{-}$, $p\text{-MeC}_6\text{H}_4$, $1\text{-C}_{10}\text{H}_7$, $2\text{-C}_{10}\text{H}_7$ (269, 270); see also (225)

The reaction of PhPCl_4 and alkoxyureas under normal condition follows Eq. (81) up to 80% yield [(448), see also (137)]. If the reaction is carried out *in vacuo* reasonable yields of $\text{ROCON}=\text{PPhCl}_2$ are obtained

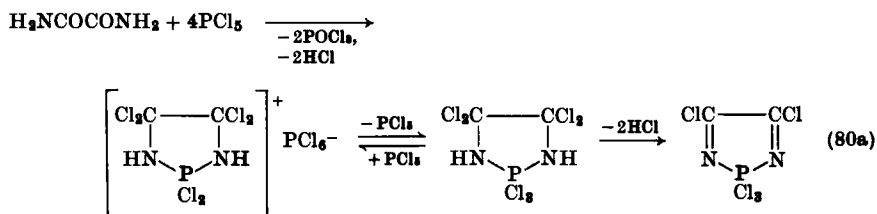


(474). These latter compounds may also be obtained from *N,N*-dichlorocarbamates and PhPCl_4 (449). The isocyanate $\text{CCl}_3\text{PO}(\text{NCO})\text{Cl}$ is obtained without formation of the phosphazo compound by reaction of

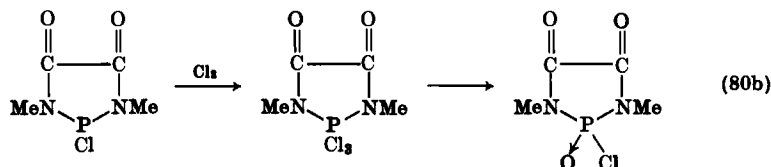


MeOCONH_2 with CCl_3PCl_4 (472). Similarly $\text{MeOP}(\text{O})(\text{Cl})\text{NCO}$ is obtained using MePCl_4 (470), and a mixture of $\text{ClCH}_2\text{PO}(\text{NCO})\text{Cl}$ and $\text{ClCH}_2\text{POCl}_2$ is formed using $\text{ClCH}_2\text{PCl}_4$ (471a).

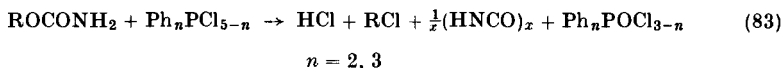
* Chlorination and ring-closure reaction to 1,3,2-diazaphospholanes occurs with PCl_5 and oxamide (451):



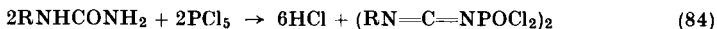
Other authors (41) obtained in this reaction four- and five-membered fused ring systems. *N,N'*-Dimethyloxamide and PCl_3 , followed by chlorination and intermolecular reaction, give the product shown in Eq. (80b) (41).



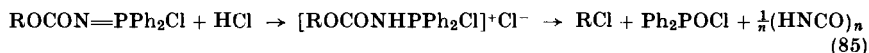
Alkoxyureas and Ph_2PCl_3 (*in vacuo*) give only 3% yield of $\text{ROCON}=\text{PPh}_2\text{Cl}$; with Ph_3PCl_2 instead, only isocyanuric acid and triphenylphosphine oxide are obtained (449).



In an analogous manner only Ph_3PO and unidentified products result from PhNHCONH_2 and Ph_3PCl_2 (544), instead of the expected $\text{PhNHCON}=\text{PPh}_3$; this latter compound is obtained from $\text{Ph}_3\text{P}=\text{NH}$ and PhNCO (544). In contrast, $\text{PhNHCSN}=\text{PPh}_3$ is synthesized from PhNHCSNH_2 and Ph_3PCl_2 (545). Compounds RNHCONH_2 ($\text{R} = \text{Me}, \text{Et}, \text{Ph}, p\text{-MeOC}_6\text{H}_4, p\text{-BrC}_6\text{H}_4$) and PCl_5 react with intramolecular rearrangement to give phosphorylated diazetidines (343a).



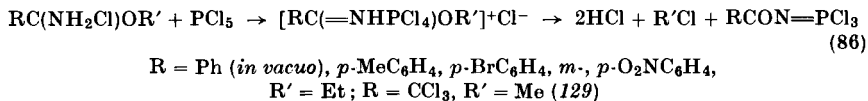
In order to obtain phosphazo compounds, the HCl formed during the reaction has to be removed; for example, $\text{ROCON}=\text{PPh}_2\text{Cl}$ reacts with HCl in the following way:



Similar results are obtained with $(\text{PhO})_3\text{PCl}_2$ (96).

Finally, alkyltetrachlorophosphoranes and perfluorinated carbonyl amides give $\text{R}_f\text{CON}=\text{PRCl}_2$ (327).

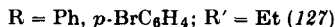
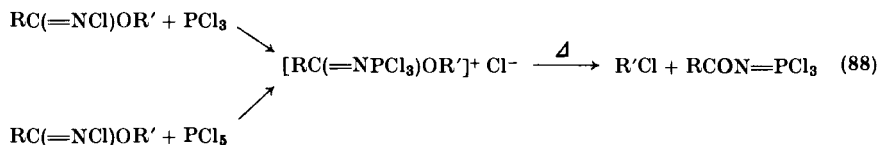
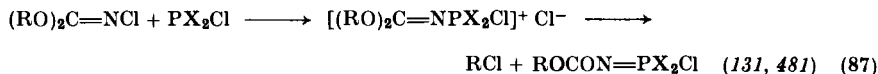
Imidoalkylcarbamates $\text{RC}(=\text{NH})\text{OR}'$ or their hydrochlorides react with PCl_5 to form an ionic compound and then to give carbonylphosphazotrichlorides (129, 134, 247).



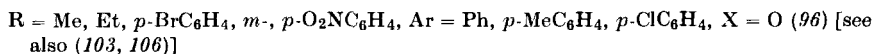
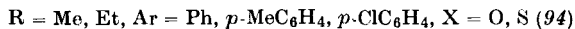
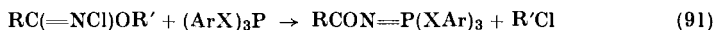
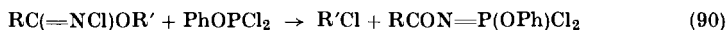
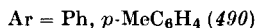
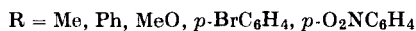
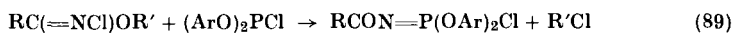
With $\text{R} = \text{Me}$, decomposition giving EtCl , HCl , POCl_3 and MeCN occurs; with $\text{R} = \text{R}' = \text{Et}$ no reaction takes place.

Analogous behavior is observed with PhPCl_4 [$\text{R} = \text{Ph}, p\text{-ClC}_6\text{H}_4, p\text{-BrC}_6\text{H}_4, m\text{-}, p\text{-O}_2\text{NC}_6\text{H}_4$ (132), CHCl_2 , CCl_3 (466)] and Ph_2PCl_3 ($\text{R} = \text{CHCl}_2$, CCl_3) (466). Compounds $\text{RCN}=\text{PPh}_2\text{Cl}$ may alternatively be prepared by the phosphine-azide reaction (90).

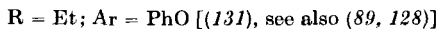
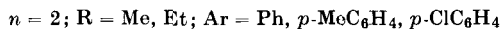
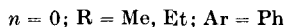
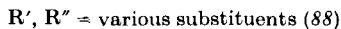
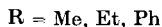
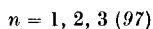
Another route toward carbonylphosphazotrichlorides consists in the action of phosphorus(III) halides on *N*-chloroiminocarbamates, involving an ionic intermediate (96).



The following reactions are known in detail:



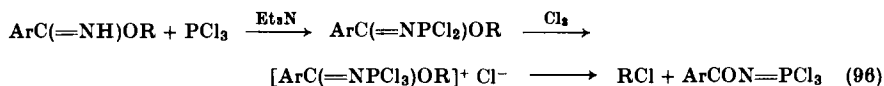
Interaction of $\text{NCC}(=\text{NCl})\text{OEt}$ and $(\text{ArO})_3\text{P}$ ($\text{Ar} = \text{Ph}, p\text{-MeC}_6\text{H}_4, p\text{-ClC}_6\text{H}_4$) gives $\text{NCCON}=\text{P}(\text{OAr})_3$. With trialkylphosphites and at $75^\circ\text{--}80^\circ$ a Michaelis–Arbuzov rearrangement, giving $\text{NCC}[=\text{NPO}(\text{OR})_2]\text{OEt}$, takes place (91).



With PCl_3 , instead, the reaction stops at $[(\text{RO})_2\text{C}=\text{NPCl}_3]^+\text{Cl}^-$ ($\text{R} = \text{Me}$, Et) (127).

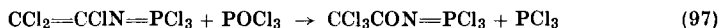
The analogous reaction (100° – 120°) of $(\text{EtO})_2\text{C}=\text{NCl}$ with PR_2Cl [$\text{R} = \text{Ph}$ (100, 126), $p\text{-ClC}_6\text{H}_4$ (126)] or PRCl_2 [$\text{R} = p\text{-ClC}_6\text{H}_4$, Ph_2PN (126), Ph (100, 126)] gives via the (assumed) intermediate phosphazo compound the appropriate isocyanates $\text{RP}(\text{O})\text{CINCO}$ or $\text{R}_2\text{P}(\text{O})\text{NCO}$ with elimination of EtCl ; see also (79, 82, 124, 257).

In a similar way carbonylphosphazotrichlorides are obtained (130).



Finally, compounds $\text{RCON}=\text{PCl}_3$ are formed, as listed in Section VI, B, as intermediates in the interaction of sulfonylphosphazotrichlorides with acyl chlorides [(231), cf. also (71, 72, 221, 222, 235, 372, 375)].

$\text{CCl}_3\text{CON}=\text{PCl}_3$ may also be obtained from $\text{CCl}_2=\text{CCIN}=\text{PCl}_3$ (obtained itself from dichloroacetonitrile and PCl_5 , Section VIII, B, 1) and POCl_3 (307).



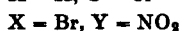
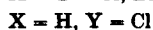
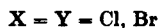
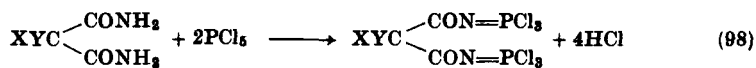
For the reactions of substituted ureas with PCl_5 , see Section IX.

Only few bis(trichlorophosphazoaclys) are known. Urea reacts with 2 moles of PCl_5 on both amide groups,* giving $\text{CO}(\text{N}=\text{PCl}_3)_2$ (233); the analogous compounds $m\text{-C}_6\text{H}_4(\text{CON}=\text{PCl}_3)_2$ (244), $p\text{-C}_6\text{H}_4(\text{CON}=\text{PCl}_3)_2$ (367), $(\text{F}_2\text{C})_n(\text{CON}=\text{PCl}_3)_2$ [$n = 3$ (122, 387e), 4 (387e)], and $(\text{F}_2\text{C})_n(p\text{-C}_6\text{H}_4\text{CON}=\text{PCl}_3)_2$ ($n = 1, 2$) (123, 387e) are known. Similarly, the compounds $\text{A}(\text{CON}=\text{PCl}_3)_2$ [$\text{A} = \text{CCl}_2$, $(\text{CCl}_2\text{CH}_2)_2$, $(\text{CH}_2)_6(\text{CCl}_2)_2$] have been prepared (387e). As for the compounds with one $-\text{CON}=\text{PCl}_3$ group, bis(carbonylphosphazotrichlorides) may be postulated as intermediates in the action of dicarbonyldichlorides on sulfonylphosphazotrichlorides (235, 367). The compound $\text{Cl}_2\text{PPh}=\text{NCOCON}=\text{PPhCl}_2$ is formed from PhPCl_2 and $\text{EtOC}(=\text{NCl})\text{C}(=\text{NCl})\text{OEt}$ (91).

A mixed carbonyl- and sulfonylphosphazotrichloride $p\text{-Cl}_3\text{P}=\text{NSO}_2\text{C}_6\text{H}_4\text{CON}=\text{PCl}_3$ is obtained (367) from p -sulfonamidobenzamide and phosphorus(V) chloride.

Substituted malonic acid diamides and PCl_5 yield bis(carbonylphosphazotrichlorides) (450) without chlorination of the CO group as in the case of the oxalic ester amides.

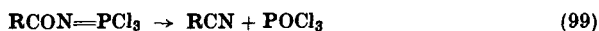
* By-products of this reaction are described (207) in Section IV, C, 1.



Analogous compounds $\text{R}(\text{CON}=\text{PCl}_2)_2$ ($\text{R} = -\text{CCl}_2-, -\text{CCl}_2(\text{CH}_2)_n\text{CCl}_2-, n = 2, 5, 6$) have been described recently (387f).

B. REACTIONS

Nitriles and POCl_3 result from the pyrolysis of carbonylphosphazotrichlorides.



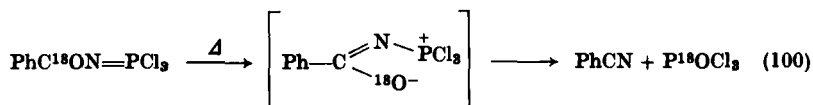
$\text{R} = \text{Ph}$ [(223, 260), cf. also (298)], *o*-, *m*-, *p*- $\text{O}_2\text{NC}_6\text{H}_4$, *o*-, *p*- ClC_6H_4 , *p*- BrC_6H_4 ,

2,4-(O_2N) $_2\text{C}_6\text{H}_3$, 3,5-(O_2N) $_2\text{C}_6\text{H}_3$, 2,4- $\text{Cl}(\text{O}_2\text{N})\text{C}_6\text{H}_3$, 2,4- $\text{Cl}_2\text{C}_6\text{H}_3$ (260), CCl_3 (240),

Ph_2CCl (243), *p*- MeC_6H_4 , 1- C_{10}H_7 , 2- C_{10}H_7 (244)

Hydrogen chloride acts catalytically in the same way at lower temperatures (240).

^{18}O -Labeling in $\text{PhC}^{18}\text{ON}=\text{PCl}_2$ showed that ^{18}O migration from the CO group to the phosphorus atom is involved [via a cyclic mechanism (298)]; the same results apply to $\text{Et}^{18}\text{OC}^{18}\text{ON}=\text{PCl}_2$ (3).



Alkoxy carbonylphosphazotrichlorides $\text{ROCON}=\text{PCl}_2$ give alkyl chlorides and dichlorophosphorylisocyanates on heating.



$\text{R} = \text{Et}$ (3, 223), Me (135, 264)

The compound $\text{PhOCON}=\text{PCl}_2$ decomposes *in vacuo* (80°) to POCl_3 , triphenylecyanurate, cyanuric chloride and PhOPOCl_2 (265).

Similarly, $\text{ROCON}=\text{PX}_2\text{Cl}$ compounds decompose (131, 448) as shown in Eq. (102). Several other papers [(100, 124, 126, 266, 481), see



also (79)] dealing with this formation of isocyanates without isolation of the corresponding carbonylphosphazotrichloride have been published.

Hydrolysis of carbonylphosphazotrichlorides with HCOOH or moist air leads to RCONHPOCl₂. This reaction has been carried out with the



following R: EtOCCl₂, BuOCCl₂ (268); Ph [(223, 259); cf. also (368) and earlier (491)]; *o*-, *m*-, *p*-O₂NC₆H₄, *o*-, *p*-ClC₆H₄, 2,4-(O₂N)₂C₆H₃, 3,5-(O₂N)₂C₆H₃, 2,4-Cl(O₂N)C₆H₃, 2,4-Cl₂C₆H₃ (259); CCl₃ (240); Ph₂CCl, Ph₃C (243); PhOCCl₂, *o*-, *m*-, *p*-MeC₆H₄OCCl₂, 1-C₁₀H₇OCCl₂, 2-C₁₀H₇OCCl₂ (270); Ph₂N (274); *p*-MeC₆H₄, 1-C₁₀H₇, 2-C₁₀H₇ (244); CHF₂CF₂, CHClCF₂, CHCl₂CF₂ (147); CF₃ (210, 330); CNCH₂ (450); C₃F₇ (330); ClCH₂CCl₂, ClCH₂CHCl (117); MeCCl₂ (119); Me₂C(CN), Et₂C(CN), Pr₂C(CN), Bu₂C(CN), Am₂C(CN), and (Me₂CHCH₂CH₂)₂-C(CN) (427).

Similarly RCONHP(O)(CCl₃)Cl (R = CHCl₂, CCl₃, CF₃, *p*-O₂NC₆H₄) (469) and MeOCONHP(O)PhCl (482) have been prepared; EtCCl=NPOCl₂ and PhCCl=NPOCl₂ are synthesized from nitriles and PCl₃ in presence of oxygen (66).

Further hydrolysis [(262), see also (491)] of RCONHPOCl₂ gives the free amides RCONHPO(OH)₂ [R = Ph, *o*-, *m*-, *p*-O₂NC₆H₄, 3,5-(O₂N)₂-C₆H₃, 2,4-(O₂N)₂C₆H₃, *o*-, *p*-ClC₆H₄, 2,4-Cl₂C₆H₃ (262, 454), 2,4-Cl(O₂N)C₆H₃ (262), Ph₂N (274)].

Thermolysis of PhCONHPOCl₂ (1 hr/150°) results in a quantitative yield of PhCN, POCl₃, and HCl (259); Ph₃CONHPOCl₂ shows analogous behavior (243).

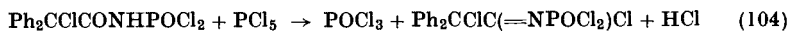
Interaction of RCONHPOCl₂ and PCl₅ gives, in addition to POCl₃, the compounds RCl=NPOCl₂ (XVII) ["isophosphazo compounds," *N*-(dichlorophosphoryl)acylimidochlorides] [R = CCl₃ (240); CF₃ (122); MeCCl₂ (119); *p*-O₂NC₆H₄ (243); Ph, *p*-MeC₆H₄, *o*-, *p*-ClC₆H₄, *o*-, *m*-, *p*-O₂NC₆H₄, 3,5-(O₂N)₂C₆H₃, 2,4-Cl(O₂N)C₆H₃, 2,4-Cl₂C₆H₃, 1-C₁₀H₇, 2-C₁₀H₇ (244); *p*-BrC₆H₄ (296)]. The compound *p*-C₆H₄(CONHPOCl₂)₂ gives similar reactions (367).

The fluorides ArNHCONHPOF₂ (Ar = *p*-ClC₆H₄, *p*-BrC₆H₄, *p*-MeC₆H₄, *p*-MeOC₆H₄, *m*-, *p*-O₂NC₆H₄, 2-C₁₀H₇) and ArNHCONHPOClF (Ar = Ph, *p*-O₂NC₆H₄) react similarly to ArNHC(=NPOF₂)Cl and ArNHC(=NPOFCl)Cl, respectively (114).

The former compounds (XVII) (RCl=NPOCl₂) [R = CCl₃ (240); Ph, *p*-MeC₆H₄, *o*-, *p*-ClC₆H₄, *o*-, *m*-, *p*-O₂NC₆H₄, 3,5-(O₂N)₂C₆H₃, 2,4-Cl(O₂N)C₆H₃, 2,4-Cl₂C₆H₃, 1-C₁₀H₇, 2-C₁₀H₇ (244)] give on thermolysis RCN and POCl₃; with ArONa the corresponding esters are obtained (245).

Compounds ArNHCON=PCl₃ (formed from ArNHCONH₂ plus PCl₅) (Ar = Ph, *p*-MeC₆H₄, *p*-MeOC₆H₄, *p*-BrC₆H₄) rearrange after some time

to *N*-phosphorylchloroformamidines $\text{ArNHC(=NPOCl}_2\text{)Cl}$ (115). The latter compounds may also be obtained from ArNHCONHPOCl_2 and PCl_5 [$\text{Ar} = \text{Ph}$, *o*-, *p*- MeC_6H_4 , *m*-, *p*- ClC_6H_4 , *p*- BrC_6H_4 , *p*- IC_6H_4 , *o*-, *m*-, *p*- $\text{O}_2\text{NC}_6\text{H}_4$, *p*- $\text{F}_3\text{CC}_6\text{H}_4$, 4,3(Me) $\text{O}_2\text{NC}_6\text{H}_3$] (138) and in the aliphatic series from RNHCONH_2 ($\text{R} = \text{Me}$, Et) and phosphorus(V) chloride (113). Analogies (243) are described.



The reaction of phenol with RCON=PCl_3 [$\text{R} = \text{Ph}$, *p*- $\text{O}_2\text{NC}_6\text{H}_4$, 3,5-(O_2N) $_2\text{C}_6\text{H}_3$] gives RCON=P(OPh)Cl_2 or RCON=P(OPh)_3 (105). The synthesis of triesters, i.e., without the isolation of partially chlorinated products, has been described with the following R and Ar substituents: $\text{R} = \text{CCl}_3$, $\text{Ar} = \text{Ph}$, *p*- ClC_6H_4 , Et , Me (241); 1- C_{10}H_7 , 4- $\text{ClC}_{10}\text{H}_6$ (242); $\text{R} = \text{Ph}_2\text{CCl}$, *p*- $\text{O}_2\text{NC}_6\text{H}_4$, $\text{Ar} = 1\text{-C}_{10}\text{H}_7$ (243); $\text{R} = \text{Ph}$, $\text{Ar} = \text{Ph}$ (96, 223, 246); $\text{R} = 1\text{-C}_{10}\text{H}_7$, *p*- ClC_6H_4 , 3,5-(O_2N) $_2\text{C}_6\text{H}_3$, 2,4- $\text{Cl(O}_2\text{N)C}_6\text{H}_3$, $\text{Ar} = \text{Ph}$; $\text{R} = \text{Me}$, *p*- BrC_6H_4 , *m*- $\text{O}_2\text{NC}_6\text{H}_4$, $\text{Ar} = \text{Ph}$, *p*- MeC_6H_4 , *p*- ClC_6H_4 (96); $\text{R} = \text{p-O}_2\text{NC}_6\text{H}_4$, $\text{Ar} = \text{Ph}$ (96, 246); $\text{R} = \text{Ph}_2\text{N}$, $\text{Ar} = \text{Ph}$, *o*-, *p*- ClC_6H_4 , *o*-, *p*- $\text{O}_2\text{NC}_6\text{H}_4$, 1- C_{10}H_7 (274); $\text{R} = \text{Ph}_2\text{CCl}$, $\text{Ar} = 1\text{-C}_{10}\text{H}_7$ (243); $\text{R} = \text{p-FC}_6\text{H}_4$, *m*- $\text{CF}_3\text{C}_6\text{H}_4$, $\text{Ar} = \text{Me}$, Et , Ph , *p*- FC_6H_4 , *p*- ClC_6H_4 , *p*- $\text{O}_2\text{NC}_6\text{H}_4$ (522). Reaction of several carbonylphosphazotrichlorides RCON=PCl_3 ($\text{R} = \text{Ph}$, *p*- ClC_6H_4 , alkyls) with various alcohols, phenol, thiophenol, and amines have been described recently (368a, 387c, 387g).

Some triesters $\text{CF}_3\text{CON=P(OAr)}_3$ are claimed to have been obtained from the reaction of $\text{CF}_3\text{CONHPOCl}_2$ with 3 moles of ArOH ($\text{Ar} = \text{Ph}$, *p*- BrC_6H_4) (122); $\text{CF}_3\text{CON=P(OEt)}_3$ is prepared from an azide-phosphine reaction [(210); see also (478a)].

Dieters RCONHP(O)(OMe)_2 [$\text{R} = \text{CCl}_3$, Ph , *p*- ClC_6H_4 , *m*-, *p*- $\text{O}_2\text{NC}_6\text{H}_4$, 3,5-(O_2N) $_2\text{C}_6\text{H}_3$] can be prepared by direct action of alcohols, e.g., methanol (133, 263); extension to higher alcohols is mentioned in the literature (464).



The analogous reactions of RCON=P(Ar)Cl_2 (466), $\text{RCON=P(CCl}_3\text{)Cl}_2$ (469), RCON=P(OPh)Cl_2 (105), and ArCON=P(Ar')Cl_2 (95) are described.

Alcoholysis in presence of triethylamine yields the free dichlorides (465); the use of sodium alcoholates (241) or excess alcohol (264) gives the triesters, some of which, however, have been obtained on another way (210).

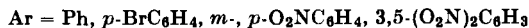
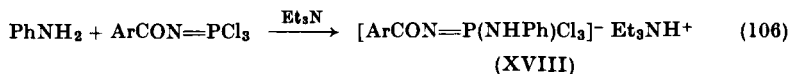
The compounds ArNHCON=P(OR)_3 are only obtained by a phosphine-azide reaction (112).

Finally, it must be mentioned that esters of the type $\text{ROCON}=\text{P}(\text{OR}')_3$ isomerize to $\text{ROCONR}'\text{P}(\text{O})(\text{OR}')_2$ on heating (477).

Excess of aromatic amines with carbonylphosphazotrichlorides (6:1) readily give the amides $\text{ArCON}=\text{P}(\text{NHAr}')_3$ [$\text{Ar} = p\text{-BrC}_6\text{H}_4$, m -, $p\text{-O}_2\text{NC}_6\text{H}_4$, $\text{Ar}' = p\text{-MeC}_6\text{H}_4$ (93); $\text{Ar} = \text{Ar}' = \text{Ph}$ [(93, 104), see also (288a)] in contrast to the very increased difficulty with sulfonylphosphazotrichlorides; $\text{ArCON}=\text{P}(\text{NHAr}')_3$ compounds hydrolyze to $\text{ArCONHPO}(\text{NHAr}')_2$.

The compound $\text{CCl}_3\text{CON}=\text{PCl}_3$ forms 1:1 complexes with DMF or DMA (297d).

Molar ratios of aniline and $\text{ArCON}=\text{PCl}_3$ lead to the monoanilides (ionic form) (XVIII) (107); these salts give,



on hydrolysis (HCOOH , H_2O), $\text{ArCONHPO}(\text{NHPh})\text{Cl}$ and subsequently $\text{ArCONHPO}(\text{NHPh})\text{OH}$; diesters $\text{ArCON}=\text{P}(\text{NHPh})(\text{OPh})_2$ are formed from (XVIII) and PhONa .

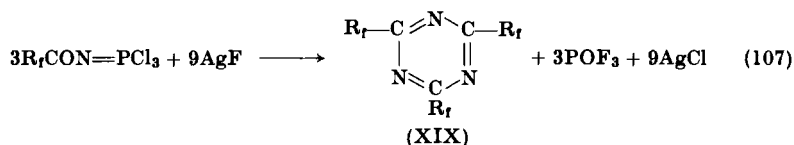
Trisaziridines $\text{ArCON}=\text{P}(\text{NC}_2\text{H}_4)_3$ ($\text{Ar} = \text{Ph}$, o -, $p\text{-ClC}_6\text{H}_4$, o -, $p\text{-BrC}_6\text{H}_4$, m -, $p\text{-O}_2\text{NC}_6\text{H}_4$) are obtained from $\text{ArCON}=\text{PCl}_3$ and ethylenimine at $3^\circ\text{--}7^\circ$ (296); $\text{PhNHCON}=\text{P}(\text{NC}_2\text{H}_4)_3$ and $\text{MeOCON}=\text{P}(\text{NC}_2\text{H}_4)_3$, among others, have been obtained by a phosphine-azide reaction (109).

The compound $p\text{-FC}_6\text{H}_4\text{CON}=\text{PCl}_3$ gives with ethylenimine, in the presence of alcohols ROH ($\text{R} = \text{Me}$, Et , Pr , $i\text{-Pr}$, Bu , $n\text{-C}_6\text{H}_{13}$), compounds of the type $p\text{-FC}_6\text{H}_4\text{CON}=\text{P}(\text{OR})(\text{NC}_2\text{H}_4)_2$ (369a).

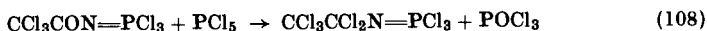
Excess phenylhydrazine and $\text{RCON}=\text{PCl}_3$ ($\text{R} = \text{CCl}_3$, MeCCl_2 , ClCH_2CHCl , $\text{ClCH}_2\text{CCl}_2$, m -, $p\text{-FC}_6\text{H}_4$, $p\text{-BrC}_6\text{H}_4$) give the corresponding hydrazides (387b).

The arylation of arylcarbonylphosphazotrichlorides yields $\text{ArCON}=\text{PPh}_3$ ($\text{Ar} = \text{Ph}$, $p\text{-ClC}_6\text{H}_4$, $p\text{-BrC}_6\text{H}_4$) (92). $\text{NCCON}=\text{PPh}_3$ may be prepared from PPh_3 and $\text{NCC}(=\text{NCl})\text{OEt}$ (91).

The fluorination of $\text{R}_f\text{CON}=\text{PCl}_3$ ($\text{R}_f = \text{CF}_3$, CF_3CF_2 , $\text{CF}_3\text{CF}_2\text{CF}_2$, $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2$) with AgF results in elimination of POF_3 and a ring closure (370) to 2,4,6-tris(perfluoroalkyl)-1,3,5-triazine (XIX).



Chlorination of $\text{CCl}_3\text{CON}=\text{PCl}_3$ with PCl_5 or Cl_2 yields $\text{CCl}_3\text{CCl}_2\text{N}=\text{PCl}_3$ (424).



The compounds $(\text{CF}_2)_3(\text{CON}=\text{PCl}_3)_2$ and $(\text{CF}_2)_n(p\text{-C}_6\text{H}_4\text{CON}=\text{PCl}_3)_2$ ($n = 1, 2$) react with HCOOH to give $(\text{CF}_2)_3(\text{CONHPOCl}_2)_2$ and $(\text{CF}_2)_n(p\text{-C}_6\text{H}_4\text{CONHPOCl}_2)_2$, respectively. Reaction of these compounds with sodium alcoholates and amines has been mentioned (123). The interaction of $\text{R}(\text{CON}=\text{PCl}_3)_2$ with various alcohols, amines, etc., is described (387d, 387f); *m*- and *p*- $\text{C}_6\text{H}_4(\text{CON}=\text{PCl}_3)_2$ and ethylenimine give the corresponding hexamides *m*- and *p*- $\text{C}_6\text{H}_4[\text{CON}=\text{P}(\text{NC}_2\text{H}_4)_3]_2$ (367). Thermolysis of *m*- $\text{C}_6\text{H}_4(\text{CON}=\text{PCl}_3)_2$ gives POCl_3 and isophthalic dinitrile; its hydrolysis (HCOOH) leads to *m*- $\text{C}_6\text{H}_4(\text{CONHPOCl}_2)_2$ (244).

A compound $\text{Et}_2\text{C}(\text{Br})\text{CONHP}(\text{O})(\text{NHPOCl}_2)_2$ has been reported in the literature (168). Finally, $\text{Ph}_3\text{P}=\text{NCOCON}=\text{PPh}_3$ is formed from PPh_3 and $\text{EtOC}(=\text{NCl})\text{C}(=\text{NCl})\text{OEt}$ (91).

C. SPECTROSCOPIC INVESTIGATIONS

Only a few spectroscopic data for carbonylphosphazotrichlorides are available.

The $\nu_{\text{P}=\text{N}}$ of $\text{RCON}=\text{PCl}_3$ ($\text{R} = \text{CCl}_3, \text{CF}_3, \text{Ph}, p\text{-ClC}_6\text{H}_4$) is found in the range $1290\text{--}1360\text{ cm}^{-1}$ (98); for $\text{CF}_3\text{CON}=\text{PCl}_3$ the assignment has been made at 1381 cm^{-1} (210).

An infrared investigation of $^{14}\text{N}/^{15}\text{N}$ -labeled compounds $\text{RCON}=\text{PCl}_3$ ($\text{R} = \text{CF}_3, \text{CCl}_3, \text{Ph}, p\text{-ClC}_6\text{H}_4, p\text{-O}_2\text{NC}_6\text{H}_4, p\text{-FC}_6\text{H}_4, p\text{-MeC}_6\text{H}_4, \text{MeO}, \text{EtO}$) has been made recently (475).

The $\text{P}=\text{N}$ band in the esters $\text{ArCON}=\text{P}(\text{OR})_3$ ($\text{Ar} = \text{Ph}, m\text{-}, p\text{-O}_2\text{NC}_6\text{H}_4$; $\text{R} = \text{Me}, \text{Et}, \text{Pr}, i\text{-Pr}$; $\text{Ar} = \text{Ph}, \text{R}' = \text{Me}, \text{Ph}$) has been found (90) to be typical at $1340\text{--}1360\text{ cm}^{-1}$; another paper (210) gives a wider range of $1317\text{--}1415\text{ cm}^{-1}$. The $\nu_{\text{P}=\text{N}}$ for $\text{MeCON}=\text{P}(\text{OEt})_3$ lies at $1350\text{--}1385\text{ cm}^{-1}$ (212). Infrared spectra of $\text{CCl}_3\text{CON}=\text{PPh}(\text{OPh})_2$ (467), $\text{MeOCON}=\text{P}(\text{OPh})_2(\text{NHPh})$, and $\text{MeOCON}=\text{P}(\text{OPh})_2\text{NH}_2$ (102) have been reported.

Matrosov (331) carried out a calculation of the IR spectra of $\text{CCl}_3\text{CON}=\text{PCl}_3$ and $(\text{EtO})_3\text{P}=\text{NP}(\text{O})(\text{OEt})_2$ and assigns the $\nu_{\text{P}=\text{N}}$ to a range of $1290\text{--}1415\text{ cm}^{-1}$, in accordance with experimental results. It is mentioned that the $\nu_{\text{P}=\text{N}}$ is strongly dependent on the substituents at the nitrogen atoms and to a lesser extent on those at the phosphorus atom [see also (295)]. The compounds $\text{PhCON}=\text{PR}_3$ exhibit the $\nu_{\text{P}=\text{N}}$ at 1332 cm^{-1} ($\text{R} = \text{Ph}$) and at 1341 cm^{-1} ($\text{R} = \text{Bu}$), $\text{PhCON}=\text{PPh}_2\text{Et}$ at 1337 cm^{-1} , and $\text{EtOCON}=\text{PPh}_3$ at 1268 and 1281 cm^{-1} , respectively (520).

Only a few ^{31}P NMR chemical shifts have been measured (475): $\text{CCl}_3\text{CON}=\text{PCl}_3$ ($\delta_{\text{P}} = -25.1$ ppm), $\text{PhCON}=\text{PCl}_3$ ($\delta_{\text{P}} = -13.2$ ppm), $p\text{-O}_2\text{NC}_6\text{H}_4\text{CON}=\text{PCl}_3$ ($\delta_{\text{P}} = -18.7$ ppm), $p\text{-FC}_6\text{H}_4\text{CON}=\text{PCl}_3$ ($\delta_{\text{P}} = -15.0$ ppm), $p\text{-MeC}_6\text{H}_4\text{CON}=\text{PCl}_3$ ($\delta_{\text{P}} = -12.2$ ppm), $\text{MeOCON}=\text{PCl}_3$ ($\delta_{\text{P}} = -8.9$ ppm), and $\text{EtOCON}=\text{PCl}_3$ ($\delta_{\text{P}} = -7.3$ ppm).

VIII. Aryl- and Alkylphosphazotrihalides

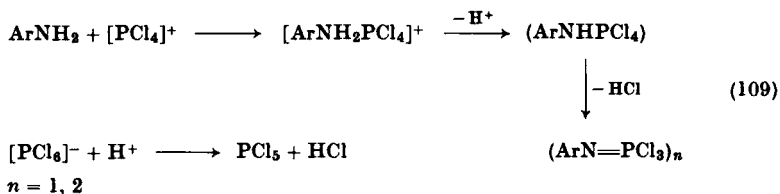
A. TRICHLOROPHOSPHAZOARYLS

1. Syntheses

Gilpin (172) described the reaction of equimolar amounts of PCl_5 and aniline hydrochloride at 170° , but the resulting compound $\text{C}_6\text{H}_5\text{NPCl}_3$ was not further characterized. The same compound is mentioned without further specification in some patents (322). Recent work uses PCl_5 and primary aromatic amines (or their hydrochlorides) in CCl_4 (535) or a twice molar ratio of the amine in CCl_4 (538).

As found from infrared spectra and molecular weight measurements, dimerization of the resulting compounds occurs when the amine used has a basicity constant K_{B} (in aqueous solution) greater than 10^{-10} . If $K_{\text{B}} = 10^{-10}$ – 10^{-13} , the compounds are dimeric in the solid state, but monomeric in benzene solution; with amines of $K_{\text{B}} = 10^{-14}$ – 10^{-19} , only monomeric compounds are obtained (535).

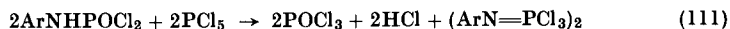
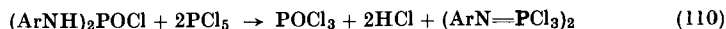
The following steps for this reaction have been proposed :



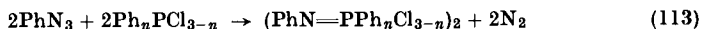
The following $(\text{ArN}=\text{PCl}_3)_2$ ($n = 1$ or 2) have been obtained: Ar = Ph, *o*-, *p*- MeC_6H_4 , *o*-, *m*-, *p*- ClC_6H_4 (535, 538), * *m*- MeC_6H_4 , *o*-, *m*-, *p*- BrC_6H_4 , 2,4- $\text{Cl}_2\text{C}_6\text{H}_3$, 2,4- $\text{Br}_2\text{C}_6\text{H}_3$, 3,5- $\text{Me}_2\text{C}_6\text{H}_3$, *p*- MeOC_6H_4 , *p*- EtOC_6H_4 , 3,5- $\text{Cl}_2\text{C}_6\text{H}_3$, *o*-, *m*-, *p*- $\text{O}_2\text{NC}_6\text{H}_4$, 2,4-(O_2N) $_2\text{C}_6\text{H}_3$, 2,4,6- $\text{Cl}_3\text{C}_6\text{H}_2$, 2,4,6- $\text{Br}_2\text{C}_6\text{H}_2$, 2,4,6- $\text{Cl}_2(\text{O}_2\text{N})\text{C}_6\text{H}_2$ (535), *o*-, *m*-, *p*- FC_6H_4 , 2,4- $\text{F}_2\text{C}_6\text{H}_3$, 2,5- $\text{F}_2\text{C}_6\text{H}_3$, 2,3,4,5- $\text{F}_4\text{C}_6\text{H}$, 2,3,5,6- $\text{F}_4\text{C}_6\text{H}$ [(502), see also (500)], $\text{ClSO}_2\text{C}_6\text{H}_4$ (50, 354), *o*-, *m*-, *p*- $\text{CF}_3\text{C}_6\text{H}_4$, 2-F,5- $\text{CF}_3\text{C}_6\text{H}_3$ (46), *o*-, *m*-, *p*- $\text{Me}_2\text{NSO}_2\text{C}_6\text{H}_4$ (549), 5-Me, 2-NCC $_6\text{H}_3$ (401).

* *p*- $\text{ClC}_6\text{H}_4\text{N}=\text{PCl}_3$ has also been isolated (510) as a by-product of $\text{PhNHSO}_2\text{N}=\text{PCl}_3$ and PCl_5 (Section VI,B) and from another reaction (361a) (Section VIII,B,1).

Arylphosphazotrichlorides can also be obtained by phosphorylation (PCl_5) of ArNHPOCl_2 , $\text{ArNHPO}(\text{OPh})_2$, $\text{ArNHPO}(\text{OPh})\text{Cl}$, $(\text{ArNH})_2\text{POCl}_2$, and $(\text{ArNH})_3\text{PO}$ (535, 536) or of $\text{ArNHPO}(\text{Cl})\text{NArPOCl}_2$ ($\text{Ar} = \text{Ph}$, $p\text{-MeC}_6\text{H}_4$, $p\text{-BrC}_6\text{H}_4$, $3,5\text{-Me}_2\text{C}_6\text{H}_3$) (536).



Compounds $\text{PhN}=\text{PPh}_n\text{Cl}_{3-n}$ ($n = 0, 1, 2$) may be generated from an azide-phosphine reaction using $\text{Ph}_n\text{PCl}_{3-n}$ and phenyl azide (65).



$(\text{PhN}=\text{PCl}_3)_2$ should be formed as an intermediate in the thermolysis of 2-phospha-1,3-diazetidin-4-ones as well as isocyanate. These two products react further to form a carbodiimide and POCl_3 (495-498).

Finally, dimeric arylphosphazotrichlorides (1,3,2,4-diaryldiazadi-phosphetidines) are obtained on chlorination (Cl_2) of arylaminothio-phosphoryldichlorides (99).

In an analogous manner PhPCl_4 reacts with ArNH_3Cl [$\text{Ar} = \text{Ph}$, o -, m -, $p\text{-MeC}_6\text{H}_4$, o -, m -, $p\text{-ClC}_6\text{H}_4$, $p\text{-MeOC}_6\text{H}_4$, $p\text{-EtOC}_6\text{H}_4$, $2,4\text{-Cl}_2\text{C}_6\text{H}_3$, $2,4,6\text{-Cl}_3\text{C}_6\text{H}_2$, o -, m -, $p\text{-BrC}_6\text{H}_4$, $2,4\text{-Br}_2\text{C}_6\text{H}_3$, $2,4,6\text{-Br}_3\text{C}_6\text{H}_2$, o -, m -, $p\text{-O}_2\text{NC}_6\text{H}_4$, $2,4\text{-(O}_2\text{N)}_2\text{C}_6\text{H}_3$, $2,4,6\text{-Cl}_2\text{(O}_2\text{N)C}_6\text{H}_2$] to give $\text{ArN}=\text{PPhCl}_2$ (537). With Ph_2PCl_3 and only in presence of pyridine the corresponding compounds $\text{ArN}=\text{PPh}_2\text{Cl}$ ($\text{Ar} = \text{Ph}$, $o\text{-MeC}_6\text{H}_4$, o -, $p\text{-ClC}_6\text{H}_4$, $2,4\text{-Cl}_2\text{C}_6\text{H}_3$, $p\text{-BrC}_6\text{H}_4$, $p\text{-EtOC}_6\text{H}_4$, m -, $p\text{-O}_2\text{NC}_6\text{H}_4$) are obtained [(537, 540); see also (192a)].



Similarly MePCl_4 gives $(\text{ArN}=\text{PCl}_2\text{Me})_n$ ($n = 1$, $\text{Ar} = p\text{-ClC}_6\text{H}_4$, o -, $p\text{-BrC}_6\text{H}_4$, $o\text{-MeC}_6\text{H}_4$, $2,4\text{-Cl}_2\text{C}_6\text{H}_3$, $p\text{-O}_2\text{NC}_6\text{H}_4$, $2,4\text{-(O}_2\text{N)}_2\text{C}_6\text{H}_3$; $n = 2$, $\text{Ar} = o$ -, $p\text{-ClC}_6\text{H}_4$, $o\text{-BrC}_6\text{H}_4$) (526). $\text{C}_6\text{F}_5\text{N}=\text{PCl}_3$ is obtained from the reaction of PCl_5 with $\text{C}_6\text{F}_5\text{NSO}$ (188c).

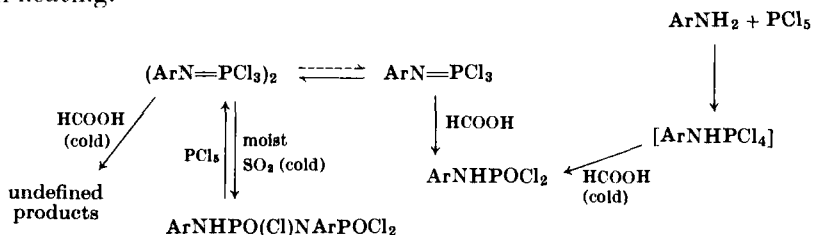
A difluorotetrachlorodiazadiphosphetidine $(\text{FCl}_2\text{P}=\text{NPh})_2$ has been synthesized (37) from aniline hydrochloride and PCl_2F_3 (see also Section VIII, C).

Aminobenzenesulfonamides o -, m -, $p\text{-H}_2\text{NSO}_2\text{C}_6\text{H}_4\text{NH}_2$ react with PCl_5 at both amino groups to form o -, m -, $p\text{-Cl}_3\text{P}=\text{NSO}_2\text{C}_6\text{H}_4\text{N}=\text{PCl}_3$ (549) (Section VI, A). The para isomer has also been synthesized independently (354, 489); only the ortho isomer is dimeric, the meta and para isomers are monomeric.

2. Reactions

The monomeric and dimeric forms of $(\text{ArN}=\text{PCl}_3)_n$ ($n = 1, 2$) show different behaviors upon hydrolysis.

$\text{ArN}=\text{PCl}_3$ compounds hydrolyze with HCOOH to form ArNHPOCl_2 [$\text{Ar} = 2,4,6\text{-Cl}_3\text{C}_6\text{H}_2$, $2,4,6\text{-Br}_3\text{C}_6\text{H}_2$, $2,4\text{-(O}_2\text{N)}_2\text{C}_6\text{H}_3$, $2,4,6\text{-Cl}_2(\text{O}_2\text{N})\text{-C}_6\text{H}_2$ (536); Ph , o -, p - MeC_6H_4 , m -, p - ClC_6H_4 , $2,4\text{-Cl}_2\text{C}_6\text{H}_3$, $2,4\text{-Br}_2\text{C}_6\text{H}_3$ (538); o - ClC_6H_4 (297a, 538); o - $\text{Me}_2\text{NSO}_2\text{C}_6\text{H}_4$ (549)]. In contrast, hydrolysis of the dimers in the cold results in ring opening to yield $\text{ArNHPO}(\text{Cl})\text{NArPOCl}_2$ ($\text{Ar} = \text{Ph}$, p - MeC_6H_4 , p - BrC_6H_4 , $3,5\text{-Me}_2\text{C}_6\text{H}_3$) (536). The temperature control of this hydrolysis reaction is probably the most important factor, because the dimeric products monomerize in solution on heating.



Compounds $\text{ArN}=\text{PPhCl}_2$ hydrolyze similarly to $\text{ArNHP}(\text{O})\text{PhCl}$ (539).

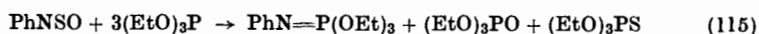
Ammonolysis of $(\text{PhN}=\text{PCl}_3)_2$ gives an ionic compound $[\text{PhNHP}(\text{NH}_2)_2]_2\text{N}^+\text{Cl}^-$ (504). The reaction with methylamine yields only a polymeric substance (219) (see also Section VIII, B, 2); fluorophenylphosphazotrichlorides also give saltlike compounds with liquid ammonia (502).

Polymers with $[\text{HN}=\text{P}(\text{Cl})\text{N}]_n$ units have been obtained by the reaction of $(\text{PhN}=\text{PCl}_3)_2$ with urea or melamine at elevated temperatures (525a).

By the action of diethylamine on $(\text{PhN}=\text{PCl}_3)_2$ gradual substitution of the chlorine atoms occurs to monomeric compounds $\text{PhN}=\text{P}(\text{NEt}_2)_{3-n}\text{Cl}_n$ ($n = 0, 1, 2$) (184); analogous substances $\text{PhN}=\text{P}(\text{X})\text{Cl}_2$ [$\text{X} = \text{NMe}_2$, NBu_2 , $\text{N}(\text{Me})\text{CH}_2\text{Ph}$] have been synthesized (501) which give, on ammonolysis, tetraminophosphonium salts $[\text{PhNHP}(\text{X})(\text{NH}_2)_2]^+\text{Cl}^-$ [$\text{X} = \text{NMe}_2$, NEt_2 , NBu_2 , $\text{N}(\text{Me})\text{CH}_2\text{Ph}$] (501). The reaction of $\text{PhN}=\text{P}(\text{NEt}_2)\text{Cl}_2$ with other secondary amines leads to $\text{PhN}=\text{P}(\text{NEt}_2)\text{YCl}$ ($\text{Y} = \text{NMe}_2$, NEt_2 , NPr_2 , NBu_2 , morpholine, piperidine, pyrrolidine) which hydrolyze to unsymmetrical phosphine oxides $\text{PhNHP}(\text{O})(\text{NEt}_2)\text{Y}$ (47).

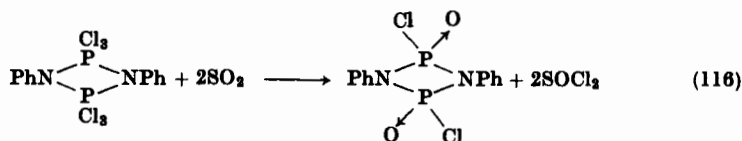
Trisaziridines $\text{ArN}=\text{P}(\text{NC}_2\text{H}_4)_3$ have only been obtained from the phosphine $\text{P}(\text{NC}_2\text{H}_4)_3$ and the corresponding azide ($\text{Ar} = \text{Bu}$, Ph , p - PhC_6H_4 , p - BrC_6H_4 , p - MeC_6H_4 , o -, m -, p - $\text{O}_2\text{NC}_6\text{H}_4$) (109).

Trichlorophosphazoyls give with PhONa the triesters $\text{ArN}=\text{P}(\text{OPh})_3$ [$\text{Ar} = \text{Ph}$, *o*-, *m*-, *p*- MeC_6H_4 , *o*-, *m*-, *p*- BrC_6H_4 , *o*-, *m*-, *p*- $\text{O}_2\text{NC}_6\text{H}_4$, *o*-, *m*-, *p*- ClC_6H_4 , *p*- MeOC_6H_4 , *p*- EtOC_6H_4 , 3,5- $\text{Me}_2\text{C}_6\text{H}_3$, 2,4- $\text{Cl}_2\text{C}_6\text{H}_3$, 2,5- $\text{Cl}_2\text{C}_6\text{H}_3$, 2,4- $\text{Br}_2\text{C}_6\text{H}_3$, 2,4-(O_2N) $_2\text{C}_6\text{H}_3$, 2,4,6- $\text{Cl}_3\text{C}_6\text{H}_2$, 2,4,6- $\text{Br}_3\text{C}_6\text{H}_2$, 2,6,4- $\text{Cl}_2(\text{O}_2\text{N})\text{C}_6\text{H}_2$] (546), which with water yield the diesters $\text{ArNHPO}(\text{OPh})_2$ [see also (549)]. Some $\text{ArN}=\text{P}(\text{OPh})_3$ [$\text{Ar} = \text{Ph}$, *p*- $\text{O}_2\text{NC}_6\text{H}_4$, 2,4-(O_2N) $_2\text{C}_6\text{H}_3$, 3,4-(O_2N) $_2\text{C}_6\text{H}_3$, 5- O_2N , 2-pyridyl- C_6H_3 , 2,4,6-(O_2N) $_3\text{C}_6\text{H}_2$] are also obtained from $(\text{PhO})_3\text{P}$ and the corresponding amine; $\text{PhN}=\text{P}(\text{OPh})_3$ is also obtained from $(\text{PhO})_3\text{PCl}_2$ and aniline (534). Compounds $\text{PhN}=\text{P}(\text{OR})_3$ ($\text{R} = \text{Me}$, Et , Pr , Me_2CH) have only been prepared by an azide-phosphine reaction (208); $\text{PhN}=\text{P}(\text{OEt})_3$ may also be prepared (518) using the method indicated in Eq. (115).



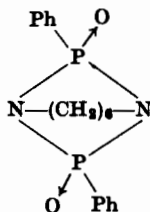
2,2,2,4,4,4-Hexachloro-1,3-diphenyl-1,3,2,4-diazadiphosphetidine reacts with phenylisocyanate at 150° (with postulated monomerization) to give diphenylcarbodiimide* (494–496, 498). With CO_2 or CS_2 the corresponding isocyanate and thioisocyanate are obtained (494).

Reaction of $(\text{PhN}=\text{PCl}_3)_2$ with sulfur dioxide yields 2,4-dichloro-2,4-dioxo-1,3-diphenyl-1,3,2,4-diazadiphosphetidine (181). This compound



was made previously by Michaelis (334, 335) from POCl_3 and aniline. Action of HCl on it produces a ring opening to $\text{ArNHP}(\text{O})\text{ClNArPOCl}_2$ ($\text{Ar} = \text{Ph}$, *p*- MeC_6H_4 , *p*- ClC_6H_4) (297a), also obtained by hydrolysis of $(\text{ArN}=\text{PCl}_3)_2$.

Analogous compounds, such as $(\text{RN}=\text{P}(\text{O})\text{R}')_2$ ($\text{R} = \text{Ph}$, $\text{R}' = \text{Et}$) and



(from PhPOCl_2 and hexamethylenediamine), are known (53).

* Isocyanates do not react with alkylsulfonylphosphazotrichlorides (495, 496).

The monomeric compound $o\text{-Me}_2\text{NSO}_2\text{C}_6\text{H}_4\text{N}=\text{PCl}_3$ gives with HCOOH a quantitative yield of $o\text{-Me}_2\text{NSO}_2\text{C}_6\text{H}_4\text{NHPOCl}_2$, whereas the (dimeric) meta and para isomers do not react in this way (549). Reaction with RONa in absolute alcohol gives the diesters $o\text{-}$, $m\text{-}$, $p\text{-Me}_2\text{NSO}_2\text{-C}_6\text{H}_4\text{NHP(O)(OR)}_2$ ($\text{R} = \text{Me}$; for the ortho isomer also $\text{R} = \text{Ph}$) (549).

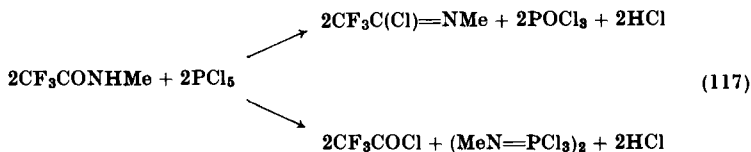
For the reactions of $o\text{-}$, $m\text{-}$, $p\text{-Cl}_3\text{P}=\text{NSO}_2\text{C}_6\text{H}_4\text{N}=\text{PCl}_3$, see Section VI, B.

B. ALKYLPHOSPHAZOTRICHLORIDES

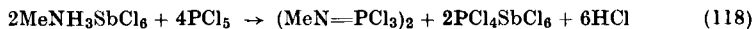
1. Syntheses

2,2,2,4,4,4-Hexachloro-1,3-dimethyl-1,3,2,4-diazadiphosphetidine, $(\text{MeN}=\text{PCl}_3)_2$, was first synthesized independently by Haasemann (186) and Chapman and co-workers (69) from the reaction of methylamine hydrochloride and PCl_5 in symmetric $\text{C}_2\text{H}_2\text{Cl}_4$. The heat of formation was found to be -217.3 ± 0.5 kcal/mole (166); the energy of this P-N bond is 74.3 kcal/mole (166) and thus lies between the energy of a single bond (66.8 kcal/mole) and a double bond (98 kcal/mole), so that in some extent delocalization of the nitrogen electron pair can be assumed (519) (see also Section VIII, D, 3).

Other routes to the synthesis of $(\text{MeN}=\text{PCl}_3)_2$ are the action of PCl_5

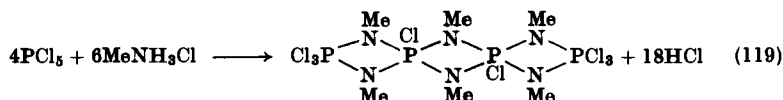


on N -methyltrifluoroacetamide (352) and the (indirect) synthesis from $[\text{MeNH}_3]^+\text{SbCl}_6^-$ (395).



Minor amounts of $(\text{MeN}=\text{PCl}_3)_2$ are formed in the reaction of MeNH_3Cl with PCl_5 in presence of BCl_3 (34) or AlCl_3 (509a) (where six-membered ring compounds are formed, see Section IV, A, 2) and by the action of PCl_5 on N,N' -dimethylsulfamide (36b, 510), as well as by the reaction of PCl_5 or PhPCl_4 with $\text{Me}_3\text{SiN}(\text{Me})\text{PCl}_2=\text{NSO}_2\text{Cl}$ (50b). Another way is the chlorination of methylaminothiophosphoryldichloride (99).

A by-product (3%) of the normal synthesis of $(\text{MeN}=\text{PCl}_3)_2$ ($\text{MeNH}_3\text{Cl} + \text{PCl}_5$) is formed according to Eq. (119) (31, 32).



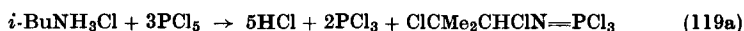
Higher alkylphosphazotrichlorides $(\text{RN}=\text{PCl}_3)_n$ ($n = 1, 2$) are known with the following R: Et, Pr, Bu, Am (185, 528); $n\text{-C}_6\text{H}_{13}$ to $n\text{-C}_{10}\text{H}_{21}$ (185); $\text{ClCMe}_2\text{CHCl}$, $\text{ClCMe}_2\text{CH}_2$, Me_3C (528); *i*-Pr (185); *i*-Bu* (142); $\text{Me}_2\text{CClCH}_2$ (528); Me_3C (527c, 528); Me_3CCH_2 (529); Et_2CH (527a, 529); $\text{Me}_3\text{CCH}_2\text{CH}_2$, Et_2CH , PhCH_2 , PhCH_2CH_2 , $\text{Me}_3\text{CCCl}_2\text{CHCl}$, † $(\text{ClCH}_2)_2\text{CH}$, † ClCH_2CH_2 † (529); $\text{Me}_2\text{CHCH}_2\text{CH}_2$, $\text{EtCH}(\text{Me})\text{CH}_2$ (185); Ph_2CH (543); $(\text{CF}_3)_2\text{CH}$, $(\text{CF}_3)_2\text{CCl}$, $(\text{CF}_3)_3\text{C}$ (295); $\text{ClSO}_2(\text{CH}_2)_n$ ($n = 2-4$) (542).

It has been shown (185) that in the case of isoalkylamines not only the basicity of the amine involved (as for the arylamines), but also the place of branching, influences whether the monomer or the dimer is formed. Thus, α -branched isoamines yield monomeric compounds (with the exception of $(i\text{-PrN}=\text{PCl}_3)_2$), β -branched amines yield either monomeric or dimeric species, and γ -branched amines yield only the dimeric compounds.

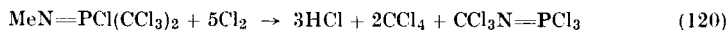
Similarly $(\text{RN}=\text{PPhCl}_2)_2$ compounds ($\text{R} = \text{Me, Et, Pr, Bu}$) are prepared from PhPCl_4 and alkylammonium chlorides (527); $(\text{MeN}=\text{PPh}_2\text{Cl})_2$ has only been synthesized from the azide and Ph_2PCl (196), whereas MeNH_3Cl and Ph_2PCl_3 yield only the ionic compound $[\text{MeNHPClPh}_2]^+\text{Cl}^-$ (192a, 519), which is also obtained from Ph_2PONHMe and PCl_5 (192a). Interaction of $(\text{CCl}_3)_2\text{PCl}_3$ and aliphatic amines gives the monomeric compounds $(\text{CCl}_3)_2\text{CIP}=\text{NR}$ ($\text{R} = \text{Me, Et, Pr, } i\text{-Pr, Bu, C}_6\text{H}_{11}$) (294b).

Partially or fully halogenated trichlorophosphazohaloalkyls are known: $(\text{CH}_2\text{ClN}=\text{PCl}_3)_2$ is formed in 40–63% yield by the reaction of aminomethanesulfonic acid with a 3.5-fold excess of PCl_5 (338, 542); tris(chloromethyl)amine $\text{N}(\text{CH}_2\text{Cl})_3$ is also formed in the reaction (338). $(\text{CH}_2\text{ClN}=\text{PCl}_3)_2$ results also on careful chlorination of $(\text{MeN}=\text{PCl}_3)_2$ (141a). The attempted synthesis of $(\text{CHCl}_2\text{N}=\text{PCl}_3)_n$ ($n = 1$ or 2) by the action of PCl_5 on HCN failed (44). The fully chlorinated monomeric compound $\text{CCl}_3\text{N}=\text{PCl}_3$ may be prepared by chlorination (UV) of $(\text{MeN}=\text{PCl}_3)_2$ (142, 294), thiophosphoric triisocyanate (162), or $\text{MeN}=\text{PCl}(\text{CCl}_3)_2$ (294b). Smaller yields of $\text{CCl}_3\text{N}=\text{PCl}_3$ are formed in the

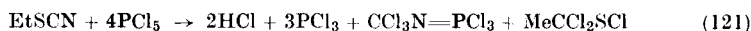
* *i*- BuNH_3Cl reacts with excess PCl_5 to give $\text{CCl}_2=\text{C}(\text{CHCl}_2)\text{N}=\text{PCl}_3$ (527b) or $\text{ClCMe}_2\text{CHClN}=\text{PCl}_3$ (528):



† Only when excess PCl_5 is used during the reaction (529).



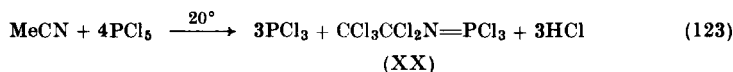
thermolysis (120° – 130°) of $[\text{EtSCCl-NPCl}_3]^+\text{PCl}_6^-$ along with HCl , MeCHClSCl , and PCl_3 (442) and by the action of excess PCl_5 on EtSCN or ArSCN ($\text{Ar} = \text{Ph}$, $p\text{-MeC}_6\text{H}_4$, $p\text{-O}_2\text{NC}_6\text{H}_4$) (442, 443). It can also be obtained from the reaction of Cl_2CNCNCl with PCl_3 (188a).



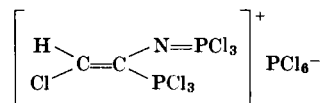
Higher aminoalkanesulfonic acids and excess PCl_5 react with partial chlorination of the SO_3H group and formation of the following $\text{RN}=\text{PCl}_3$ compounds (542): $\text{R} = \text{CCl}_3\text{CHCl}$, $\text{Me}_2\text{CCl}_2\text{CHCl}$, $\text{EtCCl}_2\text{CHCl}$, and $\text{Me}_2\text{CClCHCl}$; see also the phosphorylation of nitriles.

Because of the numerous publications in the field, the phosphorylation of nitriles is considered somewhat in detail.

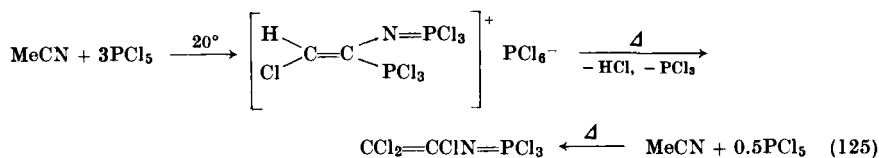
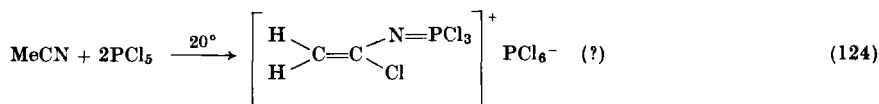
Acetonitrile and chloroacetonitrile give with PCl_5 different products depending on temperature and ratio of the reactants (425).



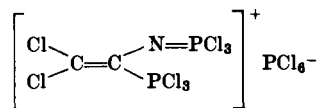
Acetonitrile and PCl_5 (2:1) at 80° give an intermediate compound, $\text{CH}_2=\text{CCIN} \cdot \text{PCl}_3$, which may be chlorinated to (XX) (425). Other workers (307), in contrast, find the action of MeCN and PCl_5 (1:3) at room temperature to give only the ionic compound



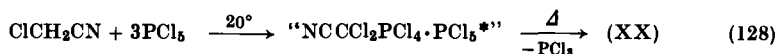
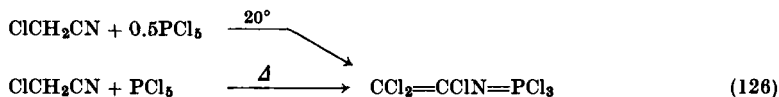
(see Section IV, D, 1), which decomposes at 130° – 150° to $\text{CCl}_2\text{-CCIN} \cdot \text{PCl}_3$; the same result is found in later work by Shevchenko and Bodnar-chuk (423).



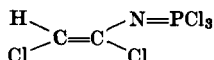
Chloroacetonitrile and PCl_5 (1:3) react at room temperature to form



which decomposes on heating to give compound (XX) (307, 423). Kirsanov and co-workers describe various products which are obtained by this reaction (239, 425).



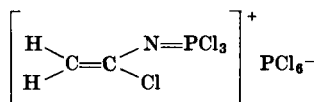
Chloroacetonitrile and PCl_5 (2:1) at elevated temperature give



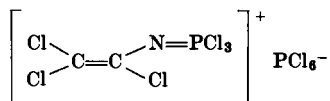
(307); fluoroacetonitrile under the same conditions gives $\text{FClCHCCl}_2\text{N}=\text{PCl}_3$ (239, 280, 425).

Phosphorylation of dichloroacetonitrile with PCl_5 (1:0.4) in the cold yields $\text{CCl}_2=\text{CClN}=\text{PCl}_3$, which upon chlorination with Cl_2 or PCl_5 gives (XX) (239, 281, 307, 424); $\text{CCl}_2=\text{CClN}=\text{PCl}_3$ may also be obtained from

* Rather to be formulated as



and



respectively.

thermolysis of $[\text{Cl}_3\text{P}=\text{NCCl}=\text{CHPCl}_3]^+\text{PCl}_6^-$ (Section IV, D, 2) (423) or by heating $\text{Cl}_3\text{P}=\text{NCCl}_2\text{CCl}_2\text{POCl}_2$ at $150^\circ\text{--}170^\circ$ (423).

Compound (XX) is also obtained from $\text{CCl}_3\text{CON}=\text{PCl}_3$ and PCl_5 [Eq. (108)] or from $\text{CCl}_3\text{CCl}=\text{NPOCl}_2$ and PCl_5 (424), as well as from thermo-



lysis of $[\text{Cl}_3\text{P}=\text{NCCl}=\text{CClPCl}_3]^+\text{PCl}_6^-$ besides PCl_3 (423). The same compound (XX) is obtained from the interaction of trichloroacetonitrile* and PCl_5 (1:1) at $140^\circ\text{--}150^\circ$ (291) and from the chlorination (UV) of $(\text{EtN}=\text{PCl}_3)_2$ (142) or $\text{CHCl}_2\text{CCl}(\text{COCl})\text{N}=\text{PCl}_3$ at $200^\circ\text{--}210^\circ$ (532). It results also as a by-product of the reactions of $\text{CHCl}(\text{COCl})\text{N}=\text{PCl}_3$ (532)



and $\text{NCCCl}_2\text{CCl}_2\text{N}=\text{PCl}_3$ or $\text{CCl}_2(\text{CN})_2$ (290c) with PCl_5 .

The compound $\text{CF}_3\text{CCl}_2\text{N}=\text{PCl}_3$ is obtained from CF_3CFCINO and PCl_3 (336); $(\text{CF}_3)_2\text{CCIN}=\text{PCl}_3$ results from the chlorination of $(\text{CF}_3)_2\text{CHN}=\text{PCl}_3$ (295), and $\text{PhCCl}=\text{CCIN}=\text{PCl}_3$ (239, 281) and $\text{PhCCl}_2\text{CCl}_2\text{N}=\text{PCl}_3$ (239) have also been described.

Higher nitriles upon reaction with PCl_5 (1:3) at room temperature, give, besides the ionic compounds $[\text{Cl}_3\text{P}=\text{NCCl}=\text{CRPCl}_3]^+\text{PCl}_6^-$ (Section IV, D, 1) in 25–45% yield, substances of the formula $\text{RCCl}_2\text{N}=\text{PCl}_3$ ($\text{R} = \text{MeCCl}_2, \text{ClCH}_2\text{CCl}_2, \text{EtCCl}_2, \text{PrCCl}_2, i\text{-PrCHCl}, \text{BuCCl}_2, i\text{-BuCCl}_2, \text{AmCCl}_2$) (445), which are obtained directly when the reaction is carried out under heating. Contrary to these results other authors (307) found only the ionic compound $[\text{MeC}(\text{Cl})=\text{C}(\text{PCl}_3)\text{N}=\text{PCl}_3]^+\text{PCl}_6^-$ in the reaction of propionitrile with PCl_5 .

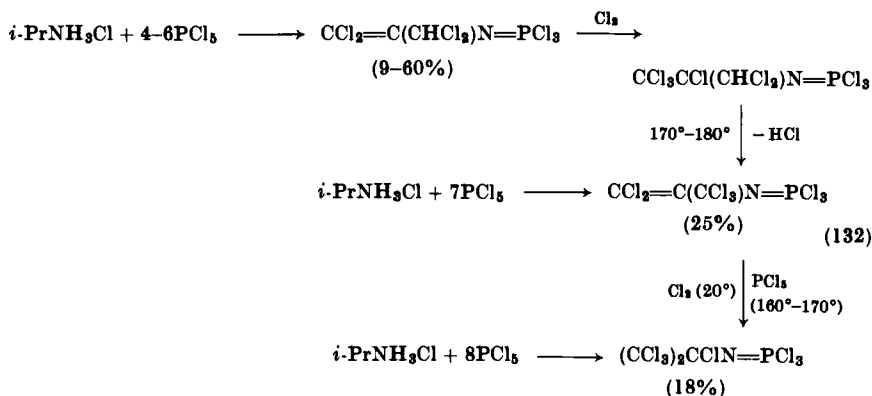
Aromatic-aliphatic cyanides $\text{RC}_6\text{H}_4\text{CH}_2\text{CHClCN}$ ($\text{R} = \text{H}, o\text{-}, p\text{-Cl}, p\text{-Br}, o\text{-}, p\text{-NO}_2, m\text{-}, p\text{-Me}, p\text{-MeO}$) with PCl_5 give $\text{RC}_6\text{H}_4\text{CH}_2\text{CCl}_2\text{CCl}_2\text{N}=\text{PCl}_3$ directly (444a).



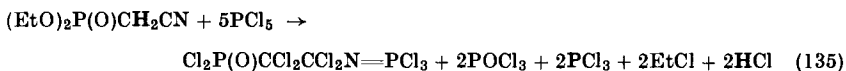
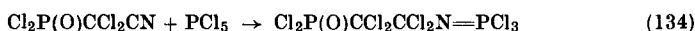
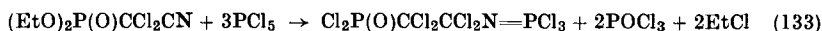
Isopropylecyanide and PCl_5 give, besides HCl , PCl_3 , and Me_2CClCN , poor yields of $\text{Me}_2\text{C}=\text{CCIN}=\text{PCl}_3$ (432); excess of PCl_5 produces $\text{Me}_2\text{CClCCl}_2\text{N}=\text{PCl}_3$ (307, 432).

Other secondary nitriles with PCl_5 (1:2) give $\text{MeRCClCCl}_2\text{N}=\text{PCl}_3$ ($\text{R} = \text{ClCH}_2, \text{CH}_2\text{Br}, \text{Et}$) (432) via a postulated ionic compound. Excess PCl_5 and isopropylamine [the equimolar reaction follows the usual route (185)] produce various compounds (530).

* Trichloroacetonitrile with SbCl_5 gives only the adduct $\text{CCl}_3\text{CN} \cdot \text{SbCl}_5$ (125).



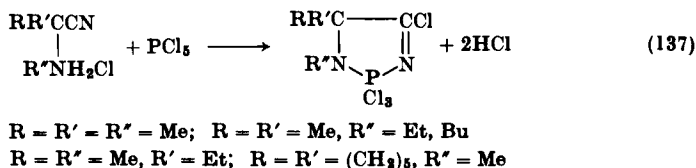
The compound $\text{Cl}_2\text{P}(\text{O})\text{CCl}_2\text{CCl}_2\text{N}=\text{PCl}_3$ is prepared (59) according to Eqs. (133)–(135).



α -Cyanoamine hydrochlorides $\text{RR}'\text{C}(\text{CN})\text{NH}_3\text{Cl}$ react with PCl_5 to form either monomeric or dimeric compounds $(\text{RR}'\text{C}(\text{CN})\text{N}=\text{PCl}_3)_n$ ($n = 1, 2$) [$\text{R} = \text{Me}, \text{Et}$; $\text{R}' = \text{Me}, \text{Et}$; $\text{RR}' = (\text{CH}_2)_4, (\text{CH}_2)_5$] (362). The monomeric species may also be prepared from α -*N,N*-dichloroamino-nitriles (365).



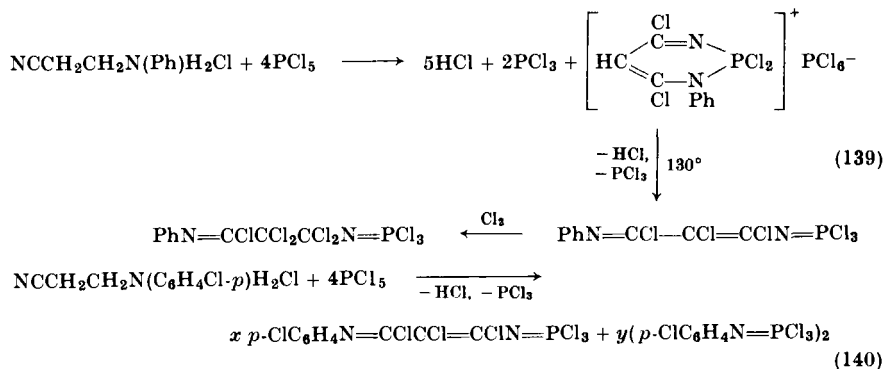
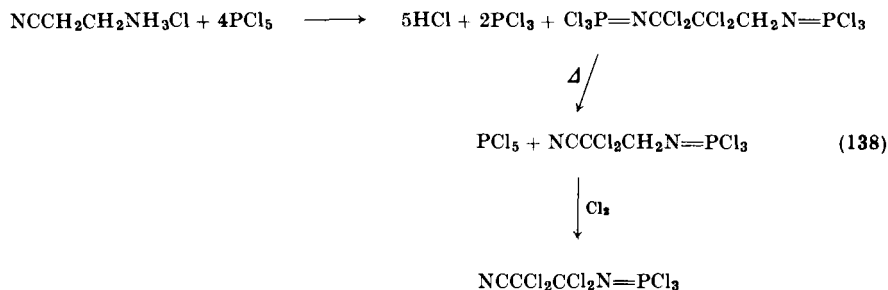
The reaction of $\text{RR}'\text{C}(\text{CN})\text{NH}_2\text{R}'\text{Cl}$ and PCl_5 gives a five-membered ring (364).



The aminonitriles $\text{RArC}(\text{CN})\text{NH}_2$ ($\text{R} = \text{Me}, \text{Et}, \text{Pr}, i\text{-Pr}, \text{Bu}, \text{Ar} = \text{Ph}$; $\text{R} = \text{Me}, \text{Ar} = p\text{-MeC}_6\text{H}_4, p\text{-ClC}_6\text{H}_4, 2,4\text{-Me}_2\text{C}_6\text{H}_3, 2,5\text{-Me}_2\text{C}_6\text{H}_3$) with PCl_5 yield the monomeric compounds $\text{R}(\text{Ar})\text{C}(\text{CN})\text{N}=\text{PCl}_3$ (363). With $\text{R} = \text{Me}$ and $\text{Ar} = \text{Ph}$ the dimer can also be isolated in small yields (3–5%). $\text{ArCH}=\text{C}(\text{CN})\text{CONH}_2$ and PCl_5 yield $\text{ArCH}=\text{C}(\text{CN})\text{CON}=\text{PCl}_3$

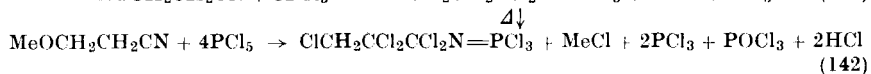
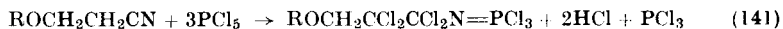
(427*b*). The reaction of enamines $XYC=C(R)NH_2$ ($X=Y=COOR$, CN or $X=COOR$, $Y=CN$, $COMe$; $R=CHCl_2$, CCl_3 , CF_3) with $PhPCl_4$, $MePCl_4$, and Ph_2PCl_3 has been described (57*a*).

β -Cyanoamine hydrochlorides and PCl_5 give the following reactions (361*a*):



The phosphorylation of *N*-alkyl(aryl)-3-aminopropionitriles has been described recently (292*a*).

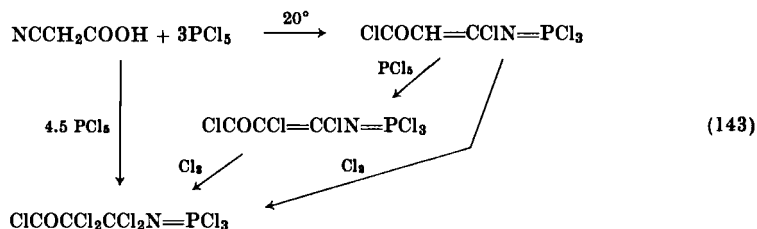
The CH_2 groups of the alkoxynitriles are partially chlorinated by PCl_5 at elevated temperatures and the amine group shows the normal reaction to form $ROCH_2CCl_2CCl_2N=PCl_3$ ($R=Pr, Bu, Ph$). Heating to 175° gives $ClCH_2CCl_2CCl_2N=PCl_3$; the latter compound is also obtained from $MeOCH_2CH_2CN$ and excess of PCl_5 via the intermediate formation of $ClCH_2CH_2CN$ (439).



The similar reaction of $EtOCH_2CH_2CN$ and PCl_5 gives intractable mixtures of $EtOCH_2CCl_2CCl_2N=PCl_3$ and $ClCH_2CCl_2CCl_2N=PCl_3$ (439).

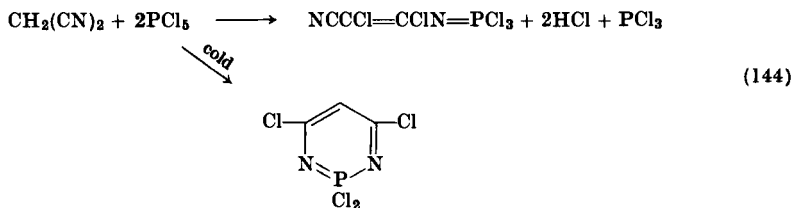
Aminoacetic acid reacts with a twofold excess of PCl_5 with chlorination of the carboxyl group and Kirsanov reaction on the amine side to give $(\text{ClCOCH}_2\text{N}=\text{PCl}_3)_2$ (531, 532) and $\text{CHCl}(\text{COCl})\text{N}=\text{PCl}_3$ (532). The former compound with excess PCl_5 gives $\text{ClCOCHClN}=\text{PCl}_3$, which may also be obtained directly from glycine and PCl_5 (1:3) (531, 532). Further chlorination at $160^\circ\text{--}170^\circ$ yields $\text{CCl}_2(\text{COCl})\text{N}=\text{PCl}_3$ (532). α -Amino acids $\text{RCH}(\text{NH}_2)\text{COOH}$ ($\text{R} = \text{Me, Et}$) give upon phosphorylation (1:4–6 PCl_5) $\text{MeCHClCCl}(\text{COCl})\text{N}=\text{PCl}_3$ or $\text{CHCl}=\text{C}(\text{COCl})\text{N}=\text{PCl}_3$ and $\text{CHCl}_2\text{CCl}(\text{COCl})\text{N}=\text{PCl}_3$, respectively (530–532). Higher α -amino acids (α -methylalanine, valine, leucine) give $\text{Me}_2\text{C}(\text{COCl})\text{N}=\text{PCl}_3$, $\text{Me}_2\text{CClCCl}(\text{COCl})\text{N}=\text{PCl}_3$, and $i\text{-PrCCl}_2\text{CCl}(\text{COCl})\text{N}=\text{PCl}_3$, respectively (532).

Cyanoacetic acid and PCl_5 at room temperature yield $\text{ClCOCH}=\text{CCIN}=\text{PCl}_3$; on heating or with excess PCl_5 $\text{ClCOCCl}=\text{CCIN}=\text{PCl}_3$ is obtained. The chlorination (PCl_5 or Cl_2) of these two latter compounds gives $\text{ClCOCCl}_2\text{CCl}_2\text{N}=\text{PCl}_3$ (429).



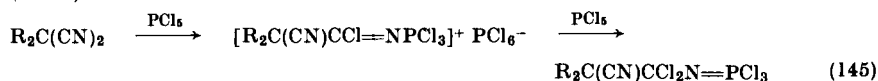
α -Cyanocarbonic acids $\text{RCH}(\text{CN})\text{COOH}$ with PCl_5 give in the initial step $\text{RCH}(\text{CN})\text{COCl}$ and then $\text{RC}(\text{COCl})=\text{CCIN}=\text{PCl}_3$ ($\text{R} = \text{Me}$), whereas excess PCl_5 produces $\text{RCCl}(\text{COCl})\text{CCl}_2\text{N}=\text{PCl}_3$ ($\text{R} = \text{Me, Et, Pr, } i\text{-Pr}$) (431). The compounds $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{CN}$ and $(\text{EtO})_2\text{P}(\text{O})\text{CCl}_2\text{CN}$ with excess PCl_5 give $\text{Cl}_2\text{P}(\text{O})\text{CCl}_2\text{CCl}_2\text{N}=\text{PCl}_3$ (59) [Eqs. (133–135)].

Malonic dinitrile and PCl_5 (1:1) give 1,1,3,5-tetrachloro-1,2,6-phosphadiazine (239), whereas with a 3:2 ratio at elevated temperatures besides HCl and small amounts of 1,1,3,4,5-pentachloro-1,2,6-phosphadiazine, the compound $\text{NCCl}=\text{CCIN}=\text{PCl}_3$ is obtained (239, 430). A



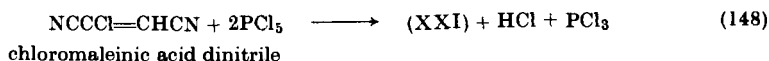
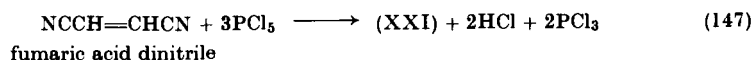
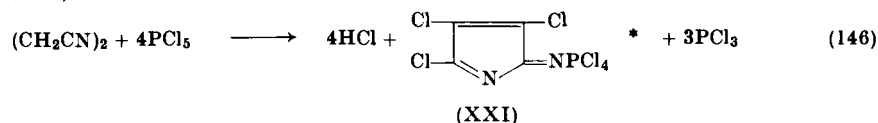
higher ratio of PCl_5 (1:2) at elevated temperatures produces $\text{NCCl}=\text{CClN}=\text{PCl}_3$; chlorination (Cl_2 or PCl_5) of both linear compounds leads to $\text{NCCl}_2\text{CCl}_2\text{N}=\text{PCl}_3$ (430).

Alkylmalonic dinitriles react with PCl_5 (2:1) to form 1,1,3,5-tetrachloro-4-alkyl-1,2,6-phosphadiazines and $\text{RC}(\text{CN})=\text{CClN}=\text{PCl}_3$ ($\text{R} = \text{Me, Et, Pr, } i\text{-Pr, Bu}$) (428); chlorination of these phosphazotrichlorides results in $\text{RCCl}(\text{CN})\text{CCl}_2\text{N}=\text{PCl}_3$. Other substituted malonic dinitriles $\text{R}_2\text{C}(\text{CN})_2$ ($\text{R} = \text{Me, Et, Pr, Cl}$) with PCl_5 give $\text{R}_2\text{C}(\text{CN})\text{CCl}_2\text{N}=\text{PCl}_3$ (290c).

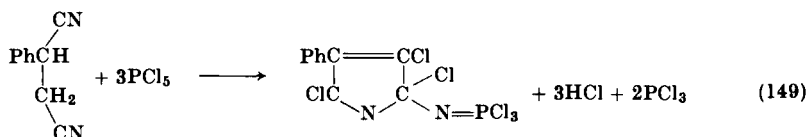


Phosphorylation (PCl_5) of 1,1-dicyano-2-amino-2-arylethylenes, $(\text{NC})_2\text{C}=\text{CArNH}_2$ ($\text{Ar} = \text{Ph, } p\text{-MeC}_6\text{H}_4, p\text{-ClC}_6\text{H}_4, p\text{-O}_2\text{NC}_6\text{H}_4$) also yields cyclic compounds (290a).

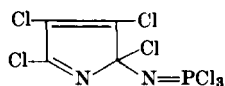
Succinic acid dinitrile and PCl_5 undergo a ring closure to form (XXI) (436); the same compound is obtained starting from fumaric acid dinitrile (1:3) (436, 441) or chloromaleinic acid dinitrile and PCl_5 (1:2) (436).



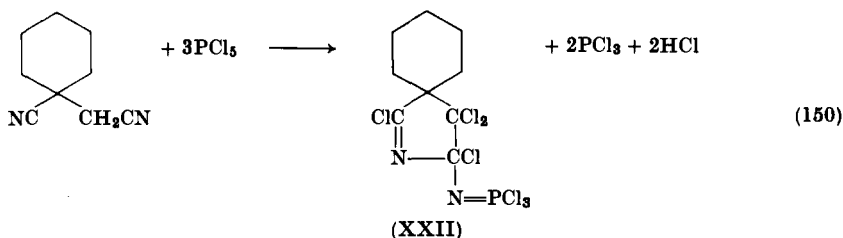
Phenylsuccinic acid dinitrile (441) and other derivatives $\text{RR}'\text{C}(\text{CN})\text{-CH}_2\text{CN}$ [$\text{R} = \text{Ph, R}' = \text{H}$ (441); $\text{R} = \text{Me, R}' = \text{Me, Et, Bu, } sec\text{-Bu, Ph}$; $\text{R} = \text{R}' = \text{Et, Pr}$; $\text{RR}' = (\text{CH}_2)_4, (\text{CH}_2)_5$ (441a)] also give five-membered rings.



* Better formulated as

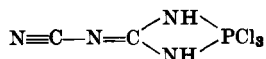


A spiro compound (XXII) is obtained (441) from Eq. (150).



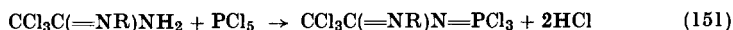
It is interesting to note that other derivatives of maleinic acid, i.e., $\text{RR}'\text{C}=\text{CR}''\text{NH}_2$, react with PCl_5 only to give $\text{RR}'\text{C}=\text{CR}''\text{NHCl}$ ($\text{R}, \text{R}' = \text{EtOCO}, \text{R}'' = \text{CCl}_3$) (58).

The reaction of dicyandiamide with PCl_5 (1:2) gives via the postulated intermediates



(26b, 207) and $\text{NCN}=\text{C}(\text{Cl})\text{NHPCl}_3\text{N}=\text{PCl}_3$ a compound $\text{C}_2\text{H}_4\text{P}_2\text{Cl}_6$ [2-(trichlorophosphazyl)-2,4,6-trichloro-2-phospha-1,3,5-triazine] (Section V,A), also described by other authors (110); the corresponding hydrochloride may also be isolated (26b).

Other trichlorophosphazidoalkyls are obtained from the phosphorylation (PCl_5) of amidines: while only 1:1 adduct formation between trichloroacetamidine $\text{CCl}_3(\text{=NH})\text{NH}_2$ and PCl_5 occurs, the corresponding *N*-alkyl- or *N*-aryltrichloroacetamidines or their hydrochlorides react with PCl_5 in the expected manner.

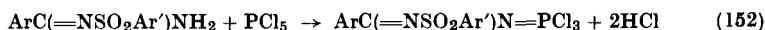


$\text{R} = \text{Me}, \text{Et}, \text{PhCH}_2$ (118), $\text{Bu}, \text{COCCl}_3, \text{MeP}(\text{O})\text{NMe}_2, \text{POCl}_2$ (120), Ph (116a, 121),

$p\text{-MeC}_6\text{H}_4, p\text{-BrC}_6\text{H}_4, p\text{-MeOC}_6\text{H}_4$ (121)

Compounds $\text{CF}_3\text{C}(\text{=NPh})\text{N}=\text{PCl}_3$ (120) and $\text{PhC}[\text{=NP}(\text{O})(\text{OPh})_2]\text{N}=\text{PCl}_3$ (84) have also been described.

For the reaction of amidinium salts with PCl_5 , see Section IV,C,1. *N*-Sulfonylarylamidines and PCl_5 yield the phosphazo compounds.

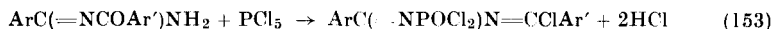


$\text{Ar} = \text{Ph}, \text{Ar}' = \text{Ph}, p\text{-MeC}_6\text{H}_4, p\text{-ClC}_6\text{H}_4, p\text{-O}_2\text{NC}_6\text{H}_4, 1\text{-C}_{10}\text{H}_7, 2\text{-C}_{10}\text{H}_7$ (84)

$\text{Ar} = p\text{-O}_2\text{NC}_6\text{H}_4, \text{Ar}' = \text{Ph}$ (87)

Contrary to the reactions above, *N*-carbonylarylamidines $\text{ArC}(\text{=NCOAr}')\text{NH}_2$ do not form the phosphazo compound, but (with a

probable intramolecular rearrangement) only phosphorylated amidines $\text{ArC}(=\text{NPOCl}_2)\text{N}=\text{CClAr}'$ ($\text{Ar} = \text{Ph}$, $p\text{-BrC}_6\text{H}_4$, $\text{Ar}' = \text{Ph}$, $p\text{-MeC}_6\text{H}_4$,



$p\text{-BrC}_6\text{H}_4$), which decompose upon heating to form $\text{ArC}(=\text{NPOCl}_2)\text{Cl}$ and $\text{Ar}'\text{CN}$ (101).

Kirsanov and co-workers (115, 116) also report the reaction of *N*-arylureas ArNHCONH_2 ($\text{Ar} = \text{Ph}$, $p\text{-ClC}_6\text{H}_4$, $p\text{-MeC}_6\text{H}_4$) with PCl_5 at room temperature to yield, via $\text{ArNHCON}=\text{PCl}_3$ and subsequent rearrangement, phosphorylated formamidines (see also Section VII, A).



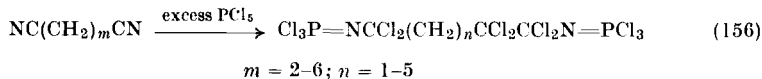
Introduction of a sulfonyl group, i.e., with $\text{ArSO}_2\text{NHCONH}_2$ ($\text{Ar} = \text{Ph}$, $p\text{-O}_2\text{NC}_6\text{H}_4$), leads to phosphazotrichlorides (80).



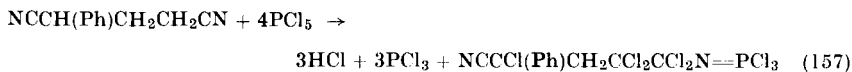
An analogous reaction has been described (81).

Similarly, *N*-chloroalkylamidines give with $(\text{ArO})_3\text{P}$, $(\text{PhO})_2\text{PCl}$, PhOPCl_2 , or PCl_3 the substances $\text{R}(\text{C}(\text{NH})\text{N}=\text{P}(\text{OAr})_n\text{Cl}_{3-n})$ ($\text{R} = \text{Me}$, CCl_3 ; $\text{Ar} = \text{Ph}$, $p\text{-ClC}_6\text{H}_4$; $n = 1, 2, 3$) (103). Variation of the method leads to $\text{ROC}(=\text{NH})\text{N}=\text{PCl}_3$ [(257), see also (114)].

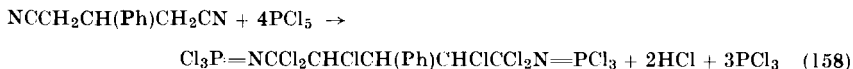
When dinitriles of higher dicarbonic acids are heated with excess PCl_5 , they react at both nitrile groups and with partial chlorination of the methylene groups (437).



Other dinitriles *o*-, *m*-, $p\text{-C}_6\text{H}_4(\text{CH}_2\text{CN})_2$ give *o*-, *m*-, $p\text{-C}_6\text{H}_4(\text{CCl}_2\text{CCl}_2\text{N}=\text{PCl}_3)_2$ (427c), whereas dinitriles of the type $\text{NCCH}(\text{Ph})\text{CH}_2\text{CH}_2\text{CN}$ react only at one cyanide group with PCl_5 (427b).



Both nitrile groups are attacked in $\text{NCCH}_2\text{CH}(\text{Ph})\text{CH}_2\text{CN}$ (427b).



Bis(trichlorophosphazo)tetrachloroethane $(\text{CCl}_2\text{N}=\text{PCl}_3)_2$ is obtained from isothiocyanic acid and PCl_5 (41); 3-aminopropionitrile and PCl_5 give $\text{Cl}_3\text{P}=\text{NCCl}_2\text{CCl}_2\text{CH}_2\text{N}=\text{PCl}_3$ (297c).

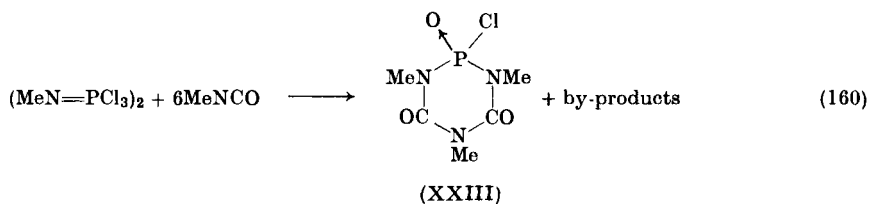


Phenyldichlorophosphazopolychloroalkenes have been obtained recently (59a). Only one amino group in $(\text{CF}_3)_2\text{C}(\text{NH}_2)_2$ reacts with MePF_4 to give $(\text{CF}_3)_2(\text{NH}_2)\text{CN}=\text{PMeF}_2$ (143a).

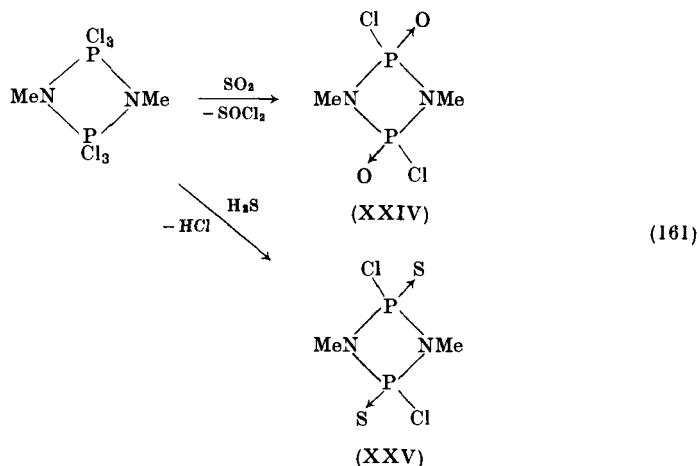
Finally, $\text{Cl}_3\text{P}=\text{NSO}_2(\text{CH}_2)_2\text{N}=\text{PCl}_3$ (542) can also be considered as a sulfonylphosphazotrichloride (see Section VI, A).

2. Reactions

Heating of $(\text{MeN}=\text{PCl}_3)_2$ should result in monomerization (186); this is in accordance with the reaction with phenylisocyanate at 150° producing an unsymmetrical carbodiimide (494). Milder conditions give ring enlargement (305) to the six-membered ring compound (XXIII), also obtained in other ways (299, 300, 304) (Section IX). It is interesting to note that $(\text{MeN}=\text{PPhCl}_2)_2$ and $(\text{MeN}=\text{PPh}_2\text{Cl})_2$ with methylisocyanate



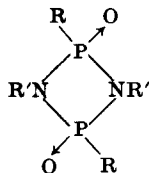
lead only to the formation of PhPOCl_2 and Ph_2POCl , respectively (196). Reaction of $(\text{MeN}=\text{PCl}_3)_2$ with CO_2 and CS_2 gives the corresponding isocyanates and isothiocyanates, respectively (494).



The P-N ring system is preserved in the interaction of $(\text{MeN}=\text{PCl}_3)_2$ with SO_2 and H_2S giving (XXIV) (2,4-dioxo-2,4-dichloro-1,3-dimethyl-1,3,2,4-diazadiphosphetidine) and the thio analog (XXV), respectively [(32, 181), cf. also (297a)].

The compounds $(\text{EtN}=\text{PCl}_3)_2$ and $(\text{PrN}=\text{PCl}_3)_2$ (181) react similarly with liquid SO_2 , as does $\text{P}_4(\text{NMe})_6\text{Cl}_8$ (32) with SO_2 or H_2S to give the group $\text{>P} \begin{smallmatrix} \text{Cl} \\ \diagup \\ \text{X} \end{smallmatrix}$ (X = O, S).

Analogous compounds to (XXIV)



R = PhO, R' = Me (52)

R = $\text{C}_6\text{H}_{11}\text{O}$, R' = C_6H_{11} (54)

R = Bu, R' = *p*- ClC_6H_4 , PhCH_2 ; R = $\text{Cl}(\text{CH}_2)_4$, R' = *p*- MeSC_6H_4 , *m*-, *p*- ClC_6H_4 (193)

R = Me, C_6H_{11} , Ph, PhCH_2 ; R' = Et, Ph, PhCH_2 (53)

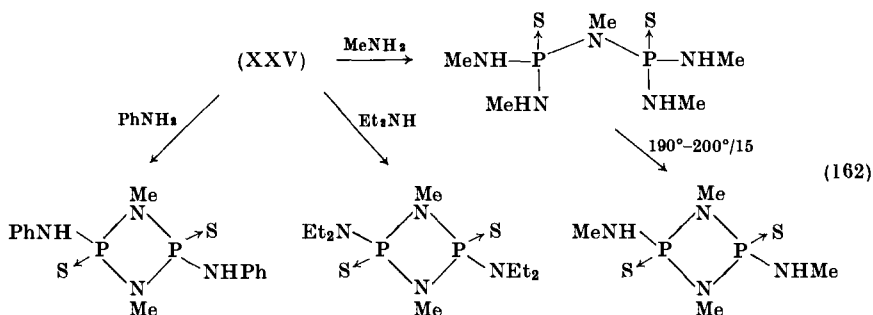
have generally been prepared from the amine and a phosphoric ester dichloride or phosphonic dichloride. Other compounds $[\text{R}'\text{NP}(\text{O})\text{R}]_2$ (R = Me_2N , Et_2N , PhNH ; R' = Ph, *p*- BrC_6H_4 , *p*- MeC_6H_4 , *p*- MeOC_6H_4) are isolated from the thermolysis of phosphoric trianilide or from the reaction of phosphoric trianilide or phenylphosphonic dianilide with phosphoric tris(dialkylamides) [(216), cf. also (359)]. Chain polymers with four-membered P-N ring units are known (348, 358, 359).

Similar compounds to (XXV), $[\text{R}'\text{NP}(\text{S})\text{R}]_2$, result from the thermal degradation of $\text{R}'\text{NHP}(\text{S})\text{RCl}$ (R = Me, R' = Me, Et, Ph, *p*- MeC_6H_4 , *m*-, *p*- ClC_6H_4 , *p*- MeOC_6H_4 , *p*- EtOC_6H_4 ; R = Ph, R' = Me, *i*-Pr, Ph, *p*- EtOC_6H_4) (333). Elimination of amine from $\text{PhP}(\text{S})(\text{NHR})_2$ [R = PhCH_2 (492), Me (201, 492), Et,* Pr, Bu (201)] results in formation of the corresponding diazadiphosphetidines; with R = H the corresponding $[\text{PhP}(\text{S})\text{NH}]_2$ can only be isolated as a by-product (419).

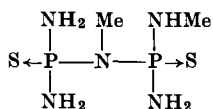
Some of the above-mentioned compounds have previously been described by Michaelis (334, 335) ("phosphazoles") and a monomeric or a dimeric form was assigned to them. Bock and Wiegräbe, however (57), showed that only the dimeric form is present [see also (63)].

* With R = Et, the *cis*- and *trans*-1,3-diethyl-2,4-diphenyl-2,4-dithiocyclo-diphosphazanes have been observed (152).

Of some interest are further reactions of (XXV) with replacement of the two chlorine atoms (32).



The interaction of (XXV) with ethanol also gives substitution without affecting the P-N ring system (391). Linkage with catechol, resorcinol, hydroquinone, and their derivatives gives chainlike, thermally quite stable polymers which still contain some four-membered rings (197). The ammonolysis of (XXV) yields (XXVI) (391), the structure of which



has been established (553).

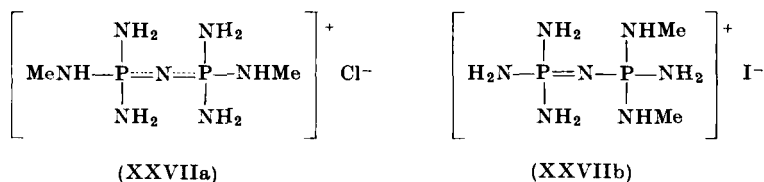
The compounds (XXIV) and (XXV) react with MeNCO to form six-membered ring compounds [analogous to (XXIII) (305)]. Dimethyl-amino or thiomethyl groups are introduced by the action of (XXIV) with Me₃SiNMe₂ or Me₃SiSMe, respectively (181); azide groups may also be introduced (196c).

The ammonolysis of (MeN=PCl₃)₂ (and its higher homologs) with liquid ammonia (185) gives in the case of the methyl compound an ionic product C₂H₁₆N₇P₂Cl (XXVII), to which a symmetrical structure (XXVIIa) (as for the phenyl compound) was assigned.



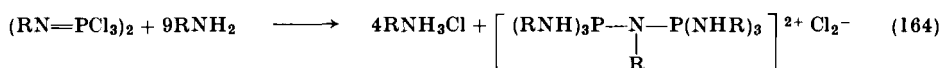
Ziegler (550, 551) carried out an X-ray investigation of the iodide (391) and rather surprisingly found an unsymmetrical structure (XXVIIb). Evidence for both the symmetrical structure (mechanism, ³¹P NMR spectrum) and the unsymmetrical structure of the iodide (X-ray investigation) is available, and a definitive answer concerning the structure is not yet possible. An ammonolysis mechanism formerly suggested (185)

has now been given up in favor of another involving the intermediate formation of a tetraminophosphonium salt (501).

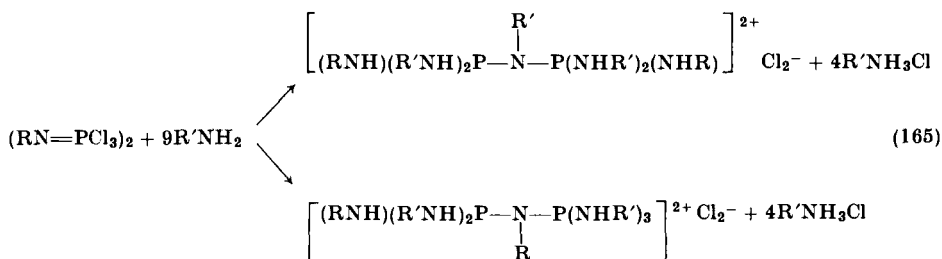


Ammonolysis of $(\text{RN}=\text{PCl}_3)_2$ ($\text{R} = \text{Me}, \text{Ph}$) with NH_4Cl at 180° yields high polymers of the proposed formulas $[\text{P}(\text{NR})\text{ClNH}]_n$ (525b).

The similar reactions of $(\text{RN}=\text{PCl}_3)_2$ with primary amines have been described (143).

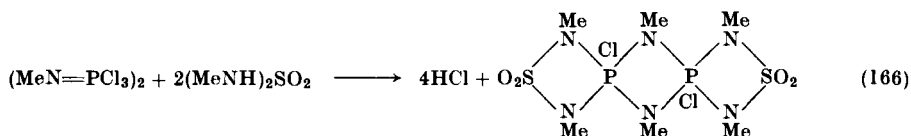


$\text{R} = \text{Pr}, \text{Bu}, i\text{-Bu}$

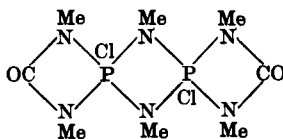


$\text{R} = \text{Et}, \text{Pr}, \text{Bu}, i\text{-Bu}; \text{R}' = \text{Et}, \text{Bu}, i\text{-Bu}$ (some salts as iodides)

The attempted isolation of $\text{MeN}=\text{P}(\text{NMe}_2)_3$ [by aminolysis of $(\text{MeN}=\text{PCl}_3)_2$ with Me_2NH] failed (45, 187); this compound has only been prepared by an azide-phosphine reaction (187). The compound $\text{Et}_2\text{CHN}=\text{PCl}_3$ with MeNH_2 (1:5) gives the salt $(\text{Et}_2\text{CHNH})(\text{MeNH})_3\text{PCl}$ (143). It is found that $(\text{MeN}=\text{PCl}_3)_2$ gives with N,N' -dimethylsulfamide (36b, 37, 510) a compound containing three four-membered rings [Eq. (166)].



With *N,N'*-dimethylurea



is similarly obtained (36a). In the reaction between $(\text{MeN}=\text{PCl}_3)_2$ and NaN_3 the hexazide is formed (196c); with NH_4NCS correspondingly the hexaisothiocyanate results (51b).

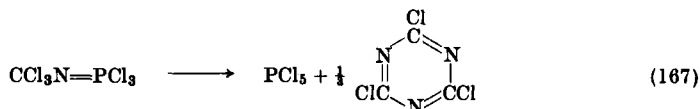
Interaction of $(\text{MeN}=\text{PCl}_3)_2$ and $\text{Cr}(\text{CO})_6$ yields a blue-red product $(\text{OC})_4\text{Cr}(\text{MeN}=\text{PCl}_3)_2$, which on thermal degradation gives a polymer $(\text{Cr}_7\text{P}_5\text{N}_2)_x$ (198).

Chlorination (UV) of $(\text{MeN}=\text{PCl}_3)_2$ gives $\text{CCl}_3\text{N}=\text{PCl}_3$ (142, 294). Fluorination with Na_2SiF_6 gives both $(\text{MeN}=\text{PF}_3)_2$ and partially fluorinated compounds (for these, see Section VIII, C); with KSO_2F (187) $(\text{MeN}=\text{PF}_3)_2$ is obtained. Fluorination of $(\text{RN}=\text{PCl}_3)_2$ [$\text{R} = \text{Me}$ (142, 294), Et , Pr (142)] with SbF_3 leads to the corresponding hexafluoro-diazadiphosphetides; $(\text{BuN}=\text{PCl}_3)_2$ and $(i\text{-BuN}=\text{PCl}_3)_2$ were fluorinated with AsF_3 to the corresponding fluoro compounds (142).

Hydrolysis of higher alkylphosphazotrichlorides $\text{RN}=\text{PCl}_3$ [$\text{R} = \text{Me}_3\text{C}$ (527c, 533), Me_3CCH_2 , Et_2CH , $\text{ClCMe}_2\text{CH}_2$, $\text{CCl}_2=\text{C}(\text{CHCl}_2)$, $\text{CCl}_2=\text{CCCl}_3$, $\text{ClCMe}_2\text{CHCl}$, $\text{Me}_3\text{CCCl}_2\text{CHCl}$, ClCOCHCl , $\text{CHCl}_2\text{CCl}(\text{COCl})$ (533)] with moist air, formic acid, or acetic acid leads to the corresponding alkylaminophosphonic acid dichlorides. $\text{ClCMe}_2\text{CH}=\text{NPOCl}_2$ is obtained by elimination of HCl from $\text{ClCMe}_2\text{CHClNHPOCl}_2$; $\text{ClCMe}_2\text{CH}=\text{NPOCl}_2$ and $\text{Me}_3\text{CCCl}_2\text{CH}=\text{NPOCl}_2$ are formed from $\text{ClCMe}_2\text{CHClN}=\text{PCl}_3$ and $\text{Me}_3\text{CCCl}_2\text{CHClN}=\text{PCl}_3$ with SO_2 at $140^\circ\text{--}150^\circ$, respectively (533).

Finally, the compounds $\text{MeN}=\text{P}(\text{OEt})_3$ (187) (phosphine-azide reaction) and $(\text{CF}_3)_3\text{CN}=\text{PPh}_3$ and $(\text{CF}_3)_3\text{CN}=\text{P}(\text{OEt})_3$, prepared from Ph_3P or $(\text{EtO})_3\text{P}$ with $(\text{CF}_3)_3\text{CNO}$ (336), are known.

The reactions of the phosphorylation products of nitriles are well studied. $\text{CCl}_3\text{N}=\text{PCl}_3$ decomposes at room temperature, at a faster rate at 150° to cyanuric chloride and PCl_5 (162):



With SO_2 at room temperature $\text{CCl}_2=\text{NPOCl}_2$ is obtained (294, 442), whereas compound (XX) reacts analogously only at $180^\circ\text{--}200^\circ$ (442).

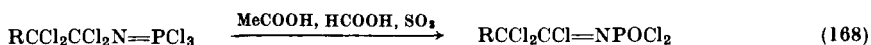
Other perchloroalkylphosphazotrichlorides $\text{RCCl}_2\text{N}=\text{PCl}_3$ [$\text{R} = \text{MeCCl}_2$, $\text{ClCH}_2\text{CCl}_2$, EtCCl_2 , PrCCl_2 , $i\text{-PrCHCl}$, BuCCl_2 , $i\text{-BuCCl}_2$,

AmCCl_2 (445), Me_2CCl (432)] give (180° – 220°) the corresponding chlorinated nitriles, PCl_5 , HCl , and PCl_3 on thermolysis (445).

ω -Cyanoalkylphosphazotrichlorides (from malonic acid dinitriles and PCl_5) undergo an intermolecular ring closure to form six-membered rings upon heating (430).

Hydrolysis of $\text{CCl}_2=\text{C}(\text{CHCl}_2)\text{N}=\text{PCl}_3$ or $\text{CCl}_2=\text{C}(\text{CCl}_3)\text{N}=\text{PCl}_3$ with excess water produces $(\text{CHCl}_2)_2\text{CO}$ or $\text{CHCl}_2\text{COCCl}_3$ (530), respectively. A mechanism has been suggested [(445), cf. also (442)] which involves fission of the $\text{P}=\text{N}$ bond leading finally to chlorinated nitriles.

A unique feature is observed in the controlled hydrolysis (formic or acetic acid, or, in some cases, SO_2) of perchloroalkylphosphazotrichlorides; no formation of $-\text{CCl}_2\text{NHPOCl}_2-$ from $-\text{CCl}_2\text{N}=\text{PCl}_3$ occurs, but the $\text{>C}=\text{NPOCl}_2$ group is formed instead, with intermolecular elimination of HCl .



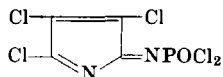
$\text{R} = \text{Cl}$ (290c, 445), ClCH_2 , Me, Et, Pr, Bu, *i*-Bu, Am (445), COCl (429)

It is interesting to note that β -cyanoperchloroalkylphosphazotrichlorides react in the same way (428).

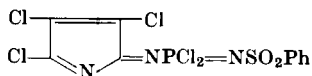


$\text{R} = \text{Me, Et, Pr, } i\text{-Pr, Bu}$

Compound (XXI) gives upon acidolysis (acetic acid) or with SO_2 the compound



(436), but compound (XXII) reacts with formation of a $-\text{NHPOCl}_2$ group (441). Action of PhSO_2NH_2 on (XXI) leads to



(436).

Alcoholysis of $\text{CCl}_3\text{CCl}_2\text{N}=\text{PCl}_3$ (XX) with 1 mole of ROH ($\text{R} = \text{Bu}$, $n\text{-C}_8\text{H}_{17}$) leads to $\text{CCl}_3\text{CCl}_2\text{N}=\text{PCl}_2\text{OR}$; with 3 moles of ROH the diesters $\text{CCl}_3\text{CCl}=\text{NPO}(\text{OR})_2$ or $\text{CCl}_3\text{C}(\text{OR})=\text{NPO}(\text{OR})\text{Cl}$ ($\text{R} = \text{Me, Et, Pr, Bu, } i\text{-Bu, Am, } i\text{-Am}$) are obtained (433). The reaction at 80° gives with (XX) only the orthoesters $\text{CCl}_3\text{C}(\text{OR})_3$ ($\text{R} = \text{Me, Et, Pr, Bu, Am}$), not decomposed even upon distillation (434). Higher phosphazo compounds $\text{RCCl}_2\text{CCl}_2\text{N}=\text{PCl}_3$ ($\text{R} = \text{Et, Pr}$) with 1 mole of R'OH eliminate R'Cl and

give only $\text{RCCl}_2\text{CCl}=\text{NPOCl}_2$; with a molar ratio of 1:3 the diesters $\text{RCCl}_2\text{CCl}=\text{NPO}(\text{OR}')_2$ ($\text{R} = \text{R}' = \text{Me, Et}$; $\text{R} = \text{Et, R}' = \text{Pr}$) (435) are obtained. A 1:4 ratio leads at room temperature to $\text{RCCl}_2\text{C}(\text{OR}')=\text{NPO}(\text{OR}')_2$ ($\text{R} = \text{Me, Et, Pr}$; $\text{R}' = \text{Me, Et, Pr, Bu}$); a tenfold excess of alcohol gives in addition to NH_4Cl only $\text{RCCl}_2\text{COOR}'$ ($\text{R} = \text{R}' = \text{Me, Et, Pr}$) (435), also obtained from $\text{RCCl}_2\text{C}(\text{OR}')=\text{NPO}(\text{OR}')_2$ and HCl . However, the reaction of $\text{RCCl}_2\text{N}=\text{PCl}_3$ ($\text{R} = \text{CCl}_3, \text{MeCCl}_2, \text{EtCCl}_2, \text{PrCCl}_2$) with phenols $\text{XC}_6\text{H}_4\text{OH}$ ($\text{X} = \text{H, } p\text{-Cl, } m\text{-NO}_2, p\text{-Me}$) gives $\text{RCCl}_2\text{N}=\text{P}(\text{OC}_6\text{H}_4\text{X})_3$ (435b).

α -Cyanoalkylphosphazotrichlorides $\text{RR}'\text{C}(\text{CN})\text{N}=\text{PCl}_3$ hydrolyze to $\text{RR}'\text{C}(\text{CN})\text{NHPOCl}_2$ [$\text{R} = \text{R}' = \text{Me, Et}$; $\text{RR}' = (\text{CH}_2)_4, (\text{CH}_2)_5$ (362); $\text{R} = \text{Et, Pr, } i\text{-Pr, Bu, R}' = \text{Ph}$; $\text{R} = \text{Me, R}' = \text{Ph, } p\text{-MeC}_6\text{H}_4, p\text{-ClC}_6\text{H}_4, 2,4\text{-Me}_2\text{C}_6\text{H}_3, 2,5\text{-Me}_2\text{C}_6\text{H}_3$ (363)]. With excess water the free amines $\text{RR}'\text{C}(\text{CONH}_2)\text{NH}_3\text{Cl}$ are obtained as salts.

The action of arenesulfonamides on $\text{CCl}_3\text{CCl}_2\text{N}=\text{PCl}_3$ (XX) leads to $\text{ArSO}_2\text{N}=\text{C}(\text{CCl}_3)\text{N}=\text{PCl}_3$ ($\text{Ar} = \text{Ph, } p\text{-ClC}_6\text{H}_4, p\text{-BrC}_6\text{H}_4, p\text{-MeC}_6\text{H}_4, m\text{-, } p\text{-O}_2\text{NC}_6\text{H}_4, 4\text{-Cl, } 3\text{-O}_2\text{NC}_6\text{H}_4, 2\text{-C}_{10}\text{H}_7$) (297e) which hydrolyze to $\text{ArSO}_2\text{N}=\text{C}(\text{CCl}_3)\text{NHPOCl}_2$; the reaction of (XX) with carboxylic amides was recently described (297c). Reaction of (XX) with DMF gives the compound $\text{Me}_2\text{NCH}=\text{NPOCl}_2$ (297d).

The alcoholysis of 2,4,4,5-tetrachloro-5-(trichlorophosphazo)-3,3-dialkylpyrrolidines is briefly described (435a).

Ethylenimino derivatives of substituted phenyldichlorophosphazovinyls have been described recently (369b).

The reactions of the phosphorylated amidines follow the usual pattern: hydrolysis with HCOOH (or acetic acid) of $\text{RC}(=\text{NR}')\text{N}=\text{PCl}_3$ gives $\text{RC}(=\text{NR}')\text{NHPOCl}_2$ [$\text{R} = \text{CCl}_3, \text{R}' = \text{Bu, COCCl}_3, \text{MeP}(\text{O})\text{NMe}_2, \text{POCl}_2$ (120); $\text{R} = \text{CF}_3, \text{R}' = \text{Ph}$ (120); $\text{R} = \text{CCl}_3, \text{R}' = \text{Ph, } p\text{-MeOC}_6\text{H}_4, p\text{-MeC}_6\text{H}_4, p\text{-BrC}_6\text{H}_4$ (121); $\text{R} = \text{Ph, R}' = \text{P}(\text{O})(\text{OPh})_2$ (84)]. The same results are obtained for $\text{PhC}(=\text{NSO}_2\text{Ar})\text{N}=\text{PCl}_3$ [$\text{Ar} = \text{Ph, } p\text{-MeC}_6\text{H}_4, p\text{-ClC}_6\text{H}_4, p\text{-O}_2\text{NC}_6\text{H}_4, 1\text{-C}_{10}\text{H}_7, 2\text{-C}_{10}\text{H}_7$ (84)], but reaction with water leads to phosphoric acid, HCl , and the corresponding amidine. However, $\text{PhC}(=\text{NH})\text{N}=\text{PCl}_3$ and acetic acid yield only $\text{PhC}(=\text{NPO}(\text{OH})\text{Cl})\text{NH}_2$ (103).

Reaction of $\text{CCl}_3\text{C}(=\text{NAr})\text{N}=\text{PCl}_3$ with $\text{Ar}'\text{OH}$ [$\text{Ar}' = \text{Ph, } p\text{-ClC}_6\text{H}_4$ (121)] gives the triesters; analogously $p\text{-O}_2\text{NC}_6\text{H}_4\text{C}(=\text{NSO}_2\text{Ph})\text{N}=\text{P}(\text{OPh})_3$ has been prepared (87), as well as $\text{PhC}(=\text{NSO}_2\text{Ar})\text{N}=\text{P}(\text{OAr}')_3$ ($\text{Ar} = \text{Ph, } p\text{-MeC}_6\text{H}_4; \text{Ar}' = \text{Ph, } p\text{-ClC}_6\text{H}_4; \text{Ar} = p\text{-ClC}_6\text{H}_4, \text{Ar}' = \text{Ph}$) (85), which hydrolyze to $\text{PhC}(=\text{NSO}_2\text{Ar})\text{NHPO}(\text{OAr}')_2$.

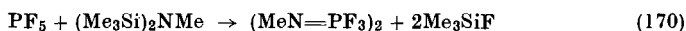
Primary amines react with $\text{PhC}(=\text{NSO}_2\text{Ar})\text{N}=\text{PCl}_3$ to $\text{PhC}(=\text{NSO}_2\text{Ar})\text{N}=\text{P}(\text{NHAr}')_3$ ($\text{Ar} = \text{Ph, } p\text{-MeC}_6\text{H}_4, p\text{-O}_2\text{NC}_6\text{H}_4, 1\text{-C}_{10}\text{H}_7, 2\text{-C}_{10}\text{H}_7, \text{Ar}' = \text{Ph}$; $\text{Ar} = p\text{-MeC}_6\text{H}_4, \text{Ar}' = \text{Ph, } p\text{-MeC}_6\text{H}_4, p\text{-ClC}_6\text{H}_4$; $\text{Ar} = \text{Ph,}$

$\text{Ar}' = p\text{-BrC}_6\text{H}_4$) (86), which upon hydrolysis yield the diamides $\text{PhC}(=\text{NSO}_2\text{Ar})\text{NHPO}(\text{NHAr}')_2$ and subsequently ArSO_2NH_2 and $\text{PhCONHPO}(\text{NHAr}')_2$.

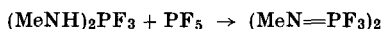
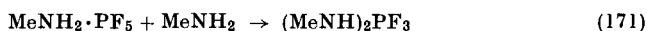
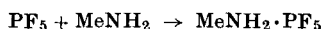
Acidolysis of $\text{Cl}_3\text{P}=\text{NCCl}_2(\text{CH}_2)_n\text{CCl}_2\text{CCl}_2\text{N}=\text{PCl}_3$ ($n = 2-4, 6$) results in solvolysis of the $-\text{N}=\text{PCl}_3$ group and an intermolecular HCl elimination to form $\text{Cl}_2\text{OPN}=\text{CClCCl}_2(\text{CH}_2)_n\text{CCl}_2\text{CCl}=\text{NOPCl}_2$ (437). The latter compounds with water give $\text{H}_2\text{NCOCCl}_2(\text{CH}_2)_n\text{CCl}_2\text{CONH}_2$, also obtained directly from $\text{CCl}_3\text{P}=\text{NCCl}_2(\text{CH}_2)_n\text{CCl}_2\text{CCl}_2\text{N}=\text{PCl}_3$ ($n = 1-6$) (438); excess alcohol produces the esters $(\text{CH}_2)_n[\text{CCl}_2\text{C}(\text{OR})=\text{NPO}(\text{OR})_2]_2$ ($\text{R} = \text{Me, Et}$; $n = 2, 4-6$) (297b). Fluorination with KF or NaF leads only to the dinitriles $\text{NCCl}_2(\text{CH}_2)_n\text{CCl}_2\text{CN}$ ($n = 2-6$) and PF_5 (440).

C. PHOSPHAZOTRIFLUORIDES

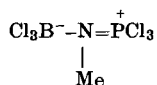
Some compounds of the type $(\text{RN}=\text{PF}_3)_n$ ($n = 1, 2$) have been described; $(\text{MeN}=\text{PF}_3)_2$, for example, may be prepared by several different methods: fission of the $\text{Si}-\text{N}$ bond with PF_5 (76, 77, 408-410):



direct reaction of PF_5 with methylamine in presence of a tertiary amine (187); this reaction has been formulated as proceeding in the steps (188d):



fluorination of $(\text{MeN}=\text{PCl}_3)_2$ with SbF_3 (142, 294), KSO_2F (187), Na_2SiF_6 (503), and PbF_2 (142), and fluorination (AsF_3) of

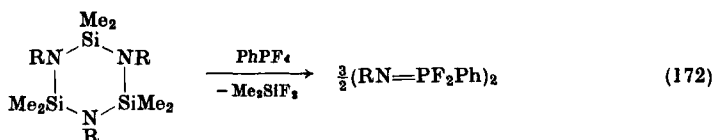


(Section IV, C, 1) (51h), as well as in minor amounts as a decomposition product of $\text{F}_2\text{PNMePF}_4$ and MeNHPF_4 (188e).

Higher dimeric alkylphosphazotrifluorides $(\text{RN}=\text{PF}_3)_2$ with the following R are known: $\text{R} = \text{Et, Bu, } i\text{-Bu}$ (142); Pr (142, 190); *tert*- Bu (190). The aryl compound $(\text{PhN}=\text{PF}_3)_2$ has also been synthesized (189, 190), as well as derivatives with $\text{Ar} = 2,4\text{-Me}_2\text{C}_6\text{H}_3$, $2,6\text{-Me}_2\text{C}_6\text{H}_3$, and $2,6\text{-Et}_2\text{C}_6\text{H}_3$ (190).

The analogous compounds $(\text{RN}=\text{PF}_2\text{R}')_2$ [$\text{R} = \text{Me, R}' = \text{Me, ClCH}_2$, $\text{Et, } 2,5\text{-Me}_2\text{C}_6\text{H}_3$, $3\text{-CF}_3\text{C}_6\text{H}_4$; $\text{R} = \text{Ph, R}' = \text{Me, Ph}$; $\text{R} = \text{Et, R}' = \text{Ph}$ (409-411); $\text{R} = \text{Me, R}' = \text{Ph}$ (62, 409)] are also known.

An interesting synthesis for $(\text{RN}=\text{PF}_2\text{Ph})_2$ ($\text{R} = \text{Me}, \text{Et}$) has been described (411).



The reaction of heptamethyldisilazane with Ph_2PF_3 gives the monomeric compound $\text{MeN}=\text{PFPh}_2$ (409); $\text{PhN}=\text{PPh}_2\text{F}$ has been prepared by an azide-phosphine reaction (62a). Finally, the compounds $\text{NCN}=\text{PPhF}_2$ and $\text{NCN}=\text{PPh}_2\text{F}$ have been obtained from bis(trimethylsilyl)carbodiimide with PhPF_4 and Ph_2PF_3 , respectively (175).

Phosphazotrifluorides have been described (190, 410) as quite stable to water (?). The halogen exchange between $(\text{MeN}=\text{PCl}_3)_2$ and $(\text{MeN}=\text{PF}_3)_2$ yields mixed chlorofluorodiazadiphosphetidines $(\text{MeN}=\text{P})_2\text{Cl}_n\text{F}_{6-n}$ ($n = 1-5$) (503). The compound $(\text{MeN}=\text{PFCl}_2)_2$ is also obtained in the reaction of $(\text{MeN}=\text{PCl}_3)_2$ with BF_3 (51c). Apart from these, only $(\text{PhN}=\text{PCl}_2\text{F})_2$ (from PhNH_3Cl and PF_3Cl_2) is known (37).

D. PHYSICAL INVESTIGATIONS

1. Infrared Studies

A band near 850 cm^{-1} is assigned as characteristic of a $\text{P}-\text{N}-\text{P}$ vibration in $(\text{MeN}=\text{PCl}_3)_2$ (69, 492) and is also found in all other dimeric alkylphosphazo compounds (181, 185, 338, 502, 519). A normal coordinate analysis (523) of $(\text{MeN}=\text{PCl}_3)_2$, assuming a C_{2h} structure (cf. Section VIII, D, 3), has been carried out.

The monomeric compounds $\text{ArN}=\text{PCl}_3$ [$\text{Ar} = 2,4\text{-Br}_2\text{C}_6\text{H}_3$, $2,6,4\text{-Cl}_2(\text{O}_2\text{N})\text{C}_6\text{H}_2$, 2-Br , $2,6\text{-Cl}_2\text{H}_6\text{H}_2$] have $\nu_{\text{P}=\text{N}}$ at $1325\text{--}1385\text{ cm}^{-1}$ (541), in sharp contrast to a former report (199). The $\text{P}=\text{N}$ vibration for $\text{Ph}_3\text{P}=\text{NPh}$ has been definitely found at 1344 cm^{-1} [(521), cf. also (520)].

For the following compounds $\nu_{\text{P}=\text{N}}$ have been correlated: $\text{CCl}_2=\text{CClN}=\text{PCl}_3$ and $\text{CCl}_3\text{CCl}_2\text{N}=\text{PCl}_3$ (XX)* at 1375 cm^{-1} (123), $\text{CF}_3\text{CCl}_2\text{N}=\text{PCl}_3$ at 1388 and 1450 cm^{-1} (^{14}N) and 1364 and 1400 cm^{-1} (^{15}N) (475), $(\text{CF}_3)_2\text{CHN}=\text{PCl}_3$, $(\text{CF}_3)_2\text{CClN}=\text{PCl}_3$, and $(\text{CF}_3)_3\text{CN}=\text{PCl}_3$ between 1300 and 1500 cm^{-1} (295). More detailed studies were made on $\text{CCl}_3\text{N}=\text{PCl}_3$, $\text{CCl}_3\text{CCl}_2\text{N}=\text{PCl}_3$, and $(\text{CCl}_3)_2\text{CClN}=\text{PCl}_3$ (220) and the $\nu_{\text{P}=\text{N}}$ assignments made at 1357 , 1372 , and 1465 cm^{-1} , respectively. $\text{CF}_3\text{CCl}_2\text{N}=\text{PCl}_3$,

* The $\nu_{\text{P}=\text{N}}$ for ^{14}N - and ^{15}N -labeled $\text{CCl}_3\text{CCl}_2\text{N}=\text{PCl}_3$ are found at 1373 and 1455 cm^{-1} and at 1345 and 1408 cm^{-1} , respectively (475).

$(\text{CF}_3)_2\text{CClN}=\text{PCl}_3$ and $(\text{CF}_3)_3\text{CN}=\text{PCl}_3$ exhibit their $\nu_{\text{P}=\text{N}}$ at 1390, 1435, and 1500 cm^{-1} , respectively (220a).

IR spectra of $\text{ClCOCH}=\text{CClN}=\text{PCl}_3$, $\text{ClCOCCl}=\text{CClN}=\text{PCl}_3$, and $\text{ClCOCCl}_2\text{CCl}_2\text{N}=\text{PCl}_3$ are reported in the literature (429). The $\nu_{\text{P}=\text{N}}$ for $\text{RCCl}(\text{COCl})\text{CCl}_2\text{N}=\text{PCl}_3$ ($\text{R} = \text{Me, Et, Pr, } i\text{-Pr}$) are found at 1360 cm^{-1} (431). In the analogous compounds $\text{ArN}=\text{PCl}_2\text{Me}$ ($\text{Ar} = o\text{-ClC}_6\text{H}_4$, $o\text{-BrC}_6\text{H}_4$) the $\nu_{\text{P}=\text{N}}$ lies between 1370 and 1380 cm^{-1} (526).

The $\text{P}=\text{N}$ absorptions for the compounds $\text{MeN}=\text{P}(\text{OR})_3$ ($\text{R} = \text{Et, Pr, Bu}$) and $\text{PhN}=\text{PR}'(\text{OR})_2$ [$\text{R} = \text{Et, R}' = \text{Ph}$; $\text{R} = \text{Pr, R}' = \text{Et, Pr}$; $\text{R} = \text{Bu, R}' = \text{Me, Et, Pr, Bu, } (\text{CH}_2)_5$] are found at 1325–1385 cm^{-1} (212).

A planar centrosymmetrical molecule (C_{2h}) is attributed to $(\text{MeN}=\text{PF}_3)_2$, according to infrared and Raman studies (141, 523); a discussion of the spectra is also given elsewhere (187).

2. NMR Investigations

Nuclear magnetic resonance, in particular ^{31}P NMR, has proved to be a very valuable method for the elucidation of structures containing $-\text{N}=\text{PCl}_3$ groups. In general, the chemical shifts for four-coordinate phosphorus in these compounds are between -40 and ~ 40 ppm, for five-coordinate phosphorus between 55 and 80 ppm (mostly centered around 80 ppm), and for six-coordinate phosphorus (e.g., PCl_6^-) at 290 to 310 ppm (external standard 85% H_3PO_4). Some papers dealing in part with the ^{31}P NMR of some compounds of Section VIII have appeared (160, 301, 411).

Hexachlorodiazadiphosphetidines $(\text{RN}=\text{PCl}_3)_2$ [$\text{R} = \text{Me}$ (157, 196b), Et to $n\text{-C}_{10}\text{H}_{21}$, $\text{Et}(\text{Me})\text{CHCH}_2$, $i\text{-Am}$ (185), Ph (301), o -, m -, $p\text{-FC}_6\text{H}_4$, $2,4\text{-F}_2\text{C}_6\text{H}_3$, $2,5\text{-F}_2\text{C}_6\text{H}_3$ (502), m -, $p\text{-CF}_3\text{C}_6\text{H}_4$ (46), CH_2Cl (338)] exhibit a chemical shift of the phosphorus nucleus between 77 and 82 ppm (85% H_3PO_4), thus proving the dimeric structure.

The ^1H NMR spectrum of $(\text{MeN}=\text{PCl}_3)_2$ (1:2:1 triplet) ($J_{\text{PH}} = 20$ Hz) (492) is also characteristic of the dimeric form; the same applies to higher diazadiphosphetidines (185).

Four-membered $\text{P}-\text{N}$ rings with tetracoordinate phosphorus atoms (sp^3 hybridization), as in (XXIV) and (XXV) (32) or $(\text{MeN}=\text{P}(\text{S})\text{Ph})_2$ (492), give shifts somewhat beyond the above limits; thus $\delta_{\text{P}} = 5.3$ ppm for (XXIV) and $\delta_{\text{P}} = -51.5$ ppm for (XXV). It is, however, interesting to note that $(\text{MeN})_6\text{P}_4\text{Cl}_8$ gives only one signal at $\delta_{\text{P}} = 74.5$ ppm (32).

The following chemical shifts for the monomeric phosphazotrihalides have been found: $\text{CCl}_3\text{N}=\text{PCl}_3$ ($\delta_{\text{P}} = 16.3 \pm 0.5$ ppm) (162) (17.4 ppm) (220a), $\text{Et}(\text{Me})\text{CHN}=\text{PCl}_3$ ($\delta_{\text{P}} = 38.7$ ppm) (185), $2,3,4,5\text{-F}_4\text{C}_6\text{HN}=\text{PCl}_3$ ($\delta_{\text{P}} = 37.8$ ppm), and $2,3,5,6\text{-F}_4\text{C}_6\text{HN}=\text{PCl}_3$ ($\delta_{\text{P}} = 31.6$

coordination at the phosphorus atoms; the chlorine atoms have one axial and two equatorial positions. The compound crystallizes in monoclinic form, space group $P_{21/n}$, molecular symmetry C_{2h} ; $a = 6.013 \pm 0.015$ Å; $b = 14.04 \pm 0.03$ Å; $c = 6.918 \pm 0.015$ Å; $\beta = 98.5 \pm 0.2^\circ$; $V = 579$ Å³; $Z = 2$; $d = 1.90$ g/cm³ (194) (see Fig. 6).

Equal P-N distances (1.67 Å) are surprisingly found in compound (XXV) (516).

The X-ray structure of (MeN)₆P₄Cl₈ has been determined (515), and it was shown to consist of three planar four-membered rings with nonequivalent P-N distances (delocalized π bonding).

The structure of (MeN=PF₂Ph)₂ (73) is in analogy a parallelogram with the fluorine atoms being in axial and equatorial position.

An electron diffraction study (4a) of (MeN=PF₃)₂ in the vapor phase shows the four-membered ring system.

An examination of MeN=PPh₂F proves its monomeric structure (1).

4. Other Physical Investigations

The heats of melting, evaporation, and sublimation of (MeN=PCl₃)₂ are known (187). Vapor pressure data for (MeN=PF₃)₂ have been published (77, 187), as well as its Trouton constant (25.5 cal/mole/deg) (77).

Ultraviolet spectra of compounds with phosphazo groups show the P=N bond to give an auxochromic effect (146, 547). The spectra of the compounds RN=PXYZ (R = Ph, *p*-O₂NC₆H₄, *p*-MeC₆H₄, *p*-CF₃C₆H₄, *p*-Me₂NC₆H₄; X, Y, Z = Ph, OPh, *p*-CF₃C₆H₄, *p*-Me₂NC₆H₄) have also been investigated (326), as well as their mass spectral fragmentation (491a).

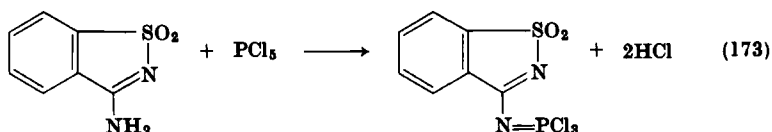
Dipole moments of RN=PCl₃ [R = CCl₃CCl₂, MeCCl₂CCl₂, ClCH₂-CCl₂CCl₂, (CCl₃)₂CCl, ClCMe₂CCl₂, ClCH₂CMeClCCl₂, 2,4-(O₂N)₂C₆H₃, 2,6,4-Cl₂(O₂N)₂C₆H₂, CCl₃, CF₃CCl₂, (CF₃)₂CCl, (CF₃)₃C] have been determined (220a, 325).

No signal for (MeN=PCl₃)₂ is found in the ³⁵Cl NQR spectrum between 20 and 45 MHz (516a).

The mass spectra of chlorofluorodiazadiphosphetidines (MeN=P)₂-Cl_nF_{6-n} ($n = 1-5$) show the presence of all possible isomers (499).

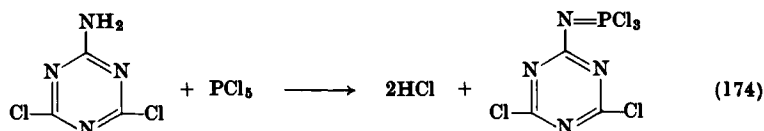
IX. Miscellaneous Compounds

3-Amino-1,2-benzisozulfonazole reacts with PCl₅ in a normal Kirsanov reaction (87).



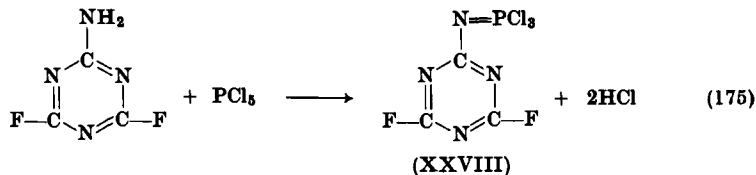
Correspondingly, $\text{FSO}_2\text{N}=\text{S}(\text{O})\text{FNH}_2$ gives $\text{FSO}_2\text{N}=\text{S}(\text{O})\text{FN}=\text{PCl}_3$ (385b).

Phosphorus pentachloride and 2-amino-4,6-dichloro-1,3,5-triazine react with introduction of a $-\text{N}=\text{PCl}_3$ group (83); with 2,4-diamino-6-chloro-1,3,5-triazine two $-\text{N}=\text{PCl}_3$ groups are introduced, and three with



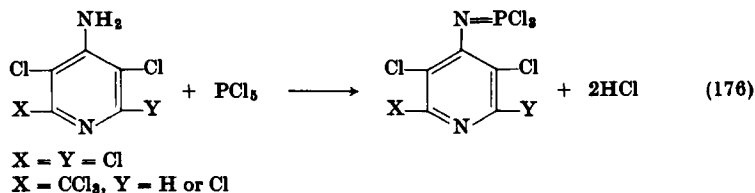
melamine (83). Tris(trichlorophosphazo)melamine may also be obtained from 2,4,6-tris(chloramino)-1,3,5-triazine and 3 moles of PCl_3 (179). Hydrolysis of these compounds with formic acid converts the $-\text{N}=\text{PCl}_3$ groups into $-\text{NHPOCl}_2$, $-\text{NHP}(\text{O})(\text{OH})\text{Cl}$, and finally $-\text{NHP}(\text{O})(\text{OH})_2$ groups (83). Interaction with NaOPh produces the esters (64).

Cyanuric fluoride amide reacts with PCl_5 (381), $\text{Ph}_n\text{PCl}_{5-n}$ ($n = 1, 2, 3$) (380) or PF_3Cl_2 (385) in the usual way, e.g.,



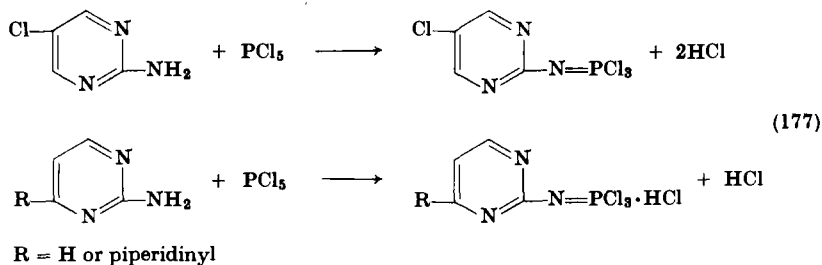
Acidolysis (HCOOH) of (XXVIII) introduces a $-\text{NHPOCl}_2$ group (380, 381), whereas substitution to a $-\text{NHSO}_2\text{F}$ group occurs with fluoro-sulfonic acid (380).

The reaction with several 4-aminopyridines with PCl_5 is described



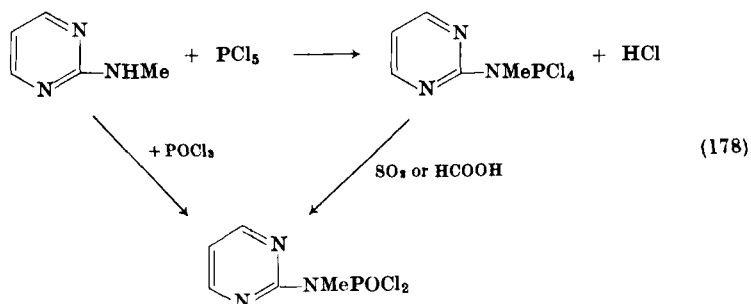
(359a); as well as their reactions with alcohols, phenols and formic acid. The similar reaction of 2-aminopyridines and PCl_5 is known (390a).

Substituted 2-aminopyrimidines react in an analogous manner (297).

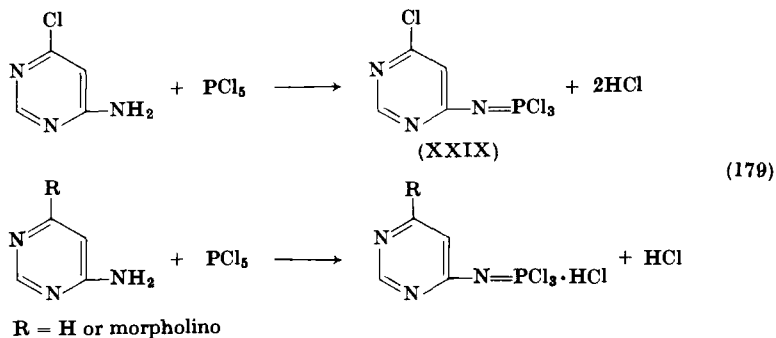


Two of the three chlorine atoms may be replaced by cyclic amines, such as morpholine or piperidine (297).

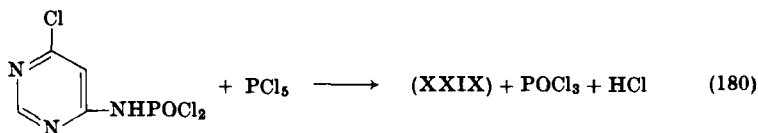
2-Methylaminopyrimidines react as expected with PCl_5 (297).



The behavior of 4-aminopyrimidines and some 4-methylaminopyrimidines with PCl_5 is described (390), as well as their subsequent reactions with HCOOH , SO_2 , or amines.

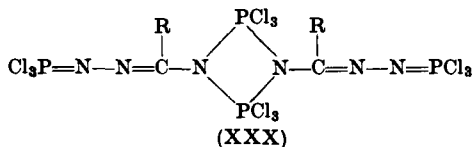


Compound (XXIX) may also be prepared (390) as in Eq. (180). The reactions of 5-aminopyrimidines with PCl_5 are similar (328).



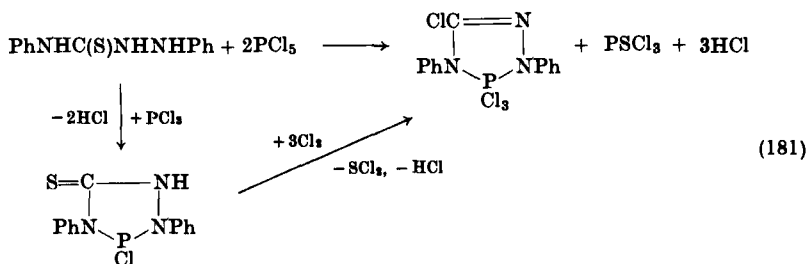
Hydrazine hydrochloride reacts with PCl_5 in POCl_3 as solvent to yield $\text{Cl}_3\text{P}=\text{N}-\text{N}=\text{PCl}_3$, which upon hydrolysis (HCOOH) gives hydrazido- N,N' -bis(phosphoryldichloride) (38). In contrast, Ph_2PCl_3 reacts with hydrazine hydrochloride to give nitrogen, HCl , and $[\text{Ph}_2\text{PCl}]_2\text{N}^+\text{Cl}^-$ (192b).

Semicarbazide, $\text{H}_2\text{NCONHNH}_2$, which possesses a hydrazide and an amide functional group, interacts with PCl_5 (solvent POCl_3) to give the interesting compounds (XXX) (39); depending on conditions the



substances with $\text{R} = \text{Cl}$ or $\text{R} = \text{OPOCl}_2$ may be obtained. Reactions of (XXX) with SO_2 give ill-defined substances.

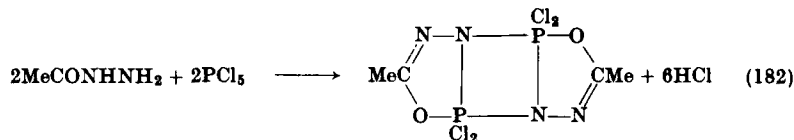
Diphenylthiosemicarbazide reacts with 2 moles of PCl_5 to produce a five-membered heterocyclic (195a) (for analogous systems, see Section VIII, B, 1).



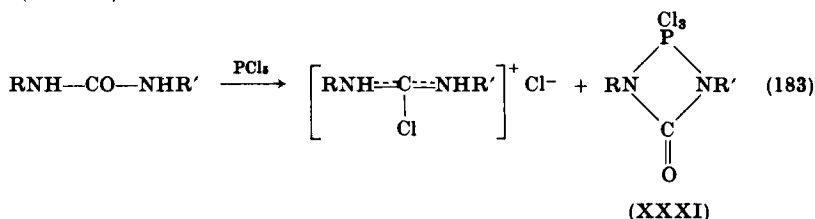
Interaction of PCl_5 with phenylsulfonylhydrazine (at room temperature or elevated temperature) gives the poorly defined compounds $(\text{C}_6\text{H}_7\text{N}_2\text{O}_2\text{S})_2\text{PCl}_3$ or $(\text{C}_6\text{H}_6\text{N}_2\text{O}_2\text{S} \cdot \text{PCl}_3)_n$, respectively (510).

Benzohydrazide, PhCONHNH_2 , reacts to give $\text{PhCONHN}=\text{PCl}_3$, which on heating reacts further with excess PCl_5 , probably via formation of a five-membered heterocyclic and fission of the $\text{P}=\text{N}$ -bond, to yield

PhCHCl_2 , HCl , and other products (332). Acetohydrazide and equimolar amounts of PCl_5 gives rise to a tricyclic system (145).



1,3-Disubstituted ureas react with PCl_5 giving 1,3,2-diazaphosphetidinones* (XXXI).



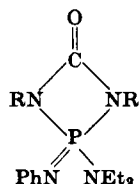
$\text{R} = \text{R}' = \text{Me, Bu}$ (495, 498), $\text{Ph, 1-C}_{10}\text{H}_7$ (111)

$\text{R} = \text{Ph, R}' = \text{Bu}$ (495, 498)

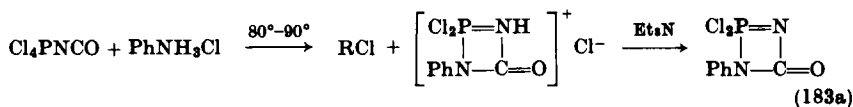
The structure of (XXXI) has been established by means of infrared and ^1H NMR spectra (498); $\delta_{\text{P}} = 60.05 \pm 0.5$ ppm (196) for (XXXI) ($\text{R} = \text{R}' = \text{Me}$), thus proving pentacoordinate phosphorus and the ring structure.

The HCl adduct of (XXXI) ($\text{R} = \text{R}' = \text{Me}$) may be obtained from PCl_5 and methyl isocyanate; its hydrolysis gives compound (XXIII), POCl_3 , and trimethylisocyanuric acid; its interaction with SO_2 (300) or with MeNCO (304) also gives (XXIII).

Attempts to make a diazaphosphetidinone with tetracoordinated phosphorus atom

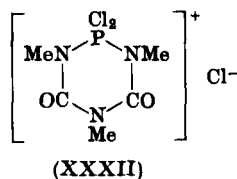


* Formation of a phosphadiazacyclobutenone is found in the reaction of Cl_4PNCO with PhNH_3Cl (288).



from the reaction of $\text{PhN}=\text{P}(\text{NEt}_2)\text{Cl}_2$ with N,N' -disubstituted ureas failed (47a).

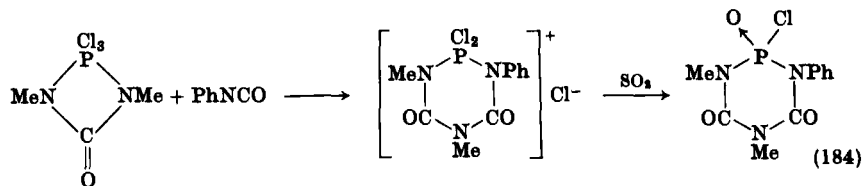
Heating (XXXI) ($\text{R} = \text{R}' = \text{Me}$) to $160^\circ\text{--}180^\circ/0.01$ Torr produces (XXXII) (299); (XXXI) ($\text{R} = \text{R}' = \text{Me}$) and MeNCO yield (XXIII)



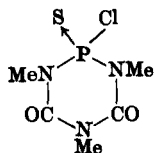
(299); the same compound (XXIII) may also be obtained from $(\text{MeN}=\text{PCl}_3)_2$ and MeNCO (305) (cf. Section VIII, B, 2).

Other authors (495, 498) assume that the thermolytic decomposition of 1,3,2-diazaphosphetidinones first produces trichlorophosphazo compounds and isocyanates, which, in turn, react with formation of carbodiimides and POCl_3 [(494), cf. also (497)]. Derkach and Narbut (111) observed the same effect upon heating (XXXI) ($\text{R} = \text{R}' = \text{Ph}$, $1\text{-C}_{10}\text{H}_7$) at $100^\circ\text{--}200^\circ$.

Interaction of (XXXI) and PhNCO proceeds over the following steps (196):

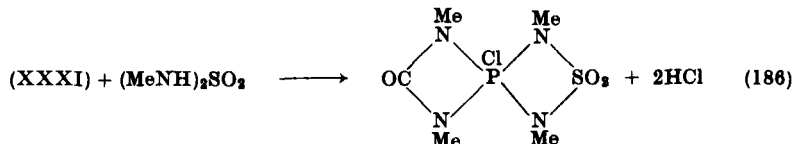
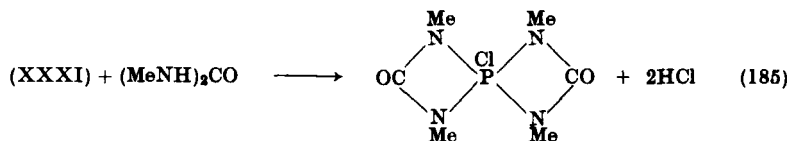


the mechanism [insertion of a PhNCO molecule between the phosphorus atom in (XXXI) and its adjacent nitrogen atom] has been established. Reaction of (XXXI) with methyl isothiocyanate gives only the thio analog to (XXIII), namely,



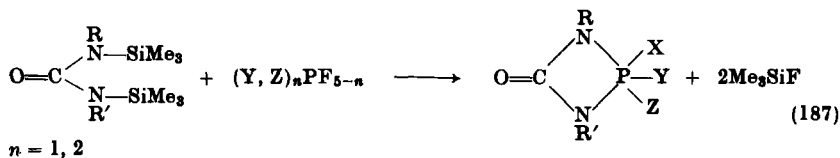
and (XXXIII); with MeNCCl_2 only (XXXIII) is obtained (196a). A six-membered ring is also obtained from (XXXI) and ClSO_2NCO (306a).

Compound (XXXI) ($R = R' = \text{Me}$) reacts with N,N' -dimethylurea or N,N' -dimethylsulfamide forming compounds containing two four-membered rings (36a).



The latter compound is the chloro analog of compound (XXXVI).

Replacement of the three chlorine atoms in (XXXI) ($R = R' = \text{Ph}$, $1\text{-C}_{10}\text{H}_7$) with phenol has been described (111); its hydrolysis at 100° gives H_3PO_4 and diarylureas, whereas at 15° the compounds $\text{ArNHCON-ArPO}(\text{OH})_2$ are obtained. Fluorination of (XXXI) ($R = R' = \text{Me}$) with SbF_3 gives 2,2,2-trifluoro-2-phospha-1,3-dimethyl-1,3-diazetidine-one [(144), cf. also (342)]; its structure has been established based on ^{19}F and ^{31}P NMR spectra. A positional exchange of the fluorine atoms has been shown to occur. Other 2-fluoroalkyl(or aryl)-2-phospha-1,3-dialkyl-1,3-diazetidinones may be prepared from N,N' -bis(trimethylsilyl)ureas with alkyl- or arylfluorophosphoranes (144).

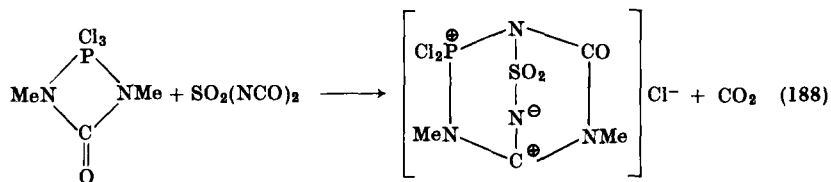


$R = R' = \text{Me}$, $X = Y = \text{F}$, $Z = \text{Me, Et, Ph, NMe}_2, \text{NEt}_2$; $X = \text{F}$, $Y = Z = \text{Me, Ph}$

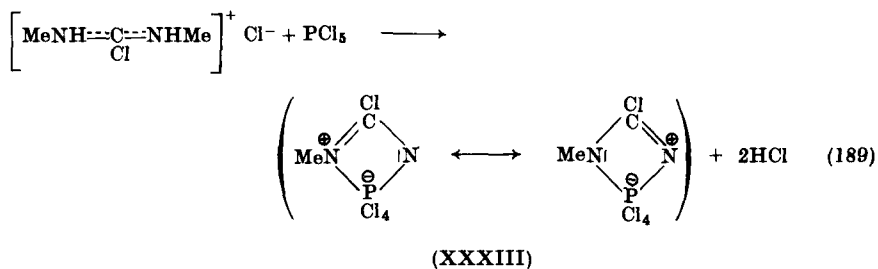
$R = \text{Me}$, $R' = \text{Ph}$, $X = Y = \text{F}$, $Z = \text{Me, Et}$

The NMR spectra (^1H , ^{19}F , ^{31}P) of these compounds (143b, 144) are consistent with the proposed structures. The mass spectra of some of these compounds have been recorded (8). The similar reaction of N,N' -bis(trimethylsilyl)ureas with POCl_3 , MePOF_2 , etc., failed to yield the desired diazaphosphetidinones (143c). The compound $\text{MeNPF}_3\text{NMeC}(\text{O})$ reacts with methyl isocyanate to give a spiro-phosphonium hexafluorophosphate (144).

A six-membered heterocyclic is formed by the reaction of 2,2,2-trichloro-1,3-dimethyl-2,1,3-phosphadiazetidione (XXXI) with sulfur diisocyanate (306).



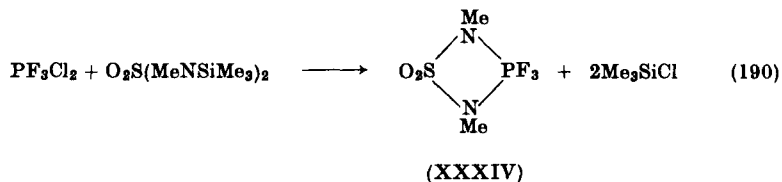
Interaction of *N,N'*-dimethylchloroformamidinium chloride with PCl_5 leads to compound (XXXIII) with hexacoordinate phosphorus



atom (303), shown by its ^1H and ^{31}P NMR spectrum ($\delta_{\text{P}} = 202 \pm 1$ ppm, $J_{\text{PH}} = 20 \pm 1$ Hz) and later by an X-ray structure determination (552).

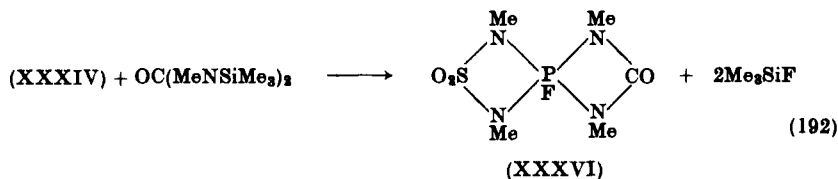
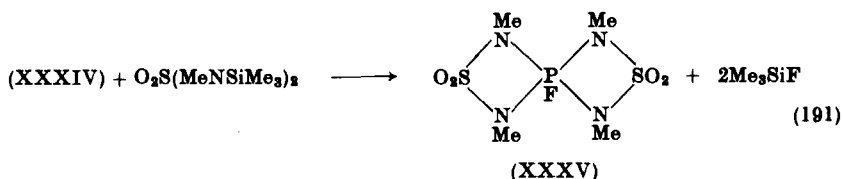
The reaction of $\text{HN}(\text{SO}_2\text{Cl})_2$ with PCl_5 (1:1) yields a compound $\text{P}_4\text{Cl}_6\text{N}_2\text{S}_2\text{O}_4$ (388) to which, on the basis of electric conductance studies in nitromethane (1:1 electrolyte) and its ^{31}P NMR spectrum ($\delta_{\text{P}} = -87 \pm 1$ ppm) (26a), the ionic structure $[\text{PCl}_4]^+[\text{N}(\text{SO}_2\text{Cl})_2]^-$ is assigned.

N,N'-Bis(trimethylsilyl)-*N,N'*-dimethylsulfamide and PF_3Cl_2 give the four-membered ring system (XXXIV) (37, 40).

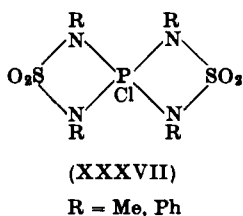


The action of excess $\text{O}_2\text{S}(\text{MeNSiMe}_3)_2$ on (XXXIV) produces (XXXV), whereas *N,N'*-bis(trimethylsilyl)-*N,N'*-dimethylurea and (XXXIV) give (XXXVI) (37, 40).

The ^{31}P NMR spectra of (XXXIV) ($\delta_{\text{P}} = 76.8$ ppm), (XXXV) ($\delta_{\text{P}} = 85.0$ ppm), and (XXXVI) ($\delta_{\text{P}} = 67.0$ ppm) prove the ring structure (40)

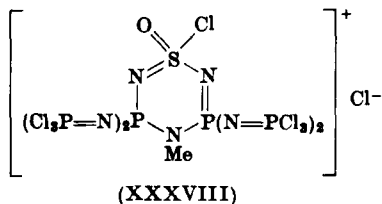


(pentacoordinated phosphorus atoms with trigonal-bipyramidal arrangement of the ligands); the ^{19}F NMR spectrum of (XXXIV) shows equivalence of the fluorine atoms, thus showing positional exchange of the fluorine atoms [analogous to $(\text{MeN}=\text{PF}_3)_2$, Section VIII, D]. Phosphorus pentachloride reacts in a similar manner with 2 moles of *N,N'*-dimethylsulfamide or *N,N'*-diphenylsulfamide to give



(36b, 37, 510).

Finally, the Kirsanov reaction with a cyclic sulfurylphosphazochloride gives compound (XXXVIII) (50a).



X. Applications

$[\text{Cl}_3\text{P}=\text{NPCl}_2=\text{NPCl}_3]^+\text{Cl}^-$ (VII) as well as $(\text{MeN}=\text{PCl}_3)_2$, $(\text{PhN}=\text{PCl}_3)_2$, 2,4- $(\text{O}_2\text{N})_2\text{C}_6\text{H}_3\text{N}=\text{PCl}_3$, $\text{PhCON}=\text{PCl}_3$, $\text{MeN}=\text{P}(\text{OPh})\text{Cl}_2$, $\text{PhN}=\text{P}(\text{OMe})_2$, Cl , $\text{PhCON}=\text{P}(\text{NMe}_2)\text{Cl}_2$, $\text{PhCON}=\text{P}(\text{OPh})_3$, and $\text{PhCON}=\text{P}\left[\text{N}\begin{array}{c} \diagup \text{CO} \\ \diagdown \text{(CH}_2)_5 \end{array}\right]_3$ are patented for use as cocatalysts in the anionic polymerization of ϵ -caprolactam (490). The amido derivative of (VII) has been suggested as a flame-proofing agent for tissues (51).

Compounds of the type $[\text{Cl}(\text{Cl}_2\text{P}=\text{N})_n\text{PCl}_3]^+\text{ZnCl}_3^-$ ($n = 1-10$) (Section IV, B, 2) have been found useful as high-temperature lubricants (345). Compounds of the types $[\text{Cl}(\text{Cl}_2\text{P}=\text{N})_n\text{PCl}_3]^+\text{M}_m^+\text{Cl}_{m+1}$ ($\text{M} = \text{Nb}$, Mo , Ta , $n = 3-15$), $[\text{Cl}(\text{Cl}_2\text{P}=\text{N})_n\text{PCl}_2]^+\text{M}_m^+\text{Cl}_{m+2}$ ($\text{M} = \text{Pt}$, W , Ru ; $n = 3-15$; $m = \text{valence state}$) (341), $[\text{Cl}(\text{PNCl}_2)_n\text{PCl}_3]^+\text{Y}$, or $[\text{Cl}(\text{PNCl}_2)_n\text{PCl}_2]^{2+}\text{Y}_2$ ($n = 3-15$, $\text{Y} = \text{ArO}$, RO , RNH , $\text{RN}=\text{}$) (374) have remarkable thermolytic and hydrolytic stability. Temperature-resistant oils of the formula $[\text{Cl}_3\text{P}(=\text{NPCl}_2)_n\text{N}=\text{PCl}_3]^+\text{Cl}^-$ ($n = 10-15$) have been suggested as high-temperature fluids (50c). The compound $\text{Cl}_3\text{P}=\text{NPOCl}_2$ (V) is an intermediate for lubricant additives, flame-proofing agents, corrosion inhibitors (214, 413), and softeners (214); the use of (V) for the polymerization of isobutene and tertiary olefins has been protected by a patent (213). Esters of (V), such as $(\text{RO})_3\text{P}=\text{NP}(\text{O})(\text{OR}')_2$, have been tested for pharmacological (43) and insecticidal (108, 214, 486) properties.

The pentakis(dimethylamides) of (VI) (13) and (VIII) (16a) represent effective insecticides.

The compounds $\text{ClSO}_2\text{N}=\text{PCl}_3$ (XV) and $\text{SO}_2(\text{N}=\text{PCl}_3)_2$ may be used as inhibitors for the polymerization of liquid SO_3 (171). Tetramido derivatives of $\text{ClSO}_2\text{N}=\text{PCl}_3$ have been suggested for the search of leaks in pipelines (293).

Several phosphazotrichlorides, such as $\text{MeSO}_2\text{N}=\text{PCl}_3$, $\text{CCl}_3\text{CON}=\text{PCl}_3$, $m\text{-Cl}_3\text{P}=\text{NO}_2\text{SC}_6\text{H}_4\text{CON}=\text{PCl}_3$, and their derivatives, stabilize photographic silver halide emulsions (95a).

Some sulfonylphosphazo derivatives, such as $\text{ArSO}_2\text{N}=\text{P}(\text{NC}_2\text{H}_4)_3$, have antitumor properties (108, 354, 488, 489); some have been patented for their usefulness for coating of textile fibers (373).

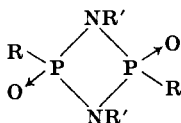
Esters of the type $\text{ArSO}_2\text{NNaPO}(\text{OR})_2$ (Section VI, B) may be utilized for the extraction of metal ions from neutral or alkaline media (468).

A compound $\text{PhSO}_2\text{N}=\text{P}(\text{OH})_2(\text{OC}_6\text{H}_4\text{NO}_2-p)$ has been described to be a good insecticide (167).

Arylsulfonylphosphazotriallyl esters have been reported to be intermediates for polymers (460).

The physiological properties of 2,3,6-Cl₃C₆H₂CONHPO(OR)₂ have been investigated (484). The toxicity and cancerostatic behavior of some carbonylphosphazo derivatives, namely, ArCON=P(NC₂H₄)₃ (Ar = Ph, *o*-, *p*-ClC₆H₄, *m*-, *p*-O₂NC₆H₄, *p*-BrC₆H₄) and ArNHCONHPO(NC₂H₄)₂ (Ar = Ph, *o*-ClC₆H₄), has been described (108, 183a). The triamides ArCON=P(NHAr')₃ (Ar = *p*-ClC₆H₄, *p*-BrC₆H₄; Ar' = Ph, *p*-MeC₆H₄) may be used as fungicides (480); several other derivatives of carbonylphosphazotrichlorides are potential insecticides (387g) or herbicides (387b). The diesters RCONHPO(OR')₂ (R = CH₂Cl, CHCl₂, MeCHCl, MeCCl₂, ClCH₂CCl₂, *o*-, *m*-, *p*-ClC₆H₄, *p*-BrC₆H₄, *p*-FC₆H₄; R' = Me, Et, Pr, Ph) have found application as herbicides (463); see (79) for general topics. The compound (PhN-PCl₃)₂, which may also be a cocatalyst for the polymerization of ϵ -caprolactam (see above), has also been suggested for use as a lubricant additive (322) [as has (MeN=PCl₃)₂] and as an inhibitor for the polymerization of SO₃ (171).

The four-membered ring compounds



R = PhO, R' = Me (52)

R = C₆H₁₁O, R' = C₆H₁₁ (54)

R = Et₂N, Pr₂N, PhNH;

R' = Et, Pr, Ph (194a)

have been described as intermediates for synthetic polymers and as flame retardants (194a). Other polymers with P-N four-membered ring units are patented (348, 358, 359).

The antiblastic properties of *p*-O₂NC₆H₄N=P(NC₂H₄)₃ have been reported recently (322a).

The phosphorylation products of nitriles may be useful starting materials for polymers (281).

Phosphorylated trichloroacetamidines have been tested for their herbicidal properties (493); they are far more active as fungicides (479).

The use of (MeN=PF₃)₂ and (MeN=PF₂R)₂ (R = Ph, *m*-CF₃C₆H₄) (62, 410) as cocatalysts for the polymerization of ϵ -caprolactam is also patented.

The trichlorophosphazopyrimidines (297, 390) have been suggested (297) for the synthesis of active cytostatics.

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LOW TEMPERATURE CONDENSATION OF HIGH TEMPERATURE SPECIES AS A SYNTHETIC METHOD

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I. Introduction

The idea of studying gaseous radicals and high temperature species by condensing them on very cold surfaces, has been employed for many years. The work of Rice and Frearno (77) on the thermal decomposition of hydrazoic acid was a spectacular example. The imine radical produced condensed to a bright blue solid at -196° which on warming to room temperature formed white ammonium azide. Various methods of trapping unstable species were reviewed in 1960 in a book by Bass and Broida (5).

An important development occurred in 1963 when Skell and Westcott (106) reported that carbon vapor, formed from a carbon arc under vacuum, reacted with organic compounds at -196° to give new compounds incorporating the carbon vapor species. The objectives of these experiments and the reaction conditions used are fundamental to the work discussed in this chapter.

The carbon was vaporized under high vacuum so that the vapor species could move away from the arc without intermolecular collisions which would have caused aggregation. The walls of the surrounding vacuum chamber were cooled with liquid nitrogen. This allowed the vapor of another compound to be passed into the chamber while the carbon was evaporating and to be condensed on the walls so rapidly that high vacuum conditions were maintained. Even with substantial rates of addition of the compound, very little of it contacted the hot carbon or interacted with carbon vapor species until the moment of condensation on the walls. The carbon vapor reacted with the other compound on the cold walls provided that thermodynamic and kinetic factors were favorable. The experiments were conducted on a scale which enabled any new compounds formed to be isolated and characterized.

This work marked the beginning of a new and fruitful phase in the exploitation of low temperature condensation reactions of high temperature species as a useful synthetic method. Since then, at least twenty atomic and molecular high temperature species have been used as reagents in chemical synthesis under conditions closely related to those described by Skell and Westcott, and many new compounds have been synthesized.

The major portion of this chapter is a review of the formation and reaction of those species which have been used in synthesis, but the total range of available species and the special features of low temperature condensation reactions are discussed first.

Most of the species considered will have been made at temperatures above 1000° , at pressures below 1 Torr, and in approximate thermal equilibrium with their surroundings. The last is a particularly important limitation in scope. Reactive chemical species can be formed by a variety of nonthermal methods including electrical discharges, photochemical excitation, and nuclear recoil. Such methods cause excitation of atoms and molecules and the formation of "high temperature" species. Usually these species are in no sense in thermal equilibrium with their surroundings (Section VI). However, the definition of approximate thermal equilibrium is broad and includes, for example, electronically excited carbon vapor species formed from an arc.

II. Species and Reaction Conditions

There are many gaseous atomic and molecular species which are thermodynamically stable with respect to condensed phases or other gaseous molecules only at high temperatures. These species have mostly been first characterized spectroscopically, and frequently equilibrium data for their formation have been obtained by mass spectrometric, effusion, and transpiration studies (55).

To be of interest to a synthetic chemist hoping to apply the low temperature condensation procedure, a high temperature species should meet two requirements. First, it must contain an element in a form which for thermodynamic and kinetic reasons is liable to be reactive at low temperatures. Second, it must be possible to form the species in a fairly pure state at the rate of at least a few millimoles an hour.

A. ATOMIC SPECIES

The largest single class of species which clearly meet the above criteria is the atoms of the elements. A gaseous atom of any element except the noble gases may be expected to be more reactive than the normal form of the element for two reasons. First, the atom can react faster because it has minimal steric requirements and generally has readily available electrons or orbitals. Second, the atom is a species of higher energy than the normal state of the element. This is shown in Table I which gives

TABLE I

HEATS OF FORMATION ($\Delta H_{298^\circ\text{K}}$) OF GASEOUS ATOMS OF THE ELEMENTS^a

H	Li	Be											B	C	N	O	F	Ne
52	39	78											134	171	113	59	19	0
	Na	Mg											Al	Si	P	S	Cl	Ar
	26	35											78	107	79	67	29	0
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
	21	42	82	113	123	95	67	100	101	103	80	31	69	90	72	54	27	0
	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
	20	39	86	145	172	159	(155)	155	133	89	68	27	58	72	63	47	25	0
	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
	19	42	104	145	187	202	186	187	160	135	88	15	43	47	50	34	—	0

^a Values in kcal/mole. Data from reference (67a), and compilation by Honig (33a).

the heats of formation of the gaseous atoms of the elements relative to their standard states at 25°. Condensation of the atoms in an isolated

form on an inert surface at -196° will not greatly change their energy, so that the values in Table I can be used when considering the energetics of low temperature condensation reactions. The extra energy possessed by atoms compared with the normal states of the elements will always make some difference to their chemistry, but a large difference is not likely until the atoms have heats of formation greater than about 40 kcal/mole. Then the atoms can react via intermediates far too endothermic to be formed from the normal states of the elements under reasonable conditions.

Thus, a reaction reported by Skell and Engel (92) in which butenes, butadiene, and methylcyclopropane were formed from carbon atoms and propane, would be impossible for solid carbon on both thermodynamic and kinetic grounds. On the other hand, none of the reactions reviewed by Mile (65) involving alkali metal atoms, which have quite low heats of formation, would have been thermodynamically impossible starting with the solid metals, only kinetically less favored.

The change in potential reactivity of elements on atomization can be further illustrated by considering the reaction of copper or sodium atoms with chlorine-containing compounds. The heats of formation of solid sodium chloride and cuprous chloride are about -98 and -32 kcal/mole, respectively, so that reactions of sodium with chlorine-containing compounds are normally much more exothermic than reactions of copper. However, the Na-Cl and Cu-Cl bond dissociation energies are much closer in value, about 98 and 87 kcal/mole, respectively. The difference between these two sets of values is almost all accounted for by the higher heat of formation of gaseous copper atoms. The implication is that when copper atoms are condensed with chlorine-containing compounds on a cold surface, they may be nearly as effective dechlorinating agents as sodium atoms (Section V, D).

Atoms of some elements, particularly those which vaporize at low temperatures in molecular forms, are not as conveniently made by thermal dissociation as by other excitation methods such as an electrical discharge (Section VI, A). The lifetimes in the gas phase of atoms of these elements are generally much longer than, for example, gaseous metal atoms. It is possible to pump atomic nitrogen at a pressure of a few Torr along tubing in a vacuum system with only slow recombination (140), whereas nickel atoms will condense immediately on collision with a surface at room temperature.

Electronically excited states of atoms will be energetically even further above the normal state of elements than are the ground state atoms. The population of excited states among atoms formed by purely thermal means below 3000° is usually low, but it may be considerable

in atoms formed by electrical discharge or photochemical methods. Skell and his associates (91, 93, 107), in their work with carbon vapor formed in an arc, have shown that different electronic states of carbon vapor species have different chemical reactivities at -196° . The lifetimes of the excited states are long enough to survive the time interval between generation in the arc and arrival on a cold surface (Section IV, B). Some excited states of transition metal atoms may be very short-lived ($<10^{-9}$ sec) and could undergo radiative decay before reaching a cold surface.

B. MOLECULAR SPECIES

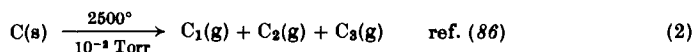
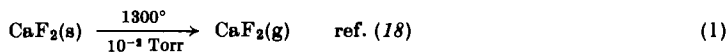
1. Formation

As there is a wide variety of known high temperature molecular species, the selection of those of possible synthetic use is more difficult than with atomic species.

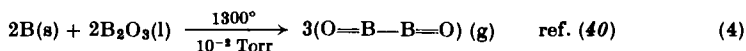
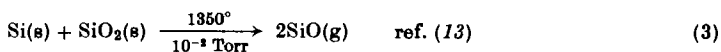
Molecular species which can be formed at high temperatures in useful amounts for synthesis generally fulfill two conditions. First, the species contain strong bonds which prevent them from undergoing dissociation to the elements at the temperature at which they are formed. Second, the process by which they are formed involves an increase in the number of gas molecules so it is favored by increasing the temperature and lowering the pressure. These conditions rule out many species known to spectroscopists which can be formed only in tiny concentrations, e.g., transition metal hydride vapors (19).

Some different processes which allow high temperature species to be formed with an increase in the number of gas molecules are shown below:

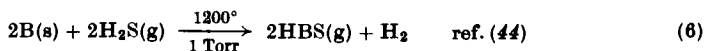
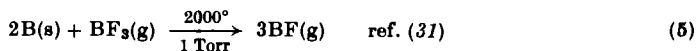
(a) The evaporation of solids or liquids, e.g.,



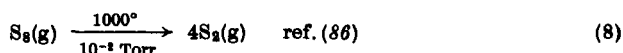
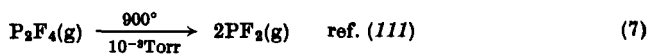
(b) Solid-solid or solid-liquid reactions, e.g.,



(c) Gas-solid reactions, e.g.,



(d) Dissociation of gases, e.g.,



Some condensed phases vaporize both as monomeric and polymeric species, the proportion of polymers in the saturated vapor increasing with increasing temperature (51). This only occurs when the heat of dimerization is less than the heat of vaporization of the element or compound in a monomeric form. An element like carbon with a very high heat of vaporization as a monomer but with strong bonds in its gaseous polymers will have a considerable concentration of polymers in its saturated vapor at high temperatures.

2. Species in Unstable Low Valencies

Equations (2), (3), (5), and (7) show the formation of low valency species unstable with respect to a higher valency of an element at ordinary temperatures. The potential in chemical synthesis for these compounds is derived from their possible conversion to the higher

TABLE II

SOME GASEOUS HIGH TEMPERATURE SPECIES OF POSSIBLE INTEREST
IN CHEMICAL SYNTHESIS AT LOW TEMPERATURES

<i>Atoms^a</i>	<i>Halides</i>	<i>Oxides, sulfides, nitrides, carbides</i>
Atoms of all elements except the noble gases (see Table I)	Nonmetals BF, ^a BCl ^a CF ₂ , ^a CCl ₂ , ^a CBr ₂ ^a	Nonmetals B ₂ O ₂ , ^b B ₂ O ₃ ^b HBS, ^b BC ₂ ^a
<i>Homonuclear molecules</i> C ₂ , ^a C ₃ , ^a C ₄ ^a P ₂ , ^b As ₂ , ^b Sb ₂ ^b S ₂ , ^b Se ₂ ^b	PF ₂ , ^a SiCl ₂ , ^a SiBr ₂ ^a PF, ^a PF ₂ ^a Metals LiF, ^b CaF ₂ , ^b AlF ₃ ^b AlF, ^a ScF, ^a LaCl ^a TiF ₂ , ^b ZrF ₂ , ^b CrF ₂ ^b	CS ^a SiO, ^a SiS, ^a SiC ^a GeO, ^b GeS ^b PN ^b Metals BeO, ^b TiO ^b ZrO ₂ ^b

^a Species containing elements in unstable low valency states.

^b Species containing elements in valency states in which they are commonly stable at ordinary temperatures.

valency state by reaction with other compounds. Thus, a compound like boron monofluoride readily combines with a variety of organic and inorganic compounds on being condensed with them at -196° , to form

a derivative of trivalent boron (119) (Section IV, A). Reactions of boron monofluoride with other compounds are able to compete successfully with its tendency to react with itself to give $(BF)_n$ or to disproportionate to boron and boron trifluoride. The heat of formation of boron monofluoride from boron and boron trifluoride is roughly 60 kcal/mole (10), and this can be taken as a crude measure of its instability relative to trivalent boron at low temperatures.

Unfortunately, not all low valency species are as reactive as boron monofluoride. For some, polymerization or disproportionation occur in preference to reactions with other compounds. There is as yet insufficient data to predict the synthetic usefulness of species, although the problem is considered again in Sections IV and V.

Table II includes a selection of known low valency gaseous high temperature species which can be formed in at least millimole quantities at temperatures above 1000° , and which appear to have potential in chemical synthesis. The inclusion of a species in Table II does not mean that equilibrium high temperature methods are the only ways of making it. An example is carbon difluoride, which can be made from trifluoromethane at 1300° (132), but is much more conveniently made by decomposition of difluorodiazirine, CF_2N_2 , at 150° (67) and from numerous other compounds at temperatures below 200° (124).

3. *Species in Normal Valencies*

Equations (1), (4), (6), and (8) show the formation of high temperature gaseous species in which the elements concerned are in valence states commonly stable at ordinary temperatures. Condensation and polymerization of these species does not involve a change in valency. The species are representatives of a large class including many metal halides, oxides, sulfides, and some homonuclear species as shown in Table II.

The potential of these species to be reagents in low temperature condensation reactions is less clear than for low valency or atomic species. It depends on whether or not effective use can be made of the energy difference between the gaseous species and the condensed, polymerized forms. For example, the heat of vaporization of zirconia is about 175 kcal/mole so that $ZrO_2(g)$ is very unstable with respect to $ZrO_2(s)$ at ordinary temperatures. It is possible that on low temperature condensation $ZrO_2(g)$ may react with acids, alcohols, etc., to which solid zirconia is very resistant. On the other hand, polymerization of $ZrO_2(g)$ to $ZrO_2(s)$ may be the only observed process under all condensation conditions. Although there is no experimental evidence yet with $ZrO_2(g)$, there are indications that at least some of the high temperature species in this class are reactive (Section IV).

4. *The Lifetimes of Species in the Gas Phase*

Species formed by vaporization of condensed phases at high temperatures will generally condense immediately on contact with solid surfaces at ordinary temperatures. This includes species formed by reactions in condensed phases such as SiO, B₂O₃, and AlF.

A greater variation in lifetime comes with molecular species formed by reactions involving gases at high temperatures. For example, silicon dichloride formed from silicon and silicon tetrachloride is a short-lived species in the gas phase. At a pressure of 0.1 Torr it will decay in a few milliseconds forming (SiCl₂)_n on contact with solid surfaces, or reacting rapidly with any silicon tetrachloride present to form perchlorosilanes (122). Silicon dibromide is similarly short-lived. In contrast, silicon difluoride has a half-life of about 150 sec at 0.1 Torr pressure (130) and it decays only on solid surfaces forming (SiF₂)_n, not perfluorosilanes. This striking difference in behavior between SiF₂ and SiCl₂ may be caused by very slight differences in electron density on the silicon atoms in the two molecules.

Other long-lived species are HBS (44) and PF₂ (111). The long lifetime of the former is particularly surprising in view of the short lifetime of HBO (74).

C. OTHER FACTORS INFLUENCING LOW TEMPERATURE CONDENSATION REACTIONS

1. *Temperature and Activation Enthalpy*

As has already been illustrated, the use of low temperatures for reacting high temperature species with other compounds is dictated by practical considerations. Under no other set of conditions can the high temperature species be brought into contact with an ordinary compound on a large scale without thermal cracking of the compound or prior aggregation of the species. It is easiest to maintain the required high vacuum conditions if the temperature used for condensation is such that the vapor pressure of all the condensed species is less than about 10⁻⁵ Torr. For the majority of inorganic and organic compounds which are reacted with high temperature species, this condition is fulfilled within the temperature range -78° (solid CO₂) to -196° (liquid N₂). Much lower temperatures, which can be obtained using liquid hydrogen (20°K) or liquid helium (4°K), are only practical for very small-scale work.

Reaction rates are strongly affected by the activation enthalpy at low temperatures. For example, at -196°, assuming an activation entropy of -10 cal·deg⁻¹·mole⁻¹, the rate constants for reactions of activation

enthalpies 1, 2, and 5 kcal/mole are very roughly 10^7 , 10^4 , and 10^{-4} sec $^{-1}$, respectively. High temperature species are observed to polymerize very rapidly on cold surfaces which indicates that these reactions may have activation enthalpies of 1 kcal/mole or less. Thus, activation enthalpies of reactions between high temperature species and ordinary compounds have to be similarly low if the reactions are to compete with polymerization of the high temperature species. Raising the temperature of the cold surface reduces the differences in reaction rates caused by small differences in activation enthalpy. The corresponding rate constants for the above reactions at -78° are very roughly 10^9 , 10^8 , and 10^5 sec $^{-1}$, respectively. This suggests that the temperature chosen for the condensation should be as high as possible. This was demonstrated by results of Bassler *et al.* (6). However, the best temperature will be a compromise between these kinetic effects and the practical considerations of available coolants, the need for low vapor pressures, and the preservation of unstable reaction products.

2. The Process of Condensation

There are three main ways in which a short-lived high temperature species can be brought into contact with another compound on a cold surface.

(a) The species and a compound with which it may react are cocondensed, i.e., condensed simultaneously, on the cold surface. This is the method which has already been described and which has been used most commonly in synthetic work.

(b) The species and at least a hundredfold excess on an inert gas are cocondensed on the cold surface, to isolate the species in an inert matrix. A compound which may react with the species is then condensed on the matrix and is allowed to diffuse into the matrix on warming.

(c) The species is condensed on to a cold sample of a potentially reactive compound in a solid, liquid, or solution form.

When a high temperature species and another vapor are cocondensed on a cold surface, several processes occur. At the moment of impact on the surface all the molecules immediately lose most of their translational energy and will very rapidly lose their excess rotational and vibrational energy. However, the surface will be in a fluid state and the molecules will move around for a short time. The period of surface motion is shorter the lower the temperature of the cold surface.

In most cases it is not known what proportion of the molecules of the high temperature species react in this stage of surface mobility, but evidence from matrix isolation experiments (see below) suggests almost complete reaction. The primary products of the reactions and unchanged

reactants will then be frozen on the surface and covered by other molecules. Secondary reactions may occur when the temperature is raised at the end of the cocondensation to give the products which are finally isolated at ordinary temperatures. In several of the reactions discussed in Sections IV and V, it is noted that some obvious change, such as evolution of gas, occurred on warming to slightly above -196° .

The yields in cocondensation reactions can nearly always be improved by using a large excess of the compound condensed with the high temperature species as this reduces the proportion of contacts between molecules of the high temperature species.

Method (b) depends on being able to prevent polymerization of a high temperature species by surrounding it with many inert atoms or molecules in a rigid matrix. Because of the surface mobility problem discussed above, this is not easily achieved. Skell and his associates (90, 91, 93, 107) were successful in isolating small quantities of carbon vapor species in neopentane matrices at -196° and subsequently reacting these with other compounds. However, Brewer *et al.* (12) failed to isolate metal atoms in sulfur hexafluoride on cocondensation at -196° . They found that by condensing the atoms and SF_6 at -250° , using a very large excess of SF_6 , they obtained isolated atoms which remained isolated on warming to -196° .

Matrix isolation of high temperature species in noble gas matrices at 4° or 20°K is a technique which has been used widely by spectroscopists (63, 136). It is possible to condense and isolate another compound along with the high temperature species in an inert matrix, and watch changes in the spectrum when diffusion is allowed to occur at a higher temperature. However, this powerful method has so far been applied to only a few of the reactions of interest to synthetic chemists (6).

Method (c) works well if a high temperature species is condensed into a cold, stirred liquid or solution (89). This is a very attractive alternative to method (a) for synthetic work when liquids of suitable vapor pressure can be chosen. Reaction of the high temperature species probably occurs in the surface layers of the liquid just as it occurs on a surface used for cocondensation. When a high temperature species is condensed on a cold solid, reaction seldom occurs. The species simply polymerizes on the surface. Hydrogen atoms are known to diffuse into solid olefins at -196° (46), but these are exceptionally mobile.

III. Experimental Methods

The basic experimental requirements for studying low temperature reactions of high temperature species are a furnace for generating the

species inside a vacuum system and a cold surface on which the species can be condensed with other compounds.

The design of an apparatus will be influenced by many variables such as the method of formation of the high temperature species, the lifetime of the species in the gas phase, the manner in which the species is condensed with other compounds, and the scale on which the experiment is to be run.

A. THE FORMATION OF HIGH TEMPERATURE SPECIES

1. *Preparation from Condensed Phases*

A considerable technology exists on the vacuum evaporation of metals, metalloids, and other condensed phases, developed by chemists

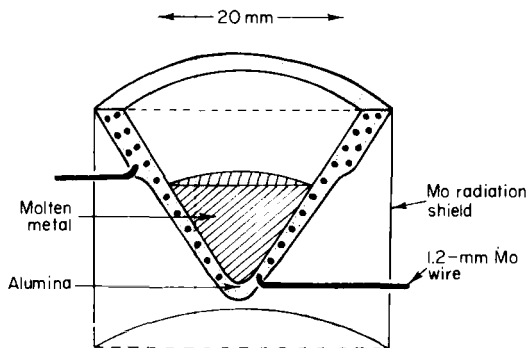


FIG. 1. Section through crucible used for evaporating metals.

and physicists interested in thin films of these materials (32). Experimentally the methods fall into two groups depending on whether or not the substance being vaporized is in contact with other hot materials. In almost all cases, the high temperature species formed are short-lived and must travel to a cold surface by a line-of-sight path.

a. Methods Employing a Hot Container. The range of materials which can be used as containers at high temperatures is rather limited. The requirements are a high melting point and resistance to corrosion. The latter is a formidable problem when heating many elements and compounds—hence the need for the “containerless” methods discussed below.

A type of container which the author has found particularly useful is shown in Fig. 1. This is a crucible made from a spiral of molybdenum wire coated with alumina cement. It is heated by passing an electric

current through the wire. The design is a development of that described by Olsen *et al.* (70). The size of crucible shown in Fig. 1 conveniently holds about 0.3 ml of molten metal. The metal is heated until its vapor pressure is 10^{-2} Torr or greater before rapid evaporation occurs. For example, 2 gm of cobalt were vaporized from the crucible under high vacuum in 30 min at a temperature of about 1650° with a power input

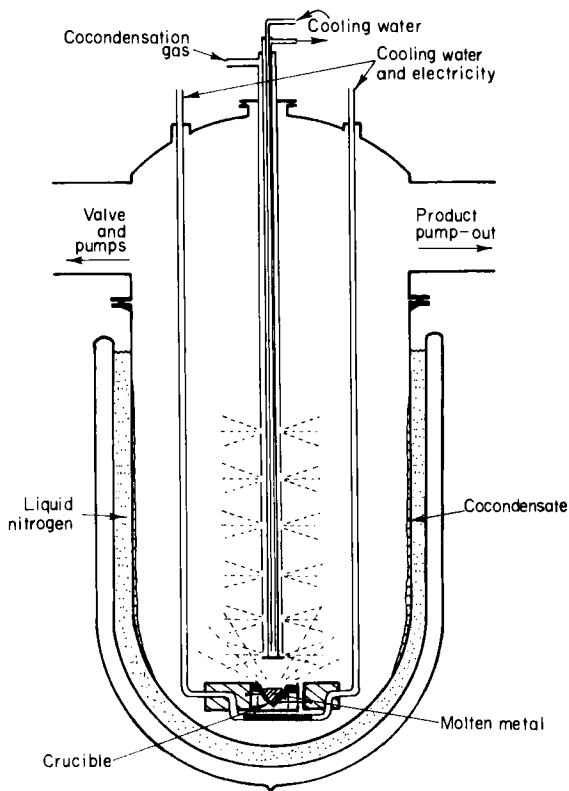


FIG. 2. Apparatus for condensing metal atoms with volatile compounds.

of 190 W. With the crucible mounted as shown in Fig. 2, roughly 90 W were radiated to the walls of the surrounding vacuum chamber, the rest of the heat was absorbed in water cooling. A larger version of the crucible with straight sides has been used to evaporate 30 gm of copper in 1 hr with a power input of 320 W.

The crucibles have been used successfully to evaporate Mn, Fe, Co, Ni, Cu, Ag, Au, and Sn as shown in Table III. Chromium has been

TABLE III

FORMATION OF HIGH TEMPERATURE SPECIES WHICH HAVE BEEN USED IN SYNTHESIS

Species	Formed from	Temperature	Method of heating	Rate of formation (mmoles/hr)	Refs.
<i>1. Vapors of Main Group Elements</i>					
B	B(l)	2300°–2500°	Electron bombardment	~50	(120)
C, C ₂ , C ₃ , . . .	C(s)	2600°–3200°	10–16 V ac arc	30–120	(22, 107, 133)
		~2600°	Resistance heated C rod	<20	(112)
Si	Si(l)	1500°–1700°	Electron bombardment	~50	(45)
	Si(s)	1350°	Resistance heated Si rod		(99)
Ge	Ge(l)	~1400°	Resistance heated graphite cloth strip	~20	(64)
Sn	Sn(l)	1400°	Resistance heated Mo-wound Al ₂ O ₃ crucible	20–100	(64)
Mg	Mg(s)	700°	ac arc	—	(88)
H	H ₂ (0.03–1.0 Torr)	1800°	Resistance heated tungsten strip		(46)
<i>2. Vapors of Transition Metals</i>					
Cr	Cr(s)	1450°	Resistance heated Mo-wound Al ₂ O ₃ crucible	20	(126, 127)
Mn	Mn(l)	1100°	Resistance heated Mo-wound Al ₂ O ₃ crucible	20–100	(126, 127)
Fe	Fe(l)	1550°	Resistance heated Mo-wound Al ₂ O ₃ crucible	20–40	(126, 127)
Co	Co(l)	1600°	Resistance heated Mo-wound Al ₂ O ₃ crucible	20–60	(126, 127)

(continued)

TABLE III—continued

Species	Formed from	Temperature	Method of heating	Rate of formation (mmoles/hr)	Refs.
Ni	Ni(l)	1600°	Resistance heated Mo-wound Al ₂ O ₃ crucible	20–40	(126, 127)
Pd	Pd(l)	1600°	Resistance heated Mo-wound Al ₂ O ₃ crucible	10–20	(127)
Cu	Cu(l)	1400°	Resistance heated Mo-wound Al ₂ O ₃ crucible	20–400	(127, 128)
Ag	Ag(l)	1200°	Resistance heated Mo strip	10–20	(121)
Au	Au(l)	1300°	Resistance heated Mo strip Resistance heated Mo-wound Al ₂ O ₃ crucible	10–20 10	(121) (28)
3. Gaseous Compounds					
BF ₃	B(s) + BF ₃ (1 Torr)	1800°–2000°	Induction heated graphite tube	100	(119)
B ₂ O ₃	B(s) + B ₂ O ₃ (l)	1300°–1400°	Resistance heated Mo-wound Al ₂ O ₃ crucible	50	(128)
CCl ₂	HCCL ₃ → HCl + CCl ₂	1400°	Resistance heated graphite tube		(89)
SiF ₂	Si(s) + SiF ₄ (1 Torr)	1200°	Kanthal-wound quartz or mullite tube	30–300	(130, 131)
SiCl ₂	Si(s) + SiCl ₄ (1 Torr)	1350°	Induction heated graphite tube	30	(122)
SiO	Commercial solid "SiO"	1400°–1500°	Resistance heated Mo-wound Al ₂ O ₃	100–250	(80)
PF ₂	P ₂ F ₄ → 2PF ₂	800°–1000°	Resistance heated nichrome wound quartz tube	20	(109, 111)

evaporated, but with slight contamination from lower aluminum oxides. More electropositive elements than chromium attack the alumina rapidly and cannot be evaporated this way. The highest temperature to which the crucible can be used is 1800° . As a consequence, it is found that metals with heats of vaporization greater than about 110 kcal (Table I) cannot be evaporated at a useful rate.

Induction heating of crucibles has been used to a limited extent. Weltner (136) has described a very simple induction furnace for depositing high temperature species in matrices of inert gases. Electron bombardment heating of crucibles and Knudsen cells has been used extensively in high temperature mass spectrometry (55) where the attainment of a very uniform, controllable temperature is important.

b. Containerless Methods. The essential feature of "containerless" methods is the introduction of energy in such a way that the material being evaporated is in contact only with cooler portions of itself or with a water-cooled metal surface with which it will not react. Such methods are mandatory for the evaporation of boron, carbon, and other elements which react with almost all possible container materials at the temperatures at which they vaporize. Containerless methods are also important for vaporizing the more refractory second- and third-row transition metals.

The most widely used containerless method for high vacuum evaporation is electron bombardment heating using a focused electron beam. An intense beam of electrons striking any solid surface will cause local heating and then vaporization. The author has used an electron gun made by Varian Associates. This draws electrons from a hot tungsten filament with a 4000-V potential and bends the electron stream through 180° magnetically to bring it to focus on a 3-mm diameter spot. The maximum power available is 2 kW. The material being vaporized is in contact only with the water-cooled body of the gun. The fastest rates of evaporation are obtained with materials which are poor conductors of heat. Using the arrangement shown in Fig. 3 in which a rod of material is fed downward into the electron beam, boron and silicon have each been vaporized at rates of about 50 mmoles/hr (45, 120). These were maximum rates compatible with retention of a drop of molten material on the end of the rod. Although the main effect of the electrons is to raise the temperature of the material they strike, there is some risk of electronic excitation or even ionization of the resulting vapor.

Heating methods such as a laser beam or focused energy from the sun or from an arc are not easily used for continuous vaporization under vacuum, as vaporized material tends to coat the window through which energy passes into the vacuum system. Schaeffer and Pearson (78) have

used a pulsed laser to vaporize small amounts of carbon and boron in the presence of other compounds.

Carbon is one of the few elements which can be evaporated successfully from an arc under high vacuum. The type of apparatus used by

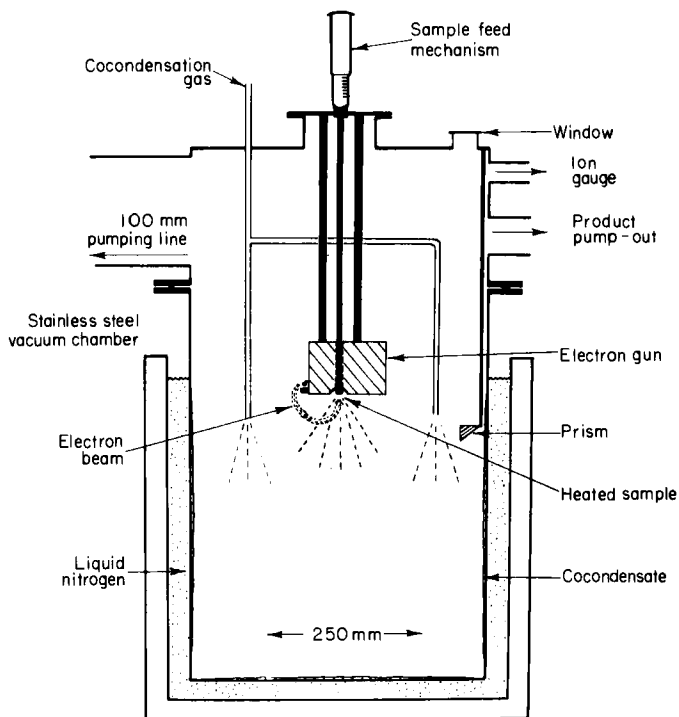


FIG. 3. Electron bombardment vaporization apparatus.

Skell and his associates, and other workers (8, 21, 22, 107), is shown in Fig. 4. Using a potential of 10–16 V and a current of 30–100 A, the carbon was vaporized at a rate of 40 to 150 mmoles/hr. The carbon vapor species were formed in ground and excited electronic states (91, 107), which would not be produced in a purely thermal process.

There have also been reports of evaporation of carbon (112) and silicon (99) by electrical resistance heating of a filament or rod of these materials. This is difficult to control, particularly for silicon, which melts

only slightly above the temperature at which appreciable vaporization occurs.

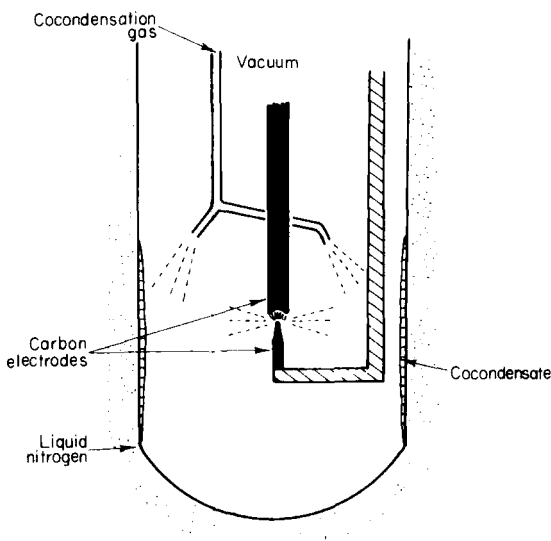


FIG. 4. Schematic of carbon arc apparatus.

2. Preparation from Gases

The formation of high temperature species by thermal dissociation of gases or by gas-solid reactions is most commonly carried out in a heated tube. The tube must be chemically resistant to the gas and to any condensed phase present. Unlike gaseous species formed by evaporation from condensed phases, some species formed from gases will survive collisions with cool surfaces or other gas molecules, without immediate condensation or polymerization (Section II). Thus, very high vacuum conditions and line-of-sight paths to cold surfaces are not always essential.

Figure 5 shows an apparatus which has been used for forming the relatively long-lived species, silicon difluoride (123, 130). The silicon was heated inside an evacuated quartz tube by an external tube furnace. Silicon tetrafluoride was passed up through the column of hot silicon and the off-gases containing SiF_2 and SiF_4 were pumped into a liquid nitrogen-cooled trap where they could be condensed with other compounds. The pressure above the silicon was maintained at 0.1–0.2 Torr.

A similar furnace system with an alumina tube was used by Kirk and Timms (44) to prepare thioborane, HBS, from boron and H_2S .

Figure 6 shows an apparatus used for preparing short-lived species such as SiCl_2 or BF by gas-solid reactions. A graphite tube containing silicon or boron was heated inductively from a 450-kHz supply with a work coil mounted inside the vacuum system. Other designs (119, 125)

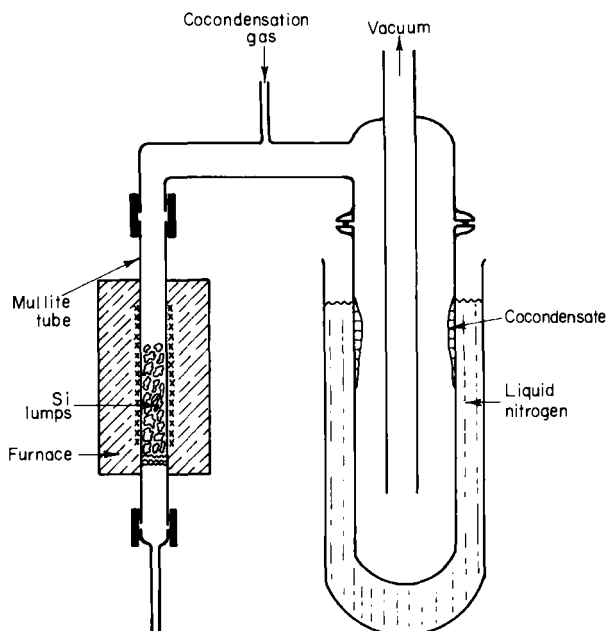


FIG. 5. Apparatus for cocondensing SiF_2 and volatile compounds.

have put the work coil outside the vacuum chamber. The vapors of the high halides were passed down through the tube at a rate which gave a pressure in the tube of 1–5 Torr. However, the gas emerging from the nozzle at the end of the tube expanded rapidly into a vacuum better than 10^{-5} Torr and passed by a line-of-sight path to a liquid nitrogen-cooled surface. This apparatus is, of course, equally suitable for preparing the longer lived species like SiF_2 (see p. 153).

Figure 7 shows the type of apparatus used by Skell and Cholod (89) for pyrolysis of chloroform at 1300° and condensation of the resulting

CCl_2 in solutions of alkenes in low-melting alkanes at about -120° . The graphite pyrolysis tube was heated by simply passing a current through it.

Atomic hydrogen has been formed by Klein and Scheer (46) and other workers (35) by thermal decomposition of H_2 on a heated tungsten ribbon mounted in the center of a flask cooled by liquid nitrogen. The

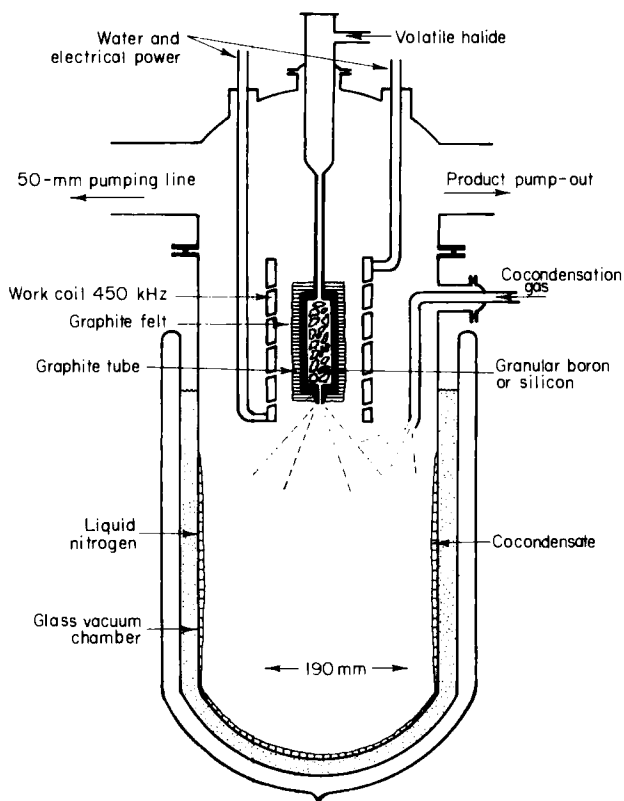


FIG. 6. Apparatus for studying reactions of short-lived boron or silicon subhalides.

walls of the flask were coated with a condensed layer of a compound which might react with the hydrogen atoms. With a hydrogen pressure of 0.05–1.0 Torr, atomic hydrogen formed on the filament diffused rapidly to the walls.

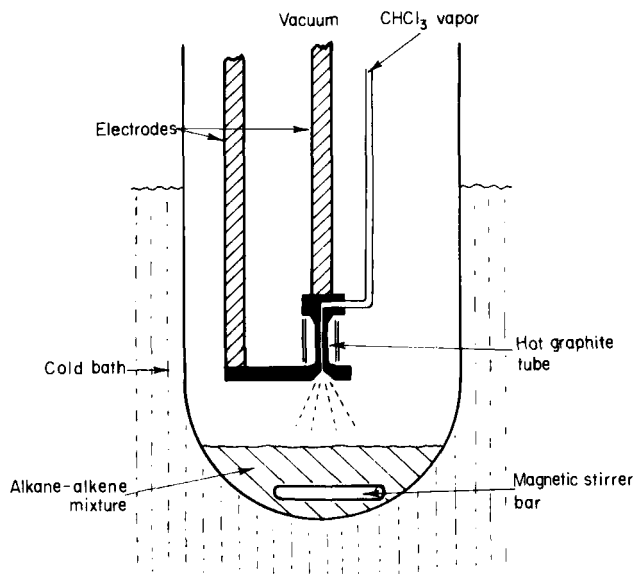


FIG. 7. Apparatus for condensation of CCl_2 in a cold alkane-alkene mixture. After Skell and Cholod (89).

B. CONDENSATION PROCEDURES

As can be seen from Figs. 2, 3, 4, and 6, the most common way of creating a cold surface on which the high temperature species can condense is by immersing part of the vacuum chamber in liquid nitrogen. This provides the largest possible cold area which is important for a number of reasons.

The surface acts as a cryogenic pump. The larger the cold area, the more quickly it pumps condensable vapors. It is then possible to pass relatively large amounts of vapors of compounds to be condensed with high temperature species, into the vacuum chamber without causing a large increase in pressure. For example, boron trichloride has been passed into the vacuum chamber shown in Fig. 2 at a rate of 3 moles/hr. During this process the pressure measured at the top of the pot was about 10^{-4} Torr. The speed of pumping of the diffusion pump assembly used to evacuate the reaction chamber is usually very low compared with the pumping speed of the cold surface for condensable vapors.

Heat is radiated to the cold surface from the source of the high temperature species. Removal of this heat is hindered by a thick layer of condensed material. The larger the surface, the thinner the deposit

of condensed material and so the surface will be cooler and act as a more efficient pump. Large vacuum chambers with cooled walls a long way from the hot source are thus most desirable, although more difficult to construct and use than smaller ones. The problem has been solved in a different way in the rotating cryostat apparatus described by Mile (65). In the apparatus shown in Fig. 5, the cold surface is shielded from the hot source and a smaller area can be used effectively.

Various forms of inlet systems for the compounds to be condensed with the high temperature species have been used, as seen in Figs. 2-6. Their purpose is to distribute the vapor over the cold surface as uniformly as possible without allowing the vapor to impinge on the furnace. With liquid nitrogen as the coolant, it is not usually possible to condense compounds with boiling points lower than about -130° without seriously raising the pressure in the vacuum chamber.

Condensation of the high temperature species into a cooled liquid avoids the use of an inlet system. Two practical problems arise using this method. First, the high temperature species has to be sprayed downward into a pool of liquid. Downward evaporation of condensed phases is slightly more difficult to achieve than upward evaporation. Second, the liquid has to have a suitable vapor pressure at the temperature of condensation, preferably less than 10^{-5} Torr, although pressures as high as 10^{-3} Torr may be acceptable. On the credit side is the possibility of reacting an involatile material in solution with a high temperature species, and the potential to work on a much larger scale than with cocondensation.

C. RECOVERY OF REACTION PRODUCTS

Normal practice with the apparatus shown in Figs. 2-6 is to remove the liquid nitrogen coolant at the end of a run and allow the condensate to warm to room temperature with continuous pumping to remove excess reactants and volatile products. It has been found advantageous to use large bore pumping lines so that sparingly volatile products can be pumped out of the vacuum chambers fairly quickly. This is particularly important if the products are unstable.

Products that are not volatile are rather difficult to recover if they are spread in a thin layer over the inside of a vacuum chamber. Under these conditions deposition of the high temperature species and the compound with which it may react on a more restricted but accessible surface can be useful.

Characterization of the reaction products has mainly been carried out using conventional instrumental analytical methods.

IV. Reactions of High Temperature Species of Main Group Elements

High temperature species of use to synthetic chemists are unequally distributed among the main group elements. Species in Group III and IV, especially boron monofluoride, carbon vapor, and the silicon dihalides have been used most extensively and so appear to dominate this section. This situation may change in a few years as the chemistry of other species is explored.

A. GROUP I, II, AND III ELEMENTS

The high temperature species of the Group I, II, and III elements which have been used in synthesis are discussed under subheadings below.

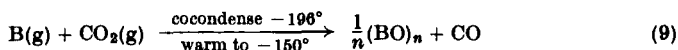
The most important species of these elements as yet untried in synthetic experiments are the atoms of beryllium, aluminum, gallium, and indium. The gaseous monohalides of the Group II elements could be reactive, although difficult to form free of the vapors of the metals (11). The gaseous aluminum monohalides have been tried in cocondensation experiments by the author and by Ehlert (24), but no reactions has been observed with inorganic or organic compounds. Among species containing the elements in normal valencies, the gaseous hydroxides KOH, RbOH, and CsOH (14) and some halides, like AlF_3 , seem potentially useful.

1. The Group I and II Metals

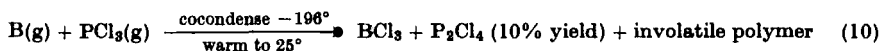
With the exception of beryllium, the Group I and II metals can be vaporized at temperatures much below 1000° under vacuum and they are strictly not high temperature species within the definition used in this chapter. The gaseous atoms appear to be highly reactive in condensation reactions at low temperatures, but they have been little used by synthetic chemists. This is mainly because the reactivity of the atoms at low temperatures is not very much greater than that of the metals used under conventional conditions. Skell (88) has reported that magnesium atoms react on condensation with alkyl halides to give alkylmagnesium halides. Klabunde *et al.* (45a) have recently described reactions of zinc atoms with perfluoroalkyl iodides. Group I metals have also been reacted with organic compounds at low temperatures, although the objectives of the experiments have generally been to obtain spectra of the radicals formed (65). Andrews and Pimentel (4) and Andrews and Carver (3, 17) have studied reactions of lithium atoms with halocarbons and oxygen in noble gas matrices at 20° – 50°K by infrared spectroscopy.

2. Boron Atoms

Boron has been vaporized by electron bombardment heating of a boron rod in an apparatus like that shown in Fig. 3 (120). The vapor species was believed to be monatomic boron in a 2P electronic state. The boron vapor was condensed with BF_3 , BCl_3 , PCl_3 , HCl , HBr , NH_3 , C_6H_6 , and CO_2 at -196° , and in each case reaction was observed. Carbon dioxide was reduced explosively to carbon monoxide when the cocondensate was warmed to about -150° . The boron and phosphorus trihalides each gave



a small yield, based on the boron atoms condensed, of the corresponding catenated tetrahalides B_2F_4 , B_2Cl_4 , and P_2Cl_4 ; e.g.,

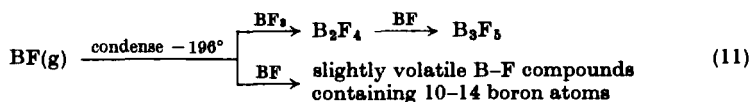


The boron atoms caused complete polymerization of benzene. Since boron atoms are an odd-electron species, they must form free radicals in initial reactions with other compounds which would promote the polymerization of many reactants. For this reason, boron atoms are not very useful in chemical synthesis.

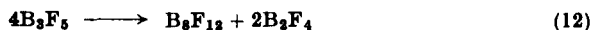
3. Boron Monofluoride and Monochloride

Boron monofluoride is the easiest of the known boron subhalide species to make at high temperatures. It has been formed in high yield by passing BF_3 over boron at 2000° (119) in an apparatus like that shown in Fig. 6. Its chemistry has proved very rich and can be considered in two parts.

a. Reactions of BF with Inorganic Compounds. When gaseous BF is condensed at -196° in the presence of a small amount of BF_3 , a sequence



of reactions occurs which is shown in Eq. (11). Cocondensation of BF and B_2F_4 gives much improved yields of B_3F_5 . This last compound is very unstable at temperatures above -50° and quickly disproportionates.



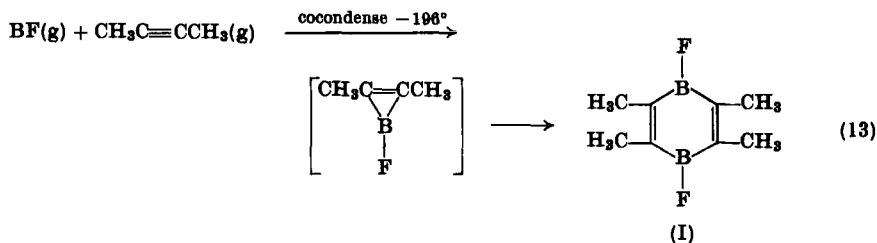
The compound B_8F_{12} is a bright yellow, volatile oil which decomposes above -10° . The most important property of the compound is its ability to react with "soft" bases (71) to form stable crystalline solids of general

formula $(\text{BF}_2)_3\text{BX}$, where X is a molecule of the base. Complexes have been formed with CO, PF_3 , PCl_3 , PH_3 , AsH_3 , and $(\text{CH}_3)_2\text{S}$ (43, 119). The structure of the complex with PF_3 was shown by X-ray crystallography to contain a tetrahedral arrangement of three BF_2 groups and the PF_3 molecule around a central boron atom (20). The complexes can also be made by cocondensation of BF and the base at -196° , although this synthesis must clearly involve complex reactions on the cold surface.

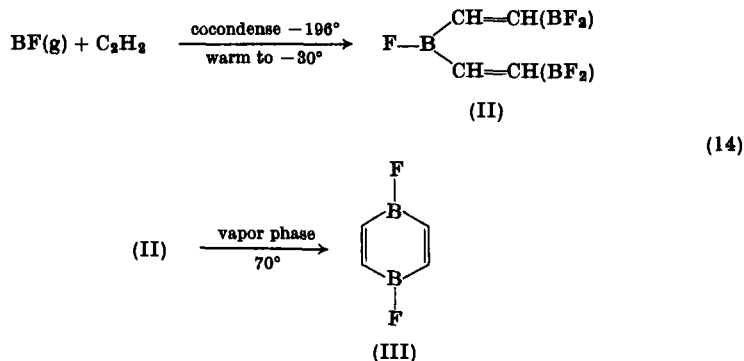
There is still some uncertainty about the structure of B_3F_{12} and the higher boron fluorides formed in the polymerization of BF on a cold surface. All spectroscopic evidence suggests that the compounds contain only $>\text{B}-\text{BF}_2$ groups and no BF groups, in contrast to the higher boron chlorides which are definitely composed of BCl groups (61).

The use of BF as a reagent in low temperature condensation reactions is presently the only way known for making the higher boron fluorides. Electrical discharge methods which work well for the higher boron chlorides do not work for boron fluorides (61).

b. Reactions of BF with Organic Compounds. Cocondensation of 2-butyne and BF gives fairly good yields of the 1,4-diboracyclohexadiene derivative (I) (124). This may be formed by a two-step process on the

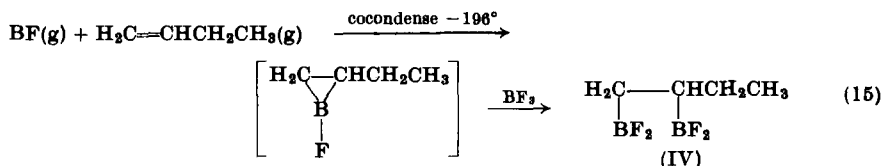


cold surface. However, the reaction between BF and acetylene on cocondensation was found to be more complex. It is not clear how (II)



was formed and whether or not an analog of (II) was a short-lived intermediate in the formation of (I). These reactions of BF (or BCl) with acetylenes are the only known way of making the 1,4-diboracyclohexadiene ring system, other methods yield *clovo*-carborane structures.

Condensation of BF with 1-butene gave good yields of (IV) (43),



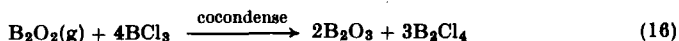
perhaps by the steps shown in Eq. (15). The same compound can be made by heating 1-butene with B_2F_4 at about 100° , but the mechanism of the reaction is probably different from that in Eq. (15).

c. *Boron Monochloride*. The formation of BCl from BCl_3 and boron requires temperatures appreciably above 2000° , beyond the eutectic point for graphite and boron. Thus, the graphite furnace shown in Fig. 6 cannot be used and the experimental problem of making BCl efficiently by this route has not been solved.

It has been found that thermal cracking of diboron tetrachloride at 1100° at 0.1–5.0 Torr pressure in a rapid flow system produces high yields of a mixture of BCl and BCl_3 . The BCl has been trapped by reaction with acetylene to give 1,4-dichloro-1,4-diboracyclohexadiene, an analog of (III) (54a). Alternatively, BCl can be made when an electric discharge is struck in B_2Cl_4 (61) and then condensed with other compounds at -196° (54a).

4. Other Boron Species

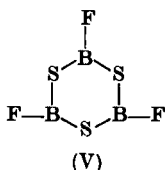
Boron monoxide gas, B_2O_2 , is formed by heating a mixture of B_2O_3 and boron. It will condense on a surface at room temperature to form a brownish solid $(\text{BO})_n$ (40). This solid is air- and moisture-sensitive, but otherwise less reactive than another polymer $(\text{BO})_n$ made by dehydrating subboric acid. The latter polymer reacts with BCl_3 at 200° to give B_2Cl_4 in 25% yield (52). Recently it has been found that cocondensation of gaseous B_2O_2 and BCl_3 at -196° gives a 60% yield of B_2Cl_4 according to (16). This work (128) suggests that gaseous B_2O_2 is much more reactive



than the polymerized forms, although it is a "normal valency" compound (Section II).

The long-lived gaseous species HBS, formed from H_2S and boron at 1300° (44) has not been used with much success in low temperature reactions. Kirk (43) obtained slight evidence for a volatile complex $\text{HBS}\cdot\text{NH}_3$ resulting from the reaction of HBS and NH_3 at -196° .

The action of SF_6 on boron at 1300° forms a gaseous compound $(\text{FBS})_2$ which has a lifetime comparable to that of silicon difluoride (Section II, B) in the gas phase. The compound polymerizes to involatile solids at room temperature, but if condensed at -196° and then allowed to warm to room temperature, good yields of the cyclic trimer (V) are formed (43).



B. SPECIES CONTAINING CARBON

The most important carbon-containing high temperature species in synthetic work are those present in carbon vapor. Much of the work with carbon vapor has been performed by Skell and his associates and is pure organic chemistry. Nevertheless, the work is central to the theme of this chapter as it represents the most detailed study of a series of condensation reactions which has yet been made.

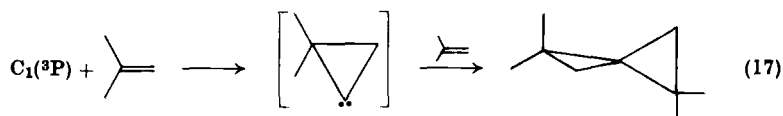
1. Reactions of Carbon Vapor Species

a. The Composition of the Vapor. The vapor species over hot carbon have been investigated mass spectrometrically by Drowart *et al.* (23) and shown to include C_1 , C_2 , C_3 , C_4 , and higher polymers. When formed under high vacuum in an arc the vapor composition does not correspond to that predicted from thermal equilibrium studies such as those of Thorn and Winslow (118). Data obtained from cocondensation experiments when carbon was vaporized from a 16-V arc, suggest an approximate composition C_1 40%, C_2 28%, C_3 <25%, C_4 2%, plus higher polymers (29, 96, 97, 103).

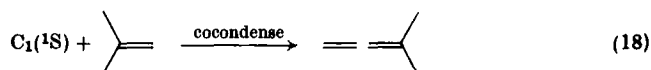
Vaporization from an arc also produces excited electronic states of all the species present. Skell and Engel (90, 91) claim that C_1 is formed in its ^3P ground state, but also in excited singlet states, ^1D and ^1S , lying 39 and 60 kcal, respectively, in energy above the ground state. The excited ^1S state probably accounts for the bulk of the C_1 formed, but it decays rapidly with a half-life of about 2 sec, on the cold surface.

Evidence for the existence of these states has been obtained by observing the changes in reactivity with time of alkane matrices of the carbon species at -196° toward olefins and other organic compounds. The C_2 and C_3 species are believed to be formed in both excited triplet and ground singlet electronic states (103, 104, 107).

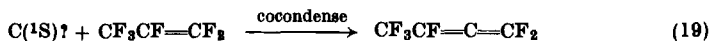
b. Reactions with Organic Compounds. Three types of reactions have been found between olefins and different carbon species. The reaction of C_1 in its 3P ground state forms spiropentanes. The 3P state was obtained by trapping carbon vapor in neopentane and allowing the excited states to decay to the ground state before adding an olefin (91). Thus, with isobutene a spiropentane is formed via a carbene intermediate. The reaction is represented in Eq. (17) showing only the carbon



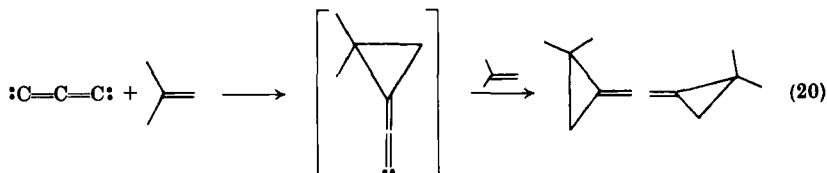
skeleton. The excited 1S state forms allenic compounds. Cocondensation of isobutene and carbon vapor on a surface at -196° gave 3-methyl-1,2-butadiene in a yield corresponding to about 40% of the evaporated



carbon (93). The cocondensation procedure lends itself to work on a much larger scale than the aging technique used to study the 3P state and it is much more convenient. As a consequence, carbon atom reactions provide a practical synthesis of some allenic compounds but not of spiropentanes. McGlinchey *et al.* (54) have reported that cocondensation reactions of fluoroolefins with carbon vapor form mainly allenic compounds. Perfluorobut-1,2-diene was obtained in 20% yield based on the carbon evaporated, from perfluoropropene.



The C_3 molecule adds to olefins to form a class of compounds which had not previously been made, the bisethanoallenes. The reaction with isobutene is shown schematically in Eq. (20). Skell *et al.* (107) report that the stereochemistry of the products is affected by aging of the carbon vapor deposited in alkane matrices, and they have interpreted this on the basis of initial deposition of a short-lived triplet state of C_3 .



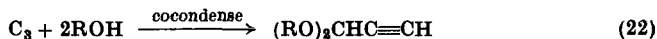
Sprung *et al.* found that cycloheptatriene and toluene were the main volatile products when carbon vapor was condensed on top of a layer of benzene at -196° . The vapor was formed in tiny amounts from a resistance heated graphite rod. The methyl group in the toluene was presumably formed by hydrogen abstraction by an initial reaction product. Hydrogen abstraction reactions giving methyl groups or free C_2 and C_4 hydrocarbons have also been reported by Skell and his associates (29, 95, 103, 105) in work with carbon vapor.

Only the excited 1S state of C_1 reacts with alkanes. Insertion occurs into C-H bonds fairly randomly, so that secondary reactions of the resulting carbenes cause many products to be formed (92). Neopentane is inert and has been much used by Skell and his associates for isolating carbon species.

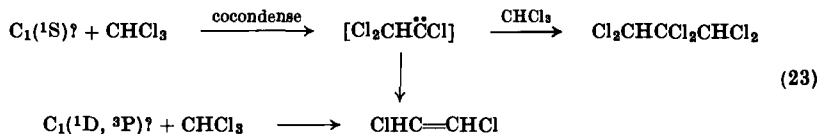
Organic compounds containing oxygen are often deoxygenated by C_1 (1S) with the formation of carbenes and carbon monoxide (73, 97, 98, 100, 101, 102). With alcohols dialkoxymethanes are formed from C_1 species.



A similar insertion occurs with C_3 species (96).



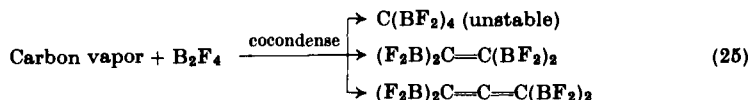
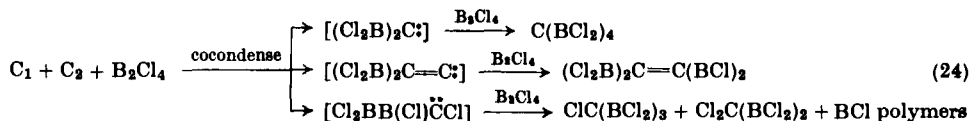
Carbon vapor species do not dechlorinate organic chloro compounds, insertion into the C-Cl bonds by C_1 species seems to be the main reaction. As in other reactions with carbon vapor, cocondensation gives slightly different products than those obtained with aged carbon matrices. This is illustrated in Eq. (23) for the reaction with chloroform (94).



c. *Reactions with Inorganic and Organometallic Compounds.* Attempts to introduce carbon into inorganic compounds by reactions with carbon vapor have been fairly successful and have established practical synthetic

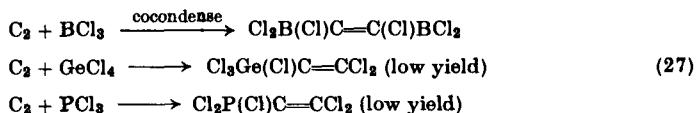
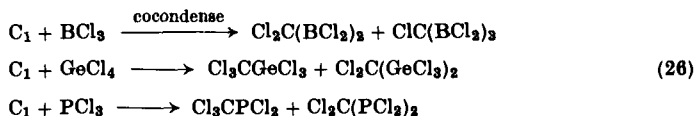
routes to some new compounds. The experiments have all been run under cocondensation conditions with no attempt to form aged matrices of carbon species in inert substrates, so that the excited electronic states of carbon must play a large part in the observed reactions.

Carbon vapor has been condensed with B_2Cl_4 and B_2F_4 at -196° and products resulting from insertion of carbon into both B-B and B-halogen bonds have been observed (22, 133). As with reactions of organic compounds, carbene intermediates were probably formed.



No C_3 product was isolated in the reaction of carbon vapor and B_2Cl_4 , but this may have been due to the low volatility of the higher chloro compounds. About 1.5 mmoles of the interesting product $C(BCl_2)_4$ were obtained per run involving the evaporation of 30 mmoles of carbon and its condensation with 150 mmoles of B_2Cl_4 over a period of 15 min (133).

Stone and his co-workers have found the reactions of carbon with BCl_3 (133), $GeCl_4$, and PCl_3 (53) to be basically similar. In each case the major products isolated contained one carbon atom,



Binenboyn and Schaeffer (8) reported that the major product from the reaction of $SiCl_4$ and carbon vapor is the acetylenic compound $ClC\equiv CSiCl_3$. The formation of this would appear to involve insertion of a C_2 molecule into a Si-Cl bond. The difference between this result and that shown for BCl_3 , $GeCl_4$, and PCl_3 in Eqs. (26) and (27), may stem from a real difference in the chemistry of the halides, but it is possible that the experimental conditions employed by the two sets of workers

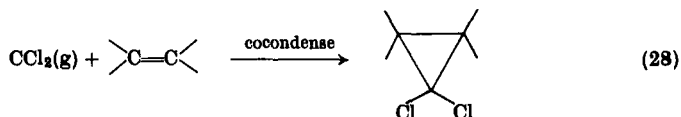
caused the difference. As was discussed in Section II, the relative rates of competing reactions can be affected by the surface temperature in the condensation which is influenced by the size of reactor and the power dissipated.

A simple insertion of C_1 into a B-C bond probably accounted for the formation of $(CH_3)_2C(BCl_2)_2$ from carbon and methyldichloroborane (22). Similarly the formation of thiophosgene from S_2Cl_2 and carbon vapor may have been the result of C_1 insertion into S-S or S-Cl bonds (53).

Condensation of carbon vapor with the less stable hydrides raises serious experimental difficulties. Hydrogen may be evolved during the codeposition which increases the pressure, allowing collisions in the gas phase. Schaeffer and his co-workers have attempted reactions of carbon vapor with B_5H_9 (75) and SiH_4 (8). From the former they isolated a small amount of a carborane, B_5CH_7 . With the latter, hydrogen evolution caused organic compounds like benzene and acetylene to be formed in greater abundance than silicon-containing products.

2. Other Species Containing Carbon

a. *Dichlorocarbene*. Westcott and Skell (137) reported the formation of CCl_2 by pyrolysis of chloroform or carbon tetrachloride at about 1500° under high vacuum conditions, which allowed the CCl_2 to be condensed with other compounds on a cold surface. They showed, for example, that CCl_2 added to olefins to form 1,1'-dichlorocyclopropanes. The work was



extended by Skell and Cholod (89), who sprayed the CCl_2 gas into a cooled, well-stirred solution of an olefin in an alkane (Fig. 7). The carbene reacted efficiently with the olefin under these conditions. However, the conclusion from the work with CCl_2 was that the compound formed at high temperatures reacted in the same way as the carbene liberated chemically at ordinary temperatures, e.g., from the decomposition of $LiCCl_3$ (66). Thus, as mentioned for CF_2 (Section II), there is little point in making CCl_2 at high temperatures.

b. *Carbon Monosulfide*. The chemistry of CS is little known. It can be formed by decomposition of CS_2 on metal surfaces at 1700° (9) or from metal sulfides and carbon at high temperatures (138). Solan (109) has found that CS appears to be reactive at low temperatures, and it seems likely that a careful study of this species would be rewarding.

C. SPECIES CONTAINING SILICON

1. Silicon Atoms

The vapor of silicon contains a much smaller proportion of polymers than the vapor of carbon, and Si_1 is the dominant species at low pressures (33).

Skell and Owen (99) vaporized silicon from a resistively heated silicon rod and condensed the vapor with trimethylsilane at -196° . The silicon atoms inserted into the Si-H bond and a trisilane was isolated in fair



yield. This seems to be one of the few reactions of silicon atoms which give good yields of products. Kirk and Timms (45) vaporized silicon by electron bombardment of a silicon rod and condensed the vapor with BF_3 , BCl_3 , and B_2F_4 . Almost no volatile products were obtained at all from the first two compounds, while the third formed the new compound $\text{FSi}(\text{BF}_2)_3$ in a 1% yield, presumably by reactions analogous to those of Eqs. (24) and (25). In each case, the main product was involatile polymeric material which contained only a small amount of elemental silicon. Other cocondensation experiments with silicon vapor have mainly failed to give volatile products, so that its future as a reagent is much less promising than that of carbon vapor.

2. Silicon Difluoride

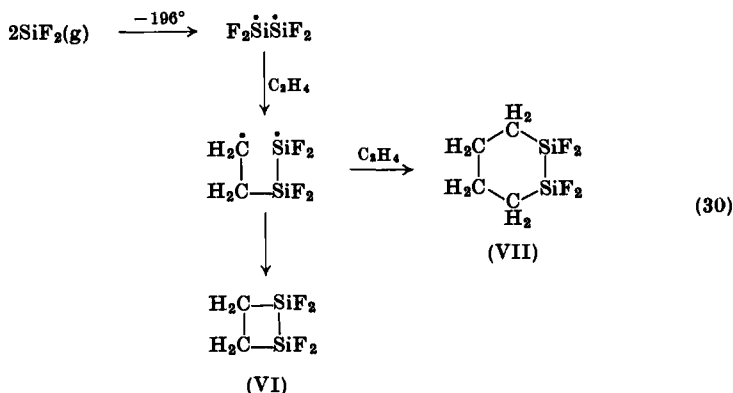
a. The Reactive Species. Silicon difluoride gas is easily prepared from SiF_4 and silicon at temperatures above 1100° under vacuum. It is also formed by thermal decomposition of Si_2F_6 at low pressures (81). It reacts with a wide range of compounds on condensation at -196° . However, its long lifetime in the gas phase is scarcely affected by the presence of the vapors of several of the compounds with which it will react at -196° (130). It exhibits the unusual behavior of being more reactive in the condensed phase at low temperatures than in the gas phase at ordinary temperatures.

A characteristic of many low temperature reactions of SiF_2 is the formation of products containing two or more silicon atoms, often with no product containing only one silicon atom. These observations suggested that in the polymerization of SiF_2 at low temperatures, the simple polymers Si_2F_4 , Si_3F_6 , etc., are more reactive than monomeric SiF_2 . Evidence to support this view was obtained from the infrared spectra of the polymerization of SiF_2 in noble gas matrices (6). The high

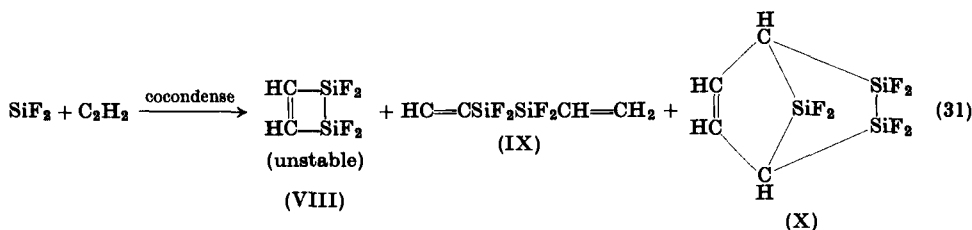
reactivity of these simple polymers indicated that they are diradical rather than olefinic species, and a further proof of this came from electron spin resonance studies of the polymerization at -196° (34).

Cocondensation reactions of SiF_2 with compounds capable of breaking the Si-Si bonds in polymers or inhibiting their formation, give products containing one silicon atom. Sometimes the yields in these reactions are much higher than in those which depend on the formation of the diradical polymers.

b. Reactions with Unsaturated Organic Compounds. Cocondensation of SiF_2 and ethylene at -196° gave small yields of the two cyclic volatile products (VI) and (VII) (115).



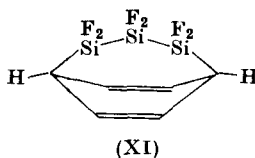
The reaction with acetylene was found to be more complicated and several products have been obtained containing Si-Si bonds. The low



stability of (VIII) may be due to ring strain. The mechanism for the formation of (IX) and (X) is not known (117).

The reaction of benzene and SiF_2 produced another unexpected bicyclic ring compound (XI) (131). Mass spectrometric evidence was obtained for a homologous series $\text{C}_6\text{H}_6(\text{SiF}_2)_n$, where $n = 2$ to at least

6, perhaps all with silicon chains bridged across the 1,4-positions of a cyclohexadiene ring.

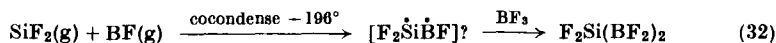


Cocondensation of SiF_2 and hexafluorobenzene at -196° gave a different type of reaction. As the condensate warmed to room temperature it emitted flashes of light (131). The products isolated were $\text{C}_6\text{F}_5\text{SiF}_3$ and mixed isomers of $\text{C}_6\text{F}_4(\text{SiF}_3)_2$, but no compounds containing Si-Si bonds. It seems quite possible in this case that the initial reaction products were of the same type as formed with benzene, but that on warming an exothermic transfer of fluorine from carbon to silicon occurred with destruction of the Si-Si bond system. Partially fluorinated aromatic and olefinic compounds show this same effect (115, 131).

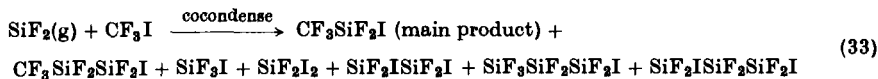
c. Reactions with Inorganic Compounds. One of the most thoroughly studied reactions of SiF_2 is that with BF_3 at low temperatures. Using the apparatus of Fig. 5, the products were $\text{SiF}_3\text{SiF}_2\text{BF}_2$, $\text{SiF}_3(\text{SiF}_2)_2\text{BF}_2$, and much smaller amounts of higher homologs in the series $\text{SiF}_3(\text{SiF}_2)_n\text{BF}_2$ (129). The compound SiF_3BF_2 was not formed in the reaction. When SiF_2 and BF_3 were simultaneously isolated in a krypton matrix at 20°K , it was shown by infrared spectroscopy that $\text{SiF}_3\text{SiF}_2\text{BF}_2$ was first formed on warming the matrix to 35°K . This was the same temperature at which new bands appeared in the infrared spectrum of matrix-isolated SiF_2 , tentatively assigned to the diradical species Si_2F_4 (6).

It has been found recently that when SiF_4 at 1-5 Torr pressure is passed over silicon or silicon carbide heated to 1200° - 1800° in the apparatus of Fig. 6, and the resulting gases are condensed with BF_3 at -196° , SiF_3BF_2 is formed in addition to the expected $\text{Si}_2\text{F}_5\text{BF}_2$ and $\text{Si}_3\text{F}_7\text{BF}_2$. It is thought that SiF_3BF_2 must be formed by a reaction of a hitherto undetected, short-lived high temperature species, perhaps triplet SiF_2 (108a).

In another experiment involving the Si-B-F system, SiF_4 was passed over boron at 1800° in the apparatus described in Fig. 6. The gas issuing from the graphite tube was believed to contain a mixture of SiF_2 , BF , and BF_3 (45). On condensing this mixture at -196° the main volatile product which could be isolated was $\text{F}_2\text{Si}(\text{BF}_2)_2$.



Silicon difluoride reacts with most halides except SiF_4 , when condensed with them at low temperatures. Sometimes the products are not stable, e.g., reactions with GeF_4 , NF_3 , PF_3 , and SF_4 (60), generally due to halogen abstraction by the silicon. The reaction with CF_3I occurs smoothly, but gives a large range of products (58). Free halogens react



quantitatively with SiF_2 in the gas phase or on condensation at low temperatures, and the reaction of SiF_2 and I_2 is the best method for making SiF_2I_2 (57).

Oxygen reacts with gaseous SiF_2 at room temperature with emission of a bright blue glow. It was found that SiF_2 could be deposited in a matrix containing 50% O_2 and 50% Kr at 20°K without reaction. Only on warming to 45°–50°K was any reaction detected using the infrared spectrum. Thus, paradoxically, SiF_2 is less reactive toward O_2 than BF_3 at very low temperatures, although the situation is quite reversed at room temperature. The final product of the reaction of SiF_2 with most oxygen-containing compounds is a complex mixture of silicon oxyfluorides (7, 116). The steps in the reactions with NO and CO have been followed by infrared spectroscopy in krypton matrices at 20°–60°K (6).

Reactions of SiF_2 with inorganic hydrides give well-defined products. Germane forms $\text{HSiF}_2\text{GeH}_3$, together with smaller amounts of $\text{HSiF}_2\text{SiF}_2\text{GeH}_3$ and less stable higher homologs (110). Similarly, H_2S forms HSiF_2SH , a little of the unstable $\text{HSiF}_2\text{SiF}_2\text{SH}$, and the corresponding S–S-bonded compounds HSiF_2SSH and $\text{HSiF}_2\text{SiF}_2\text{SSH}$ (84). Water and SiF_2 give good yields of $\text{HSiF}_2\text{OSiF}_2\text{H}$ (59).

Many of the compounds described above, formed from reactions of SiF_2 with both organic and inorganic compounds, are very difficult or impossible to make except by using SiF_2 as a reagent. The compound has an assured place among important synthetic reagents in silicon chemistry, particularly as it is long-lived as a gas and easy to make.

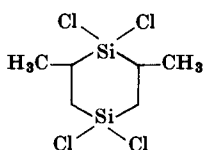
3. Silicon Dichloride and Silicon Dibromide

Monomeric SiCl_2 is formed from SiCl_4 and silicon at about 1300° under low pressure, but it is quickly converted to polymers or perchlorosilanes by collisions with the walls of the reaction vessel or with other molecules (Section II, B). Its chemistry is as much akin to that of CCl_2 as to SiF_2 . The compound behaves like other carbene analogs such as $\text{Si}(\text{CH}_3)_2$ or GeI_2 (68).

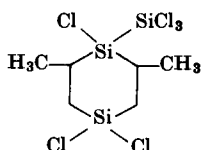
Cocondensation of SiCl_2 and olefins at -196° gives high yields of

1,4-disilacyclohexane derivatives. With propene, (XII) is the main product, together with higher homologs such as (XIII), in which SiCl_2 has inserted into an $\text{Si}-\text{Cl}$ bond in (XII). This insertion into $\text{Si}-\text{Cl}$ bonds seems the most favored reaction of SiCl_2 , and it is difficult to avoid the formation of compounds like (XII) even in the presence of excess propene (108).

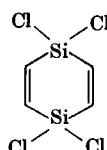
The reaction of SiCl_2 with acetylene is complex and gives a large amount of volatile polymer. The main volatile product is the 1,4-disilacyclohexadiene derivative (XIV), which is fairly unstable, but other



(XII)



(XIII)



(XIV)

compounds containing acetylenic groups are also formed. The reaction is still being investigated.

In contrast to the reaction of SiF_2 and BF_3 , cocondensation of SiCl_2 and BCl_3 forms $\text{SiCl}_3\text{BCl}_2$ in a 15% yield based on the SiCl_2 . This is much superior to the electrical discharge synthesis of this compound reported by Massey and Urch (62). The reaction with PCl_3 gives a similar yield of $\text{SiCl}_3\text{PCl}_2$ (122), but the yield of $\text{SiCl}_3\text{CCl}_3$ from SiCl_2 and CCl_4 is lower. The conversion of $\text{M}-\text{Cl}$ to $\text{M}-\text{SiCl}_3$ by a cocondensation reaction with SiCl_2 seems to be a fairly general and synthetically useful process.

Many carbenes can be formed by reactions at ordinary temperatures. This is not really possible for either SiF_2 or SiCl_2 , but the latter is implicated as an intermediate in reactions of silicon with organic chloro compounds at temperatures of 100° – 400° (27).

Silicon dibromide has been formed from SiBr_4 and silicon under very similar conditions to those used for SiCl_2 . It appears to be as short-lived as SiCl_2 and readily forms polymers and perbromosilanes. Very little of its chemistry has been studied, but there is every reason to suppose it will be like that of SiCl_2 .

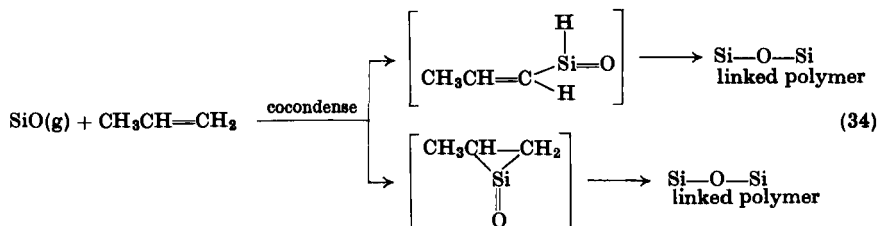
Silicon diiodide cannot be made under high vacuum conditions from silicon and SiI_4 because of dissociation to silicon and iodine atoms (79).

4. Silicon Monoxide and Other Species

Gaseous silicon monoxide is easily formed by heating mixtures of silicon and silica above 1300° under vacuum. The polymerization of SiO in noble gas matrices has been studied by two groups of workers (1, 30),

and has been shown to involve the formation of oxygen linked polymers Si_2O_2 , Si_3O_3 , etc.

Silicon monoxide has been found to react with most unsaturated organic compounds on cocondensation at -196° (80). In every case the products were infusible solids. For example, the reaction with propene yielded a transparent solid of approximate composition $\text{C}_3\text{H}_6(\text{SiO})_3$, which seems to have been formed by attack of SiO and its polymers on



propene in two ways. Benzene and SiO formed a white solid $\text{C}_6\text{H}_6(\text{SiO})_4$. This also appears to have involved insertion of SiO into C-H bonds and attack on the aromatic system to form a derivative of 1,4-cyclohexadiene, as hydrolysis yielded benzene and 1,4-cyclohexadiene. The relative reactivities of monomeric and simple polymeric forms of SiO are not known, but it is possible that the polymers are the more active species which would account for the composition of the above products.

Silicon monosulfide was reported to react with various inorganic halides at -196° to form new volatile products, but details have not yet been published (56).

Vaporization of silicon carbide is said to yield the gaseous species SiC_2 , Si_2C , and SiC , in addition to a larger amount of silicon vapor (135). Mixed B-C-Si and B-Si species were also detected. The cocondensation chemistry of these mixed species could prove very interesting.

D. SPECIES CONTAINING OTHER MAIN GROUP ELEMENTS

1. Germanium and Tin Atoms and Compounds

Both germanium and tin are fairly easily vaporized to give mainly atoms with some polymers (86). No work has been published on cocondensation reactions of these elements, but some preliminary studies have been made (64). These indicate that germanium vapor behaves like silicon vapor, reacting with many compounds at low temperatures, but not forming simple, volatile products. Tin vapor has been successfully reacted with some alkyl halides to give alkyltin halides at low temperatures.

Gaseous germanium dihalides are not true high temperature species

as they can be formed from the tetrahalides and germanium at 200° – 400° . Germanium difluoride vapor contains polymeric species (143), but the dichloride and dibromide are monomeric (134). None of these species seems to be reactive in cocondensation reactions at -196° . However, solid GeCl_2 , GeBr_2 , and GeI_2 show some carbenoid properties in reactions with organic compounds at 25° – 300° (68, 123).

Germanium and tin monoxides are formed as vapour species at temperatures of 700° – 1000° from the elements and their dioxides. Matrix isolation infrared studies on GeO and SnO have shown that their polymerization is similar to that of SiO (2). No cocondensation reactions have been attempted with the species, but there is a reasonable chance that they will prove reactive and form products similar to those from silicon monoxide.

2. Group V, VI, and VII Elements and Hydrogen

The vapors of phosphorus, arsenic, sulfur, and selenium are complex below 1000° , but at higher temperatures diatomic species predominate (86). The diatomic species P_2 , As_2 , S_2 , and Se_2 are energetic compared with the normal forms of the elements, but their use as reagents in cocondensation reactions is of uncertain value. Unlike C_2 , they contain elements in formally stable valency states, unstable only with respect to the polymerized, single bonded P_4 , As_4 , S_8 , and Se_8 , respectively. They fall in the general class of species discussed in Section II, B. Similar comments apply to the mixed species containing these elements like gaseous PN (16).

The atomic species, P, As, S, and Se, are of much greater potential interest as reagents, but they are not easily made free of the diatomic species by high temperature methods. The atoms can be made more successfully by photochemical reactions (Section VI, A).

The species PF_2 , possibly mixed with PF , was made by thermal dissociation of P_2F_4 at 800° – 1000° under vacuum (109, 111). Condensation of the gas at -196° formed small amounts of a new compound $\text{P}(\text{PF}_2)_3$. Attempts to react PF_2 with organic compounds at -196° gave no stable products.

The great majority of studies of synthetic reactions of atoms of nitrogen, oxygen, hydrogen, and the halogens have used methods such as discharges and photolysis which are outside the main scope of this chapter (see Section VI, A). The work of Klein and Scheer (46) on the mechanism of reactions of hydrogen atoms with olefins at -196° , in which the hydrogen atoms were formed on a hot filament, is an exception. Their method would seem to have potential for the synthesis of some inorganic compounds.

V. Reactions of High Temperature Species of Transition Elements

A. SPECIES OF INTEREST

1. *The Metal Vapors*

The transition metals vaporize mainly as monomeric species (86). Dimers such as Ni_2 have been seen by mass spectrometry (41), but as the metal-metal bond energies are fairly low compared with the heat of vaporization, these species form a tiny proportion of the vapor under low pressure evaporation conditions.

As discussed in Section II,A, vaporization of the first-row elements generally occurs at lower temperatures than for the second- and third-row elements. This is particularly true in the middle of the transition metal series where the binding energy of atoms in the solid lattice is extremely high for the second- and third-row elements. The metals Nb, Ta, Mo, W, Re, Os, and Ir, all require temperatures in excess of 2500° for appreciable vaporization, so their vapors are unlikely to be used in large-scale chemical synthesis. On the other hand, elements such as Cu, Ag, and Mn can be vaporized easily at rates as high as 1 mole/hr in laboratory apparatus (Fig. 2).

The synthetic uses of transition metal atoms fall into two classes (125a). The most obvious is the formation of complexes by condensation reactions with ligands at low temperatures. These will generally give products in which the metal is in a zero or other low valency state. As Pearson has pointed out (71), free transition metal atoms must be classed as "soft" acids and will be expected to combine readily with "soft" bases such as phosphines, CO, NO, and many unsaturated organic compounds. The other use of transition metal vapors in cocondensation syntheses is as dehalogenating agents. The thermodynamics of dehalogenation reactions of copper atoms compared with sodium atoms were discussed in Section II,A, and it was seen that the transition metal atoms are potentially powerful reagents. Their ability to form complexes imparts a degree of selectivity to some of their dehalogenation reactions not found with other metals and compounds.

2. *Molecular Species*

The use of high temperature molecular species of the transition metal elements as reagents in chemical synthesis is as yet entirely unexplored. The most promising species would appear to be those containing the elements in low valency states. However, it seems to be difficult to make most of the simple species known to spectroscopists free of other species

such as the metal vapors (19, 42). A possible exception is the monohalides of the rare earth elements (142).

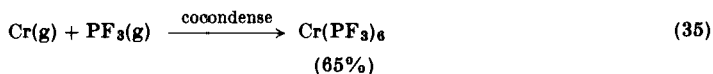
Species such as gaseous TiO , VF_2 , and CrF_2 , which are formed from condensed phases at temperatures well above 1000° , may form a range of complexes on condensation with ligands which are not accessible from reactions of these compounds at ordinary temperatures. The particular case of ZrO_2 vapor was discussed in Section II, B. The technique of low temperature condensation might also be applied usefully to reactions of vapors of CuCl and AgCl and other species which are formed in the temperature range 500° – 1000° .

B. REACTIONS OF METAL VAPORS WITH INORGANIC LIGANDS

1. Trifluorophosphine

Condensation of transition metal vapors with trifluorophosphine at -196° has been shown to be a useful way of making the zero-valent PF_3 complexes in high yields (127). On a laboratory scale, the method is an attractive alternative to the normal high pressure routes to PF_3 complexes (48).

The reactions which have been studied are shown schematically in Eq. (35). In each case the metal vapor was condensed with PF_3 in at least a 1:8 mole ratio using an apparatus similar to that of Fig. 2. The approximate yields of products based on the metal vaporized, are shown in parentheses.



Mn: no volatile product

Fe: $\text{Fe(PF}_3)_5$ (25%) + $(\text{PF}_3)_3\text{Fe(PF}_2)_2\text{Fe(PF}_3)_3$ (25%)

Co: $[\text{Co(PF}_3)_4]_x$ (50%)

Ni: $\text{Ni(PF}_3)_4$ (85–100%)

Cu: no volatile product

Pd: $\text{Pd(PF}_3)_4$ (70%)

The reaction of nickel with PF_3 is particularly efficient. The pressure in the vacuum system during codeposition of nickel vapor and PF_3 was always exceptionally low apparently due to "gettering" of the PF_3 by nickel atoms either in the gas phase or on the surface. The only other metal which showed this effect to the same extent was copper vapor. It is possible that a molecule such as Cu-PF_3 was formed in the gas phase

or on the cold surface, but that it decomposed on warming to metallic copper and PF_3 .

The reaction of iron vapor with PF_3 is very complicated. The relative amounts of the two products shown in Eq. (35) have been found to vary substantially with changes either in the temperature of the cold surface or in the ratio of $\text{Fe}:\text{PF}_3$ cocondensed. Other less stable products are also formed in small amounts, one of which may be $(\text{PF}_3)_3\text{FePF}_2\text{Fe}(\text{PF}_3)_3$ (87).

The failure to form any volatile product in the reaction of manganese and PF_3 is further proof (48) that the compound $(\text{PF}_3)_5\text{MnMn}(\text{PF}_3)_5$, analogous to $(\text{CO})_5\text{MnMn}(\text{CO})_5$, cannot be stable at room temperature. However, a slow evolution of PF_3 on warming the cocondensate from -196° indicated that some reaction had occurred at the low temperature.

The work represented by Eq. (35) demonstrated that PF_3 is an effective ligand in low temperature reactions with metal atoms. The products were conveniently volatile and easily separated from involatile solids left on the cold surface. Carbon monoxide is very similar in its properties as a ligand to PF_3 , but it could not be used in these reactions because of its high vapor pressure at -196° . As a result, PF_3 has been chosen as the best ligand to use in conjunction with other ligands in some of the reactions described below.

Cocondensation of nickel vapor and PF_2Cl gave fair yields of $\text{Ni}(\text{PF}_2\text{Cl})_4$ (127), but other metals gave no volatile products.

2. PH_3 , NO , and Ligand Precursors

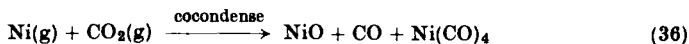
Few complexes of phosphine, PH_3 , with transition metals have been reported. Condensation of nickel vapor with PH_3 at -196° was accompanied by hydrogen evolution, and more hydrogen was evolved when the condensate was allowed to warm to room temperature. No volatile product containing nickel was obtained, suggesting that $\text{Ni}(\text{PH}_3)_4$ is very unstable. An equimolar mixture of PH_3 and PF_3 condensed with nickel at -196° formed two new volatile compounds $\text{Ni}(\text{PF}_3)_2(\text{PH}_3)_2$ and $\text{Ni}(\text{PF}_3)_3\text{PH}_3$, which were separated from $\text{Ni}(\text{PF}_3)_4$ by low temperature distillation (127). Some hydrogen was also evolved when the condensate was warmed from -196° . The compound $\text{Ni}(\text{PF}_3)_2(\text{PH}_3)_2$ decomposed slowly above 0° evolving hydrogen. When allowed to warm to room temperature in the presence of PF_3 , it was converted quantitatively to $\text{Ni}(\text{PF}_3)_3\text{PH}_3$.

The above reactions illustrate an important principle in synthesis at low temperatures. It seems likely that the ligands added randomly to the metal atoms on the cold surface in a diffusion-controlled process. Displacement of the weaker ligand, PH_3 , by the stronger ligand, PF_3 ,

did not then occur. All possible species from $\text{Ni}(\text{PF}_3)_4$ to $\text{Ni}(\text{PH}_3)_4$ may have been formed, but only $\text{Ni}(\text{PF}_3)_2(\text{PH}_3)_2$, $\text{Ni}(\text{PF}_3)_3\text{PH}_3$, and $\text{Ni}(\text{PF}_3)_4$ were stable enough to be pumped off the cold surface. There are many possibilities for the formation of complexes by condensation of a transition metal vapor with a mixture of two ligands; one a strong ligand capable of supplying a large part of the electronic requirements of the metal, the other a ligand too weak or thermally unstable to compete with the first in conventional preparative procedures.

An attempt to form the unknown compound $\text{Cr}(\text{NO})_4$ by cocondensing a mixture of chromium vapor, NO, and BF_3 , was not successful. The chromium was oxidized and formed no volatile product. The BF_3 was added merely to lower the vapor pressure of NO by forming a weak complex with it on the cold surface. More productive was the cocondensation of manganese vapor, NO, BF_3 , and PF_3 . The new compound $\text{Mn}(\text{PF}_3)(\text{NO})_3$ was formed in a 25% yield (36). This compound could not be made using conventional high pressure techniques (49).

When nickel vapor was condensed with CO_2 at -196° , the resulting solid evolved CO rapidly on being warmed above -150° . About 10% of the nickel was recovered as $\text{Ni}(\text{CO})_4$. The overall reaction was

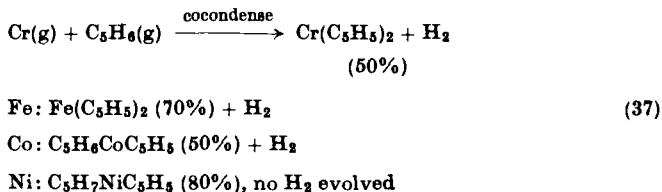


In this process, CO_2 can be considered to be the precursor of the ligand CO. Cocondensation reactions involving precursors of less common ligands, such as B_2F_4 as a source of BF (69) and Si_2Cl_6 as a source of SiCl_2 (82), are being studied currently in the author's laboratory.

A report by Burdett and Turner (14a) on the formation of nickel dinitrogen complexes, $\text{Ni}(\text{N}_2)_x$, from nickel atoms and nitrogen in a matrix at 20°K , illustrates further the range of compounds which can be made by low temperature reactions of metal atoms.

C. REACTIONS OF METAL VAPORS WITH ORGANIC LIGANDS

The condensation of chromium, iron, cobalt, and nickel vapors with cyclopentadiene at -196° has been studied (91). In each case a sandwich complex of the metal was formed as shown in Eq. (37). The yields based

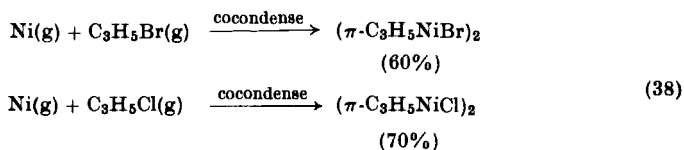


on the metal condensed are shown in parentheses. All these compounds can be made quite easily by conventional synthetic methods; so although the reactions with metal atoms are efficient, they are of little practical importance.

Chromium vapor reacted on condensation with benzene at -196° to form $\text{Cr}(\text{C}_6\text{H}_6)_2$ in about a 60% yield (126). No direct synthesis of this compound from chromium and benzene had been reported previously. Indirect preparations of $\text{Cr}(\text{C}_6\text{H}_6)_2$ have been known for many years [e.g., Fischer (26)]. A mixture of benzene and PF_3 condensed with chromium vapor at -196° gave good yields of $\text{C}_6\text{H}_6\text{Cr}(\text{PF}_3)_3$ (36).

The reaction between iron vapor and benzene at -196° was more complex than with chromium (126). A solid was formed which exploded on warming to about -40° . Iron and benzene were the main products of the explosion, but small amounts of diphenyl and hydrogen were also formed. The iron-benzene cocondensate was found to be chemically very reactive. On warming it from -196° in the presence of 1 atm hydrogen, there was no explosion and part of the benzene was reduced to cyclohexane. Condensation of cyclopentadiene onto the iron-benzene cocondensate at -196° resulted in the formation of ferrocene when the mixture was allowed to warm to room temperature. The results show that an iron-benzene complex was formed on the cold surface, but its formula and structure are not clear. There is no previous report of a zero-valent iron-benzene complex. Nickel vapor did not react at all with benzene at -196° .

It has been found that π -allylnickel halides can be formed very efficiently by condensing nickel vapor with allyl bromide or allyl chloride



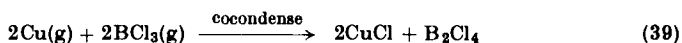
at -196° (72). These are useful preparations of these reactive complexes which compare favorably with conventional methods in speed and convenience.

Skell and Havel (97a) have reacted platinum vapor, formed in small amounts by vaporization of the metal from a tungsten filament at 1950° , with some unsaturated organic compounds at -196° . They report the formation of bis(1,5-cyclooctadiene)platinum(0) from 1,5-cyclooctadiene, $[\text{PtCl}(\text{C}_3\text{H}_5)]_4$ from allyl chloride, and ill-defined complexes with alkenes.

D. DEHALOGENATION REACTIONS OF TRANSITION METAL VAPORS

Copper is well known as a dehalogenating agent in organic chemistry. It is also used as a chlorine scavenger in the electrical discharge preparation of B_2Cl_4 (61). Thus, it seemed likely that copper vapor and possibly silver and gold vapors too, would be useful for dehalogenation in both inorganic and organic systems.

The first reaction to be studied was that between copper vapor and BCl_3 at -196° (121). Diboron tetrachloride was formed in yields varying from about 70% with a 20:1 mole ratio of BCl_3 :Cu, to 40% with a 6:1



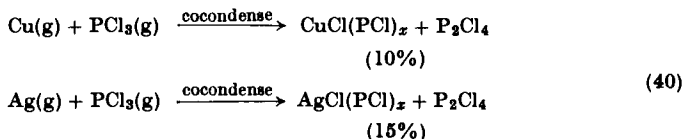
mole ratio. The work was initially carried with about 15 mmoles of copper, but it has been scaled up using the apparatus shown in Fig. 2. About 300 mmoles of copper, evaporated in 50 min, have been condensed with 2.7 moles of BCl_3 to form 57 mmoles of B_2Cl_4 (128). This is the best method available now for making B_2Cl_4 , much more rapid than the discharge methods commonly used (61).

Silver vapor also reacts with BCl_3 on cocondensation at -196° , but the yield of B_2Cl_4 is very small. No B_2Cl_4 was formed from the reaction of nickel and BCl_3 at -196° , although an involatile solid containing combined nickel, boron, and chlorine was left after excess BCl_3 had been pumped off the cold surface.

The reaction of copper with substituted chloroboranes is also useful for making B-B-bonded compounds. Methylchloroborane and copper vapor reacted at -196° to give high yields of 1,2-dichloro-1,2-dimethyldiboron, a liquid which is unstable above -10° (121).

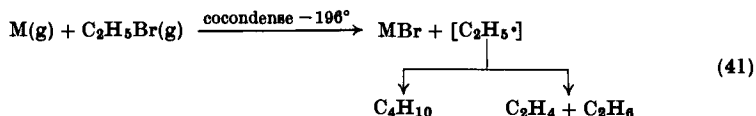
Copper vapor formed from molten copper heated in a crucible (Fig. 2) does not react with silicon-chlorine compounds at -196° . However, it has been found that if the copper vapor is formed by electron bombardment vaporization of copper, it will react with $SiCl_4$ to give perchlorosilanes. The reason for this difference in reactivity of copper vapor from the two sources is very likely the presence of excited copper atoms in the vapor formed by electron bombardment.

Both copper and silver vapors react very readily with PCl_3 at -196° . Some P_2Cl_4 can be pumped off from the cocondensates on warming, but



most of the dechlorinated phosphorus species remain coordinated to the metal in highly colored solids (108). Attempts to form more P_2Cl_4 by displacement of coordinated PCl or PCl_2 groups with other phosphine ligands have not been successful.

The simple alkyl halides such as ethyl bromide are dehalogenated efficiently by copper, silver, or gold vapors at -196° (28). The general



reaction with ethyl bromide is shown schematically in Eq. (41). Copper vapor formed mainly butane with traces of ethylene and ethane. Silver vapor gave mainly ethylene and ethane with a small amount of butane. Gold vapor gave butane and the ethylene-ethane mixture in equal amounts. These reactions are of no synthetic value, but copper does seem to be a fairly efficient reagent for causing coupling of carbon atoms rather than rearrangement of free radicals.

VI. The Method in Perspective

It was stressed in Section I that the emphasis of this chapter would be on low temperature reactions of high temperature species formed at low pressures under conditions which approximate to thermal equilibrium. This restricted scope was chosen because the synthetic uses of species formed this way have been mainly explored in the last few years. Before drawing conclusions about the value of these developments in chemical synthesis, it is important to consider some of the other synthetic techniques which involve the formation of "high temperature" chemical species as intermediates.

A. OTHER SYNTHETIC METHODS INVOLVING "HIGH TEMPERATURE" SPECIES

1. *Plasmas at Atmospheric Pressure*

Plasmas produced by an electric arc or induction heating may contain gaseous species in approximate thermal equilibrium at temperatures of 3000° – $15,000^\circ$. These have attracted much attention over the last 20 years because of their potential for chemical synthesis on a large scale. Work in the area has been thoroughly reviewed (39, 50, 76).

Very few new compounds have been synthesized with the plasmas.

The main problem is quenching the hot gases fast enough to isolate metastable compounds. This is much more difficult at 1 atm pressure than under vacuum because of the large mass of gas to be cooled. The work of Stokes and Streng (25, 113) on a liquid oxygen-quenched plasma is an exception.

2. Low Pressure Electrical Discharges

The apparent temperature of a gas in an electric discharge in the pressure range 10^{-2} to 50 Torr may be close to the ambient temperature. However, the gas will contain electrons and excited atoms and molecules with energies corresponding to temperatures of thousands of degrees (76). The excited or "high temperature" species present may not be of a type which could be formed under thermal equilibrium conditions. They will react with surrounding molecules in the gas phase or on cold surfaces. The rate of formation of the "high temperature" species is usually much lower than by thermal equilibrium methods.

Jolly (38) has reviewed the most important uses of discharges in synthetic inorganic chemistry. They have been particularly useful for forming catenated hydrides and halides, and, at low temperatures, for forming very unstable reactive compounds like oxygen and noble gas fluorides (83, 114). In most cases both reactants and products are contained in, or pass through, the discharge. This is a severe limitation on the method as many compounds are polymerized or decomposed by the discharge. Some long-lived atomic species, especially nitrogen and hydrogen atoms (38, 85), have been formed in discharges remote from the compounds with which they were reacted.

It was pointed out by Jolly (38) that discharge methods are not popular among synthetic chemists because of the complicated apparatus, the small yields of products, and the difficulty of predicting the course of reactions. These criticisms are true, in part, for all the synthetic methods involving high temperature species.

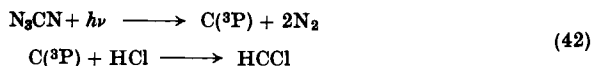
The process of sputtering metals and other materials by bombardment with excited argon atoms and ions, is another example of the formation of "high temperature" species by discharge processes (141). The species which cause transport of materials are mainly atoms or simple ions. This technique has not yet been used in the synthesis of compounds by low temperature cocondensation, although it could be very useful.

3. Photolysis

Photochemical excitation is widely used as a synthetic tool in organic chemistry, but not so much in inorganic chemistry. Excited or "high

temperature" species are formed either by direct interaction of quanta with molecules or by transfer of energy from selectively excited atoms such as mercury (15). The selection of excitation energy is much easier than with electrical discharges and the processes which occur are generally better understood. However, as with discharges, the rate of production of excited species will be lower than in thermal equilibrium methods unless intense energy sources are used.

Photolysis can be carried out at any temperature or pressure, but usually both "reactants" and products are exposed to the radiation. It has been used to generate tiny amounts of new compounds for spectroscopic identification in matrices at temperatures of -196° or lower. Thus, carbon atoms formed from photolysis of cyanogen azide at 20°K , were reacted with hydrogen chloride to give HCCl (37).



Atoms of Group VI elements can be formed conveniently photochemically. Gunning and his associates (47) have studied many reactions of sulfur atoms formed by photolysis of carbonyl sulfide.

4. "Hot Atom" Chemistry

"Hot atoms" are atoms with translational energies corresponding to temperatures of a few thousand to several hundred thousand degrees. The species of highest energy are commonly formed by nuclear transformations and recoil, e.g., ^{12}C ($n, 2n$) ^{11}C . They cannot be made on a scale which is really attractive to synthetic chemists, but the mechanisms of their reactions have been extensively studied (139). Many of the products obtained by Wolfgang and his associates from reactions of "hot" carbon atoms with organic compounds are similar to those reported by Skell and his associates using carbon atoms formed under semiequilibrium conditions from an arc. This is to be expected as the "hot atoms" can lose their excess translational energy in collisions with other molecules.

B. CONCLUSIONS

The results of the synthetic work described in Sections III, IV, and V can be summarized by three points.

1. Reactions of high temperature species have formed a large number of new compounds many of which were only isolated successfully because of the low temperatures employed.

2. The work has been carried out on a scale which forms at least millimole quantities of products.

3. Some of the species used give high yields of products and their reactions are predictable. These can now be regarded as reagents and syntheses planned around them.

There is little doubt that the use of high temperature species formed under equilibrium conditions at low pressures is a fruitful exploratory method in chemical synthesis. As the high temperature species are formed apart from the compounds with which they are to be reacted, there are few restrictions on what reactions can be tried—in fact, far less restrictions than with the other methods using “high temperature” species discussed above.

However, the change from an exploratory to a widely applied synthetic method has not yet been made. The apparatus used so far has been too complicated and the techniques too sophisticated to have appeal to most chemists. There are some hopeful signs, particularly in reactions of transition metal atoms. Great simplification of the apparatus seems possible for these without sacrificing the scale of operation or the high yields of products.

The number of high temperature species which can be regarded as potential reagents is not unlimited. At the rate at which interesting areas of research can grow throughout the world, it should be possible to make a balanced judgment on the real importance of this area of work in about 5 years time.

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TRANSITION METAL COMPLEXES CONTAINING BIDENTATE PHOSPHINE LIGANDS

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I. Introduction

The greater stability of complexes of bidentate ligands compared with the corresponding complexes containing similar monodentate ligands is well known. Jorgensen prepared ethylenediamine complexes in 1889, and Blau investigated the bipyridyl and *o*-phenanthroline complexes of iron in 1898. *o*-Phenylenebisdimethylarsine was prepared

by Chatt and Mann in 1939, and its complexes have been extensively investigated by Nyholm and co-workers. 1,2-Bis(diphenylphosphino)ethane (dPe*) was synthesized by Wymore and Bailar in 1956, and the chemistry of the metal diphosphine complexes has since been the subject of a good deal of work. In the relatively short space of 15 years a large number of complexes of diphosphine ligands have been prepared; of these dPe has been most widely used.

At the present time more than sixty diphosphines are known as ligands, but many of these have been only incompletely studied. One of the aims of this review is to focus attention on these less well-studied ligands, and with this in mind, a section has been devoted to references to the synthesis of the various diphosphines.

The coverage is intended to be comprehensive with the exception of organometallic compounds containing diphosphine ligands. Compounds of this type were included when either they were considered to be of particular interest because of the diphosphine ligand, or for comparative purposes. In the last few years a large number of organometallic compounds often containing dPe have been prepared, in which the interest centers on the metal-carbon bond and not the metal-phosphorus bond; these compounds have generally not been included.

There has been one previous review (30) in which metal-diphosphine compounds were included, and several other reviews (110, 124, 145) have included some diphosphine compounds studied from a different viewpoint. Reviews on the ligand preparations have also been published (97, 203).

II. Bonding in Metal-Phosphine Complexes

Until relatively recently consensus of opinion had it that the preference of phosphorus ligands for class (b) cations was due to the formation of π -type bonds between the metal and phosphorus atoms (30). A schematic representation of this type of bond (dative π bonding or back-bonding) is shown in Fig. 1.

A revaluation of this model has been stimulated by the work of Venanzi and co-workers, who have reported the ^{195}Pt - ^{31}P coupling constants for a series of square-planar Pt(II) complexes (224). They found that, as the ligand trans to the phosphine becomes a better trans director, the ^{195}Pt - ^{31}P coupling constant decreases. Based on some

* See Appendix for list of abbreviations used for the diphosphine ligands discussed in this review.

rather vigorous assumptions about the nature of $J(^{195}\text{Pt}-^{31}\text{P})$ (the constancy of ΔE and the constancy of the contribution of the phosphorus $3s$ orbital in the series), these authors related the magnitude of the coupling constant to the s character and strength of the Pt-P bond and concluded that, as the ligand trans to the phosphine becomes a more effective trans director, the s character and the strength of the Pt-P bond decreases. Venanzi *et al.* also concluded that phosphines have a very high trans influence which is entirely due to σ -bonding effects.

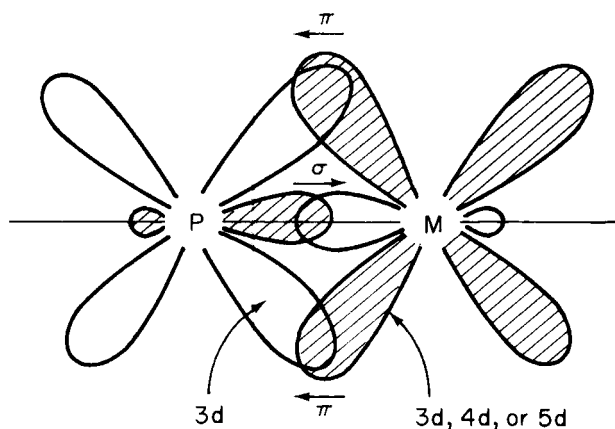


FIG. 1. Bonding in metal-phosphine complexes.

The conclusion by these workers that π bonding was not important in the phosphine complexes which they studied was mainly based on the fact that the ratio of the $^{195}\text{Pt}-^{31}\text{P}$ coupling constant in the cis complex to that in the trans complex is the same for both Pt(II) and Pt(IV) complexes. It was suggested that since π bonding is expected to be much less in Pt(IV) than in Pt(II) complexes, the similar coupling constant ratios for the two types of complexes indicate that π bonding is unimportant in both the Pt(II) and Pt(IV) complexes. Because of the difficulties, already mentioned, in interpreting J , and in the absence of any other information, this conclusion seems far from certain.

However, Zumdahl and Drago have done some extended Hückel M.O. calculations in order to investigate the π bonding in Pt(II) complexes (269). The extent of $d\pi-d\pi$ interactions between the Pt and P atoms in these complexes is hard to estimate because the energy and the Slater exponent for the phosphorus set of $3d$ orbitals are very uncertain.

However, a calculation was performed on *trans*-PtCl₂(PH₃)(NH₃) in which was included a set of phosphorus 3*d* orbitals with a Slater exponent of 0.7 and an energy of -5.0 eV, and it was felt that these parameters would overemphasize any Pt-P *d*π-*d*π bonding. The results showed that the Pt-P π-bond order is ~15% of the σ-bond order.

Thus, although it would seem that the postulation of π bonding in metal-phosphine complexes is no longer fashionable, this may only apply to metal ions in their usual oxidation states. It is possible, even likely, that π bonding may become important when ligands with strong electronegative substituents such as PF₃ are used in conjunction with Lewis acids of very low formal oxidation state, as in the complex [Pt-(PF₃)₄]. It is also likely that π bonding may be of significance in transition states (258).

III. Techniques Used to Study Metal-Phosphine Complexes

A variety of physical techniques have been used to characterize transition metal diphosphine complexes. Several of these, namely, conductivity, magnetic, and dipole moment measurements, are standard methods and will not be discussed. Much information has been obtained by application of various spectroscopic methods to these complexes, and some examples of the kind of information obtained are mentioned below.

A. MASS SPECTROSCOPY

This technique has not been widely used. Lewis and co-workers obtained the mass spectra of a number of diphosphine and phosphido-bridged dinuclear carbonyls of Cr, Mo, W, Fe, and Mn (191). Observation of the parent ions, e.g., [(OC)₅Cr(PMe₂)₂Cr(CO)₅]⁺, confirmed the dimeric formulas. The parent ions lose carbonyl groups progressively before appreciable fragmentation of the M₂P₂R₄ moiety occurs. In the diphosphine complexes the monomeric ions M(CO)_{*n*}P₂R₄⁺ and MP₂R₄⁺ are observed in low abundance, but such ions do not appear in the spectra of the phosphido-bridged complexes. This difference has been proposed as a method of distinguishing between the two types of complexes.

Mass spectroscopy has been used to study a number of other substituted carbonyl complexes. For example, Cullen *et al.* (103) found that the ffo_s and f₆fo_s complexes of iron lost carbonyl groups progressively until Fe₂(diphos)⁺ remained.

B. INFRARED SPECTROSCOPY

The metal-phosphorus vibrational frequencies occur in the far-infrared, and few assignments have been reported. Many workers have instead studied the infrared frequencies of other ligands in the complex, whose absorptions occur in regions of the spectrum where assignments are easier, e.g., carbonyl and metal-hydride vibrations. The infrared spectra of carbonyl complexes (136) and metal-halogen vibrations (86) have recently been reviewed. The few examples of metal-phosphorus vibrational assignments which have been made and some data from the study of metal-hydride frequencies and from the spectra of the free and complexed ligands are discussed next.

1. Metal-Hydride complexes

The $\nu(\text{M-H})$ frequency occurs in the range 2250–1600 cm^{-1} , and is easily observed and assigned, usually by comparing with deuteriated analogs. The $\delta(\text{M-H})$ vibrations have only rarely been assigned. The $\nu(\text{M-H})$ band is very sensitive to the nature of the trans ligand, and when H is trans to H, the $\nu(\text{M-H})$ occurs at a particularly low frequency

TABLE I
EXAMPLES OF METAL-HYDROGEN VIBRATION FREQUENCIES

Compound	$\nu(\text{M-H})^a$ (cm^{-1})	$\delta(\text{M-H})$ (cm^{-1})	Ref.
<i>trans</i> -[OsHCl(dee) ₂]	2039	—	(69)
<i>trans</i> -[OsH ₂ (dee) ₂]	1721	—	(69)
<i>trans</i> -[OsH ₂ (PEE) ₂]	1720 ^b	—	(69)
<i>trans</i> -[RuHCl(dme) ₂]	1891 ^c	—	(69)
<i>trans</i> -[RuHCl(dee) ₂]	1938 ^c	—	(69)
<i>trans</i> -[RuHCl(dPm) ₂]	1978	—	(69)
<i>trans</i> -[RuHCl(PEE) ₂]	1726 ^b	—	(69)
<i>cis</i> -[RuH ₂ (dme) ₂]	1806	—	(69)
<i>trans</i> -[RuH ₂ (dee) ₂]	1615	—	(58)
<i>trans</i> -[FeHCl(dee) ₂]	1849	656	(66)
<i>trans</i> -[FeH ₂ (PEE) ₂]	1726	716	(66)
<i>trans</i> -[FeD ₂ (PEE) ₂]	1259 $\nu(\text{Fe-D})$	—	(70)
<i>trans</i> -[FeDCl(dee) ₂]	1336 $\nu(\text{Fe-D})$	—	(70)
ReH ₄ (dPe) ₂ Cl	1950	850?	(120)
ReH ₃ (dPe) ₂	1860	850?	(120)

^a All solid mulls.

^b Benzene solution.

^c Hexane solution.

($\sim 1600\text{ cm}^{-1}$). $\nu(\text{M-H})$ are usually solvent-sensitive, except when H is trans to P, when little change is observed on varying the solvent (4).

In the $\text{RuHX}(\text{diphos})_2$ complexes $\nu(\text{Ru-H})$ increases with increasing electronegativity of the diphosphine (69). $\nu(\text{Ru-H})$ rises in the order $o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2 < \text{dme} < \text{dee} < \text{dPm} \sim \text{PEE}$. Table I contains more examples of M-H vibrational frequencies.

2. Metal-Phosphorus Frequencies

$\nu(\text{M-P})$ frequencies occur in the range $\sim 460\text{--}150\text{ cm}^{-1}$ (218). There has been a moderate number of assignments of $\nu(\text{M-P})$ in tertiary phosphine complexes, but hardly any in diphosphine complexes. With the increasing availability of infrared instruments that cover this region of the spectrum, an increasing number of reports of far-infrared spectra have appeared; but owing to the difficulty of assigning particular bands, most authors have assigned $\nu(\text{M-X})$ ($\text{X} = \text{halogen}$) (which frequencies often fall in the same region), stating that some at least of the remaining bands must be $\nu(\text{M-P})$. A major complication in diphosphine complexes is the relative complexity of the ligands. Boorman and Carty (26) studied the far-infrared region of a number of Ni(II) complexes, but were unable to assign $\nu(\text{M-P})$ in the diphosphine compounds, since the free ligands had several absorption bands in the range in which $\nu(\text{M-P})$ was expected.

3. IR Spectra of Free and Coordinated Ligands

When a diphosphine complexes with a metal ion, the electron density on the phosphorus atom changes, and the ligand is restricted in the conformation it can assume. Thus the vibrational spectra of the free and coordinated ligands differ. Ligands containing multiple bonds, VPP, DPPA, etc., are particularly suited to this kind of study since changes in $\text{C}=\text{C}$ and $\text{C}\equiv\text{C}$ bonds are easy to observe. For example, IR studies indicate that the $\text{C}\equiv\text{C}$ bond does not coordinate in metal complexes of DPPA (10, 47, 193). Similarly, Cullen *et al.* (99, 100, 103) have used IR spectra to show that ffos and f_6fos forms complexes in which the $\text{C}=\text{C}$ is coordinated, e.g., $\text{Fe}_2(\text{CO})_6\text{ffos}$, or is not coordinated, e.g., $\text{PtCl}_2\text{f}_6\text{fos}$. Vibrational spectra have also been used to distinguish between diphosphines behaving as monodentate or bidentate ligands (47).

C. NUCLEAR MAGNETIC RESONANCE

1. Proton NMR

Proton NMR has been widely used in the study of hydrido complexes. Hydrogen bonded to a transition metal exhibits a chemical shift in the range $\sim 17\text{--}45\tau$, the majority falling between $20\text{--}35\tau$ (see Table II).

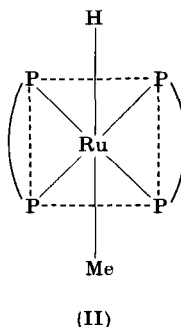
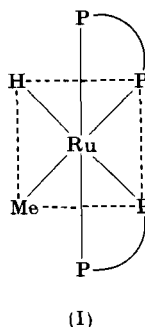
TABLE II
EXAMPLES OF PROTON NMR OF DIPHOSPHINE COMPLEXES

Compound	$\tau(\text{M-H})^a$	$J(\text{P-H})$ (Hz)	Ref.
<i>trans</i> -[FeH ₂ (PEE) ₂]	23.1	—	(66)
<i>trans</i> -[FeHCl(PEE) ₂]	41.2	49 (cis)	(70)
<i>trans</i> -[RuHBr(dee) ₂]	31.5	19 (cis)	(69)
<i>trans</i> -[OsHI(dee) ₂]	31.6	16 (cis)	(69)
<i>trans</i> -[RuHMe(dee) ₂]	18.4		(72)
<i>cis</i> -[RuHMe(dee) ₂]	18.9	19 (cis) 76 (trans)	(72)
<i>trans</i> -[IrHCl(dme) ₂]BPh ₄	32.2	17.5 (cis)	(180)
<i>trans</i> -[FeH(CO)(dee) ₂]BPh ₄	20.9	47 (cis)	(16)
<i>cis</i> -[MnH(CO) ₃ (dPe)]	17.8	45 (cis)	(29)

^a Relative to T.M.S. internal standard.

The $J(\text{P-H})$ values in the range 10–50 Hz are characteristic of *cis*-P-H, whereas $J(\text{P-H})$ values of 75–160 Hz are found for *trans*-P-H.

For the *trans*-hydrohalides of Fe, Ru, and Os the splitting pattern is a 1:4:6:4:1 quintet, which requires the presence of four equivalent ³¹P nuclei. This indicates that the structure is indeed *trans*. For *trans*-FeH₂(PEE)₂ only three bands were observed (66). The compound RuHMe(dee)₂ occurs in two forms; one has a quartet 1:3:3:1 and is thus the *cis* isomer (I), the other has a more complex pattern, probably due to coupling between the proton and the *trans*-methyl group (II).



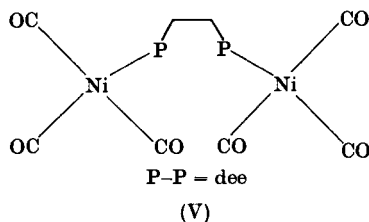
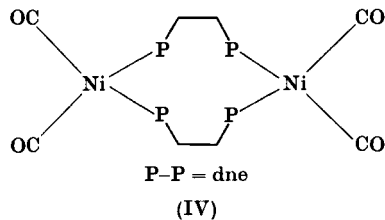
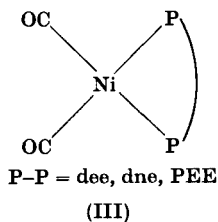
The ¹H NMR spectra of diposphine complexes show a number of absorptions due to the magnetically different protons in the molecule. The spectrum of a coordinated diposphine will differ from that of the uncoordinated ligand in that the magnetic equivalence of some of the protons may be changed, and the extent of shielding will change. The

coupling between the phosphorus and the protons in the diphosphine may also change. Recently, several groups have begun to study these effects. In VPP the absorption of the olefinic protons is hidden by that due to the phenyl protons, but in coordinated VPP the olefinic protons are clearly distinguishable from the phenyl protons. This is a reflection of the greater effect of coordination on the olefin protons compared with the phenyl protons (194). King and Efraty observed that in DPPB the CH_2 protons are coupled to both phosphorus atoms. On formation of $(\text{PtCl}_2\text{DPPB})_2$ coupling decreases; the CH_2 protons are only coupled with the phosphorus to which it is bonded. An intermediate degree of coupling is observed in the compound $(\text{AuCl})_2\text{DPPB}$ (193).

2. ^{31}P NMR

The utility of NMR spectra of the phosphorus isotope ^{31}P in chemical studies of both organic and inorganic compounds containing phosphorus has been well established (240), and metal complexes containing phosphine ligands are receiving an increasing amount of attention (134, 221). However, diphosphine complexes have not been well investigated.

High-resolution ^{31}P NMR spectra of a large number of nickel carbonyl-phosphine complexes have been obtained by Meriwether and Leto (216). It was pointed out that complex formation always causes a shift in the phosphorus resonance, δ^{P} , to a new value $\delta^{\text{P-M}}$. In most cases $\delta^{\text{P-M}}$ is more negative than δ^{P} , agreeing with the intuitive assumption that the formation of a donor bond from phosphorus to nickel results in a decrease in electron density on the phosphorus atom and thus a decrease in the shielding and in the δ value. Three monomeric diphosphine complexes (III) were studied. The values of $\delta^{\text{P-M}} - \delta^{\text{P}}$ for



these complexes (-68 to -52 ppm) were much more negative than those obtained for the unchelated complexes of similar monodentate complexes (-42 ppm). This was attributed to the presence of the phosphorus atoms in a planar 5-membered ring, in which the C-P-C and Ni-P-C bond angles are distorted from the approximately tetrahedral angles which obtain in the unchelated complexes. The reaction with dne also yielded a small amount of (IV). In this complex the $\delta^{\text{P-M}}-\delta^{\text{P}}$ was -42 ppm, proving the absence of a chelate ring. Complex (V) also exhibited $\delta^{\text{P-M}}-\delta^{\text{P}}$ in the unchelated range. The *cis*-Mo(dne)(CO)₄ exhibits a large $\delta^{\text{P-M}}-\delta^{\text{P}}$ (-74.4 ppm) value (216).

Grim *et al.* have measured the $^{31}\text{P}-^{31}\text{P}$ coupling constant in the novel *trans*-[(EtO)₃PMo(CO)₃dPe] ($J_{\text{P-P}} = 104$ Hz) (133). The $^{183}\text{W}-^{31}\text{P}$ nuclear spin coupling constant has also been measured for [W(CO)₄·dPe] ($J_{\text{W-P}} = 239.0$) (209).

D. ELECTRONIC SPECTROSCOPY

The observation and interpretation of “*d-d*” bands in the visible spectra of metal complexes have now become refined tools for “finger-printing” structural types. This is particularly true for $3d^7$ and $3d^8$ complexes, and it is for ions with these configurations that the main application of visible spectroscopy has been made.

Horrocks and co-workers, have identified a planar-tetrahedral equilibrium in complexes of nickel(II) halides with dPp (150). These workers have also identified the structures of [CoLX₂] (L = dPe, dPp; X = Cl, Br, I) as tetrahedral, and that of [CoL₂X₂] as pentacoordinate on the basis of electronic spectra (167). Dyer *et al.* have also used this technique in assigning structures to the pentacoordinate [Co(VPP)₂X]⁺ (X = Cl, Br, I) cation, and to the [Co(VPP)₂(NCS)]₂[Co(NCS)₄] complex which contains a pentacoordinate cation and a tetrahedral anion (111). McAuliffe and Meek assigned square-planar structures to [Ni(VPP)X₂] (X = Cl, Br, I, NCS), and square-pyramidal structures to [Ni(VPP)₂X]⁺ (X = Cl, Br, I) using visible spectroscopy (212).

E. ELECTRON SPIN RESONANCE

Horrocks *et al.* obtained the electron spin resonance spectra of Co(dPe)₂Cl₂ (167), Co(dPe)₂Br₂ (167), and Ni(dPp)Br₃ (150). For Ni(dPp)Br₃ $g = 2.218$ was obtained, corresponding to a magnetic moment of 1.92 B.M. The g values for the Co complexes were:

Co(dPe) ₂ Cl ₂	$g_1 = 2.257$	$g_2 = 2.056$	$g_3 = 2.041$
Co(dPe) ₂ Br ₂	$g_1 = 2.258$	$g_2 = 2.075$	$g_3 = 2.037$

which leads to $\mu = 1.84$ B.M. The ESR spectra are consistent with the ground state configuration for the pentacoordinate complexes of $|(xy)^+(xy)^-(x^2-y^2)^+|$, in agreement with electronic spectral data (167).

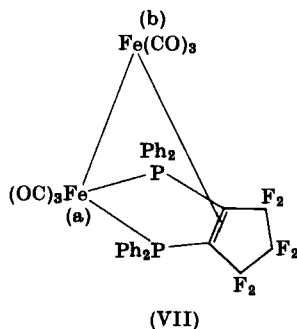
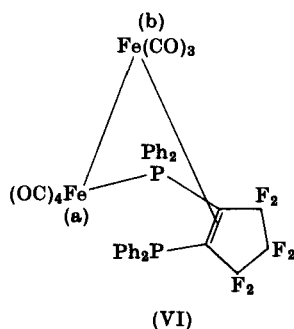
The reaction of $\text{Co(dPe)}_2\text{Cl}_2$ or $\text{Co(dee)}_2\text{Cl}_2$ with MeMgCl in 1,2-dichloroethane gave no ESR signal at a $\text{Mg}:\text{Co}$ ratio >8 , consistent with the formation of Co^{I} . The reappearance of Co^{II} was observed. The suggested explanation was that the signal was produced by Co-H interaction, i.e., that a proton from the phosphine was exchanged for a chloride ion (151).

F. MÖSSBAUER SPECTROSCOPY

Only diphosphine complexes of iron have so far been studied by this technique, although it is potentially capable of extension to a number of other transition metals, e.g., Ni, Ir, or Pt.

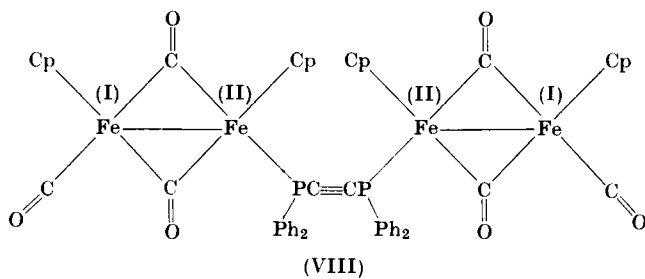
Bancroft *et al.* (15) studied a number of low-spin iron(II) complexes of the type $\text{FeX}_2(\text{diphos})_2$. They found an inverse correlation between the partial center shifts of the various ligands and their position in the spectrochemical series. The partial center shifts for the ligands dee, dme, and PEE were obtained, and the results discussed in terms of the σ -donor and π -acceptor properties of these ligands. The quadrupole splitting values have been used as a means of assigning structure in some iron complexes, but in the cases discussed, the Mössbauer data did not clearly indicate the configuration.

Cullen *et al.* (103, 105) have obtained some interesting results from the f_6fos complexes. $\text{Fe}_2(\text{CO})_7\text{f}_6\text{fos}$ and $\text{Fe}_2(\text{CO})_6\text{f}_6\text{fos}$ are believed to have the structures (VI) and (VII), respectively. The Mössbauer



spectra are in agreement with these structures and exhibit several interesting features. The isomer shifts for Fe(b) in both compounds are

identical, but Fe(a) is slightly lower in the $\text{Fe}_2(\text{CO})_7$ complex than in the $\text{Fe}_2(\text{CO})_6$ complex (lower shift corresponding to higher s -electron density). This was attributed to the greater $d\pi$ -acceptor properties of the extra carbonyl group compared with $\text{Ph}_2\text{P}-$. In both complexes the isomer shift of Fe(a) is smaller than that of Fe(b), indicating a deficiency of s -electron density on the Fe(b) nucleus. The quadrupole splitting of Fe(a) in $\text{Fe}_2(\text{CO})_6\text{fos}$ is greater than that of Fe(a) in $\text{Fe}_2(\text{CO})_7\text{fos}$. When both phosphorus atoms are coordinated to Fe(a), the P-Fe(a)-P angle is fixed, which means a distortion of the octahedron around Fe(a). In $\text{Fe}_2(\text{CO})_7\text{fos}$ the presence of one coordinated phosphorus only allowed this distortion to be minimized. Mössbauer spectra then can give information about the environment of the metal atom and the electron density on the atom.



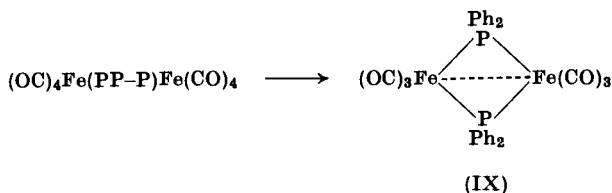
An interesting case is that of $[(\pi\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3]_2\text{DPPA}$ (52). An X-ray structural determination showed it to be (VIII), but a Mössbauer study failed to detect the nonequivalence of the iron atoms, the difference in isomer shift between Fe^{I} and Fe^{II} being too small to be resolved.

IV. X-Ray Crystallography Studies

Several diphosphine complexes have had full crystallographic structures determined, and a section is devoted to them here in order to illustrate some especially interesting features of diphosphine complexes.

Mais and co-workers have determined the structure of $[(\text{OC})_3\text{Ni}(\text{PP-P})\text{Ni}(\text{CO})_3]$ (206). Nickel is in a tetrahedral environment, and the diphosphine link has the catenary form. The molecule consists of two identical halves related by a center of symmetry. The P-P bond (2.777 Å) is longer than normal, and this was attributed to steric strain resulting from repulsion between the phenyl groups and between the phenyl and carbonyl groups. The increased length of the P-P bond suggests that this

bond may be weak, and when PP-P is complexed in the analogous iron carbonyl complex, cleavage of the P-P bond occurs.



However, the iron carbonyl complex containing MP-P is stable, and Jarvis *et al.* have published the structure of $[(\text{OC})_4\text{Fe}(\text{MP-P})\text{Fe}(\text{CO})_4]$ (187). This has the centrosymmetric pi-catenary form; a "staggered" conformation of substituents (methyl or carbonyl) about the Fe-P and P-P bonds which produce the main steric interactions. However, these steric interactions are not at all severe, and the P-P bond length (2.231 Å) is quite normal. The Fe atoms are not in an "ideal" trigonal-bipyramidal environment (two equatorial bond angles = 116° – 117° , and one equatorial bond angle = 127° , instead of three at 120°). The Fe-P bond length (2.25 Å) is less than the radius sum (2.35–2.40 Å, taking 1.25–1.30 Å as the radius for iron) by about 0.10–0.15 Å, and suggests that there is appreciable double bonding in the Fe-P bond.

Adam *et al.* investigated the structure of $[\text{MoOCl}(\text{dPe})_2] \cdot [\text{ZnCl}_3 \cdot (\text{OCMe}_2)]$ (3). The molybdenum atom is in a fairly regular octahedral environment, with bond lengths of Mo-O (1.69 Å), Mo-Cl (2.46 Å), and Mo-P (2.57 Å, mean).

The planar $[\text{Rh}(\text{dPe})_2](\text{ClO}_4)$ structure was elucidated by Hall *et al.* (138) and these workers included a valuable discussion of the torsion included in the bond angles of this and several other diphosphine complexes. The mean Rh-P bond length is 2.306 Å, and the P-Rh-P angles are 82.7° .

The oxygen adduct of $[\text{Rh}(\text{dPe})_2]^+$, $[\text{Rh}(\text{O}_2)(\text{dPe})_2]\text{PF}_6$, and the analogous iridium complex have been studied crystallographically by McGinnety *et al.* (215). The complexes have been assigned distorted trigonal-bipyramidal structures. The mean Rh-P distance (2.342 Å) is longer than in the parent complex, and the mean Ir-P distance is 2.283–2.452 Å. The bond lengths associated with the oxygen molecule are very interesting. The Rh complex can be reversibly oxygenated and the mean Rh-O distance is 2.2025 Å and O-O distance is 1.418 Å (the O_2 molecule is bonded "sideways on" to the Rh and Ir). However, oxygenation is irreversible in the Ir complex, the Ir-O bond (1.976 Å)

is distinctly shorter, and the O–O bond (1.625 Å) has lengthened compared with the Rh complex.

The complex “Ru(dme)₂(naphthalene)” was originally thought to be a complex of Ru(0), but the I.C.I. crystallographers have shown this to be a Ru(II)-hydrido complex, *trans*-[Ru(H)(naphthyl)(dme)₂]. The complex is a fairly regular octahedron, with Ru–P (2.28–2.33 Å) and an estimated Ru–H bond length of 1.7 Å (169).

The phenomenon of diphosphine ligands promoting the coordination of both thiocyanato and isothiocyanato groups in [Pd(diphos)(NCS)-(SCN)] complexes has been investigated by Meek and McAuliffe and co-workers (84). Palenik has X-rayed the complex prepared by Meek [Pd(dPe)(SCN)(NCS)] and shown the complex to be approximately square-planar (24). The complex does indeed contain both S- and N-bonded groups. The Pd–P bond *trans* to –SCN is significantly longer (2.260 Å) than the Pd–P bond *trans* to the –NCS group (2.245 Å).

[Ni(POPO)Cl₂] contains a distorted tetrahedral environment about the Ni atom (Cl–Ni–Cl = 127.1°, P–Ni–P = 107.1°). The mean Ni–Cl distance is 2.20 Å, and the mean Ni–P distance is 2.315 Å. The oxygen atom in the chelate is 3.64 Å from the metal and is thus not coordinated. This complex is therefore a rare example of an eight-membered chelate ring (132).

V. Syntheses of Diphosphines

The synthetic methods have been reviewed and will not be discussed. For completeness, references to synthesis are included in the Appendix alongside the abbreviations.

VI. Diphosphine Complexes

A. LANTHANIDES AND ACTINIDES

A light tan complex UCl₄·dme was reported (207) in 1963, but its existence has since been questioned (247). A light green complex (UCl₄)₂·dPe produced by mixing UCl₄ and dPe in THF seems authentic (247). The IR spectrum of this complex shows no evidence of P=O, P–H, or UO₂²⁺; $\mu_{\text{eff}} = 3.2$ B.M.

A pale green U^V complex, UCl₅·dPe, $\mu_{\text{eff}} = 2.7$ B.M., was synthesized by mixing UCl₅·teac with dPe in benzene (teac = Cl₂C=CCl–COCl) with exclusion of oxygen and moisture (246).

B. GROUP IVA (Ti, Zr, AND Hf)

A complex of Ti^0 (analogous to the V, Cr, Mo, and W complexes) could not be obtained; reduction of $TiCl_4 \cdot dme$ gave a black solid—probably metallic titanium (82).

Titanium tetrachloride reacts with dme, dee, and PEE in dry benzene under nitrogen to give red or orange 1:1 adducts, $TiCl_4 \cdot L$ (71). By reacting $TiCl_4$ with dPe in various ratios in benzene three red solids were obtained: $TiCl_4 \cdot dPe$ (119, 260), $(TiCl_4)_2 \cdot dPe$, and $(TiCl_4)_3(dPe)_2$ (260); their IR spectra were recorded. All are extremely moisture-sensitive. The ligand PMM reacted with $TiCl_4$ in a 2:1 ratio to produce the eight-coordinate, orange $TiCl_4(PMM)_2$ (88). Titanium tetrabromide is reported to be reduced to Ti^{III} by dPe (119).

The complexes $[CH_3TiCl_3(dPe)]$ (87) and $[Ti(CH_3)_4(dme)]$ (254) have been prepared. A compound thought to be $TiCl_3(dee)$ was obtained as a dark brown solid by refluxing the ligand with $TiCl_3$ in benzene (71).

Fowles could not obtain pure complexes from the reaction of zirconium halides with dPe (119); but the compounds $[Zr(dPe)Cl_4]$, $[Zr(dpe)Br_4]$, and $[Hf(dPe)Cl_4]$ have been obtained from MX_4 and dPe in benzene, and their IR spectra in the range 460–250 cm^{-1} reported (227).

C. GROUP VA (V, Nb, AND Ta)

Brown-black crystals of $V(dme)_3$ were obtained by reducing a mixture of VCl_3 and dme in THF with sodium naphthalenide (82). It is paramagnetic, $\mu_{eff} = 2.1$ B.M. A similar reaction with $NbCl_5$ gave only a black carbon-free sludge, presumably niobium metal.

Reaction of $V(CO)_6$ with dPe produced three different products depending on the ratio of the reactants and the temperature: the red-brown $[VL_3][V(CO)_6]$, $\mu_{eff} = 4.01$ B.M.; the dark-green $[V(CO)_4L]$, $\mu_{eff} = 2.23$ B.M.; and the red *trans*- $[V(CO)_2L_2]$, $\mu_{eff} = 1.77$ B.M. The anion $[V(CO)_4L]^-$ was also obtained (20). $V(CO)_6$ gives a phosphido derivative with PP-P, but vanadium nitrosyl carbonyl forms $[(CO)_4-(NO)V(PP-P)V(NO)(CO)_4]$ (159a).

Vanadium trichloride reacted with dme in THF to produce an apple-green solution, but no complex was isolated (82). VCl_4 is reduced by dPe (34).

Selbin investigated the reaction of $VOX_2 \cdot xH_2O$ ($X = Cl, Br$) with dPe and dPm. Green complexes $[VOBr_2(dPe) \cdot H_2O]$, $[VOBr_2(dPm) \cdot H_2O]$, and $[VOCl_2(dPe) \cdot H_2O]$ were obtained. Their electronic and IR spectra were characteristic of the VO^{2+} group. Some blue-green com-

pounds, apparently phosphine oxide complexes, produced by ligand oxidation by V^{IV} , were also formed (248).

D. GROUP VIA (Mo, Cr, AND W)

The compounds $Cr(dme)_3$, $Mo(dme)_3$, and $W(dme)_3$ were formed as yellow solids by reducing $CrCl_3$, $MoCl_5$, and WCl_6 , respectively, with $LiAlH_4$ or sodium naphthalenide in THF (82). Mo^0 complexes $[Mo(dme)_3]$, $[Mo(dPe)_3]$, and $[Mo(PEE)_3]$, were obtained by heating dibenzene-molybdenum with the ligand in a sealed tube (80). $K_6Cr(CN)_6$ reacts with dpm and dPe in liquid ammonia to give $[Cr(dpm)_3]$ and $[Cr(dPe)_3]$ (21). $[Mo(dme)_3]$ is monomeric in chloroform. All the complexes readily oxidize in the order $Cr > Mo \gg W$. An essentially octahedral structure has been proposed for these unique MP_6 compounds (see Table III).

TABLE III
GROUP VIA DIPHOSPHINE COMPLEXES

Compound	Color	M.p. ^a (°C)	Properties	Ref.
$[Cr(dme)_3]$	Yellow	293 (d)	—	(82)
$[Mo(dme)_3]$	Yellow	397	—	(80, 82)
$[W(dme)_3]$	Yellow	396 (d)	—	(82)
$[Mo(dPe)_3]$	Red-orange	281	—	(80)
$[Mo(PEE)_3]$	Red-black	236	—	(80)
$[WCl_3(dPe)]$	Brown		IR, $\mu = 1.29$	(27)
$WCl_3(dPe)_2$	Yellow		IR, $\mu = 1.48$	(27)
$[WCl_4(dPe)]$	Yellow-brown		IR, $\mu = 1.74$	(27)
$WCl_5(dPe)$	Pale green		IR, $\mu = 0.90$	(28)
$[WCl_2(dPe)_2][WCl_6]$	—		IR, $\mu = 1.09/W$ atom	(27)
$[MoCl_4(dPe)]$	Red-brown		$\mu = 2.18$	(36)
$[MoCl_4(VPP)]$	Red-brown		$\mu = 2.26$	(36)
$[(Mo_6Cl_8)Cl_3(dPe)]Cl$	—		Vis. ^b	(116)
$[(Mo_6Cl_8)Cl_3(dPe)py]Cl$	—		Vis.	(116)

^a (d), decomposes.

^b Vis., visible.

The substituted carbonyls have been extensively studied [see Table IV (110)]. Although the $M(diphos)_3$ compounds can be prepared directly, complete substitution of the CO in the carbonyls has not been achieved. Three main types of complexes are known: $[M(CO)_4\text{-}diphos]$, $[M(CO)_2(diphos)_2]$, and $[M_2(CO)_6(diphos)_3]$. The compounds

TABLE IV
SUBSTITUTED CARBONYLS OF GROUP VIA

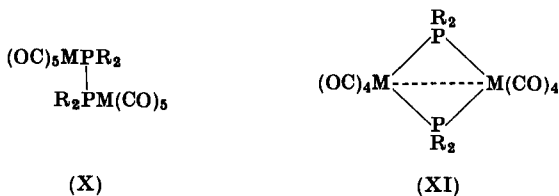
Compound	Color	M.p. ^a (°C)	Physical properties	Ref.
[Cr(CO) ₄ (dPe)]	White	211–212	IR	(81)
[Mo(CO) ₄ (dPe)]	White	193–194	IR	(81)
[W(CO) ₄ (dPe)]	Pale yellow	208–209	IR, ³¹ P NMR	(81, 209)
[Cr(CO) ₄ (dee)]	White	116	IR	(81)
[Mo(CO) ₄ (dee)]	White	107	IR	(81)
[W(CO) ₄ (dee)]	Pale yellow	122	IR	(81)
[Cr(CO) ₄ (dPm)]	Yellow	171	IR	(81)
[Mo(CO) ₄ (dPm)]	Yellow	195	IR	(81)
[W(CO) ₄ (dPm)]	Yellow	201	IR	(81)
[Cr(CO) ₄ (PEE)]	White	163	IR, D.M. = 7.6	(81)
[Mo(CO) ₄ (PEE)]	White	181	IR, D.M. = 7.8	(81)
[W(CO) ₄ (PEE)]	White	190	IR, D.M. = 8.3	(81)
<i>cis</i> -[Cr(CO) ₂ (PEE) ₂]	Orange	265	IR	(81)
<i>cis</i> -[Mo(CO) ₂ (PEE) ₂]	Bright yellow	257	IR, D.M. = 6.4	(81)
<i>cis</i> -[W(CO) ₂ (PEE) ₂]	Bright yellow	271	IR, D.M. = 6.6	(81)
<i>cis</i> -[Cr(CO) ₂ (dPe) ₂]	Pale orange	280	IR	(81)
<i>cis</i> -[Mo(CO) ₂ (dPe) ₂]	Yellow	324	IR, D.M. = 6.2	(81)
<i>cis</i> -[W(CO) ₂ (dPe) ₂]	Yellow	321	IR, D.M. = 6.7, ³¹ P NMR	(81, 209)
<i>trans</i> -[Cr(CO) ₂ (dPe) ₂]	Vermillion	279	IR	(81)
<i>cis</i> -[Cr(CO) ₂ (dPm) ₂]	Orange	289	IR	(81)
<i>trans</i> -[Mo(CO) ₃ (dPe)P(OEt) ₃]	Yellow	117	IR, ³¹ P NMR	(133)
[Cr ₂ (CO) ₁₀ (MP–P)]	Pale yellow	130	IR, UV, NMR, D.M. = 4.6	(78, 146)
[Mo ₂ (CO) ₁₀ (MP–P)]	Colorless	143	IR, UV, NMR, D.M. = 4.8	(78, 79, 146)
[W ₂ (CO) ₁₀ (MP–P)]	Colorless	163	IR, UV, NMR, D.M. = 4.6	(78, 79, 146)
[Mo ₂ (CO) ₁₀ (EP–P)]	Colorless	158(d)	IR	(79)
[W ₂ (CO) ₁₀ (EP–P)]	Colorless	188	IR	(79)

[Cr ₂ (CO) ₆ (dPe) ₃]	Yellow	263(d)	IR	(266)
[Mo ₂ (CC) ₆ (dPe) ₃]	Colorless	210(d)	IR	(266)
[W ₂ (CO) ₆ (dPe) ₃]	Yellow	194(d)	IR	(266)
[Cr(CO) ₄ (ffos)]	Orange	217	IR	(99)
[Mo(CO) ₄ (ffos)]	Yellow	194	IR	(99)
[W(CO) ₄ (ffos)]	Yellow	208(d)	IR	(100)
[Cr(CO) ₄ (f ₆ fos)]	Orange-brown	189(d)	IR	(100)
[Mo(CO) ₄ (f ₆ fos)]	Yellow	192(d)	IR	(100)
[W(CO) ₄ (f ₆ fos)]	Yellow	216(d)	IR	(100)
[Cr(CO) ₄ (f ₈ fos)]	Amber	209(d)	IR	(100)
[Mo(CO) ₄ (f ₈ fos)]	Orange	202(d)	IR	(100)
[W(CO) ₄ (f ₈ fos)]	Orange	211(d)	IR	(100)
[Cr(CO) ₄ (dHe)]	Cream	—	$\nu(\text{P-H})$ 2330 cm ⁻¹	(109)
[Mo(CO) ₄ (dHe)]	White	—	$\nu(\text{P-H})$ 2345, 2315 cm ⁻¹	(109)
[Mo(CO) ₄ (VPP)]	Yellow	174(d)	IR, NMR	(194)
[W(CO) ₄ (VPP)]	Yellow	179	IR, NMR	(194)
[Cr(CO) ₄ (VPP)]	Yellow	152	IR, NMR	(194)
[Mo(CO) ₂ (dPe) ₂] ₃	Red	201(d)	$\mu = 1.66$	(199)
[W(CO) ₂ (dPe) ₂] ₃	Red	216(d)	$\mu = 1.86$	(199)
[Mo(CO) ₂ (dPe) ₂] ₂ ClO ₄	Pink	160	$\mu = 1.61$	(199)
[W(CO) ₂ (dPe) ₂] ₂ ClO ₄	Orange	—	—	(199)
[Mo(CO) ₃ (dPe)•I ₂]	Orange-brown	208(d)	IR, $\mu = 0$	(12, 199)
[W(CO) ₃ (dPe)•I ₂]	Yellow	237(d)	IR, $\mu = 0$	(12, 199)
[Mo(CO) ₃ (dPe)•Br ₂]	Yellow	217(d)	IR	(12, 199)

^a (d), decomposes.

$[M(CO)_4\text{diphos}]$ result from heating $M(CO)_6$ with a slight deficit of the diphosphine in a sealed tube (81). The disubstituted $M(CO)_2(\text{diphos})_2$ compounds are obtained similarly with two equivalents of the diphosphine, but $[\text{Cr}(CO)_2(\text{diphos})_2]$ compounds are better prepared from tricarbonylmesitylenechromium (81). This latter method also produced the only trans isomer, *trans*- $[\text{Cr}(CO)_2(\text{dPe})_2]$. The corresponding cis isomer is obtained by recrystallization of the trans isomer from methanol. Infrared and dipole moment measurements have shown that the chromium compounds $[\text{Cr}(CO)_2(\text{diphos})_2]$ exhibit cis-trans isomerism in solution, but this is not observed with the molybdenum and tungsten analogs (81). *trans*- $[\text{Mo}(CO)_2(\text{dPm})_2]$ results on refluxing $\text{Mo}(CO)_6$ with dPm in *n*-decane (92). The dinuclear $M_2(CO)_6(\text{diphos})_3$ compounds were obtained by Zingales and Canziani from the reaction of $[M(CO)_3\text{-(cycloheptatriene)}]$ with the diphosphines (266). Some diphosphine-bridged complexes are known, e.g., $[M(CO)_5]_2 \cdot \text{dPe}$ ($M = \text{Cr}, \text{Mo}$); they react with dPe to form the $[M(CO)_4(\text{dPe})]$ compounds (17).

Diphosphines containing a direct P-P bond react rather differently from their C-linked analogs. At 180°–200° in sealed tubes, these ligands react with the hexacarbonyls to produce yellowish compounds (X) in which the P-P bond is retained. At higher temperatures the P-P

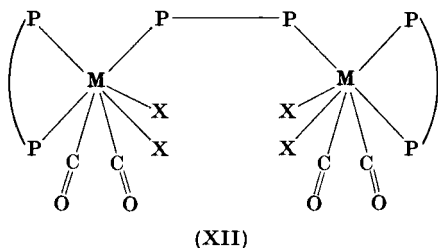


$M = \text{Cr}, \text{Mo}, \text{or W}$

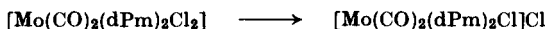
bond ruptures and phosphido-bridged complexes result (XI) (147). Phosphido-bridged $[\text{Mo}_2(CO)_8(\text{PMe}_2)_2]$ reacts with dPm, dPe, and dPb to produce compounds, $\text{Mo}_2(CO)_6(\text{PMe}_2)_2(\text{diphos})$, of unknown structure (205). With $\text{P}_f\text{P-P}$ molybdenum and chromium form white polymers $[\text{Mo}(\text{P}_f\text{P-P})(\text{CO})_4]_n$, and also low-melting white or yellow compounds $[\text{Mo}(\text{P}_f\text{P-P})(\text{CO})_5]$, in which the diphosphine acts as a monodentate ligand (131). The di(primary)phosphine, $\text{C}_2\text{H}_4(\text{PH}_2)_2$ (dHe), displaced weakly bonded bidentates from $[M(\text{bid.})(\text{CO})_4]$ ($M = \text{Cr}, \text{Mo}, \text{W}$) to produce $[M(\text{dHe})(\text{CO})_4]$ (109). Diphosphine, P_2H_4 , has been reacted with (norbornadiene) $\text{Mo}(CO)_4$ to produce $[\text{Mo}(\text{P}_2\text{H}_4)(\text{CO})_4]_n$ (17). In no case is the $>\text{C}=\text{C}<$ involved in coordination in the complexes $[M(CO)_4(\text{diphos})]$ ($M = \text{Cr}, \text{Mo}, \text{W}$; diphos = ffos, $f_6\text{fos}$, $f_8\text{fos}$) (99, 100). A large number of compounds containing other ligands as well as diphosphines are known, e.g., $[(\text{C}_5\text{H}_5)\text{Mo}(CO)_2(\text{dme})]\text{Cl}$ and $[(\text{C}_5\text{H}_5)\text{-}$

$\text{Mo}(\text{CO})_2(\text{VPP})\text{PF}_6$ (195, 196), and the reader is referred to reviews of carbonyl compounds (1) for coverage of these.

The complexes $[\text{M}(\text{CO})_2(\text{dPe})_2]$ react with three equivalents of iodine to give M^{I} complexes. The presence of univalent metal is confirmed by the preparation of the perchlorates $[\text{M}(\text{CO})_2(\text{dPe})_2]\text{ClO}_4$ ($\text{M} = \text{Mo}, \text{W}$). Lewis and Whyman observed that excess chlorine or bromine decomposed the substituted carbonyl complexes with formation of Mo^{V} , W^{VI} , and phosphine oxide complexes (199). Under controlled conditions they isolated $[\text{M}(\text{CO})_3(\text{dPe})\text{X}_2]$ ($\text{X} = \text{Br}, \text{I}$), and these nonelectrolyte complexes were assigned a seven-coordinate structure. Recently, Colton and co-workers have prepared a number of complexes of the types $[\text{M}(\text{CO})_2(\text{diphos})_2\text{X}_2]$, $[\text{M}(\text{CO})_3(\text{diphos})\text{X}_2]$, and $[\text{M}(\text{CO})_2(\text{diphos})_{1.5}\text{X}_2]_2$ ($\text{M} = \text{Mo}, \text{W}$; $\text{diphos} = \text{dPm}, \text{dPe}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) (12, 13, 91-93). The $\text{M}(\text{CO})_2(\text{diphos})_2\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$) are neutral diamagnetic, seven-coordinate complexes, in which one of the diphosphines behaves as a monodentate ligand. The structures of the $[\text{M}(\text{CO})_2(\text{diphos})_{1.5}\text{X}_2]_2$ compounds are probably given by (XII). The general methods of preparation are



from $\text{M}(\text{CO})_4\text{X}_2^+$ diphosphine, from $[\text{M}(\text{CO})_4\text{X}_3]^-$ and dPm , or by the method of Lewis and Whyman. The iodo complexes are different in several respects from the chloro and bromo complexes. $\text{M}(\text{CO})_2(\text{diphos})_2\text{I}_2$ are 1:1 electrolytes and react reversibly with CO (13, 92, 93). They may be seven-coordinate, but it is more likely that they are six-coordinate, with one diphosphine behaving as a monodentate ligand. Two isomers of $\text{M}(\text{CO})_3(\text{diphos})\text{I}_2$ and three of $\text{M}(\text{CO})_2(\text{diphos})_2\text{I}_2$ have been isolated (92, 93). The apparently irreversible isomerism occurs on dissolution of



the yellow $[\text{Mo}(\text{CO})_2(\text{dPm})_2\text{Cl}_2]$ under reflux in an inert solvent (91). The differences between the complexes formed with the different halogens and those of dPm and dPe are believed to be largely due to steric factors (91).

A *trans*-dinitrogen complex $[\text{Mo}(\text{N}_2)_2(\text{dPe})_2]$ was obtained as orange-yellow crystals by reducing molybdenum(III) acetylacetonate with iso- Bu_3Al in the presence of nitrogen and dPe (153). The $\nu(\text{N}-\text{N})$ occurs at 1970 cm^{-1} , indicative of the *trans* configuration. The orange $[\text{W}(\text{N}_2)_2(\text{dPe})_2]$, $\nu(\text{N}-\text{N})$ at 1953 cm^{-1} , has also been obtained (22).

Complexes analogous to Reinecke's salt result from the reaction of $\text{K}_3\text{Cr}(\text{NCS})_6$ (175) and $\text{K}_3\text{Mo}(\text{NCS})_6$ (171) with dCye and dee. The products are $[\text{R}_2\text{PH}(\text{CH}_2)_2\text{PHR}_2][\text{M}(\text{SCN})_4(\text{diphos})]$ ($\text{M} = \text{Cr}, \text{Mo}$). A similar complex was obtained with dPm and $\text{K}_3\text{Mo}(\text{NCS})_6$, but this ligand did not react with $\text{K}_3\text{Cr}(\text{NCS})_6$. Salts of the $[\text{M}(\text{SCN})_4(\text{diphos})]^{2-}$ anions with Cd^{2+} , Cu^{2+} , Zn^{2+} , and Cs^+ have also been prepared.

The 1:1 electrolyte $[(\text{Mo}_6\text{Cl}_8)(\text{dPe})\text{Cl}_3]\text{Cl}$ was obtained from $\text{Mo}_6\text{Cl}_{12}$ and excess dPe in THF. It forms $[(\text{Mo}_6\text{Cl}_8)(\text{dPe})(\text{py})\text{Cl}_3]\text{Cl}$ upon recrystallization from pyridine (116).

Molybdenum(IV) complexes $[\text{Mo}(\text{dPe})\text{Cl}_4]$ and $[\text{Mo}(\text{VPP})\text{Cl}_4]$ were obtained by Butcher and Chatt by adding the ligand in benzene to $[\text{MoCl}_4(\text{EtCN})_2]$ in boiling benzene (36).

Several dPe complexes of tungsten are known (27). $[\text{W}(\text{dPe})\text{Cl}_3]$ is formed from $[\text{WCl}_4(\text{MeCN})_2]$ and dPe, or from K_2WCl_6 and dPe in acetonitrile. $\text{WCl}_3(\text{dPe})_2$ results from fusing $[\text{WCl}_4(\text{PrCN})_2]$ with dPe. It is a 1:1 electrolyte in nitromethane, $[\text{WCl}_2(\text{dPe})_2]\text{Cl}$, but a non-electrolyte in chloroform. Fusion of K_2WCl_6 with dPe produces yellow-brown $\text{WCl}_4(\text{dPe})$. The green solid, $\text{WCl}_5(\text{dPe})$, formed from WCl_6 and excess dPe in benzene, rapidly decomposes in air (28). A complex which, on the basis of molecular weight and IR measurements, was formulated as $[\text{WCl}_2(\text{dPe})_2][\text{WCl}_6]$, was obtained from $[\text{WCl}_4(\text{MeCN})_2]$ and dPe in acetonitrile (28).

Complexes $[\text{MoOCl}(\text{diphos})_2]\text{X}$ (diphos = dme, dPe, VPP; $\text{X} = \text{Cl}, \text{BPh}_4, \text{BF}_4$) are obtained as violet or purple solids from $[\text{MoOCl}_2(\text{PR}_3)_3]$ and excess diphosphine in ethanol (14). With a stoichiometric amount of diphosphine $[\text{MoOCl}_2(\text{PR}_3)(\text{diphos})]$ can be isolated. The THF in $\text{MoOCl}_3(\text{THF})$ is easily replaced by dPe giving red $[\text{MoOCl}_3(\text{dPe})]$, which can be reduced with zinc in THF to the $[\text{MoOCl}(\text{dPe})_2]^+$ ion, isolated as $[\text{MoOCl}(\text{dPe})_2][\text{ZnCl}_3 \cdot \text{OCMe}_2]$ upon recrystallization from acetone (3).

E. GROUP VIIA (Mn, Tc, AND Re)

Diphosphine complexes of manganese are only formed in low oxidation states. Manganese(III) is readily reduced by phosphines.

Hieber and Freyer obtained $\text{Mn}_2(\text{CO})_8(\text{dPe})$ as yellow crystals by reaction of $\text{Mn}_2(\text{CO})_{10}$ and dPe (155). Sacco reacted dPe and $\text{Mn}_2(\text{CO})_{10}$

in benzene when paramagnetic $[\text{Mn}(\text{CO})_3(\text{dPe})]$ and $[\text{Mn}(\text{CO})(\text{dPe})_2]$, and diamagnetic $[\text{Mn}(\text{CO})_2(\text{dPe})_2][\text{Mn}(\text{CO})_5]$ and $[\text{Mn}(\text{CO})_2(\text{dPe})_2]\text{Cl}$ were obtained (232). $[\text{Mn}(\text{CO})_2(\text{dPe})_2]\text{Cl}$ can be oxidized to the green $[\text{Mn}(\text{CO})_2(\text{dPe})_2]^{2+}$, which has been isolated as the perchlorate; IR evidence suggests a trans structure (252).

Interaction of $\text{HMn}(\text{CO})_5$ and dPe in benzene produced the yellow $[\text{HMn}(\text{CO})_3(\text{dPe})]$; the NMR spectrum (triplet 1:2:1, $\tau = 17.8$, $J = 45$ Hz) is indicative of a cis structure (29). The carbonyl halides $\text{Mn}(\text{CO})_5\text{X}$ ($\text{X} = \text{Br}, \text{I}$) produce monomeric, diamagnetic, octahedral $[\text{Mn}(\text{CO})_3(\text{dPe})\text{X}]$ complexes (222). Pale cream $[\text{Mn}(\text{CO})_3(\text{PPP})\text{Cl}]$ was similarly obtained in diglyme (83). Faron and Wojcicki reported that the S-bonded thiocyanate complex $[\text{Mn}(\text{CO})_5(\text{SCN})]$ produced an N-bonded isomer upon reaction with dPe to form $[\text{Mn}(\text{CO})_3(\text{dPe})(\text{NCS})]$ (112).

There are several examples of organometallic complexes in which the diphosphine behaves either as a bridging or a chelating ligand depending on reaction conditions. On irradiation of $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3]$ and dPe in cyclohexane, the bridged $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2]_2\text{dPe}$ is formed as yellow crystals, while prolonged irradiation of the mixture in benzene produces the chelate-containing $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})(\text{dPe})]$ as orange crystals (220). Similarly, $[\text{CH}_3\text{COMn}(\text{CO})_5]$ and dPe produce either $[\text{CH}_3\text{COMn}(\text{CO})_4]_2\text{dPe}$ or $[\text{CH}_3\text{COMn}(\text{CO})_3(\text{dPe})]$ depending on the conditions (210). The same types of complexes are obtained from $[\text{CH}_3\text{Mn}(\text{CO})_5]$, but $[\text{PhMn}(\text{CO})_5]$ produces *cis*- $[\text{PhMn}(\text{CO})_3(\text{dPe})]$ (16a). The structures of the diphosphine complexes derived from methylmanganese carbonyl have been discussed (197).

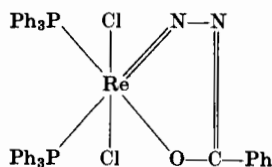
VPP displaced carbon monoxide from $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2(\text{NO})]\text{PF}_6$ to form $[\text{C}_5\text{H}_5\text{Mn}(\text{NO})(\text{VPP})]\text{PF}_6$ (192). $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})(\text{VPP})]$ was obtained from $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3]$ (194). Several diphosphines (dPe, DPPA, and DPPB) react with $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{NO}]\text{PF}_6$ to form either monodentate $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})(\text{NO})(\text{diphos})]\text{PF}_6$ or bidentate, bridged $[\{\text{C}_5\text{H}_5\text{Mn}(\text{CO})(\text{NO})\}_2(\text{diphos})](\text{PF}_6)_2$ complexes (192).

A number of diphosphine complexes of rhenium have been prepared by Freni *et al.* by reaction of $\text{Re}(\text{CO})_5\text{X}$ or $\text{Re}_2(\text{CO})_{10}$ with diphosphines (121, 123) $[\text{Re}(\text{CO})_5\text{I}]$ reacts with dPe in benzene to give *cis*- $\text{Re}(\text{CO})_3(\text{dPe})\text{I}$. A further molecule of carbon monoxide is lost on heating with dPe in a sealed tube, and on recrystallization from CH_2Cl_2 , *cis*- $[\text{Re}(\text{CO})_2(\text{dPe})_2]\text{I} \cdot \text{CH}_2\text{Cl}_2$ is obtained. By the reaction of *cis*- $[\text{Re}(\text{CO})_2(\text{dPe})_2]\text{I} \cdot \text{CH}_2\text{Cl}_2$ with excess dPe, again in a sealed tube, $\text{Re}(\text{CO})(\text{dPe})_2\text{I}$ is produced (123). $\text{Re}_2(\text{CO})_{10}$ and dPe react *in vacuo* to produce two isomers of $\text{Re}(\text{CO})_3(\text{dPe})$: a diamagnetic, nonelectrolytic, and a paramagnetic isomer. Because of magnetic and IR evidence the former is assigned as *cis*- $[\text{Re}(\text{CO})_3(\text{dPe})]_2$, and the latter as *trans*- $[\text{Re}(\text{CO})_3(\text{dPe})]$ (121). At

higher temperatures the reaction of $\text{Re}_2(\text{CO})_{10}$ and dPe produces $\text{Re}(\text{CO})_2(\text{dPe})_2$ and $\text{Re}(\text{CO})(\text{dPe})_2$. Both forms of $\text{Re}(\text{CO})_3(\text{dPe})$ react with iodine. The trans isomer behaves normally, forming *trans*- $[\text{Re}(\text{CO})_3(\text{dPe})\text{I}]$, but the cis isomer reacts with two equivalents of iodine to produce an ill-defined product. $\text{Re}(\text{CO})_2(\text{dPe})_2$ reacts with three equivalents of iodine to form a diamagnetic, nonelectrolyte $[\text{Re}(\text{CO})_2(\text{dPe})_2\text{I}_3]$. Freni *et al.* suggest (121) that, rather than nine-coordinate $\text{Re}(\text{III})$, this is a $\text{Re}(\text{I})$ compound in which one dPe is monodentate, and the uncoordinated phosphorus has been oxidized to $\text{P}(\text{V})$, i.e., $\text{Re}(\text{CO})_2(\text{dPe})\text{-}[\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{I})_2\text{Ph}_2]\text{I}$. On hydrolysis a compound $\text{Re}(\text{CO})_2(\text{dPe})\text{-}\{\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}\text{I}$ is formed, a formulation supported by the presence of two bands assigned as P–O stretching IR modes.

Upon heating $[\text{Re}(\text{CO})_6]\text{ClO}_4$ with dPe, $[\text{Re}(\text{CO})_4(\text{dPe})]^+$ is formed; it is also formed by the high-pressure carbonylation of *cis*- $[\text{Re}(\text{CO})_3(\text{dPe})\text{Cl}]$ (2). $\text{Re}(\text{CO})_5\text{I}$ reacts with PP–P to form $[(\text{PP-P})\text{Re}(\text{CO})_4\text{I}]$, in which the PP–P behaves as a monodentate ligand (161).

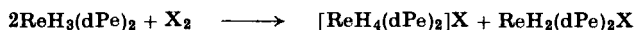
Some dinitrogen complexes of rhenium, $[\text{Re}(\text{N}_2)(\text{diphos})_2\text{Cl}]$ (diphos = dPm, dPe, VPP), have been obtained by the reaction of (XIII) with



(XIII)

diphos in methanol, or from $[\text{Re}(\text{N}_2)(\text{PPh}_3)_4\text{Cl}]$ and the diphosphine in boiling toluene (59). The dinitrogen is probably *trans* to the chlorine. The N_2 is displaced by chlorine in chloroform, but in CCl_4 $[\text{ReCl}(\text{N}_2)(\text{dPe})_2]$ forms a purple solid, probably $[\text{ReCl}(\text{N}_2)(\text{dPe})_2]\text{Cl}$.

The rhenium hydrido complexes have been studied by Chatt and Coffey (57), and Freni *et al.* (120). $[\text{ReH}_7(\text{dPe})]$ and $[\text{ReH}_5(\text{dPe})_2]$ were obtained on reducing $[\text{ReOCl}_3(\text{dPe})]$ with excess dPe and LiAlH_4 . In the presence of PPh_3 , $[\text{ReH}_5(\text{dPe})(\text{PPh}_3)]$ results. The NMR spectrum of $[\text{ReH}_5(\text{dPe})_2]$ indicates that one dPe is acting as a monodentate ligand (57). $[\text{ReH}_3(\text{dPe})(\text{PPh}_3)_2]$ is formed by displacement of PPh_3 from $[\text{ReH}_5(\text{PPh}_3)_3]$ by dPe in benzene (120). In a sealed, evacuated tube dPe displaces all the PPh_3 to form $[\text{ReH}_3(\text{dPe})_2]$. Both $[\text{ReH}_3(\text{dPe})(\text{PPh}_3)_2]$ and $[\text{ReH}_3(\text{dPe})_2]$ can be protonated by acids to give $[\text{ReH}_4(\text{dPe})(\text{PPh}_3)_2]^+$ and $[\text{ReH}_4(\text{dPe})_2]^+$ cations, the reaction being reversed by alkali. With halogens in benzene solution the following reactions



occur. Freni *et al.* also reported the formation of $\text{ReH}_2(\text{dPe})_2\text{X}$ from reduction of $[\text{Re}(\text{dPe})_2\text{X}_2]$ or $[\text{ReO}_2(\text{dPe})_2]\text{X}$ with LiAlH_4 , but Chatt and Coffey were only able to isolate $[\text{Re}(\text{dPe})_2\text{X}_2]$ from the reaction mixture. $[\text{ReH}_3(\text{dPe})(\text{PPh}_3)_2]$ reacts with chlorine to give $[\text{Re}(\text{dPe})\text{Cl}_4]$ and PPh_3O , but $[\text{ReH}_3(\text{dPe})_2]$ forms $[\text{Re}(\text{dPe})_2\text{Cl}_2]\text{Cl}$ (120). Some properties of these hydrides are shown in Table V.

There was a good deal of confusion in the older literature about the formulation of rhenium complexes, due to the failure to recognize the presence of oxygen in many complexes prepared by reduction of Re_2O_7 or KReO_4 . $[\text{ReCl}_2(\text{dPe})_2]$ was produced by reducing $[\text{ReCl}_2(\text{dPe})_2]\text{Cl}$ with NaBH_4 in ethanol (75). A red complex of approximate composition $\text{Re}_3\text{Cl}_9(\text{dPe})_{1.5}$ has been obtained, but its structure is uncertain (96, 114).

The compound $[\text{ReCl}_3(\text{dPe})(\text{PEt}_2\text{Ph})]$ is formed on boiling *cis*- $[\text{ReOCl}_3(\text{PEt}_2\text{Ph})_2]$ with dPe in propanol (75). $[\text{ReCl}_2(\text{dPe})_2]\text{Cl}$ was obtained by Chatt and Rowe by reduction of KReO_4 with concentrated hydrochloric acid and dPe in propanol (75); Cotton *et al.* obtained this compound from $[\text{Re}_2\text{Cl}_8]^{2-}$ (95). The latter workers found that $[\text{Re}_2\text{Cl}_8]^{2-}$ and dPe react in acetonitrile to give a very insoluble red isomer $[\text{ReCl}_3(\text{dPe})_2]$. The $[\text{ReX}_2(\text{dPe})_2]\text{X}$ ($\text{X} = \text{Br}, \text{Cl}$) compounds are converted to $[\text{ReX}_2(\text{dPe})_2]\text{ClO}_4$ by HClO_4 or NaClO_4 in methanol. The red $[\text{ReCl}_3(\text{dPe})_2]$ absorbs oxygen when refluxed in CH_2Cl_2 with free access of air to form green $[\text{Re}(\text{dPe})\text{OCl}_3]$ (95). A blue $[\text{Re}(\text{dPe})\text{OCl}_3]$ had previously been obtained (75), and it is possible that these are *cis* and *trans* isomers. A blue $[\text{Re}(\text{dee})\text{OCl}_3]$ is also known (75).

On boiling $[n\text{-Bu}_4\text{N}]_2[\text{Re}_2\text{Br}_8]$ with dPe and 70% HClO_4 in methanol $[\text{ReO}_2(\text{dPe})_2](\text{ClO}_4)$ is formed (95). HReO_4 reacts with dPe to form *trans*- $[\text{ReO}_2(\text{dPe})_2]^+$, which can be isolated as the Cl^- , Br^- , I^- , I_3^- , ClO_4^- , ReO_4^- , or NO_3^- salts (122) (see Table VI). Acids in acetone solution form Re(V) derivatives $[\text{ReO}(\text{OH})(\text{dPe})_2]^{2+}$, but in ethanol diamagnetic $[\text{ReO}(\text{OEt})(\text{dPe})_2]^{2+}$ is formed. $\text{ReO}(\text{dPe})\text{X}_3$ and $[\text{Re}(\text{dPe})\text{X}_2]\text{X}$ were also prepared.

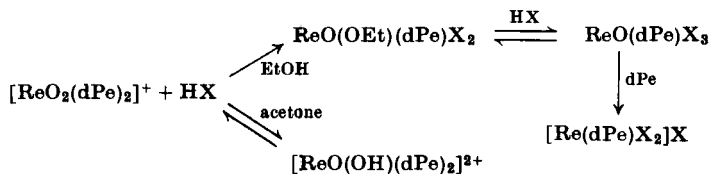


TABLE V
RHENIUM-HYDRIDO COMPLEXES (57, 120)

Compound	Color	M.p.(°C)	$\nu(\text{Re-H})$ (cm ⁻¹)	$\tau(\text{Re-H})$	$J(\text{P-H})$ (Hz)	Dipole moment (D)
ReH ₇ (dPe)	White	161	1967, 1916	Triplet 15.71 ^a Triplet 15.77 Triplet 16.60	13.5 13.0 13.0	6.57 — —
ReH ₅ (PPh ₃)(dPe)(THF)	White	190(d)	1943, 1926	Quartet 15.73 Quartet 16.36	16.0	3.59
ReH ₅ (dPe) ₂ (THF)	White	197(d)	1972, 1934, 1890	Quartet 16.76	17.2	3.06
ReH ₃ (dPe)(PPh ₃) ₂	Yellow	164	1960, 1900, 1820	Singlet 16.27 ^b quintet 16.75	24	8.26
ReH ₃ (dPe) ₂	Yellow	202	1860	Quintet 17.97 ^c	17	4.95
[ReH ₄ (dPe)(PPh ₃) ₂]Cl	White	170	1970	Quintet 13.88 ^c	22.1	—
[ReH ₄ (dPe) ₂]Cl	White	172	1950	Quintet 15.34 ^d	19.9	—
ReH ₂ (dPe) ₂ Cl	Yellow	172(d)	2040, 2020	Quintet 17.9 ^e	14.4	4.20
ReH ₂ (dPe) ₂ Br	Yellow	178	2010, 2030	Quintet 20	16	4.43
ReH ₂ (dPe) ₂ I	Yellow	185(d)	2050	Quintet 21.6	24	4.89

^a THF.

^b 100 MHz CS₂.

^c 60 MHz CS₂.

^d 100 MHz (CD₃)₂CO.

^e 60 MHz C₆D₆.

TABLE VI
 RHENIUM AND TECHNETIUM DIPHOSPHINE COMPLEXES

Compound	Color	M.p. (°C)	Physical Properties	Ref.
<i>cis</i> -Re(CO) ₃ (dPe)I	White	133	IR, D.M. = 6.9	(123)
<i>cis</i> -[Re(CO) ₂ (dPe) ₂]I	White	282	IR, D.M. = 5.6	(123)
<i>cis</i> -[Re(CO) ₃ (dPe) ₂]	Cream	195	IR	(123)
<i>trans</i> -Re(CO) ₃ (dPe)	Pale yellow	325(d)	IR	(121)
<i>cis</i> -Re(CO) ₂ (dPe) ₂	White	136	IR, D.M. = 5.01	(121)
Re(CO)(dPe) ₂	White	308(d)	IR	(121)
<i>trans</i> -Re(CO) ₃ (dPe)I	Orange	335	IR	(121)
<i>cis</i> -Re(CO) ₂ (dPe)(dPeI ₂)I	Yellow	172	IR	(121)
<i>cis</i> -Re(CO) ₂ (dPe)(dPeO)I	White	152	IR, D.M. = 6.30	(121)
[Re(CO) ₄ (dPe)]ClO ₄	White	—	IR, ¹ H NMR	(2)
[ReCl ₂ (dPe) ₂]	Yellow	225	—	(63)
Re ₃ Cl ₉ (dPe) _{1.5}	Red	—	UV, $\mu = 0.63/\text{Re}$	(96, 114)
[ReCl ₃ (PEt ₂ Ph)(dPe)]	Yellow	195(d)	—	(63)
[ReCl ₂ (dPe) ₂]	Yellow	219(d)	Vis. ^a	(63, 95)
[ReCl ₃ (dPe) ₂]	Purple-red	—	Vis.	(95)
[ReCl ₂ (dPe) ₂]ClO ₄	Yellow	—	Vis.	(95)
[ReBr ₂ (dPe) ₂]Br	Red-orange	—	Vis.	(95)
[ReBr ₂ (dPe) ₂]ClO ₄	Orange	—	Vis.	(95)
[ReCl ₂ (dPe) ₂]Cl	Orange	245	—	(122)
[ReI ₂ (dPe) ₂]I	Violet	236	—	(122)
[Re(NPh)(dPe)Cl ₃]	Blue-green	291	—	(60, 95)
[Re(NMe)(dPe)Cl ₃]	Blue-violet	261	IR	(60)
[Re(NPh)(dee)Cl ₃]	Green	248	IR	(63)
[ReOCl ₃ (dPe)]	Blue	260(d)	$\nu(\text{Re-O})$ 976 cm ⁻¹	(63)
[ReOCl ₃ (dPe)]	Green	—	$\nu(\text{Re-O})$ 980 cm ⁻¹	(95)
[ReOCl ₃ (dee)]	Blue	241(d)	$\nu(\text{Re-O})$ 984 cm ⁻¹	(63)
[ReO ₂ (dPe) ₂]ClO ₄	Orange	Explodes	$\nu(\text{Re-O})$ 789 cm ⁻¹	(95, 122)
[ReO(OEt)(dPe) ₂]Cl ₂	Violet	234	$\nu(\text{Re-O})$ 958 cm ⁻¹	(122)
[ReO ₂ (dPe) ₂]ReO ₄	Yellow	250(d)	$\nu(\text{Re-O})$ 785 cm ⁻¹	(122)
[ReO ₂ (dPe) ₂]Cl	Yellow	230	$\nu(\text{Re-O})$ 790 cm ⁻¹	(122)
[ReO ₂ (dPe) ₂]Br	Yellow	239	$\nu(\text{Re-O})$ 790 cm ⁻¹	(122)
[ReO ₂ (dPe) ₂]I	Yellow	232(d)	$\nu(\text{Re-O})$ 788 cm ⁻¹	(122)
[ReO ₂ (dPe) ₂]NO ₃	Yellow	245	$\nu(\text{Re-O})$ 787 cm ⁻¹	(122)
[ReO(dPe)Br ₃]	Green	258	—	(122)
[ReO(OH)(dPe) ₂]Cl ₂	Orange	194	—	(122)
[ReO(OH)(dPe) ₂]Br ₂	Orange	189	—	(122)
[ReO(OH)(dPe) ₂]I ₂	Orange	202(d)	—	(122)
[ReO(OH)(dPe) ₂](ReO ₄) ₂	Orange	230	—	(122)
[TcCl ₂ (dPe) ₂]	Yellow-green		$\mu = 2.05$ B.M.	(115)
[TcBr ₂ (dPe) ₂]	Yellow		$\mu = 2.28$ B.M.	(115)
[TcCl ₂ (dPe) ₂]Cl	Red-orange		$\mu = 2.74$ B.M.	(115)
[TcBr ₂ (dPe) ₂]Br	Red-orange		$\mu = 3.04$ B.M.	(115)

^a Vis., visible.

Two arylimido complexes, $[\text{Re}(\text{NPh})(\text{dPe})\text{Cl}_3]$ and $[\text{Re}(\text{NPh})(\text{dee})\text{Cl}_3]$, are formed from $[\text{ReOCl}_3(\text{diphos})]$ and aniline, or by displacing PPh_3 from $[\text{ReCl}_3(\text{NPh})(\text{PPh}_3)_2]$ (63, 95). Violet-blue $[\text{Re}(\text{NMe})(\text{dPe})\text{Cl}_3]$ has recently been obtained (60).

Technetium complexes have only recently been prepared (113, 115). $\text{Tc}(\text{III})$ complexes, $[\text{Tc}(\text{dPe})_2\text{X}_2]\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$), are produced by reaction of TcX_4 with dPe. They are 1:1 electrolytes. The reaction of these with NaBH_4 produces $[\text{Tc}(\text{dPe})_2\text{X}_2]$, which are presumably octahedral (see Table VI).

F. GROUP VIII (Fe, Ru, AND Os)

Brown, diamagnetic $[\text{Fe}(\text{dme})_2]$ was obtained by reduction of *trans*- $[\text{Fe}(\text{dme})_2\text{Cl}_2]$ with sodium naphthalenide. It reacts normally with iodine to produce *trans*- $[\text{Fe}(\text{dme})_2\text{I}_2]$ (82).

Several hydrido complexes are known. Iron powder reacts with PEE in the presence of hydrogen to form $[\text{FeH}_2(\text{PEE})_2]$ in low yield (66). A much higher yield is obtained from the reduction of $[\text{Fe}(\text{PEE})_2\text{Cl}_2]$ with LiAlH_4 (70). The aliphatic diphosphine complexes $[\text{Fe}(\text{diphos})_2\text{Cl}_2]$ (diphos = dme, dee) are only reduced to $[\text{FeHCl}(\text{diphos})_2]$ by LiAlH_4 . Attempted further reduction produced yellow oils (70). *trans*- $[\text{FeHCl}(\text{PEE})_2]$ can be prepared by the reaction between *trans*- $[\text{FeH}_2(\text{PEE})_2]$ and one equivalent of hydrogen chloride in ether. The chlorine in *trans*- $[\text{FeHCl}(\text{dee})_2]$ is labile; reaction with NaI in acetone yielding *trans*- $[\text{FeHI}(\text{dee})_2]$ (70). $[\text{FeHCl}(\text{dee})_2]$, in the presence of sodium tetraphenylborate in acetone solution, forms a number of complexes containing cationic hydrides, *trans*- $[\text{FeH}(\text{L})(\text{dee})_2]\text{BPh}_4$ [$\text{L} = \text{N}_2, \text{CO}, \text{PhCN}, \text{MeCN}, p\text{-MeOC}_6\text{H}_4\text{NC}, \text{Me}_3\text{CNC}, \text{P}(\text{OPh})_3, \text{P}(\text{OMe})_3$] (16). Analogous Ru and Os complexes are known, and structures were assigned on the basis of IR and ^1H NMR studies. In the phosphite complexes the NMR pattern shows a further doublet splitting due to the *trans*-phosphite, in addition to the quintet due to the four equivalent ^{31}P in the diphosphine ligands (16).

An interesting reaction occurs between $\text{Fe}(\text{acac})_3$, dPe, and ethoxy-diethylaluminum (143). $[\text{Fe}(\text{dPe})_2\cdot\text{C}_2\text{H}_4]$ is formed, and on irradiation with UV light the hydride $[\text{HFe}(\text{C}_6\text{H}_4\text{PPhCH}_2\text{CH}_2\text{PPh}_2)(\text{dPe})]$ is produced. Hydrogen at atmospheric pressure produced $[\text{FeH}_2(\text{dPe})_2]$. The complex formed between iron and dPe is the first example in iron chemistry of the transfer of a proton from the ligand to the metal. A similar effect was observed in the Ru-dme complex, but not in the Fe-dme system. The hydrogen in the Fe-H bond in $[\text{HFe}(\text{C}_6\text{H}_4\text{PPhCH}_2\text{CH}_2\text{PPh}_2)(\text{dPe})]$ is labile and returns to the ligand with ease (see Fig. 2).

An investigation of the closely analogous system, $\text{Fe}(\text{acac})_3 + 2\text{dPe} + 3\text{Et}_3\text{Al}$, by Bowden and Johnson has yielded a yellow solid, $[\text{Fe}(\text{acac})_2(\text{dPe})]$, which has a high-spin configuration, and is an intermediate in the reduction process (33). These workers have also isolated a series of complexes, $[\text{Fe}(\text{dPe})_2(\text{olefin})]$ (olefin = propene, pent-1-ene, styrene) and $[\text{Fe}(\text{dPp})_2(\text{C}_2\text{H}_4)]$.

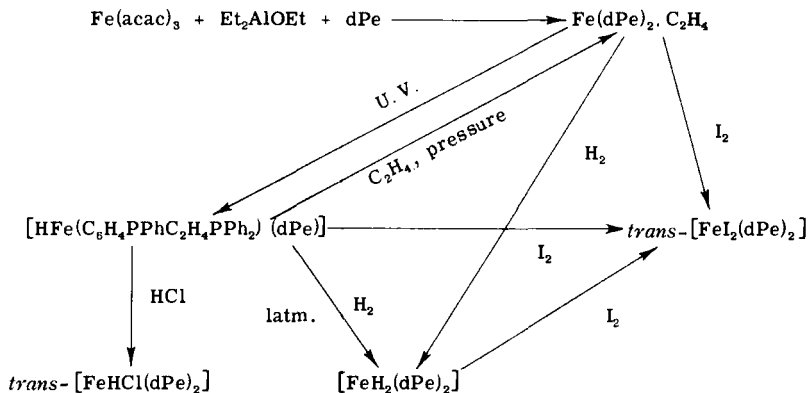
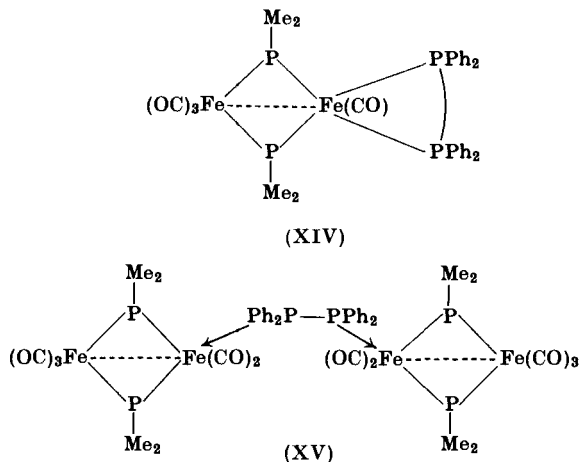
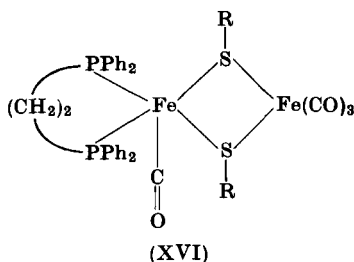


FIG. 2. Reactions of Fe-dPe complexes (143).

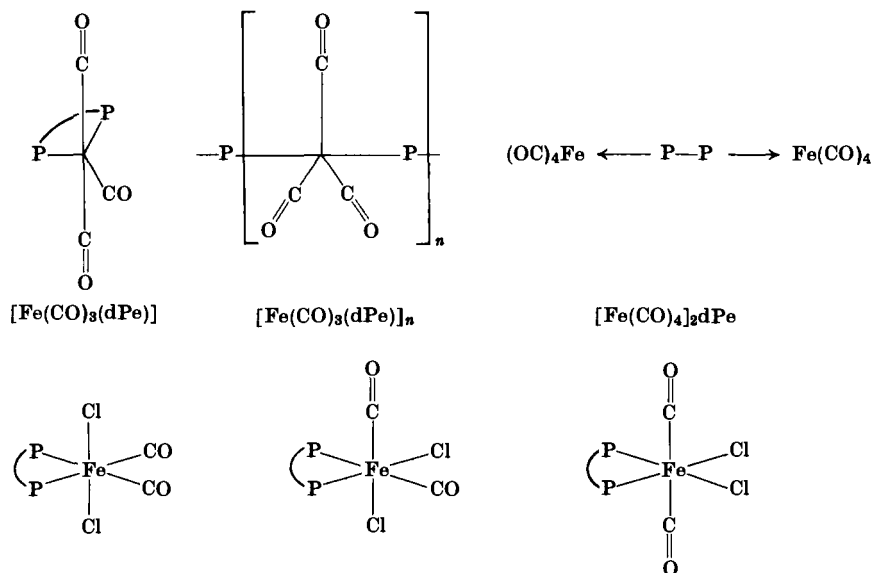
Diphosphines containing a P-P bond react with iron pentacarbonyl to produce phosphido- and diphosphine-bridged complexes [cf. Cr, Mo, and W (79, 146, 147, 157, 178)]. The nature of the product can be controlled to a great extent by varying the conditions. The reaction of dPe with the phosphido-bridged $[\text{Fe}_2(\text{PMe}_2)_2(\text{CO})_6]$ produces (XIV) and (XV) (255). The structure of $[(\text{OC})_4\text{Fe}(\text{MP-P})\text{Fe}(\text{CO})_4]$ has been determined;



there is a staggered configuration about the P-P and Fe-P bonds (187). An interesting complex related to (X) is the S-bridged complex (XVI) (162). $\text{Fe}(\text{CO})_5$ and dPe produce $[\text{Fe}(\text{CO})_4]_2\text{dPe}$ (198). Manuel obtained

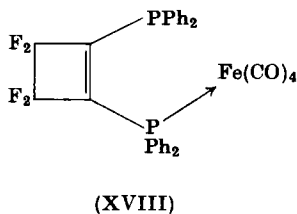
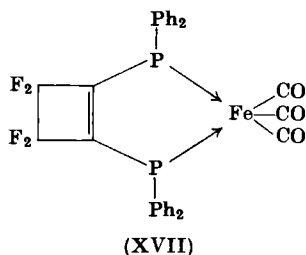


two forms of $[\text{Fe}(\text{CO})_3(\text{dPe})]$ from $\text{Fe}(\text{CO})_5$, $\text{Fe}_3(\text{CO})_{12}$, or [(cyclooctatetraene) $\text{Fe}(\text{CO})_3$] and dPe (208). Zingales *et al.* obtained $[\text{Fe}(\text{CO})_3(\text{dne})]$ (268). Ferrous chloride, CO, and dPe in benzene or THF produce $[\text{Fe}(\text{CO})_2(\text{dPe})\text{Cl}_2]$ (various isomers) (208). Cullen and Harbourn have recently reinvestigated the reactions of the iron carbonyls with dPe. In each case $[\text{Fe}(\text{CO})_3(\text{dPe})]$ and $[\text{Fe}(\text{CO})_4]_2\text{dPe}$ were obtained in varying amounts (101). All these complexes are yellow or orange and are very air-sensitive. On the basis of IR measurements Manuel suggested the following structures:

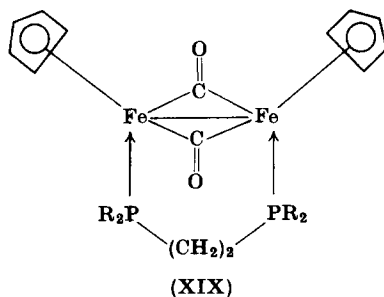


Cullen *et al.* have prepared a number of carbonyl complexes with ffos, f_6fos , and f_8fos (100, 103-105). Only $[(\text{f}_8\text{fos})\text{Fe}(\text{CO})_3]$ is obtained with

$f_8\text{fos}$, and the >C=C< is not involved in the bonding. The complexes $[(f\text{fos})\text{Fe}(\text{CO})_3]$, $[(f\text{fos})\text{Fe}_2(\text{CO})_6]$, $[(f_6\text{fos})\text{Fe}(\text{CO})_3]$, $[(f_6\text{fos})\text{Fe}_2(\text{CO})_6]$, $[(f_6\text{fos})\text{Fe}_2(\text{CO})_7]$, and $[(f\text{fos})\text{Fe}(\text{CO})_4]$ were obtained. On the basis of IR, NMR, mass spectroscopic, and Mössbauer data, the structures (VI), (VII), (XVII), and (XVIII) were suggested. $[\text{Fe}(\text{CO})_3(\text{VPP})]$ has been obtained by irradiation of $\text{Fe}_2(\text{CO})_9$ and VPP in hexane (194).



A large number of other derivatives of iron carbonyls are known which contain $\pi\text{-C}_5\text{H}_5$, etc., as well as diphosphines (I). $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2(\text{diphos})$ (diphos = dPm, dPe, dPp) has a structure containing both carbonyl and diphosphine bridges (XIX) (137). The complex formed by DPPA, $[(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3]_2(\text{DPPA})$, has structure (VIII) (50, 52).



A number of substituted iron nitrosyl compounds are known. $[\text{Fe}(\text{NO})_2(\text{dPe})]$ and $[\text{Fe}(\text{NO})_2(\text{CO})]_2 \cdot \text{dPe}$ are formed from $[\text{Fe}(\text{NO})_2(\text{CO})_2]$ and dPe (210, 213). The complexes $[\text{Fe}(\text{PMe}_2)(\text{NO})_2]_2$, $[\text{Fe}_2(\text{CO})_2(\text{MP-P})(\text{NO})_4]$, and $[\text{Fe}_2(\text{MP-P})_2(\text{NO})_4]$ are formed from MP-P and $[\text{Fe}(\text{CO})_2(\text{NO})_2]$ (149). The reduction of $[\text{Fe}(\text{NO})_2\text{I}]_2$ with sodium amalgam in the presence of dPe produces $[\text{Fe}(\text{NO})_2(\text{dPe})]$ (160). However, the reaction with PP-P is more complex; $[\text{Fe}(\text{NO})_2\text{Br}]_2$ reacted with PP-P in THF to form $[\text{Fe}(\text{NO})_2(\text{PP-P})_2]$, $[\text{Fe}(\text{NO})_2(\text{PP-P})]$, and other products (158).

Compared with the other Group VIII metals, iron does not form a large number of diphosphine complexes. The yellow-green *trans*-[Fe(diphos)₂X₂] (X = Cl, Br, I; diphos = dme, dee, PEE) compounds were obtained by Chatt and Hayter from FeX₂ and the appropriate diphosphine (70). When dPm and dPe were used unstable, not well-defined complexes resulted. The chlorine in *trans*-[Fe(dee)₂Cl₂] is readily replaced on treatment with LiX to form *trans*-[Fe(dee)₂X₂] (X = NCO, NCS, N₃, Br, I); with SnCl₂ the blue *trans*-[Fe(dee)₂(SnCl₃)Cl] was obtained (15). A series of these octahedral [FeX₂(dee)₂] complexes have been studied by Mössbauer spectroscopy (15). Isslieb and Hohlfeld have prepared [Fe(diphos)₂Br₂] (diphos = dCyp, dCyf) (176).

The ferric complexes [Fe(diphos)₂Cl₂][FeCl₄] (diphos = dme, dee, PEE) are stable, dark red or green solids, readily soluble in polar organic solvents, but insoluble in water (70) (see Table VII).

The carbonyl Ru₃(CO)₁₂ reacts with ffos and f₆fos under a variety of conditions to give red [Ru₃(CO)₈(ffos)₂], white [Ru₂(CO)₆(ffos)], white [Ru₂(CO)₆(f₆fos)], and brown [Ru(CO)₃(f₆fos)]. The products were characterized by IR and ¹⁹F NMR (102). [Ru(CO)₂(dPe)]I₂ has been obtained from Ru(CO)₂(*p*-MeC₆H₄NH₂)₂I₂ and dPe, and IR and NMR data indicate that the product has a *cis* structure (156, 189).

Chatt and Hayter prepared an extensive series of octahedral complexes of ruthenium and osmium, [M(diphos)₂XY] (M = Ru, Os; X, Y = halogen; diphos = dme, dee, dPe, PEE, dPm) (68, 70, 72). The *trans*-[M(diphos)₂Cl₂] complexes are obtained by refluxing a slight excess of the diphosphine in aqueous ethanol with RuCl₃ or (NH₄)₂OsCl₆. The *cis* isomers are obtained on heating [M₂Cl₃(PR₃)₆]Cl with the diphosphine in the absence of a solvent. In the case of dPe a good yield of *trans*-[Ru(dPe)₂Cl₂] was obtained, probably due to steric interaction between the phenyl groups in the *cis* isomer. The corresponding *cis*- or *trans*-[M(diphos)₂X₂] are obtained from the chloro-complex and M¹X (X = Br, I, SCN, CN, OAc); isomerization does not occur. Only the *cis*-[Os(diphos)₂X₂] are appreciably air-sensitive. *cis*- and *trans*-[Ru(dee)₂Cl₂]ClO₄ form on treating *cis*- or *trans*-[RuCl₂(diphos)₂] with HClO₄ in ethanol (68). The formation of various isomers from the reaction of 1,2-bis(methylphenylphosphino)ethane with RuCl₃ has been studied by Bercz *et al.* (24a).

trans-Hydrido complexes, [MHX(diphos)₂] (M = Ru, Os; X = Cl, Br, I, SCN, CN, NO₂), were obtained by reduction of the *cis*-[MX₂(diphos)₂] with LiAlH₄ (X = Cl, Br, I) or by metathesis from *trans*-[MHCl(diphos)₂] (X = SCN, CN, NO₂). The *trans*-[MX₂(diphos)₂] complexes are not reduced by LiAlH₄. The structures of *trans*-[MHX(diphos)₂] were established by ¹H NMR and dipole moment studies.

TABLE VII
DIPHOSPHINE COMPLEXES OF IRON

Compound	Color	M.p.(°C)	Properties	Ref.
[Fe(dme) ₂]	Brown	205	$\mu = 0$	(82)
<i>trans</i> -[FeH ₂ (PEE) ₂]	Orange	248	IR, NMR, M, $\mu = 1.80$	(15, 66, 70)
<i>trans</i> -[FeH ₂ (dPe) ₂]C ₆ H ₆	Yellow	219	IR	(143)
[HFe(C ₆ H ₄ PPhC ₂ H ₄ PPh ₂)(dPe)]	Orange-brown	179	IR, NMR	(143)
<i>trans</i> -[FeHCl(dme) ₂]	Red	180(d)	IR	(70)
<i>trans</i> -[FeHCl(dee) ₂]	Red	155	IR, NMR, M, D.M. = 4.23	(15, 70)
<i>trans</i> -[FeHCl(PEE) ₂]	Red	231	IR, NMR	(70)
<i>trans</i> -[FeHI(dee) ₂]	Red-brown	173(d)	IR, NMR, M	(15, 70)
<i>trans</i> -[FeH(N ₂)(dee) ₂]BPh ₄	Yellow-red	—	IR, NMR, M	(16)
<i>trans</i> -[FeH(CO)(dee) ₂]BPh ₄	Yellow-red	—	IR, NMR, M	(16)
{Fe(CO) ₄ } ₂ (MP-P)	Orange-yellow	147(d)	IR, NMR	(79, 146)
[Fe(CO) ₃ (dPe)]	Yellow	143	IR, mass spec.	(101, 208)
[Fe ₂ (CO) ₈ (dPe)]	Yellow	186	IR, mass spec.	(101)
[Fe(CO) ₃ (dPe)] _n	Red-brown	203(d)	IR	(208)
{Fe(CO) ₄ } ₂ (dPe)	Yellow	171	IR	(198, 208)
[Fe(CO) ₃ (VPP)]	Yellow-orange	139	IR, NMR	(194)
[Fe ₂ (CO) ₆ (ffos)]	Orange	220(d)	IR, NMR, M, mass spec.	(103-105)
[Fe ₂ (CO) ₆ (f ₆ fos)]	Orange	226		
[Fe ₂ (CO) ₇ (f ₆ fos)]	—	—		
[Fe(CO) ₃ (ffos)]	Brown	179		
[Fe(CO) ₄ (ffos)]	Yellow	130		
[Fe ₂ (CO) ₃ (f ₆ fos)]	Brown	211	—	(100)
[Fe(CO) ₃ f ₆ fos]	—	—		
[Fe(NO) ₂ (dPe)]	Red-brown	148(d)	IR	(210, 213)
{Fe(NO) ₂ (CO)} ₂ (dPe)	Deep red	140	IR	(210)

^a M is Mössbauer.

(continued)

TABLE VII—*continued*

Compound	Color	M.p.(°C)	Properties	Ref.
<i>trans</i> -[FeI ₂ (dPe) ₂]	Yellow-green	376	—	(82)
<i>trans</i> -[FeCl ₂ (dee) ₂]	Green	170	M, D.M. = 1.3	(15, 70)
<i>trans</i> -[FeCl ₂ (dme) ₂]	Green	258	M	(15, 70)
<i>trans</i> -[FeCl ₂ (PEE) ₂]	Green	192	M	(15, 70)
<i>trans</i> -[FeBr ₂ (dee) ₂]	Yellow-green	—	M	(15)
<i>trans</i> -[FeCl(SnCl ₃)(dee) ₂]	Blue	—	M	(15)
<i>trans</i> -[FeBr ₂ (PEE) ₂]	Yellow	—	M	(15)
<i>trans</i> -[Fe(NCO) ₂ (dee) ₂]	Purple	—	M	(15)
<i>trans</i> -[Fe(NCS) ₂ (dee) ₂]	—	—	M	(15)
<i>trans</i> -[Fe(N ₃) ₂ (dee) ₂]	—	—	M	(15)
<i>trans</i> -[FeI ₂ (dee) ₂]	Orange-yellow	—	M	(15)
<i>trans</i> -[FeI ₂ (dPe) ₂]	Yellow	143	M	(143)
<i>trans</i> -[FeCl ₂ (dee) ₂][FeCl ₄]	Dark red	149	—	(70)
<i>trans</i> -[FeCl ₂ (dme) ₂][FeCl ₄]	Purple	236	—	(70)
<i>trans</i> -[FeCl ₂ (PEE) ₂][FeCl ₄]	Dark green	150	—	(70)

The dPm and dPe complexes tend to crystallize as solvates from benzene. In air the hydridohalides tend to decompose slowly in the order [*o*-C₆H₄-(AsMe₂)₂] > dPe > dee > PEE = dPm. Excess of LiAlH₄ reduces the *trans*-[MHX(diphos)₂] complex to the dihydrides, *trans*-[MH₂(diphos)₂] (72). *cis*-[RuH₂(dme)₂] was obtained from *trans*-[RuHBr(dme)₂] and sodium naphthalenide. A series of σ -bonded alkyl and aryl derivatives, *cis*-[MR₂(diphos)₂] and *cis*- and *trans*-[MRX(diphos)₂] (M = Ru, Os) were synthesized from alkyl- or aryllithium reagents or trialkylaluminums (72). These compounds vary in stability from [MMe₂(dme)₂] and [M(Aryl)X(dme)₂], which decompose slowly in air and hydrolyze immediately in water, to the [M(alkyl)X(dPm)₂] and [M(alkyl)X(dPe)₂], which have high resistance to oxidation and hydrolysis. The [MRX-(diphos)₂] compounds are reduced to [MRH(diphos)₂] by LiAlH₄. The metal-carbon bond is cleaved by HCl or halogens, usually with retention of configuration. *trans*-[MHCl(dee)₂] reacts with NaBPh₄ and various ligands in acetone (or with N₂ in CHCl₃) to form colorless [MH-(L)(dee)₂]BPh₄, analogous to the iron complexes (16) (see Table VIII).

Chatt and Davidson observed (58) that, unlike iron, the ruthenium and osmium complexes, [M(dme)₂Cl₂], reduced with sodium naphthalenide, retained naphthalene in the product. *cis*- or *trans*-[Ru(dme)₂Cl₂] reacted with sodium arenes (arene = naphthalene, anthracene, phenanthrene, or benzene) in THF to produce [Ru(arene)(dme)₂]. Physical measurements indicate that they are *cis*-[RuH(aryl)(dme)₂], but chemically they behave as [Ru(arene)(dme)₂]. The naphthalene compound has $\nu(\text{Ru-H})$ at 1820 cm⁻¹, and $\tau(\text{Ru-H})$ at 17.6 and 19.8. On heating *in vacuo* naphthalene is lost, and with iodine no HI was detected—both of which are consistent with [Ru(naphthalene)(dme)₂]. The fact that one of the hydrogens on the naphthalene becomes attached to the metal was confirmed by the preparation of deuterium analogs. Clearly the system is tautomeric. The X-ray structure shows that in the solid state

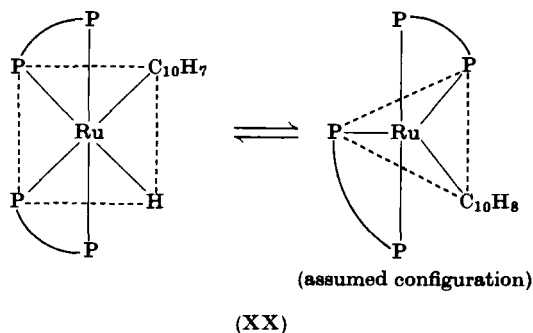


TABLE VIII
RUTHENIUM AND OSMIUM COMPLEXES (68, 69, 72)

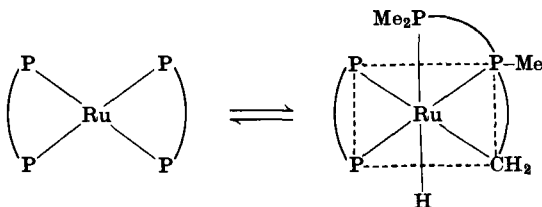
Compound	Color	M.p.(°C)	Properties
<i>trans</i> -[RuCl ₂ (dee) ₂]	Yellow	241 ^d	D.M. = 0.85
<i>trans</i> -[RuCl ₂ (dme) ₂]	Yellow	294 ^d	D.M. = 0.75
<i>trans</i> -[RuCl ₂ (dPe) ₂]	Pale Yellow	284(d)	—
<i>trans</i> -[RuCl ₂ (dPm) ₂]	Orange	277(d)	—
<i>trans</i> -[RuCl ₂ (PEE) ₂]	Yellow	241(d)	D.M. = 0.7
<i>trans</i> -[RuI ₂ (dee) ₂]	Orange-brown	269(d) ^d	—
<i>trans</i> -[RuBr ₂ (dme) ₂]	Orange	288(d) ^d	—
<i>trans</i> -[RuI ₂ (dme) ₂]	Red	303(d) ^d	—
<i>trans</i> -[RuBr ₂ (dee) ₂]	Pale orange	265 ^d	—
<i>trans</i> -[Ru(CN) ₂ (dme) ₂]·H ₂ O	Colorless	>350	—
<i>trans</i> -[Ru(OAc) ₂ (dme) ₂]·H ₂ O	Colorless	247 ^d	—
<i>cis</i> -[RuCl ₂ (dee) ₂]	Lemon yellow	214	D.M. = 9.75
<i>cis</i> -[RuCl ₂ (dme) ₂]	Yellow	263 ^d	—
<i>cis</i> -[RuCl ₂ (dPm) ₂]	Canary yellow	273(d)	D.M. = 9.5
<i>cis</i> -[RuCl ₂ (PEE) ₂]	Yellow	233(d)	—
<i>cis</i> -[RuBr ₂ (dee) ₂]	Yellow	191(d)	—
<i>cis</i> -[RuI ₂ (dee) ₂]	Orange-brown	263 ^d	D.M. = 10.35
<i>cis</i> -[Ru(SCN) ₂ (dee) ₂]	Colorless	325(d) ^d	—
<i>cis</i> -[RuBr ₂ (dme) ₂]	Yellow	242(d)	—
<i>cis</i> -[RuI ₂ (dme) ₂]	Golden yellow	290(d)	—
<i>cis</i> -[Ru(SCN) ₂ (dme) ₂]	Colorless	328(d)	—
<i>cis</i> -[RuI ₂ (PEE) ₂]	Yellow	247(d)	—
<i>trans</i> -[RuCl ₂ (dee) ₂]ClO ₄	Dark green	173(d)	—
<i>cis</i> -[RuCl ₂ (dee) ₂]ClO ₄	Dark green	168(d)	—
<i>trans</i> -[RuHCl(dee) ₂]	Colorless	175	IR, NMR, D.M. = 4.91
<i>trans</i> -[RuHBr(dee) ₂]	Yellow	189(d)	IR, NMR, D.M. = 5.65
<i>trans</i> -[RuHI(dee) ₂]	Yellow	220(d)	IR, NMR, D.M. = 5.8
<i>trans</i> -[RuH(SCN)(dee) ₂]	Colorless	247(d)	IR
<i>trans</i> -[RuH(CN)(dee) ₂]	Colorless	—	IR
<i>trans</i> -[RuH ₂ (dee) ₂]	Colorless	149	IR, D.M. = 2.1
<i>trans</i> -[RuHCl(dme) ₂]	Colorless	219	IR, D.M. = 4.8
<i>trans</i> -[RuHBr(dme) ₂]	Yellow	217(d)	IR
<i>trans</i> -[RuHI(dme) ₂]	Yellow	322(d)	IR
<i>trans</i> -[RuH(SCN)(dme) ₂]	Colorless	240(d)	IR
<i>trans</i> -[RuH(CN)(dme) ₂]	Yellow	230(d)	IR
<i>trans</i> -[RuH(NO ₂)(dme) ₂]	Yellow	240(d)	IR
<i>trans</i> -[RuHCl(PEE) ₂]	Yellow	253(d)	IR, D.M. = 4.45
<i>trans</i> -[RuHI(PEE) ₂]	Brown	280(d)	IR
<i>trans</i> -[RuH ₂ (PEE) ₂]	Yellow	277(d)	IR, D.M. = 1.2
<i>trans</i> -[RuHCl(dPm) ₂]·½C ₆ H ₆	Yellow	284	IR, D.M. = 4.95
<i>cis</i> -[RuMe ₂ (dme) ₂]	Colorless	285	D.M. = 4.35
<i>trans</i> -[RuMe ₂ (dme) ₂]	Yellow	315	D.M. = 3.7
<i>cis</i> -[RuMe ₂ (dPe) ₂]	Yellow	253	D.M. = 3.45
<i>cis</i> -[RuIme(dPe) ₂]·½C ₆ H ₆	Orange	329	D.M. = 7.8

TABLE VIII—*continued*

Compound	Color	M.p.(°C)	Properties
<i>trans</i> -[RuClEt(dPe) ₂]	Lemon yellow	230	D.M. = 4.7
[RuClPr(dPe) ₂]	Yellow	333	D.M. = 4.85
[RuClPh(dme) ₂]	Colorless	295	D.M. = 1.75
[RuPh ₂ (dPm) ₂]	Yellow	177	—
<i>cis</i> -[RuHMe(dPe) ₂]	Colorless	249	IR, NMR, D.M. = 3.25
<i>trans</i> -[RuHMe(dPe) ₂]	Colorless	292	IR, NMR, D.M. = 2.95
<i>cis</i> -[RuHEt(dPe) ₂]	Colorless	291	IR, D.M. = 3.25
<i>cis</i> -[RuHPr(dPe) ₂]	Colorless	279	IR, D.M. = 3.15
<i>trans</i> -[RuHPh(dme) ₂]	Colorless	160	IR, D.M. = 3.90
[RuH(p-tolyl)(dme) ₂]	Colorless	148	IR
<i>trans</i> -[RuH(N ₂)(dee) ₂]BPh ₄ ^a	Colorless	—	NMR
[Ru(CO) ₂ (dPe)Br ₂] ^b	Yellow	>170	—
[Ru(CO) ₂ (dPe)I ₂] ^b	Orange	150	IR, NMR
<i>trans</i> -[OsCl ₂ (dee) ₂]	Yellow	248	—
<i>trans</i> -[OsCl ₂ (dme) ₂]	Yellow	299(d) ^d	—
<i>trans</i> -[OsCl ₂ (dPe) ₂]	Orange	294(d)	—
<i>trans</i> -[OsCl ₂ (dPm) ₂]	Gold-yellow	>350	—
<i>cis</i> -[OsCl ₂ (dee) ₂]	Colorless	210	D.M. = 9.3
<i>cis</i> -[OsCl ₂ (dme) ₂]	Colorless	300(d)	—
<i>cis</i> -[OsCl ₂ (dPe) ₂]	Pale yellow	290(d)	D.M. = 8.3
<i>cis</i> -[OsCl ₂ (PEE) ₂]	Pale yellow	265(d)	—
<i>trans</i> -[OsI ₂ (dee) ₂]	Orange	273 ^d	—
<i>cis</i> -[OsI ₂ (dee) ₂]	Pale yellow	223(d)	—
OsCl ₃ (PMe ₂ Ph)(dPe) ^c	Orange	140(d)	—
<i>trans</i> -[OsHCl(dee) ₂]	Colorless	171	IR, NMR, D.M. = 4.6
<i>trans</i> -[OsHI(dee) ₂]	Yellow	227	IR, NMR
<i>trans</i> -[OsH(SCN)(dee) ₂]	Colorless	200(d)	IR
<i>trans</i> -[OsH ₂ (dee) ₂]	Colorless	152	IR
<i>trans</i> -[OsHCl(dme) ₂]	Colorless	198(d)	IR D.M. = 5.05
<i>trans</i> -[OsHCl(dPe) ₂]·C ₆ H ₆	Yellow	316(d)	IR
<i>trans</i> -[OsHCl(dPm) ₂]·C ₆ H ₆	Yellow	296(d)	IR, D.M. = 3.85
<i>trans</i> -[OsH ₂ (PEE) ₂]	Lemon	295	IR
[OsMe ₂ (dPm) ₂]	Pale yellow	254	—
<i>cis</i> -[OsClMe(dPm) ₂]	Orange	196	D.M. = 6.6
<i>trans</i> -[OsClMe(dPm) ₂]·½C ₆ H ₆	Pale yellow	286	D.M. = 5.5
<i>trans</i> -[OsClEt(dPm) ₂]·½C ₆ H ₆	Gold-yellow	296	D.M. = 4.95
<i>cis</i> -[OsPh ₂ (dPm) ₂]·½C ₆ H ₆	Pale yellow	237	D.M. = 6.1
<i>cis</i> -[OsClMe(dPe) ₂]·½C ₆ H ₆	Pale yellow	295	D.M. = 6.6
[OsClEt(dPe) ₂]	Pale yellow	312	—
[OsHMe(dPe) ₂]·C ₆ H ₆	Pale yellow	150	IR
[OsHEt(dPe) ₂]·½C ₆ H ₆	Pale yellow	313	IR
<i>trans</i> -[OsH(N ₂)(dPe) ₂]BPh ₄ ^a	Colorless	—	NMR

^a Bancroft *et al.* (16).^b Hieber and John (156) and John (189).^c Johnson *et al.* (190).^d Sublimed before melting.

it exists as *cis*-[RuH(C₁₀H₇)(dme)₂]. The C₁₀H₇(dme)₂ forms a square-pyramid, and although location of the proton was difficult, it is thought to be *trans* to the phosphorus with Ru–H = 1.7 Å. [Ru(dme)₂], formed on heating [RuH(C₁₀H₇)(dme)₂] *in vacuo* also exhibits tautomerism. It has an infrared absorption at 1791 cm⁻¹ [ν (Ru–H)], but was not sufficiently soluble for NMR studies. Chemically, it behaves as [Ru(dme)₂] (58). The tautomerism is



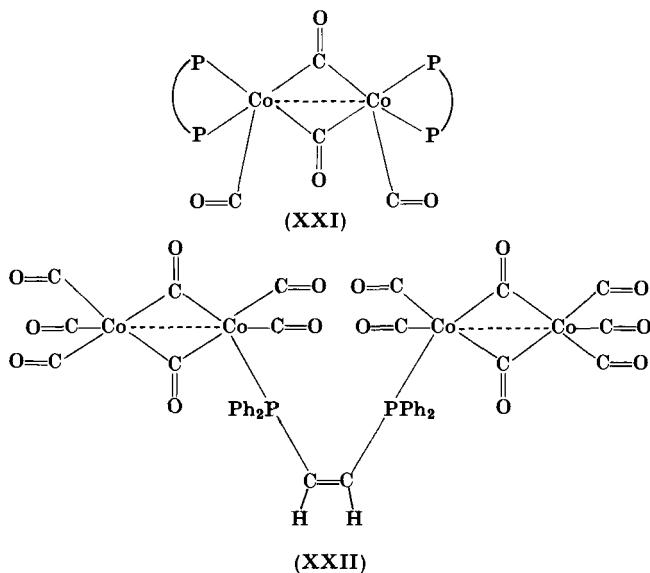
[Fe(dme)₂] does not exhibit tautomerism (82), but [Fe(dPe)₂] does (143).

G. GROUP VIII (Co, Rh, AND Ir)

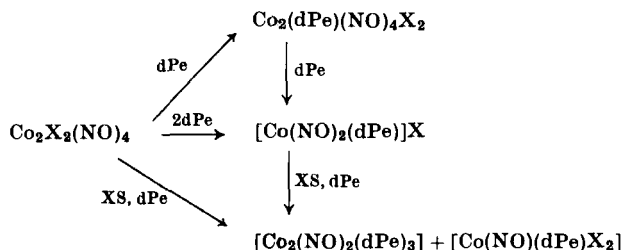
The compound [Co(dme)₂] was reported (82) as orange needles resulting from the reduction of CoCl₂ with sodium naphthalenide in the presence of dme. There were no IR bands attributable to ν (Co–H). Finely powdered cobalt reacts with PEE on heating in nitrogen or hydrogen to give [Co(PEE)₂] (66). Heating [Co(dPe)₂Br₂] with KOH in aqueous ethanol under nitrogen produced [Co(dPe)₂] (234). By reduction of [CoBr₂(dPe)₂] with NaBH₄ in aqueous ethanol, Chatt *et al.* obtained red crystals which they formulated as [Co(dPe)₂] (66); no ν (Co–H) was present in the IR spectrum. Zingales *et al.* examined the reaction using LiAlH₄ in place of NaBH₄, and obtained a compound of almost identical properties, but which contained a band at 1884 cm⁻¹ which was assigned to ν (Co–H) (267). An investigation of the reaction by Sacco and Ugo using NaBH₄ led to a product characterized as [CoH(dPe)₂]. This compound was diamagnetic if great care was taken in the preparation (236). In HClO₄ solution [CoH₂(dPe)₂]ClO₄ was formed [ν (Co–H) = 1940, 1985 cm⁻¹], and this reaction was reversed by alkalis. Reduction of Co(acac)₃ with Al(OEt)Et₂ in the presence of dPe also produced [CoH(dPe)₂] (143). Both the Co(0) compounds and the hydrides are readily decomposed by air.

A number of carbonyls and nitrosyls are known. Co₂(CO)₈ reacts with dPe to produce yellow [Co₂(CO)₄(dPe)₃][Co(CO)₄]₂. The cation has also been isolated as the iodide, perchlorate, and tetraphenylborate (232). Diamagnetic [Co₂(CO)₄(dPe)₂] was obtained from [(norbornadiene)₂Co₂(CO)₄] and dPe (19). The solid has structure (XXI). It adds

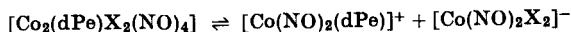
iodine to produce $[\text{Co}_2(\text{CO})_4(\text{dPe})\text{I}]$. The anion $[\text{Co}(\text{CO})_2(\text{dPe})]^-$ is also known (19). VPP reacts with $\text{Co}_2(\text{CO})_8$ in benzene to produce the red-brown diphosphine-bridged complex (XXII) (49). As with the other metal carbonyls there have been many studies on organometallic derivatives, e.g., $[\text{C}_5\text{H}_5\text{Co}(\text{dme})\text{I}]\text{PF}_6$ (195). A ligand-bridged complex, $[(\text{OC})_3\text{Co}(\text{PP-P})\text{Co}(\text{CO})_3]$, is formed from PP-P (242).



$[\text{Co}(\text{NO})(\text{CO})_3]$ and dPe form two orange solids, $[\text{Co}(\text{NO})(\text{CO})_2]_2\text{dPe}$ and $[\text{Co}(\text{NO})(\text{CO})(\text{dPe})]$ (210). The orange $[\text{Co}(\text{NO})(\text{CO})(\text{dPm})]$ and red $[\text{Co}(\text{NO})(\text{CO})(\text{dPp})]$ were obtained similarly (150). PP-P reacts with $[\text{Co}(\text{NO})_2\text{X}]_2$ (X = halogen) to produce $[\text{X}(\text{NO})_2\text{Co}(\text{PP-P})\text{Co}(\text{NO})_2\text{X}]$ and phosphido-bridged derivatives (158). Nitrosyl complexes containing dPe have also been prepared (25, 160). Bianco *et al.* reported (25) the following reactions:



$[\text{Co}_2(\text{NO})_2(\text{dPe})_3]$ has also been obtained by reduction of $[\text{Co}_2(\text{NO})_4(\text{dPe})\text{Cl}_2]$ with Zn/EtOH in the presence of dPe (160). $\text{Co}_2\text{X}_2(\text{NO})_4(\text{dPe})$ are believed to exist in two forms due to the equilibrium (25).



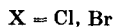
Four- and five-coordinate $\text{Co}(\text{I})$ complexes are known (235). On heating $[\text{Co}(\text{dPe})_2]$ with $\text{Co}(\text{dPe})_2\text{Br}_2$ in a 1:1 ratio under nitrogen, brown $[\text{Co}(\text{dPe})_2\text{Br}]$ is formed. By metathesis with NaClO_4 or NaBPh_4 in ethanol, green four-coordinate $[\text{Co}(\text{dPe})_2]\text{X}$ ($\text{X} = \text{ClO}_4$, BPh_4) can be prepared. $\text{Co}(\text{I})$ complexes add hydrogen to give $[\text{CoHX}(\text{dPe})_2]\text{X}$ and $[\text{CoH}_2(\text{dPe})_2]\text{X}$. $[\text{Co}(\text{CO})(\text{dPe})_2]\text{X}$ ($\text{X} = \text{Cl}$, Br , I) was also obtained (235).

The diphosphine complexes of $\text{Co}(\text{II})$ have recently been the subject of a great deal of interest. $\text{Co}(\text{II})$ combines with diphosphines in the ratios 1:1, 1:2, and, occasionally, 1:1.5. The first investigation was by Wymore and Bailar on *dee* complexes, published in 1960 (264). Complexes having empirical formulas $\text{Co}(\text{dee})_2\text{Br}_2$ (green) and $\text{Co}(\text{dee})_2\text{I}_2$ (brown) were isolated. The iodide is probably six-coordinate in the solid state, but behaves as a 1:1 electrolyte in nitrobenzene, suggesting penta-coordination in solution, $[\text{Co}(\text{dee})_2\text{I}]\text{I}$. On heating over P_2O_5 it turns green, with loss of some *dee*, and its physical properties then become more like the bromide. The bromide was formulated as $[\text{Co}(\text{dee})_2][\text{CoBr}_4]$ containing planar $[\text{Co}(\text{dee})_2]^{2+}$.

The complexes with dCyp , dCyb , and dCyf are tetrahedral $[\text{CoX}_2(\text{diphos})]$ (176), with magnetic moments in the range 3.5–4.7 B.M. Isslieb and Schwager studied the CyP-P and PP-P complexes (181, 182). The latter gives rise to $\text{Co}(\text{PP-P})_2\text{X}_2$, in which the bromide has $\mu_{\text{eff}} = 2.28$ B.M. and a dipole moment of 6.66 D; it was assigned a square planar structure in which the ligands are monodentate. The iodide has $\mu_{\text{eff}} = 4.16$ B.M. and appears to be tetrahedral. CoCl_2 did not yield a crystalline product. CyP-P forms complexes of type $[\text{Co}(\text{CyP-P})\text{X}_2]$ ($\text{X} = \text{Cl}$, Br , I) (182); all are monomeric and nonelectrolytes. The blue chloride, $\mu_{\text{eff}} = 4.48$ B.M., is tetrahedral; the very dark brown iodide, $\mu_{\text{eff}} = 2.25$ B.M., has a dipole moment of 8.7 D, consistent with a square-planar structure. Two isomers of the bromide exist, a green square-planar, and a blue tetrahedral form. Unlike PP-P , CyP-P behaves as a chelating ligand towards cobalt(II).

The dPe complexes of cobalt(II) have been most studied; 1:1 complexes, $[\text{Co}(\text{dPe})\text{X}_2]$, are difficult to obtain. They crystallize on long standing from solutions of $[\text{Co}(\text{dPe})_2\text{X}_2]$ in CH_2Cl_2 , CHCl_3 , or acetone. Pseudotetrahedral structures are indicated by the magnetic moments and electronic spectra (167). dPp , dPb , and dPf form only 1:1 complexes,

Complexes of type $\text{Co}(\text{dPe})_2\text{X}_2$ are well known, and the structures depend on the nature of X. When $\text{X} = \text{ClO}_4$, the cobalt is four-coordinate and square-planar, $[\text{Co}(\text{dPe})_2](\text{ClO}_4)_2$, and related $[\text{Co}(\text{dPe})_2][\text{CoX}_4]$ complexes are also known. When X is an anion capable of coordinating to the cobalt, pentacoordinate $[\text{Co}(\text{dPe})_2\text{X}]^+$ complexes are formed. Sacco and Gorieri assigned five-coordinate structures, on the basis of conductivity and magnetic measurements, to the complexes $[\text{Co}(\text{dPe})_2\text{X}]^+$, $[\text{Co}(\text{dPe})_2\text{Cl}]_2[\text{CoCl}_4]$, and $[\text{Co}(\text{dPe})_2(\text{NCS})]_2[\text{Co}(\text{NCS})_4]$ (233). Horrocks *et al.* obtained electronic and ESR spectra which were consistent with a five-coordinate structure (167). It was also noted that the electronic spectrum of $[\text{Co}(\text{dPe})_2\text{I}]\text{BPh}_4$ differed slightly from that of $\text{Co}(\text{dPe})_2\text{I}_2$, and it was suggested that there were two coordinated iodides in the latter complex. Dyer *et al.* (111) have discovered the interesting system



The red isomer becomes green in solution and has the same electronic spectrum as the green isomer in solution, which is indicative of the same pentacoordinate structure in solution. In the solid state the electronic spectral bands differ in relative intensity, but not in energy, and again pentacoordination is observed. It is likely that the red and green isomers are either square-pyramidal and trigonal-bipyramidal isomers, or that some subtle chelate carbon-chain conformation makes the isomers crystallize in the red and green forms. The blue isomer, $[\text{CoX}_4][\text{Sn}(\text{dPe})_2]$, is a rare example of $[\text{SnP}_4]$ coordination. Interestingly, Dyer and co-workers could only obtain the green $[\text{CoL}_2\text{X}]^+$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$) and $[\text{CoL}_2(\text{NCS})_2][\text{Co}(\text{NCS})_4]$ when $\text{L} = \text{VPP}$ (*III*). Ramaswamy *et al.* have obtained the square planar $[\text{Co}(\text{VPP})_2]\text{Y}_2$ ($\text{Y} = \text{ClO}_4, \text{NO}_3$) (*225*) (see Table IX).

TABLE IX
DIPHOSPHINE COMPLEXES OF COBALT

Compound	Color	M.p.(°C)	Properties	Ref.
[Co(dme) ₂]	Pale orange	101	—	(82)
[Co(dPe) ₂]	Red	228	D.M. = 1.2	(234)
[Co(PEE) ₂]	Deep purple	—	—	(66)
[CoH(dPe) ₂]	Red	265	$\mu = 0$	(66, 143) (236, 267)
[Co ₂ (CO) ₄ (dPe) ₂]	Light brown	—	$\mu = 0$	(49)
[{Co ₂ (CO) ₇ } ₂ (VPP)]	Red-brown	221	—	(247)
[{Co(CO) ₃ } ₂ (PP-P)]	—	140	—	(242)
[{Co(CO) ₂ (NO)} ₂ (dPe)]	Orange	146	—	(210)
[Co(CO)(NO)(dPe)]	Orange	166	—	(210)
Co ₂ Cl ₂ (NO) ₄ (dPe)	Brown	188(d)	IR	(25, 160)
Co ₂ I ₂ (NO) ₄ (dPe)	Brown	169(d)	IR	(25)
[Co(NO) ₂ (dPe)]Cl	Red	117(d)	IR	(25)
[Co(NO) ₂ (dPe)]BPh ₄	Red	188(d)	IR	(25)
[Co ₂ (NO) ₂ (dPe) ₃]	Brown-red	314(d)	IR	(25)
[Co(dPe) ₂ Cl]Cl	Green	—	$\mu = 2.212$, ESR, vis.	(166, 233)
[Co(dPe) ₂ Br]Br	Green	118	$\mu = 1.86$, ESR, vis.	(166, 233)
[Co(dPe) ₂ I]I	Dark brown	148	$\mu = 1.92$, ESR, vis.	(166, 233)
[Co(dPe) ₂][CoI ₄]	Light green	—	—	(166, 233)
[Co(dPe)Cl ₂]	Blue	—	$\mu = 4.41$, ESR, vis.	(166, 233)
[Co(dPe)Br ₂]	Blue	—	$\mu = 4.66$, ESR, vis.	(166, 233)
[Co(dPe)I ₂]	Blue	—	$\mu = 4.63$	(166, 233)
[Co(dPe) ₂ I]BPh ₄	Red	192	$\mu = 2.31$	(233)
[Co(dPe) ₂](ClO ₄) ₂	Yellow	237	$\mu = 2.50$	(233)
[Co(dPe) ₂ (NO ₃)]NO ₃	Red	139	$\mu = 2.30$	(233)
[Co(dPe) ₂ (NO ₃)]BPh ₄	Orange	—	—	(233)

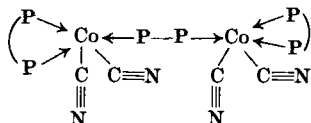
[Co(dPe) ₂ I]NO ₃	Maroon	133	—	(233)
[Co(dPe) ₂ Br]ClO ₄	Green	190	$\mu = 2.22$	(233)
[Co(dPe) ₂ (NCS)]NCS	Maroon	152	$\mu = 2.30$	(233)
[Co(dPe) ₂ (NCS)] ₂ [Co(NCS) ₄]	Green	154	—	(233)
[Co(dPe) ₂][CoCl ₄]	Green	173	$\mu = 3.35/\text{Co atom}$	(233)
[Co(dPe) ₂ Cl] ₂ [CoCl ₄]	Green	179	—	(233)
[Co(dPe) ₂ Cl]ClO ₄	Green	—	$\mu = 1.97, \text{vis.}$	(111)
[Co(dPe) ₂ Cl]SnCl ₃	Green	—	$\mu = 1.97, \text{vis.}$	(111)
[Co(dPe) ₂ Cl]SnCl ₃	Red	—	$\mu = 2.36, \text{vis.}$	(111)
[Co(dPe) ₂ Br]SnBr ₃	Green	—	$\mu = 1.96, \text{vis.}$	(111)
[Co(dPe) ₂ Br]SnBr ₃	Dark red	—	$\mu = 2.37, \text{vis.}$	(111)
Co(dee) ₂ I ₂	Brown	—	$\mu = 2.2$	(264)
Co(dee) ₂ I ₂	Green	—	$\mu = 3.9$	(264)
[Co(dee) ₂][CoBr ₄]	Green	—	$\mu = 3.7$	(264)
[Co(VPP) ₂ Cl]BPh ₄	Green	—	$\mu = 1.91, \text{vis.}$	(111)
[Co(VPP) ₂ Cl]SnCl ₃	Green	—	$\mu = 1.94, \text{vis.}$	(111)
[Co(VPP) ₂ Br]BPh ₄	Green	—	$\mu = 1.90, \text{vis.}$	(111)
[Co(VPP) ₂ I]BPh ₄	Green-black	—	$\mu = 1.98, \text{vis.}$	(111)
[Co(VPP) ₂ (NCS)]BPh ₄	Green	—	$\mu = 1.97, \text{vis, IR}$	(111)
[Co(VPP) ₂ (NCS)] ₂ [Co(NCS) ₄]	Green	—	$\mu = 2.33/\text{Co atom}$	(111)
[Co(POPO)Cl ₂]	Blue	—	$\mu = 4.5$	(237)
[Co(POPO)Br ₂]	Blue	—	$\mu = 4.55$	(237)
[Co(POPO)I ₂]	Green	—	$\mu = 4.61$	(237)
[Co(POPO)(NCS) ₂]	Green	—	$\mu = 4.41$	(237)
[Co(dPp)Cl ₂]	Blue	—	$\mu = 4.43, \text{vis.}$	(167)
[Co(dPp)Br ₂]	Blue-green	—	$\mu = 4.47, \text{vis.}$	(167)
[Co(dPp)I ₂]	Brown	—	$\mu = 4.56, \text{vis.}$	(167)
[Co(dPp) _{1.5} (CN) ₂]	Pink	—	$\mu = 2.30$	(228)
[Co(dPp) _{1.5} (CNS) ₂]	Brown	—	$\mu = 2.7$	(228)
[Co(dPb)Br ₂]	Blue	—	$\mu = 4.5$	(237, 238)
[Co(dPb)(NCS) ₂]	Green	160	$\mu = 4.56$	(237)
[Co(dPb) _{1.5} (CN) ₂]	Pink	—	$\mu = 2.40$	(228)

(continued)

TABLE IX—*continued*

Compound	Color	M.p.(°C)	Properties	Ref.
[Co(dPb) _{1.5} (CNS) ₂]	Brown	—	$\mu = 2.2$	(228)
[Co(dPf)Br ₂]	Turquoise	—	$\mu = 4.49$	(237)
[Co(dCyp)Br ₂]	Blue	210	$\mu = 4.41$	(176)
[Co(dCyp)I ₂]	Dark brown	194	$\mu = 4.40$, D.M. = 10.11	(176)
[Co(dCyb)Br ₂]	Blue	—	$\mu = 4.59$	(176)
[Co(dCyb)I ₂]	Yellow-green	290	$\mu = 3.52$	(176)
[Co(dCyf)Cl ₂]	Blue	—	$\mu = 4.72$	(176)
[Co(dCyf)Br ₂]	Blue	215	$\mu = 4.38$	(176)
[Co(dCyf)I ₂]	—	175	D.M. = 7.95	(176)
Co(dP _{se}) ₂ Cl ₂	Green	172	—	(185)
Co(dP _{se}) ₂ Br ₂	Green	178	—	(185)
Co(dP _{se}) ₂ I ₂	Green	175(d)	—	(185)
Co(de _{se}) ₂ Br ₂	Blue-violet	157(d)	—	(185)
[Co(CyP-P)Cl ₂]	Blue	129	$\mu = 4.48$	(182)
[Co(CyP-P)Br ₂]	Green	214	$\mu = 3.52$, D.M. = 4.67	(182)
[Co(CyP-P)Br ₂]	Blue	158	$\mu = 3.90$, D.M. = 7.52	(182)
[Co(CyP-P)I ₂]	Dark brown	220	$\mu = 2.25$, D.M. = 8.7	(182)
Co(PP-P) ₂ Br ₂	Black	162	$\mu = 2.28$, D.M. = 6.66	(181)
Co(PP-P) ₂ I ₂	Dark brown	—	$\mu = 4.16$	(181)
[Co(dee) ₂ Cl ₂] ₂ Cl	Green	—	$\mu = 0$	(264)
[Co(dee) ₂ Br ₂]Br	Green	—	$\mu = 0$	(264)
[Co(dee) ₂ I ₂]I	Brown	—	$\mu = 0$	(264)
[CoH ₂ (dPe) ₂]ClO ₄	Yellow	185(d)	$\mu = 0$	(236)
[Co(dP _{se}) ₂ Br ₂]Br	Dark red	187(d)	—	(185)

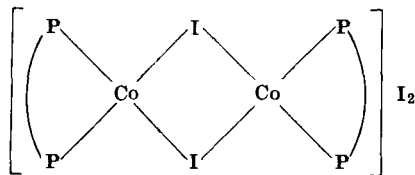
The unusual $\text{Co(diphos)}_{1.5}\text{X}_2$ complexes (diphos = dPp, dPb; $\text{X} = \text{CN}, \text{NCS}$) were prepared by Rigo *et al.* (228). The isothiocyanato complexes were prepared directly from Co(NCS)_2 and diphos, but the cyano derivatives were obtained by passing a solution of CoBr_2 and diphos through an anionic resin in the CN^- form. Infrared spectra rule out the presence of bridging CN^- or NCS^- , and the molecular weights of the cyanides indicate a dimeric formula.



Diphosphinocarborane derivatives are known. Smith *et al.* isolated $[\text{Co(dPC)(B}_{10}\text{H}_{10}\text{C}_2\text{S}_2)]$ and $[\text{Co(dPe)(B}_{10}\text{H}_{10}\text{C}_2\text{S}_2)]$, but said they were unable to isolate simple dPC complexes (251). However, Hill and McAuliffe have isolated the green, pentacoordinate $[\text{Co(dPC)}_2\text{X}]^+$ ($\text{X} = \text{Br}, \text{I}, \text{NCS}$) (163); these compounds were very difficult to isolate, and would not form at all in most solvents.

Chow and McAuliffe have isolated a complex of empirical formula Co(PPPhen)(NCS)_2 , but no structural data are yet available (84).

Isslieb and Weichmann found (185) that the disecundary phosphines, de_se and dP_se , are strong chelating agents toward Co(II) . The hexacoordinate $[\text{Co(diphos)}_2\text{X}_2]$ complexes ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) have magnetic moments in the range 1.77–1.99 B.M. A complex $[\text{Co}_2(\text{diphos})_2\text{I}_2]\text{I}_2$ was obtained, which has the probable structure



Air oxidation of Co(II) salts in the presence of dee produced Co(III) complexes, $[\text{CoX}_2(\text{dee})_2]\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). The iodide is insoluble but the green chloro and bromo complexes dissolve in water and undergo slow hydrolysis to produce yellow solutions. The brown iodo complex turns green on long heating over P_2O_5 *in vacuo* (264). $[\text{Co(dP}_s\text{e)}_2\text{Br}_2]\text{Br}$ is formed by bromination of the Co(II) complex (185).

The compound $\text{Rh}_4(\text{CO})_{10}(\text{dPe})$ has been obtained from $\text{Rh}_4(\text{CO})_{12}$ (262), while $\text{Rh}_6(\text{CO})_{16}$ adds three equivalents of dPe to give $\text{Rh}_6(\text{CO})_{10}(\text{dPe})_3$, which almost certainly retains the Rh_6 cluster (190).

The diphosphines dPm and dPe react with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ to form $[\text{Rh}(\text{CO})_2\text{Cl}]_2(\text{diphos})$, $[\text{Rh}(\text{CO})\text{Cl}(\text{diphos})]$, $[\text{Rh}(\text{CO})\text{Cl}(\text{dPm})]_n$, and $[\text{Rh}(\text{dPe})_2]\text{Cl}$ (159). Mague and Mitchener reported that dPm also formed $[\text{Rh}(\text{CO})(\text{dPm})\text{Cl}]_2$ (200). They also found that TVPP and DPPA, which cannot chelate, formed polymers, $[\text{Rh}(\text{CO})\text{Cl}(\text{diphos})]_n$, whereas a 2:1 ratio of VPP: $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ produced $[\text{Rh}(\text{VPP})_2][\text{Rh}(\text{CO})_2\text{Cl}_2]$. Excess VPP or POP gave $[\text{Rh}(\text{diphos})_2]\text{Cl}$. The $[\text{Rh}(\text{CO})_2\text{X}_2]^-$ complexes are approximately 1:1 electrolytes in CH_3CN , and the infrared spectra are essentially identical with that of $n\text{-Bu}_4\text{N}[\text{Rh}(\text{CO})_2\text{Cl}_2]$ (200). PP-P and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ form both phosphido and diphosphine complexes (159). Cullen and Thompson found (106) that $[\text{Rh}(\text{CO})_2\text{X}]_2$ ($\text{X} = \text{Cl}, \text{Br}$) reacted with ffos or f_6fos to form $[\text{Rh}(\text{diphos})_2][\text{cis-Rh}(\text{CO})_2\text{X}_2]$, whereas a fourfold excess of ffos, f_6fos , or f_8fos formed $[\text{Rh}(\text{diphos})_2]\text{Cl}$. $[\text{Rh}(\text{ffos})_2]\text{Cl}$ reacted with hydrogen chloride in CH_2Cl_2 to form $[\text{RhHCl}(\text{ffos})_2]\text{Cl}$, which exhibited $\nu(\text{Rh-H})$ at 2080 cm^{-1} . All the complexes are 1:1 electrolytes and ^{19}F NMR data were also reported (106).

Heating rhodium with PEE in hydrogen led to very small yields of an orange-yellow compound, $\text{Rh}_2\text{H}_n(\text{PEE})_3$ ($n \geq 0$) (66). $[\text{RhH}(\text{dPe})_2]$ was obtained on reducing $[\text{Rh}(\text{dPe})_2]\text{Cl}$ with NaBH_4 or LiAlH_4 (200, 236). Unlike the cobalt analog, it decomposes in perchloric acid to form $[\text{Rh}(\text{dPe})_2]\text{ClO}_4$ and hydrogen. Upon reaction of $[\text{RhH}(\text{dPe})_2]$ with hydrogen chloride in ether, $[\text{RhHCl}(\text{dPe})_2]\text{Cl}$ results. $[\text{Rh}(\text{dPe})_2]\text{Cl}$ can be converted to $[\text{Rh}(\text{dPe})_2]\text{ClO}_4$ by HClO_4 , and the latter complex has been shown to be square-planar by X-ray analysis (138).

When $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ reacts with dme under nitrogen a mixture of *cis*- and *trans*- $[\text{Rh}(\text{dme})\text{Cl}_2]\text{Cl}$ is formed (41). The pure *trans* isomer can be obtained from *mer*- $[\text{RhCl}_3(n\text{-Bu}_3\text{P})_3]$ and dme, but *mer*- $[\text{RhBr}_3(n\text{-Bu}_3\text{P})_3]$ gives the *cis* isomer. *cis*- $[\text{Rh}(\text{dme})_2\text{Cl}_2]\text{Cl}$ is formed from $[\text{Rh}(\text{dme})_2]\text{Cl}$ and chlorine, or by reaction with CCl_4 or CHCl_3 ; *trans*- $[\text{Rh}(\text{dme})_2\text{Br}_2]\text{Cl}$ results from treating $[\text{Rh}(\text{CO})(\text{dme})_2]\text{Cl}$ with bromine in CCl_4 . *trans*- $[\text{Rh}(\text{dme})_2\text{Cl}_2]\text{Cl}$ is reduced to the metal by LiAlH_4 , but the milder reductant NaBH_4 forms *trans*- $[\text{RhHCl}(\text{dme})_2]\text{Cl}$, which can also be obtained from $[\text{Rh}(\text{CO})(\text{dme})_2]\text{Cl}$ and HCl (41). $[\text{Rh}(\text{dme})_2]\text{Cl}$ forms from $[\text{RhCl}(\text{PPh}_3)_3]$ and dme in benzene (41, 56). It is a 1:1 electrolyte and takes up hydrogen chloride reversibly to form $[\text{RhH}_2(\text{dme})_2]\text{Cl}$, $\nu(\text{Rh-H})$ at 1900 and 1870 cm^{-1} . RhCl_3 and ffos react to form $[\text{RhCl}_3(\text{ffos})_2]$ (99).

In contrast to $[\text{Rh}(\text{dPe})_2]\text{Cl}$, which does not react with CO, $[\text{Rh}(\text{dme})_2]\text{Cl}$ takes up CO reversibly to give $[\text{Rh}(\text{CO})(\text{dme})_2]\text{Cl}$ (56). Solid

[Rh(dme)₂]Cl takes up oxygen, apparently to form [Rh(O₂)(dme)₂]Cl containing O₂²⁻ (56). [Rh(O₂)(dPe)₂]PF₆ was obtained from [Rh(dPe)₂]Cl, NH₄PF₆, and O₂ in anhydrous methanol (215). The oxygen is lost on boiling in CH₂Cl₂ or CH₃OH solution.

Interaction of [Ir(CO)₂Cl(py)] and PP-P gives yellow Ir(PP-P)₂-(CO)₂Cl and a phosphido complex (159). From the reaction between dPm and [Ir(CO)₂Cl(py)] were obtained [Ir(CO)₂Cl]₂(dPm) and [Ir(CO)-(dPm)₂]Cl, whereas dPe gave [Ir(CO)₂Cl(dPe)], [Ir(CO)(dPe)₂]Cl, and [Ir(dPe)₂]Cl (154, 159). [Ir(CO)(dPe)₂]Cl, which reversibly loses CO, has a distorted trigonal-bipyramidal structure (186). *In vacuo* CO is lost and the red, diamagnetic four-coordinate [Ir(dPe)₂]Cl is formed (235).

trans-[Ir(CO)Cl(PPh₃)₂] reacts readily with dme in THF to form hygroscopic *trans*-[Ir(CO)(dme)₂]Cl (170). With methanol or ethanol unusual hydridoalkoxycarbonyl complexes of Ir(III) are formed, [IrH(CO₂R)(dme)₂]⁺ (R = Me, Et), which have been isolated as the tetraphenylborates. These are stable in alkalis, but lose an alkoxide group in dilute acids to form [IrH(CO)(dme)₂]⁺. On refluxing *trans*-[Ir(CO)(dme)₂]Cl in wet ethanol, CO is lost to form [IrHCl(dme)₂]⁺, isolated as the tetraphenylborate, $\nu(\text{Ir-H}) = 2162 \text{ cm}^{-1}$. The complex [Ir(CO)-(dPe)₂]Cl does not form a hydride under similar conditions (170).

Vaska and Catone found (257) that [Ir(dPe)₂]Cl, which they obtained from [Ir(CO)Cl(PPh₃)₂] and dPe, readily adds a number of small molecules to give 5- and 6-coordinated complexes. Among the reactions studied were those with HCl and HBr to give the hexacoordinate [IrHX(dPe)₂]Cl, and with CO, O₂, and PF₃ to form the pentacoordinate [Ir(L)(dPe)₂]Cl. [Ir(dPe)₂]Cl adds carbon subsulfide at -70° to form yellow [Ir(dPe)₂(C₃S₂)]Cl, a 1:1 electrolyte, whereas in refluxing CH₂Cl₂, purple [Ir(dPe)₂(C₃S₂)₂]Cl_n results (124a). Molecular hydrogen forms [IrH₂(dPe)₂]BPh₄, which, on the basis of IR evidence, probably has the *cis* structure. It also appears to be possible to add NO, probably to produce [Ir(NO)₂(dPe)₂]Cl, since in air [Ir(NO₂)₂(dPe)₂]Cl is formed (257). The X-ray structure of [Ir(O₂)(dPe)₂]PF₆ has been reported, and the Ir atom is in a trigonal-bipyramidal environment (214, 215). *trans*-[Ir(CO)(PPh₃)₂X] and excess dPe give [Ir(dPe)₂]X on heating in benzene under nitrogen, but at room temperature in the presence of carbon monoxide [Ir(CO)(dPe)₂]X is formed, in contrast to [Rh(dPe)₂]⁺ which does not take up CO. The CO can be removed by passing nitrogen through the solution. [Ir(CO)(dPm)₂]X is obtained similarly, but it does not lose CO to form [Ir(dPm)₂]X (253) (see Table X).

The compound [IrH₂(PPh₃)(dPe)]ClO₄ (11a) and the germyl complex [IrH₂(CO)(dPe)(GeEt₃)] (127) have been prepared.

TABLE X
DIPHOSPHINE COMPLEXES OF RHODIUM AND IRIIDIUM

Compound	Color	M.p.(°C)	Properties	Ref.
[Rh(ffos) ₂][Rh(CO) ₂ Cl ₂]	Yellow	200(d)	¹⁹ F NMR	(106)
[Rh(f ₆ fos) ₂][Rh(CO) ₂ Cl ₂]	Yellow	170(d)	¹⁹ F NMR	(106)
[Rh(ffos) ₂]Cl	Yellow	200(d)	¹⁹ F NMR	(106)
[Rh(f ₈ fos) ₂]Cl	Light orange	187	¹⁹ F NMR	(106)
[RhHCl(ffos) ₂]Cl	Yellow	192	¹⁹ F NMR, IR	(106)
[Rh(VPP)(CO)Cl]	Yellow	184(d)	IR	(200)
[Rh(VPP) ₂]BPh ₄	Yellow	—	—	(200)
[Rh(POP) ₂]BF ₄	Yellow	225(d)	—	(200)
[Rh(TVPP)(CO)Cl]	Yellow	246(d)	IR	(200)
[Rh(dPm)(CO)Cl] ₂	Orange	221(d)	IR	(159, 200)
[Rh(VPP) ₂][Rh(CO) ₂ Cl ₂]	Yellow	238(d)	IR	(200)
[RhH(dPe) ₂]	Orange	280(d)	D.M. = 4.35	(236)
[RhHCl(dPe) ₂]Cl	Yellow	181	—	(236)
[Rh(dPe)(CO)Cl]	Yellow	135	μ = 0, IR	(159)
[Rh(dPe) ₂]Cl	Yellow	215	—	(236)
[Rh(dPe) ₂]ClO ₄	Yellow	282	—	(236)
Rh(ffos) ₂ Cl ₃	Yellow	231	—	(99)
[Rh(CO)(dme) ₂]Cl	Yellow	110(d)	IR	(41)
[Rh(dme) ₂]Cl	Yellow	245(d)	—	(41)
<i>cis</i> -[RhH ₂ (dme) ₂]Cl	White	—	IR	(41)
<i>trans</i> -[RhHCl(dme) ₂]Cl	White	185	IR	(41)

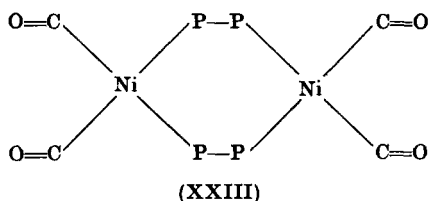
<i>trans</i> -[Rh(dme) ₂ Cl ₂]Cl	Yellow	189(d)	—	(41)
<i>cis</i> -[Rh(dme) ₂ Cl ₂]Cl	Yellow	295(d)	—	(41)
<i>cis</i> -[Rh(dme) ₂ Br ₂]Br	Yellow	334	—	(41)
<i>trans</i> -[Rh(dme) ₂ Cl ₂]Br	Yellow	186(d)	—	(41)
<i>trans</i> -[Rh(dme) ₂ Br ₂]Cl	Yellow	335(d)	—	(41)
<i>trans</i> -[Rh(dme) ₂ Cl ₂]BPh ₄	Pale yellow	181	—	(41)
[Ir(CO) ₂ Cl] ₂ dPm	Yellow	180	IR	(159)
[Ir(CO)(dPm) ₂]Cl	Yellow	195	IR	(159)
[Ir(CO) ₂ (dPe)]Cl	Yellow	162	IR	(154)
[Ir(CO)(dPe) ₂]Cl	Yellow	320	IR	(170)
<i>trans</i> -[Ir(CO)(dme) ₂]Cl	Cream	105	NMR	(170)
<i>trans</i> -[IrH(CO)(dme) ₂](BPh ₄) ₂	White	237	IR, NMR	(170)
<i>trans</i> -[IrHCl(dme) ₂]BPh ₄	White	225	IR, NMR	(170)
[Ir(dPe) ₂]Cl	Orange	225	—	(257)
[Ir(dPe) ₂]BF ₄	Orange	270	IR	(257)
[Ir(CO)(dPe) ₂]Cl	White	260	IR	(257)
[Ir(dPe) ₂ (PF ₃)]Cl	White	270	IR	(257)
[Ir(dPe) ₂ (O ₂)]Cl	Cream	185	$\nu(\text{Ir}-\text{O}_2)$ 845 cm ⁻¹	(257)
[Ir(dPe) ₂ (O ₂)]BPh ₄	Cream	175	$\nu(\text{Ir}-\text{O}_2)$ 844 cm ⁻¹	(257)
[IrH ₂ (dPe) ₂]BPh ₄	White	220	IR	(257)
[IrHCl(dPe) ₂]Cl	White	270	IR	(257)
[Ir(dPe) ₂ (NO ₂) ₂]Cl	Cream	163	IR	(257)
[IrH ₂ (dPe)PPh ₃]ClO ₄	Colorless	183(d)	IR	(11a)
IrH ₂ (CO)(dPe)GeEt ₃	White	196	IR, NMR	(127)

H. GROUP VIII (Ni, Pd, AND Pt)

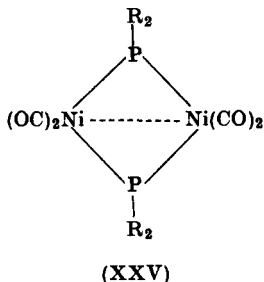
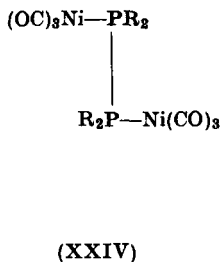
Nickel(0) complexes, $[\text{Ni}(\text{diphos})_2]$, were obtained by Chatt *et al.* by reduction $[\text{Ni}(\text{diphos})_2\text{X}_2]$ with NaBH_4 or sodium naphthalenide (67). Aromatic, but not aliphatic, diphosphines can replace all the CO from $\text{Ni}(\text{CO})_4$, while $[\text{Ni}(\text{PEE})_2]$ and $[\text{Ni}(\text{dPe})_2]$ can also be obtained by heating Raney nickel with the diphosphine at 160° (64). Van Hecke and Horrocks used the reaction of nickelocene with the diphosphine to prepare $[\text{Ni}(\text{dPe})_2]$ and $[\text{Ni}(\text{dPp})_2]$, a method which avoids using the highly toxic $\text{Ni}(\text{CO})_4$ (150). The Ni(0) complex $\text{K}_4\text{Ni}(\text{CN})_4$ reacts with dPm and dPe in liquid ammonia to form the $[\text{Ni}(\text{diphos})_2]$ compounds (21).

The reaction of $\text{Ni}(\text{CO})_4$ with most diphosphines produces $[\text{Ni}(\text{CO})_2(\text{diphos})]$ complexes, although aromatic diphosphines (dPe, PEE, PPP) can react further (64). Among the diphosphines which produce $[\text{Ni}(\text{CO})_2(\text{diphos})]$ are dee (64, 210, 217), dPe, dPp, dPm (166, 210), dne (217), PMM, PEE, PPP (64), ffos (217), and VPP (251). In general, all these complexes have good thermal stability, but oxidize readily in air. The ligands $\text{dm}_{\text{f}}\text{e}$ (39) and $\text{dm}_{\text{f}}\text{e}_{\text{f}}$ (40) have also been used, the complex with the former being volatile without decomposition in contrast to most of the $[\text{Ni}(\text{CO})_2(\text{diphos})]$ complexes.

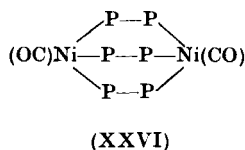
The bridged derivatives of type (XXIII) have also been obtained as biproducts of the reaction of $\text{Ni}(\text{CO})_4$ and diphosphines (64, 217).



With MP-P, EP-P, PP-P (146), CyP-P (178), and M_fP-P (38, 201) both diphosphine (XXIV) and phosphido (XXV) complexes are formed



(188, 206). From Ni(CO)_4 or $[\pi\text{-C}_5\text{H}_5\text{Ni(CO)}]_2$ and DPPA and DPPB, bridged complexes were obtained, the triply bridged $[\text{Ni}_2(\text{CO})_2(\text{DPPA})_3]$, (XXVI), and $[\text{Ni(CO)}_3]_2\text{DPPA}$ were also isolated (51, 193). Orange



or yellow $[\text{Ni(CO)}_2(\text{diphos})]$ (diphos = deC, dPC) complexes react with a further mole of ligand to form $[\text{Ni(diphos)}_2]$ compounds (230). The halogenated *o*-carboranediphosphines were investigated. With $\text{B}_{10}\text{H}_{10-n}\text{X}_n(\text{PPh}_2)_2$ ($n = 1, 2$, or 3) $[\text{Ni(CO)}_2\text{L}]$ formed which, on reaction with halogens, gave $[\text{Ni(L)X}_2]$ and $[\text{NiL}_2]\text{X}_2$ (265). The unusual $[\text{Ni(diphos)}_{1.5}(\text{CN})_2]$ (diphos = dPp, dPb) complexes are reduced by NaBH_4 in ethanol to the yellow $\text{Ni(diphos)}_{1.5}(\text{CN})$, $\mu_{\text{eff}} = 2.0\text{--}2.3$ B.M. (94). These complexes are dimeric, $[(\text{diphos})(\text{CN})\text{Ni(diphos)Ni(CN)}\text{---}(\text{diphos})]$. Hieber *et al.* (18, 158, 160) have prepared several nitrosyl complexes, e.g., the red-violet $[\text{Ni(NO)(dPe)I}]$ and $[\text{Ni(NO)C(CN)}_3(\text{dPe})]$, as well as the more unusual $[\text{X(PPh}_3)(\text{NO})\text{Ni(dPe)Ni(NO)(PPh}_3)\text{X}]$, obtained from $[\text{Ni(NO)(PPh}_3)\text{X}]_2$ and dPe. PP-P reacts with $[\text{Ni(NO)X}]_4$ to form the halogen-bridged $[\text{Ni}_2(\text{NO})_2(\text{PP-P})_2\text{X}_2]$ and phosphido complexes.

Nickel(II) complexes are of four main types: $[\text{Ni(L)X}_2]$, $[\text{Ni(L)}_2\text{X}_2]$, $[\text{Ni(L)}_2\text{X}]\text{Y}$, and $[\text{Ni(L)}_2]\text{X}_2$. The general methods of preparation include the reaction of NiX_2 with the diphosphine in aqueous ethanol, acetone, dichloromethane, etc.; the action of halogens on $[\text{Ni(diphos)(CO)}_2]$ (64); or from the chloride by metathesis with LiX . Aqueous acids convert $[\text{Ni(diphos)}_2]$ to the nickel(II) complexes (46). $\text{Ni(dme)}_2\text{X}_2$ are readily obtained as alcohol-soluble complexes; reaction with NiX_2 converts them to the insoluble Ni(dme)X_2 (31). Wymore and Bailar (264) obtained diamagnetic $[\text{Ni(dee)X}_2]$ ($\text{X} = \text{Cl, Br}$) and $[\text{Ni(dee)}_2](\text{ClO}_4)_2$. Booth and Chatt found that $\text{Ni(dee)}_2\text{X}_2$ were formed initially, but only when $\text{X} = \text{I}$ was the product stable (31). $\text{Ni(PEE)}_2\text{Br}_2$ was obtained as a dark red complex from the action of bromine on $[\text{Ni(PEE)}_2]$; the solid is diamagnetic, and is a 1:1 electrolyte in nitrobenzene (64). The same compound is formed from NiCl_2 and PEE in aqueous ethanol, and then treatment of the product with NaBr . It crystallizes from solution as the octahydrate. In $[\text{Ni(dPm)}_2\text{X}_2]$ the ligand appears to function as a monodentate (31, 150). Because dPm is bidentate in $[\text{Ni(CO)}_2(\text{dPm})]$, it was suggested (150) that halogenation of this complex might produce the bidentate nickel(II) halide derivatives, but this suggestion has not yet

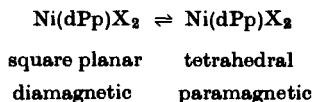
been carried out. However, dPm is bidentate in $[\text{Ni}(\text{dPm})_2]\text{Y}_2$ ($\text{Y} = \text{NO}_3, \text{ClO}_4, \text{BF}_4$) (118).

The ligand dPe forms 1:1 complexes, $[\text{NiX}_2(\text{dPe})]$, readily and 2:1 complexes, $\text{Ni}(\text{dPe})_2\text{X}_2$ ($\text{X} = \text{Br}, \text{I}$), under forcing conditions (31). Booth and Chatt assigned hexacoordinate structures to the latter complexes in the solid state (31), but no magnetic or spectral evidence was produced in confirmation; moreover, these complexes are almost 1:1 conductors in nitrobenzene, and so their octahedral structural assignment is questionable. Van Hecke and Horrocks concluded (150) on the basis of the difference in optical spectra of the solids and the solutions that in CH_2Cl_2 solution the reaction



occurs. Optical spectra rule out the presence of a five-coordinate species, which have never been observed with dPe (150, 212). Hudson *et al.* obtained $[\text{Ni}(\text{dPe})_2]\text{Y}_2$ ($\text{Y} = \text{NO}_3, \text{ClO}_4$) complexes, which are square-planar ($\mu_{\text{eff}} = 0-0.4$ B.M.) 1:2 electrolytes (168). Small magnetic moments in the range 0-0.4 B.M. have been reported for several apparently square-planar Ni(II) complexes, but no satisfactory explanation has been forthcoming. The isolation of two forms of $\text{Ni}(\text{dPe})\text{Cl}_2$ has been claimed (31): a yellow-brown diamagnetic plates form and a paramagnetic ($\mu_{\text{eff}} = 1.34$ B.M.) dull orange crystalline form, but other workers have only isolated the diamagnetic compound.

Solid $[\text{Ni}(\text{dPp})\text{X}_2]$ complexes are planar, diamagnetic compounds. On dissolution in CH_2Cl_2 , PhNO_2 , or CHCl_3 magnetic moments in the range 2.12-2.73 B.M. were reported. The difference in optical spectra between solid $\text{Ni}(\text{dPp})\text{I}_2$ and solutions of $\text{Ni}(\text{dPp})\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) were studied, and it was concluded that in the solution the equilibrium

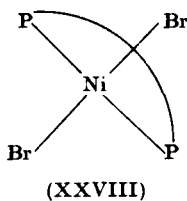
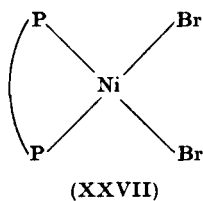


exists (150). On the basis of spectral evidence the proportion of tetrahedral isomer present decreases in the order $\text{I} > \text{Br} > \text{Cl}$. Solid tetrahedral complexes have not been obtained. The thermodynamic parameters for the equilibrium were determined by NMR (150). Sacconi and Gelsomini found that dPb and dPf formed pseudotetrahedral 1:1 complexes with nickel halides (237). The isolation of these paramagnetic ($\mu_{\text{eff}} = 3.3$ B.M.) complexes is not unexpected; since an increase in chelate chain length from dPe \rightarrow dPp produced complexes which exhibited square-planar \rightleftharpoons tetrahedral equilibrium in solution, then further in-

crease in chain length to dPb and dPf leads to tetrahedral compound formation.

McAuliffe and Meek obtained the planar $[\text{Ni}(\text{VPP})\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$) and the diamagnetic, pentacoordinate $[\text{Ni}(\text{VPP})_2\text{X}]\text{BPh}_4$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), which were assigned square-pyramidal structures on the basis of electronic spectra (212). $[\text{Ni}(\text{VPP})_2(\text{NCS})]\text{BPh}_4$ is paramagnetic ($\mu_{\text{eff}} = 1.86 \text{ B.M.}$) in the solid state, and in solution the electronic spectrum resembled the other pentacoordinate $[\text{Ni}(\text{VPP})_2\text{X}]^+$ complexes, but the solid spectrum was different. Six-coordinate VPP complexes could not be obtained (212). $[\text{Ni}(\text{VPP})_2](\text{ClO}_4)_2$ and $[\text{Ni}(\text{VPP})_2](\text{NO}_3)_2$ show interesting differences (225). The former exhibits normal magnetic behavior and follows the Curie-Weiss Law. The latter, however, is an example of the so-called "anomalous behavior of nickel." It does not obey the Curie-Weiss Law, and magnetic susceptibility measurements indicate an equilibrium between the spin-free and spin-paired electronic ground states. The differences between these two complexes has been explained in terms of the greater coordinating ability of the nitrate ions, which produce axial perturbation along the z axis. The poorer coordinating perchlorate ions do not produce this effect. This explanation is supported by the observation that in concentrated solutions of the complexes, ion-pairing occurs in the nitrate, but not in the perchlorate, complex (225). This difference has been observed in other nickel complexes (128). $[\text{Ni}(\text{VPP})(\text{NCS})_2]$ (226) and also $[\text{Ni}(\text{diphos})(\text{NCS})_2]$ [diphos = dPp (229), dPb (237)] are planar, diamagnetic complexes (see Table XI).

Nickel(II) bromide reacts with dCyp to form $[\text{Ni}(\text{dCyp})\text{Br}_2]$, a planar complex with a dipole moment of 11.13 D, indicating a *cis* structure (XXVII). The complex with dCyb is probably analogous,



but with dCyf a *trans* planar structure (XXVIII) is indicated, D.M. = 2.37 D (176).

CyP-P reacts with NiX_2 ($\text{X} = \text{Cl}, \text{Br}$) to form $[\text{Ni}(\text{CyP-P})\text{X}_2]$ in which the ligand is bidentate (182), but PP-P forms $[\text{Ni}(\text{PP-P})_2\text{X}_2]$, a diamagnetic nonelectrolyte with a dipole moment of 5.97 D, indicating a *cis* square-planar structure with monodentate PP-P ligands (176).

TABLE XI
DIPHOSPHINE COMPLEXES OF NICKEL

Compound	Color	M.p.(°C)	Properties	Ref.
[Ni(PPP) ₂]	Red-orange	—	—	(64)
[Ni(dme) ₂]	White	120	D.M. = 1.65	(67)
[Ni(dPe) ₂]	Orange	253(d)	D.M. = 1.5	(67)
[Ni(PEE) ₂]	Red-orange	241	—	(67)
[Ni(dPp) ₂]	Red-orange	—	—	(150)
[Ni(CO) ₂ (PMM)]	White	123	IR, D.M. = 5.40	(64, 150)
[Ni(CO) ₂ (PPP)]	Yellow	226	IR, D.M. = 5.39	(64)
[Ni(CO) ₂ (dPe)]	White	139	IR, D.M. = 4.81	(64)
[Ni(CO) ₂ (PEE)]	White	65	IR, D.M. = 5.48	(64)
[Ni(CO) ₂ (dee)]	White	13	IR	(64, 217)
[Ni(CO) ₂ (dm _{re})]	Colorless	5	IR	(39)
[Ni(CO) ₂ (dme)]	Cream	71	IR	(31)
[Ni ₂ (CO) ₄ (dee) ₂]	White	116	IR, D.M. = 1.6	(64)
[Ni ₂ (CO) ₆ (mrP-P)]	Red-black	105	IR	(38)
[Ni(CO) ₂ (ffos)]	Yellow	—	IR	(99)
[Ni(CO) ₂ (dne)]	Cream	132	IR, ³¹ P NMR	(217)
[Ni ₂ (CO) ₆ (PP-P)]	Yellow	195	IR, NMR	(146)
[Ni ₂ (CO) ₆ (MP-P)]	Yellow	12	IR	(146)
[Ni(CO) ₂ (VPP)]	Yellow	156	IR	(251)
[Ni ₂ (CO) ₄ (DPPA) ₂]	White	190	IR	(51)
[Ni ₂ (CO) ₂ (DPPA) ₃]	Yellow	264(d)	IR	(51)
[Ni(CO) ₂ (dm _{re})]	Colorless	30	IR	(40)
[Ni ₂ (CO) ₄ (DPPB) ₂]	Yellow	80	IR	(193)
[Ni(CO) ₂ (dPC)]	Yellow	119	IR	(230)
[Ni(CO) ₂ (deC)]	Yellow	206(d)	IR	(230)
[Ni(dPC) ₂]	Orange	268(d)	—	(230)

[Ni(deC) ₂]	Yellow	288(d)	—	(230)
[Ni(CO) ₂ (dPp)]	White	—	IR	(166)
[Ni(CO) ₂ (dPm)]	Yellow-white	—	IR	(166)
[Ni(dme)Cl ₂]	Yellow	—	$\mu = 1.23$	(31)
Ni(dme) ₂ Cl ₂	Orange	—	—	(31)
[Ni(dPm) ₂ Cl ₂]	Dark brown	—	$\mu = 0$, vis.	(31, 150)
[Ni(dPm) ₂ Br ₂]	Red	116	$\mu = 0$, vis.	(150)
[Ni(dPm) ₂ I ₂]	Purple	—	$\mu = 0$, vis.	(150)
[Ni(dPm) ₂](NO ₃) ₂	Yellow	286	—	(118)
[Ni(dPm) ₂](ClO ₄) ₂	Yellow	178	—	(118)
[Ni(dPm) ₂](BF ₄) ₂	Yellow	280(d)	—	(118)
[Ni(dee)Cl ₂]	Yellow-brown	—	$\mu = 0$	(264)
[Ni(dee)Br ₂]	Red-brown	—	$\mu = 0$	(264)
Ni(dee) ₂ I ₂	Dark red	—	—	(64)
[Ni(dee) ₂](ClO ₄) ₂	Yellow	—	—	(264)
[Ni(dPe)Cl ₂]	Orange	—	$\mu = 0.3$, IR	(31, 168)
[Ni(dPe)Br ₂]	Red	—	$\mu = 0.4$, IR	(31, 167, 168, 212)
[Ni(dPe)I ₂]	Mauve	—	$\mu = 0.3$	(166, 168, 212)
[Ni(dPe)(NCS) ₂]	Yellow	276	$\mu = 0.4$, IR, vis.	(168, 226)
[Ni(dPe)(CN) ₂]	Yellow	—	Vis.	(229)
[Ni(dPe) ₂](ClO ₄) ₂	Yellow	248	$\mu = 0.3$	(67, 168)
[Ni(dPe) ₂](NO ₃) ₂	Yellow	218	$\mu = 0.4$	(31, 168)
[Ni(dPe) ₂]Br ₂	Yellow	—	$\mu = 0.3$	(31, 168)
[Ni(dPe) ₂]I ₂	Yellow	—	$\mu = 0.3$	(31, 168)
[Ni(PEE)Cl ₂]	Brown	339(d)	$\mu = 0$	(64)
[Ni(PEE)Br ₂]	Brown	333(d)	—	(64)
[Ni(PEE)I ₂]	Red-black	279	—	(64)
[Ni(PEE) ₂]Br ₂	Dark red	—	$\mu = 0$	(64)
[Ni(PEE) ₂](NO ₃) ₂	Yellow	210	—	(67)
[Ni(VPP)Cl ₂]	Light brown	—	$\mu = 0$, vis.	(212)
[Ni(VPP)Br ₂]	Red-brown	—	$\mu = 0$, vis.	(212)
[Ni(VPP)I ₂]	Black	—	$\mu = 0$, vis.	(212)

(continued)

TABLE XI—*continued*

Compound	Color	M.p.(°C)	Properties	Ref.
[Ni(VPP)(NCS) ₂]	Yellow	—	$\mu = 0$, IR, vis.	(212, 226)
[Ni(VPP) ₂ Cl]BPh ₄	Purple	—	$\mu = 0$, vis.	(212)
[Ni(VPP) ₂ Br]BPh ₄	Purple	—	$\mu = 0$, vis.	(212)
[Ni(VPP) ₂ I]BPh ₄	Black	—	$\mu = 0$, vis.	(212)
[Ni(VPP) ₂ (NCS)]BPh ₄	Light brown	—	$\mu = 1.66$, IR, vis.	(212)
[Ni(VPP) ₂](ClO ₄) ₂	Yellow	286	$\mu = 1.50$, IR, vis	(225)
[Ni(VPP) ₂](NO ₃) ₂	Yellow	200	$\mu = 1.67$, IR, vis.	(225)
[Ni(BPEP)Cl ₂]	Purple	167	D.M. = 9.3, vis., NMR	(9)
[Ni(BPEP)Br ₂]	Deep blue	149	$\mu = 2.8$ B.M., vis. NMR	(9)
[Ni(BPEP)I ₂]	Dark brown	176	$\mu = 3.08$ B.M., D.M. = 9.4, NMR	(9)
[Ni(BPEP)(NCS) ₂]	Red-brown	183	vis.	(9)
Ni(PP-P) ₂ Br ₂	Red-brown	155	$\mu = 0$, D.M. = 5.97	(181)
Ni(CyP-P)Cl ₂	Red	203	$\mu = 0$, D.M. = 3.72	(182)
Ni(CyP-P)Br ₂	Red	193	$\mu = 0$, D.M. = 2.24	(182)
[Ni(dCyp)Br ₂]	Red	235	$\mu = 0$, D.M. = 11.13	(176)
[Ni(dCyf)Cl ₂]	Red	164	$\mu = 0$, D.M. = 2.37	(176)
[Ni(de _e e) ₂ Cl]Cl	Yellow	138	—	(185)
[Ni(de _e e) ₂ Br]Br	Red	157	—	(185)
[Ni(de _e e) ₂ I]I	Red	161	—	(185)
[Ni(de _e e) ₂ Br] ₂ NiBr ₄	Dark brown	136	—	(185)
[Ni(dP _e e) ₂ Cl]Cl	Orange-red	150	—	(185)
[Ni(dP _e e) ₂ Br]Br	Orange-red	159	—	(185)
[Ni(dP _e e) ₂ I]I	Dark red	177	—	(185)

[Ni(dP _e) ₂ Br] ₂ NiBr ₄	Brown	184	—	—	(185)
[Ni(dPp)Cl] ₂	Red	—	Vis.	—	(150)
[Ni(dPp)Br] ₂	Red	—	Vis.	—	(150)
[Ni(dPp)I] ₂	Purple	—	Vis.	—	(150)
[Ni(dPp)(NCS) ₂]	Yellow	276	IR, vis.	—	(226, 229)
Ni(dPb) _{1.5} (CN) ₂	Red	—	IR, vis.	—	(229)
Ni(dPp)(PBU ₃)(CN) ₂	Red	143	IR, vis.	—	(229)
[Ni(dPb)Br] ₂	Dark green	—	$\mu = 3.30$, vis.	—	(237, 238)
[Ni(dPb)(NCS) ₂]	Brick red	212	$\mu = 0$, IR, vis.	—	(226, 237)
[Ni(dPb)(CN) ₂]	Yellow	—	—	—	(229)
Ni(dPp) _{1.5} (CN) ₂	Red	—	IR, vis.	—	(229)
[Ni(dPf)Br] ₂	Dark green	—	$\mu = 3.28$, vis.	—	(237)
[Ni(dPf)I] ₂	Maroon	—	$\mu = 3.24$, vis.	—	(237)
[Ni(POPO)Cl] ₂	Amethyst	—	$\mu = 3.26$, vis.	—	(237)
[Ni(POPO)Br] ₂	Brown	—	$\mu = 3.23$, vis.	—	(237)
[Ni(POPO)I] ₂	Brown	—	$\mu = 3.24$, vis.	—	(237)
[Ni(POPO)(NCS) ₂]	Brown	—	$\mu = 0$, IR, vis.	—	(251)
[Ni(dPC)Cl] ₂	Red	310(d)	—	—	(251)
[Ni(dPC)(B ₁₀ H ₁₀ C ₂ S ₂)]	Brown	380(d)	—	—	(251)
[Ni(dPe)(B ₁₀ H ₁₀ C ₂ S ₂)]	Yellow	375(d)	—	—	(251)
[Ni(dme)Br] ₃	Black	—	$\mu = 2.12$	—	(31)
[Ni(dee)Br] ₃	Green-black	—	$\mu = 2.0$	—	(264)
[Ni(dme) ₂ Br] ₂ Br	Dark brown	—	$\mu = 2.05$	—	(31)
[Ni(dme) ₂ Br] ₂ Br ₃	Light brown	—	$\mu = 2.02$	—	(31)
[Ni(dPe)Br] ₃	Dark brown	—	$\mu = 2.02$, ESR, vis.	—	(150)
[Ni(dPp)Br] ₃	Black	—	$\mu = 1.93$, ESR, vis.	—	(150)

PPPhen reacts with nickel(II) halides to form the planar $[\text{Ni}(\text{PPPhen})\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$) and the planar $[\text{Ni}(\text{PPPhen})_2](\text{ClO}_4)_2$ compounds (84).

The unusual diphosphine BPEP forms complexes $[\text{Ni}(\text{BPEP})\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$). The *N*-bonded isothiocyanate is planar, the dark brown iodide ($\mu_{\text{eff}} = 2.80\text{--}3.08$ B.M.) is pseudotetrahedral, while the bromide and chloride exhibit planar-tetrahedral isomerism. The magnetic moments appear to depend on previous physical treatment of the complex, are roughly temperature independent, and follow the Curie-Weiss law, which rules out the type of anomalous behavior found for $[\text{Ni}(\text{VPP})_2](\text{NO}_3)_2$. The electronic and NMR spectra support the presence of both planar and tetrahedral species in samples of the chloride and bromide (9).

Some dPC complexes have been prepared by Smith and co-workers. They include $[\text{Ni}(\text{dPC})_2]\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$), $[\text{Ni}(\text{dPC})\text{Cl}_2]$, $[\text{Ni}(\text{dPC})-(o\text{-B}_{10}\text{H}_{10}\text{C}_2\text{S}_2)]$, and $[\text{Ni}(\text{dPe})(o\text{-B}_{10}\text{H}_{10}\text{C}_2\text{S}_2)]$ (250, 251, 265).

The $[\text{Ni}(\text{POPO})\text{X}_2]$ complexes are similar to those of dPb and dPf and were assigned pseudotetrahedral structures (237). The crystal structure of the chloride has been determined, and shows that the oxygen atom is not coordinated and an eight-membered ring is present (132). This contrasts with the nitrogen and sulfur analogs ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{-NHCH}_2\text{CH}_2\text{PPh}_2$, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{PPh}_2$) which behave as terdentate ligands forming square-pyramidal complexes.

Unlike cobalt(II), nickel(II) is reluctant to form pentacoordinate complexes with the bis(diphenylphosphino)alkanes. Five-coordination has, however, been obtained with the cyanide (229). Only the four-coordinate $[\text{Ni}(\text{dPe})(\text{CN})_2]$ has been isolated, but the complex $[\text{Ni}(\text{dPe})_2(\text{CN})_2]$ has been studied by continuous variation spectrophotometry in CH_2Cl_2 solution and shown to be pentacoordinate with one dPe acting as a monodentate ligand. The presence of $[\text{Ni}(\text{dPe})_2(\text{CN})]^+$ is ruled out by the negligible conductance of the solution. With dPp and dPb the $\text{Ni}(\text{diphos})_{1.5}(\text{CN})_2$ complexes are obtained, which are probably dimeric and contain chelating and bridging diphosphines, $(\text{NC})_2(\text{diphos})\text{-Ni}(\text{diphos})\text{Ni}(\text{diphos})(\text{CN})_2$. Five-coordinate $[\text{Ni}(\text{dPp})(n\text{-Bu}_3\text{P})(\text{CN})_2]$ is also known. $[\text{Ni}(\text{dPb})(\text{CN})_2]$ is dimeric in CH_2Cl_2 , and the IR spectrum indicates *trans*- CN^- groups, and thus bridging diphosphines are indicated (229).

The only hydrido complex reported is $[\text{NiH}(\text{dPe})_2]\text{AlCl}_4$, prepared from $\text{Ni}(\text{dPe})_2$, AlCl_3 , and dry HCl in toluene. These orange crystals exhibit $\nu(\text{Ni-H}) = 1950\text{ cm}^{-1}$ and $\tau(\text{Ni-H}) = 23$ (241).

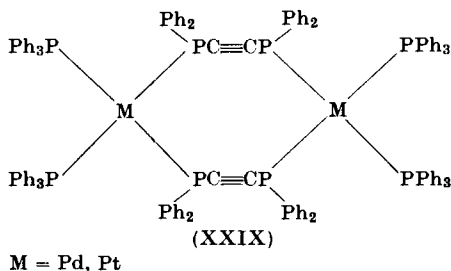
The disecundary phosphines de_se and dP_se form pentacoordinate, trigonal-bipyramidal $[\text{Ni}(\text{diphos})_2\text{X}]\text{Y}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{Y} = \text{Cl}, \text{Br}, \text{I}$,

BPh_4) complexes when reacted in a 2:1 ratio. A 1:1 diphosphine: NiBr_2 ratio produced $[\text{Ni}(\text{diphos})_2\text{Br}]_2[\text{NiBr}_4]$ (185).

Green-black $\text{Ni}(\text{dee})\text{Br}_3$ was formed on oxidizing the $\text{Ni}(\text{II})$ complex with bromine in benzene (264). It is insoluble in water and a polymeric octahedral structure has been proposed. $[\text{Ni}(\text{dme})\text{Br}_2]$ reacts with bromine to form $[\text{Ni}(\text{dme})\text{Br}_3]$, whereas the oxidation in HBr of $[\text{Ni}(\text{dme})_2\text{Br}_2]$ produced the very stable $[\text{Ni}(\text{dme})_2\text{Br}_2]\text{Br}$ (31). The latter adds bromine to form $[\text{Ni}(\text{dme})_2\text{Br}_2](\text{Br}_3)$. Booth and Chatt reported that $\text{Ni}(\text{dPe})_2\text{Br}_2$ was not oxidized (31), but Van Hecke and Horrocks obtained $\text{Ni}(\text{III})$ complexes from the 1:1 complexes $[\text{Ni}(\text{diphos})\text{Br}_2]$ (diphos = dPe , dPp) (150). These complexes have been studied by ESR and electronic spectroscopy. The magnetic moments are in good agreement with theory for a low-spin d^7 complex, but the spectra have not been unambiguously assigned. McAuliffe oxidized $[\text{Ni}(\text{VPP})\text{Br}_2]$ to $[\text{Ni}(\text{VPP})\text{Br}_3]$, and found that the latter complex is reduced to the nickel(II) complex upon standing in air (211).

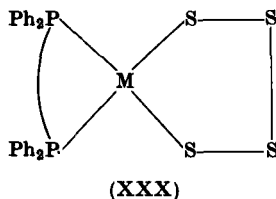
Palladium(0) and platinum(0) form $[\text{M}(\text{diphos})_2]$, thermally stable, air-sensitive complexes. Palladium also forms $\text{Pd}(\text{diphos})(\text{diphos}')$ and $\text{Pd}(\text{diphos})(\text{diars})$ (diars = chelating diarsine). $[\text{Pd}(\text{PEE})_2]$ forms on heating palladium black with PEE under nitrogen (66). Reduction of $\text{M}(\text{diphos})_2\text{X}_2$ with NaBH_4 produced $[\text{M}(\text{diphos})_2]$, while $[\text{M}(\text{dme})_2]$ was obtained from $[\text{M}(\text{dme})\text{Cl}_2]$, dme , and sodium naphthalenide in THF (67, 74). The $[\text{Pd}(\text{diphos})(\text{diphos}')] and $[\text{Pd}(\text{diphos})(\text{diars})]$ were obtained by reduction of $[\text{Pd}(\text{diphos})\text{Cl}_2]$ in the presence of an equimolar quantity of diphos' or diars . Reduction of $[\text{Pd}(\text{PEE})\text{Cl}_2]$ in the presence of PPh_3 gave only $[\text{Pd}(\text{PPh}_3)_3]$, and not $[\text{Pd}(\text{PEE})(\text{PPh}_3)_2]$ (67). $[\text{Pd}(\text{PEE})\text{MeC}(\text{CH}_2\text{PPh}_3)_3]$ has been obtained in an analogous manner to $[\text{Pd}(\text{diphos})(\text{diphos}')]$. It has been suggested that the former complex is pentacoordinate, probably square-pyramidal. $\text{K}_2\text{Pt}(\text{CN})_4$ reacts with dPe in liquid ammonia to form $[\text{Pt}(\text{dPe})_2]$ (219).$

The carbonyl complexes $[\text{Pt}_3(\text{CO})_4](\text{PEt}_3)_4]$ and $\text{Pt}(\text{CO})_2\text{Cl}_2$ are decomposed by dPe to $[\text{Pt}(\text{dPe})_2]$ (54). $[\text{M}(\text{PPh}_3)_4]$ reacts with DPPA to form $[\text{M}_2(\text{PPh}_3)_4(\text{DPPA})_2]$ (XXIX) (261). Oxidative addition



reactions of perfluoroalkyl iodides to Pd(0) and Pt(0) complexes have been reported (231).

The $[M(\text{diphos})_2]$ complexes react with HClO_4 to form $M(\text{II})$ compounds. On heating with sulfur in benzene solution the $[M(\text{dPe})_2]$ complexes take up sulfur to form tetrasulfido complexes, of probable structure (XXX) (73).



$M = \text{Pd, Pt}$

Palladium(II) and platinum(II) readily form diphosphine complexes, usually resulting in the planar configuration. Palladium(II), especially, has been complexed with many of the more unusual diphosphines (see Table XII).

Complexes $[\text{Pd}(\text{diphos})_2]\text{X}_2$ (diphos = dPm, dPe, PEE; $\text{X} = \text{Br}, \text{NO}_3$) were obtained by Chatt *et al.* by reaction of PdCl_2 or Na_2PdCl_4 with two equivalents of diphosphine and excess of NaBr , or with $\text{Pd}(\text{NO}_3)_2$ (67). Westland prepared $[\text{Pd}(\text{dPe})\text{Cl}_2]$ and found that it would react with a further molecule of dPe to form $[\text{Pd}(\text{dPe})_2]\text{Cl}_2$, from which other halide derivatives could be obtained by metathesis (259). Platinum complexes were similarly isolated. The conductivity of the halides in nitromethane is less than that of the perchlorates, but the tendency toward association to form pentacoordinate cations is much less than with the corresponding diarsine complexes. In methanol the $[\text{Pd}(\text{dPe})_2]\text{X}_2$ complexes are 1:2 electrolytes.

The 1:1 complexes $[M(\text{diphos})\text{X}_2]$ have been prepared from $[M(\text{PhCN})_2\text{Cl}_2]$, dPe, and excess LiX (168), or by reaction of the diphosphine (dme, dee, dPe) with Na_2MX_4 in ethanol to produce $[M(\text{diphos})_2][\text{MX}_4]$ complexes, which are decomposed to $[M(\text{diphos})\text{X}_2]$ on refluxing in DMF (54). These complexes are diamagnetic nonelectrolytes, and, when soluble, are monomeric in CH_2Cl_2 (168). dPm behaves as a normal chelating agent toward Pd(II) and Pt(II), in contrast to its preferred monodentate behavior with Ni(II) (55, 67).

The palladium compound $[\text{Pd}(\text{dee})\text{Cl}_2]$ was obtained from PdCl_4^{2-} and dee, but the platinum analog was isolated by displacement of Me_2S from *trans*- $[\text{Pt}(\text{SMe}_2)_2\text{Cl}_2]$ in chloroform (76). Similar reactions produce $[\text{Pd}(\text{PP-P})_2\text{Cl}_2]$ and $[\text{Pd}(\text{diphos})\text{X}_2]$ (diphos = CyP-P, V_fPP , $\text{X} = \text{Cl}$;

TABLE XII

DIPHOSPHINE COMPLEXES OF PALLADIUM AND PLATINUM

Compound	Color	M.p.(°C)	Properties	Ref.
[Pd(dme) ₂]	White	182	D.M. = 1.6	(67)
[Pd(dPm) ₂]	Scarlet	203(d)	—	(67)
[Pd(dPe) ₂]	Yellow	234	D.M. = 1.6	(67)
[Pd(PEE) ₂]	Orange	229	D.M. = 0	(66, 67)
[Pd(PEE)(dPe)]	Yellow	207	D.M. = 2.1	(67)
[Pd(PEE)MeC(CH ₂ PPh ₂) ₃]	Yellow	200	D.M. = 3.1	(67)
[Pd(PEE)C ₆ H ₄ (AsMe ₂) ₂]	Orange	141	—	(67)
[Pd(PEE)C ₆ H ₄ (AsEt ₂) ₂]	Yellow	185	D.M. = 0.95	(67)
[Pd ₂ (DPPA) ₂ (PPh ₃) ₄]	Yellow	267(d)	IR, vis., NMR	(261)
[Pd(dPe) ₂ S ₄]	Brown	234	—	(73)
[Pd(dPm) ₂]Br ₂	Yellow	314(d)	—	(67, 259)
[Pd(dPm) ₂]Br ₂ ·2H ₂ O	Orange	105	—	(67, 259)
[Pd(PEE)Cl ₂]	White	350	—	(67, 259)
[Pd(PEE) ₂]Br ₂	White	240	—	(67, 259)
[Pd(dPe)Cl ₂]	Yellow	>360	μ = 0.1, IR	(168, 259)
[Pd(dPe)Br ₂]	Yellow	—	μ = 0.2, IR	(168, 259)
[Pd(dPe)I ₂]	Brown	—	μ = 0.3	(168, 259)
[Pd(dPe)(SCN) ₂]	White	—	μ = 0.3, IR	(168, 259)
[Pd(dPe) ₂]Cl ₂	White	291	—	(259)
[Pd(dPe) ₂]Br ₂	White	248	—	(67, 259)
[Pd(dPe) ₂]I ₂	Yellow	283	—	(259)
[Pd(dPe) ₂](NO ₃) ₂	White	283(d)	—	(67, 259)
[Pd(dPe) ₂](ClO ₄) ₂	White	330(d)	—	(259)
[Pd(VPP)Cl ₂]	Cream	280	Vis.	(84)
[Pd(VPP)Br ₂]	Yellow	300	Vis.	(84)

(continued)

TABLE XII—*continued*

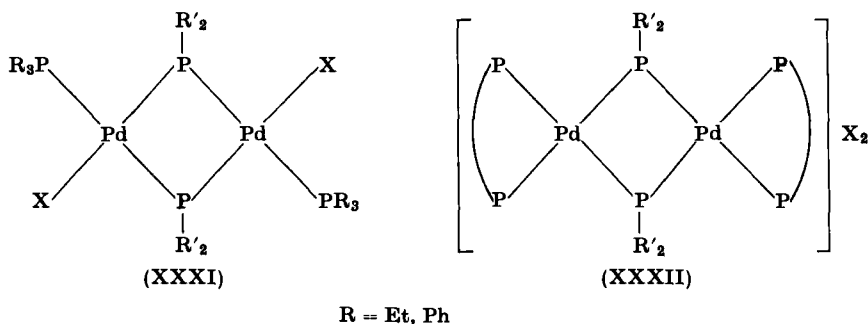
Compound	Color	M.p.(°C)	Properties	Ref.
[Pd(VPP)I ₂]	Orange-yellow	300	Vis.	(84)
[Pd(VPP)(CNS) ₂]	Pink	260	IR, vis.	(84)
[Pd(dme)Me ₂]	Colorless	125(d)	—	(32)
[Pd(dPe)MeBr]	Cream	142(d)	—	(32)
[Pd(dPe)Me ₂]	—	167	—	(42)
[Pd ₂ (DPPA) ₂ Cl ₄]	—	264	—	(47)
[Pd ₂ (DPPA) ₂ (SCN) ₄]	Orange	>300	IR	(47)
[Pd(CyP-P)Cl ₂]	Yellow	>330	—	(182)
[Pd(PP-P) ₂ Cl ₂]	Yellow	270	μ = 0	(182)
[Pd(BPEP)Br ₂]	Yellow	246	—	(9)
[Pd(ffos)Cl ₂]	Yellow	320	—	(99)
[Pd(DMBP) ₂][PdBr ₄]	Buff	200–300	—	(164)
[Pd(DMBP)Br ₂]	Orange-brown	148	—	(164)
[Pd(4MePEE)Br ₂]	Cream	>300	—	(141)
[(dPe)Pd(PPh ₂) ₂ Pd(dPe)]Cl ₂	Orange	174	—	(144)
[(dPe)Pd(PPh ₂) ₂ Pd(dPe)]I ₂	Red	182	—	(144)
[(dPe)Pd(PPh ₂) ₂ Pd(dPe)](NO ₃) ₂	Orange	203	—	(144)
[(dPe)Pd(PPh ₂) ₂ Pd(dPe)](ClO ₄) ₂	Orange	281	—	(144)
[(dPe)Pd(PPh ₂) ₂ Pd(dPe)](BPh ₄) ₂	Red	167	—	(144)
[(dPe)Pd(PEt ₂) ₂ Pd(dPe)](ClO ₄) ₂	Yellow	332	—	(148)
[(dPe)Pd(PEt ₂) ₂ Pd(dPe)](BPh ₄) ₂	Yellow	168	—	(148)
[Pt(dPm) ₂]	Yellow	>300	—	(74)
[Pt(PEE) ₂]	Red-orange	248(d)	—	(74)
[Pt(dPe) ₂]	Yellow	253	—	(74)
[Pt ₂ (DPPA) ₂ (PPh ₃) ₄]	Yellow	226(d)	IR, vis., NMR	(261)
[Pt(dPe) ₂ S ₄]	Orange	282	—	(73)

[Pt(dPm)Cl ₂]	Colorless	340(d)	—	(32)
[Pt(dme)Me ₂]	Colorless	143	—	(32)
[Pt(dee)Cl ₂]	Colorless	289	—	(32, 76)
[Pt(dee)Me ₂]	Colorless	75	D.M. = 6.7	(76, 77)
[Pt(dee)Ph ₂]	Colorless	212(d)	D.M. = 8.4	(77)
[Pt(dPe)Cl ₂]	Light yellow	360(d)	$\mu = 0.3$, IR	(32, 168, 259)
[Pt(dPe)Br ₂]	Light yellow	—	$\mu = 0.4$, IR	(32, 168, 259)
[Pt(dPe)I ₂]	Brown	—	$\mu = 0.3$	(32, 168, 259)
[Pt(dPe)Me ₂]	Colorless	219	D.M. = 6.7, IR	(32)
[Pt(dPe) ₂]Cl ₂	—	270	—	(259)
[Pt(dPe) ₂]Br ₂	—	308	—	(259)
[Pt(dPe) ₂](NO ₃) ₂	—	310(d)	—	(259)
[Pt(dPe) ₂](ClO ₄) ₂	—	367	—	(259)
<i>cis</i> -[PtHCl(dPe)]	—	143	IR	(89)
[Pt(dPe)(PEt ₃)Me]Cl·C ₆ H ₆	—	174	IR, NMR	(165)
[Pt(dPe)(PEt ₃)Et]Cl	—	140	IR, NMR	(165)
[Pt(dPe)(PEt ₃)Ph]Cl·C ₆ H ₆	—	145	IR, NMR	(165)
[PtH(dPe)(SiCl ₃)]	—	>330	IR	(61)
[Pt(dPe)(SiCl ₃) ₂]	—	>330	—	(61)
[Pt(dPe)(SiHPh ₂) ₂]	—	223(d)	IR	(61)
[Pt(dPe)(SiMePh ₂) ₂]	White	206	IR	(61)
[Pt(dPe)(GeMe ₃)Cl]	Yellow	224(d)	IR, NMR	(165)
[Pt(dPe)(GeMe ₃) ₂]	—	—	D.M. = 8.85	(35)
[PtH(dPe)(GeMe ₃)]	—	222(d)	IR	(35)
[Pt(ffos)Cl ₂]	Light brown	335	—	(99)
[Pt ₂ (DPPB) ₂ Cl ₄]	White	208	—	(193)
[Pt ₂ (DPPA) ₂ Cl ₄]	White	312	—	(47)
[Pt ₂ (DPPA) ₂ Br ₄]	Yellow	298(d)	—	(47)
[Pt ₂ (DPPA) ₂ I ₄]	—	277(d)	—	(47)

diphos = VPP, PPPhen, $X = \text{Cl, Br, I, NCS}$ (84, 182). Infrared results indicate that in $[\text{Pd}(\text{VPP})(\text{CNS})_2]$ there is an *N*- and an *S*-bonded thiocyanate group (84), and an X-ray structure has also confirmed this type of isomerism in $[\text{Pd}(\text{dPe})(\text{NCS})(\text{SCN})]$ (24).

The unusual diphosphine dne reacts with K_2PdBr_4 to form $[\text{Pd}(\text{dne})\text{Br}_2]$ in ethanol, and from solutions of DMBP and K_2PdBr_4 , is precipitated $[\text{Pd}(\text{DMBP})_2][\text{PdBr}_4]$; $[\text{Pd}(\text{DMBP})\text{Br}_2]$ can be obtained from the filtrate (164). $[\text{Pd}(\text{BPEP})\text{Br}_2]$ is a normal planar complex, unlike the nickel(II) analog (*q.v.*) (9).

Hayter (144) and Hayter and Humiec (148), found that the phosphido-bridged complexes (XXXI) reacted with dPe to form the unusual



complexes (XXXII). The structure (XXXII) was shown to be present by conductivity measurements which indicated a 1:2 electrolyte, and hence ruled out larger cations such as $[\text{Pd}_3(\text{dPe})_3(\text{PPh}_2)_3]^{3+}$. Clark *et al.* isolated the chloro-bridged complex $[\text{M}_2(\text{dPe})_2\text{Cl}_2](\text{BF}_4)_2$ ($\text{M} = \text{Pd, Pt}$) (85).

The ligands DPPA and DPPB form complexes $[\text{X}_2\text{M}(\text{diphos})_2\text{MX}_2]$ with two bridging diphosphines (47, 193). It was suggested that $\text{Pd}_2(\text{DPPA})_2(\text{SCN})_4$, obtained from KNCS and the chloro complex, contained both *N*- and *S*-bonded thiocyanate groups (47).

Platinum and palladium alkyls and aryls have been obtained by reaction of $[\text{M}(\text{diphos})\text{Cl}_2]$ with alkyl- or aryllithiums or Grignard reagents (32, 42, 76, 77).

Hooton obtained $[\text{Pt}(\text{dPe})(\text{PEt}_3)\text{R}]\text{Cl}$ ($\text{R} = \text{Me, Et, Ph}$). On heating the ethyl compound loses ethylene, but the other two lose PEt_3 . The Pt-C bonds are cleaved by iodine and HCl to $[\text{Pt}(\text{dPe})\text{I}_2]$ and $[\text{Pt}(\text{dPe})(\text{PEt}_3)\text{Cl}]\text{Cl}$, respectively (165). Interesting compounds are those formed by $\text{C}_{10}\text{H}_{12}\text{OMe}$ - (dicyclopentadienemethoxide)- $[\text{M}(\text{C}_{10}\text{H}_{12}\text{OMe})(\text{dPe})]\text{X}$ ($\text{M} = \text{Pd, Pt, X} = \text{Cl, Br}$). The organic ligand is bonded to the metal by a σ and a π bond (256).

Several hydrido complexes of platinum are known. *cis*-[PtHCl(dPe)], the first *cis*-hydridohalide of platinum, is formed by the hydrogenolysis of [Pt(dPe)(SiMe₃)Cl]. The IR spectrum exhibits a band at 2002 cm⁻¹, ν (Pt-H) (89). [PtH(dPe)(PEt₃)]Cl is formed by the hydrogenolysis of [Pt(dPe)(PEt₃)(GeMe₃)Cl] (126), or from *trans*-[PtHCl(PEt₃)₂] and dPe (135). In the latter reaction [H(PEt₃)₂Pt(dPe)Pt(PEt₃)₂H] is also obtained. Related complexes are [Pt(dPe)(PEt₃)Cl]Y (Y = Cl, SnCl₃) (135).

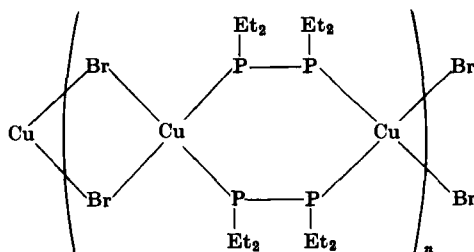
Platinum-silicon complexes have been obtained by Chatt *et al.* (61, 62). [Pt(dPe)₂] reacts with SiHCl₃, SiH₂Ph₂, and (XC₆H₄)₃SiH to form complexes such as [PtH(SiCl₃)(dPe)], [Pt(SiCl₃)₂(dPe)], and [Pt(HSiPh₂)₂(dPe)]. One equivalent of bromine reacts with [Pt(SiHPh₂)₂(dPe)] to form [Pt(SiBrPh₂)₂(dPe)], but excess bromine cleaves the Pt-Si bond. MePh₂SiLi reacts with [Pt(dPe)Cl₂] to form [Pt(MePh₂Si)₂(dPe)].

Some platinum-germanium complexes have been studied by Glockling *et al.* (35, 126). For example, [Pt(dPe)(PEt₃)(GeMe₃)Cl] is formed from [Pt(Et₃P)₂(GeMe₃)Cl] and dPe, and [Pt(dPe)(GeMe₃)₂] from [Pt(PEt₃)₂(GeMe₃)₂]. [Pt(dPe)(GeMe₃)Cl] is formed on heating [Pt(dPe)(PEt₃)(GeMe₃)Cl] (165). The platinum-germyl complexes have recently been reviewed (125).

I. GROUP IB (Cu, Ag, AND Au)

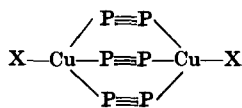
The reaction of CuI in saturated KI solution with dee, under nitrogen, produced colorless [Cu(dee)₂][Cu(dee)I₂], a 1:1 electrolyte in nitrobenzene (264). [Cu(dPe)Cl]₃, [Cu(dPe)I]₃, and Cu(dPe)BH₄ have been isolated (44). Isslieb and Hohlfeld obtained [Cu(dCyp)Br] from CuBr and dCyp in toluene. dCyf forms (CuBr)₂dCyf under similar conditions, while the intermediate ligand dCyb produces both [Cu(dCyb)Br] and (CuBr)₂dCyb (176). The 1:1 complexes contain three-coordinate copper, but the structure of the 2:1 complexes is uncertain. Colorless, diamagnetic compounds [Cu(PP-P)Cl] (182), [Cu(EP-P)Br] (139), (CuCl)₂(CyP-P), and (CuBr)₂(CyP-P) (182) have been reported. CuBr(EP-P) has structure (XXXIII), which contains alternate halogen and diphosphine bridges (139). The piperidinodiphosphine complexes of Cu(I) are reasonably stable—[Cu(diphos)Br] and (CuBr)₂(diphos) when diphos is NP-P (245) and NNP-P (243), respectively—but (CuBr)₂(NNPP-P) (244) is less stable.

A series of complexes (CuX)₂(DPPA)₃ (X = Cl, Br, I, NO₃, NCS, BH₄) has been prepared by reaction of the copper(II) salts with DPPA in ethanol (48) or by metathesis from {Cu(NO₃)₂}(DPPA) (X = I, BH₄).



(XXXIII)

All are colorless or white and melt with decomposition. A binuclear diphosphine-bridged structure (XXXIV) has been proposed. A number



(XXXIV)

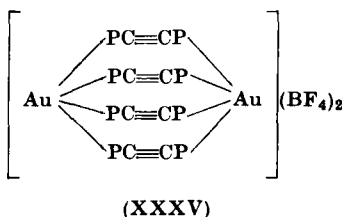
of organocopper complexes containing dPm and dPe have been prepared (43).

With chelating diphosphines silver forms complexes of the type $[\text{Ag}(\text{diphos})_2][\text{AgX}_2]$ and, less frequently, $[\text{Ag}(\text{diphos})_2]\text{X}$. Davis and Mann obtained a mixture on shaking 4Me-PEE with AgI and aqueous KI. Ethanol extraction and subsequent evaporation yielded $\text{Ag}(4\text{Me-PEE})_2\text{I}$ as colorless crystals (108). The ethanol-insoluble residue, recrystallized from DMF, gave $[\text{Ag}(4\text{Me-PEE})_2][\text{AgI}_2]$. With dee, only the diiodoargentate(I) was obtained, $[\text{Ag}(\text{dee})_2][\text{AgI}_2]$ (264).

The ligand DPPA, which cannot chelate, gave rise to three types of complex. The complexes $[\text{AgX}(\text{DPPA})]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}, \text{NO}_3$) are obtained from AgNO_3 and DPPA in ethanol, and the subsequent metathesis yields halo and pseudohalo complexes (10). Two polymeric structures have been proposed: either three-coordinate silver with monodentate nitrate groups or four-coordinate silver with bridging bidentate nitrate groups. The compounds $\text{AgX}(\text{DPPA})_2$ have been prepared for $\text{X} = \text{BF}_4$ or PF_6 . The only representative of the third type of complex is $(\text{AgCl})_2(\text{DPPA})_3$, produced by reaction of $(\text{AgNO}_3)-(\text{DPPA})$, NaCl, and DPPA in ethanol.

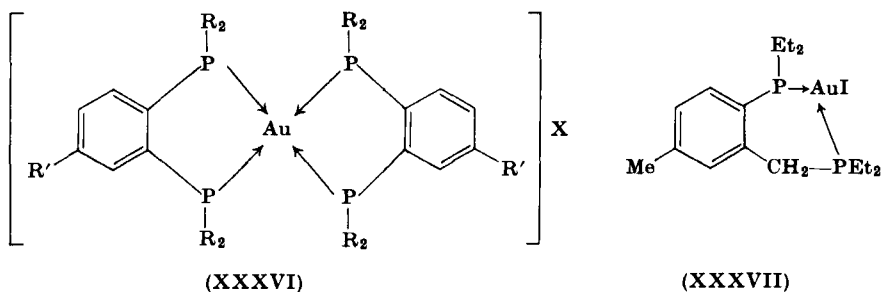
The diphosphines NP-P and NNPP-P formed $(\text{AgI})_2(\text{diphos})$; these are much more stable complexes than those of these same ligands with Cd and Zn, and resemble those of Cu(I) (243, 245). Colorless $(\text{AgI})_2-(\text{NNPP-P})$ forms from NNPP-P and AgI in benzene (244).

Carty and Efraty (48) isolated three types of gold(I) complexes with DPPA: (a) $(\text{AuX})_2(\text{DPPA})$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}$); (b) $(\text{AuX})_2(\text{DPPA})_3$ ($\text{X} = \text{I}, \text{SCN}$); and (c) $(\text{AuX})_2(\text{DPPA})_4$ ($\text{X} = \text{BF}_4, \text{PF}_6$). Type (a) was obtained from AuX_4^- and DPPA in ethanol ($\text{X} = \text{Cl}, \text{Br}$) or by metathesis from the chloride ($\text{X} = \text{I}, \text{SCN}$) and they are thought to have a linear structure with a bridging DPPA ligand. In the case of the iodide and thiocyanate it is possible to add a further two ligands to produce type (b) complexes. Reaction of $(\text{AuX})_2(\text{DPPA})$, DPPA, and the appropriate anion in ethanol produced type (c) complexes. The structure suggested was (XXXV), although a polymeric structure is also possible.



In none of the complexes was there any evidence for coordination of the triple bond. A compound $(\text{AuCl})_2(\text{DPPB})$ has recently been obtained as yellow crystals (193).

Davis and Mann obtained a number of gold(I) complexes with unsymmetrically substituted, chelating diphosphines, and attempted to resolve them into optically active forms using optically active anions (108). In no case was any resolution observed. The complexes were obtained by reacting HAuCl_4 with the diphosphine in ethanol to form the chloride, from which other complexes could be obtained by metathesis.



Mostly, complexes $[\text{Au}(\text{diphos})_2]\text{X}$ (XXXVI) were obtained (see Table XIII), but (2-diethylphosphino-4-methylbenzyl)diethylphosphine, even in excess, gave only the 1:1 adducts (XXXVII) (108).

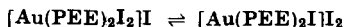
The complexes $[\text{ClAu}(\text{HMP})\text{AuCl}]$ and $[\text{Au}(4\text{-MePEE})_2]\text{I}$ decompose on heating *in vacuo* to give the pure diphosphine (141, 164).

TABLE XIII
DIPHOSPHINE COMPLEXES OF GOLD

Compound	Color	M.p.(°C)	Properties	Ref.
$[(\text{AuCl})_2\text{DPPA}]$	White	266(d)	IR, Raman	(48)
$[(\text{AuI})_2\text{DPPA}]$	White	267(d)	IR, Raman	(48)
$[(\text{AuI})_2(\text{DPPA})_3]$	White	218	IR, Raman	(48)
$(\text{AuBF}_4)_2(\text{DPPA})_4$	White	246	IR, Raman	(48)
$[(\text{AuCl})_2\text{HMP}]$	Yellow	—	—	(164)
$[(\text{AuCl})_2\text{BPPP}]$	White	287(d)	—	(83)
$[(\text{AuCl})_2\text{BPEP}]$	Yellow	292	—	(9)
$[(\text{AuCl})_2\text{dPe}]$	White	291	IR	(44)
$[\text{Au}(\text{dPe})_2]\text{Cl}$	—	245	—	(44)
$[\text{Au}_6(\text{dPe})_2\text{Cl}]\text{Cl} \cdot 2\text{H}_2\text{O}$	Brown	202	IR	(44)
$[\text{Au}_6(\text{dPe})_2\text{Cl}]\text{ClO}_4$	Red-brown	218	IR	(44)
$[\text{Au}_6(\text{dPe})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}]_n$	Red-violet	210	IR	(44)
$[\text{Au}_6(\text{dPe})_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$	Green	210	IR	(44)
$[\text{Au}_6(\text{dPe})_3](\text{ClO}_4)_2$	Green	245	IR	(44)
$[\text{Au}(\text{PEP})_2]\text{I}$	Yellow	278	—	(108)
$[\text{Au}(\text{PEE})_2]\text{Cl}$	Colorless	317	—	(108)
$[\text{Au}(\text{PEE})_2]\text{Br}$	Colorless	251	—	(108)
$[\text{Au}(\text{PEE})_2]\text{I}$	Colorless	266	—	(108)
$[\text{Au}(4\text{Me-PEE})_2]\text{I}$	Colorless	240	—	(48, 108)
$[\text{Au}(4\text{P-PEE})_2]\text{I}$	Yellow	314(d)	—	(107)
$[\text{Au}(4\text{Me-PEE})_2]\text{NO}_3 \cdot 2\text{H}_2\text{O}$	Colorless	244	—	(108)
$[\text{Au}(\text{PEE})_2]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$	Colorless	162	—	(108)
$\text{Au}(\text{PEE})_2\text{Br}_3 \cdot 2\text{H}_2\text{O}$	Green-yellow	154	—	(108)
$\text{Au}(\text{PEE})_2\text{I}_3$	Yellow-orange	180	—	(108)
$[\text{Au}(\text{PEE})_2\text{I}](\text{ClO}_4)_2$	Yellow	191	—	(108)
$[\text{Au}(4\text{Me-PEE})_2]\text{I}_3$	—	110	—	(108)

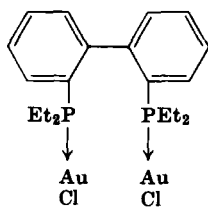
Davis and Mann also prepared a number of Au(III) complexes of PEE. HAuCl_4 reacts with two equivalents of PEE to form $[\text{Au}(\text{PEE})_2]\text{-Cl}_3$ (108). Boiling this complex in ethanol for 30 minutes the Au(I) complex is formed. The bromo and iodo complexes can be obtained from the Au(III) chloro complex and LiX, or from the Au(I) complex and free halogen. The compound $\text{Au}(\text{PEE})_2\text{I}_3$ is especially interesting. In hot, 60% perchloric acid, yellow $[\text{Au}(\text{PEE})_2\text{I}](\text{ClO}_4)_2$ is produced, whereas with sodium picrate in ethanol $[\text{Au}(\text{PEE})_2](\text{pic})_3$ is obtained. The $[\text{Au}(\text{PEE})_2\text{I}](\text{ClO}_4)_2$ complex is a 1:2 electrolyte in nitrobenzene, but

$\text{Au}(\text{PEE})_2\text{I}_3$ is intermediate between a 1:1 and 1:2 electrolyte, which suggests an equilibrium of the kind

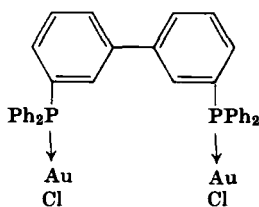


The triiodide probably exists as $[\text{Au}(\text{PEE})_2]\text{I}_3$ in ethanol, since the tri-picrate can be obtained.

With dPe Malatesta obtained some cluster complexes of gold. These were of three types: ionic, brown $[\text{Au}_6(\text{dPe})_2\text{X}]\text{Y}$; polymeric, red $[\text{Au}_6(\text{dPe})_2\text{X}_2]_n$; and ionic, green $[\text{Au}_6(\text{dPe})_3]\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}$; $\text{Y} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}, \text{ClO}_4, \text{PF}_6$) (45). $(\text{AuCl})_2(\text{dPe})$ was obtained as white crystals from HAuCl_4 and dPe in ethanol, and contains a bridging diphosphine. It is possible to prepare $[\text{Au}(\text{dPe})_2]\text{Cl}$ by varying the conditions. Reaction of $[\text{Au}(\text{dPe})_2]\text{Cl}$ with NaBH_4 produced the red-brown cluster $\text{Au}_6(\text{dPe})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ compound, in which the gold has an average oxidation number of one-third. Strongly nucleophilic ions replace both chlorides, but anions of low nucleophilicity replace only one, e.g., with perchlorate the 1:1 electrolyte $[\text{Au}_6(\text{dPe})_2\text{Cl}]\text{ClO}_4$ is obtained. The compounds $\text{Au}_6(\text{dPe})_2\text{X}_2 \cdot 2\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}$) isomerize in CH_2Cl_2 solution to form red-brown polymers, which will react with dPe to yield green complexes $[\text{Au}_6(\text{dPe})_3]\text{X}_2 \cdot \text{H}_2\text{O}$. The fact that $\text{Au}_6(\text{dPe})_2\text{Cl}_2$ only loses one Cl^- with ClO_4^- indicates the nonequivalence of these chlorines. There is IR evidence for a bridging chlorine, and thus the structures of $[\text{Au}_6(\text{dPe})_2\text{Cl}]\text{Y}$ appear to be two clusters of three gold atoms, bridged by two dPe ligands and one chlorine. In the polymeric compounds $[\text{Au}_6(\text{dPe})_2\text{X}_2]_n$ both X groups are probably involved in bridging.



(XXXVIII)



(XXXIX)

The compound $[\text{IAu}(\text{dee})\text{AuI}]$ was obtained from AuI , NaI , and dee in ethanol. The white product is oxidized to black $\text{I}_3\text{Au}(\text{dee})\text{AuI}_3$ by iodine in chloroform (264). Two interesting complexes containing bridging diphosphines are (XXXVIII) (164) and (XXXIX) (83).

J. GROUP IIB (Zn, Cd, AND Hg)

Few diphosphine complexes of zinc and cadmium have been reported. $M(dPe)X_2$ ($M = Zn, Cd$) crystallized on mixing the appropriate halide with dPe in ethanol or ethanol/propanol. Apart from melting point and $\nu(M-X)$ nothing is known about them. Presumably they have a pseudotetrahedral structure (90). Wymore and Bailar obtained $Zn(dee)Br_2$ and $(CdBr_2)_3(dee)_2$ from MBr_2 and dee (264). The latter complex dissolves in DMF and $Cd(dee)Br_2$ is precipitated by addition of water. $Cd(dee)Br_2$ reacts with $CdBr_2$ in DMF to reform $(CdBr_2)_3(dee)_2$. Zinc did not form an analogous complex (264). Seidel obtained 1:1 complexes from MI_2 ($M = Zn, Cd$) and $NNP-P$ and from CdI_2 and $NP-P$, but these are rather unstable complexes (243, 245). With $NNPP-P$ and MI_2 even less stable complexes are formed (244). Unlike mercury, zinc and cadmium do not react with DPPA (10).




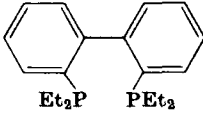
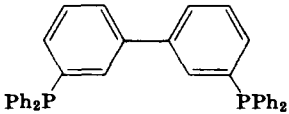
Mercuric halides HgX_2 ($X = Cl, Br, I$) form colorless, insoluble complexes with DPPA (10). The triple bond is not coordinated. Seidel obtained cream $Hg(NNP-P)I_2$, but with $NP-P$ the HgI_2 cleaved the P-P bond (243). Yellow $Hg(ffos)Cl_2$ has been prepared (99).

Wymore and Bailar found that $HgBr_2$ reacted with dee to form $Hg(dee)Br_2$ (264). The reactions of mercury(II) halides with dPe were studied by Coates and Ridley (90), and have also been investigated by Sandhu *et al.* (239). The latter workers also prepared dPb complexes. Complexes isolated were $Hg(diphos)X_2$ and $(HgX_2)_2(diphos)$; $(HgI_2)_2(dPe)$ could not be obtained (239). All are white, are insoluble in all common solvents, and are nonelectrolytes in a nitrobenzene suspension. White $(C_6F_5)_2Hg(dPe)$ forms from $(C_6F_5)_2Hg$ and dPe in benzene/hexane (53).

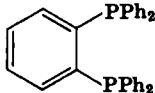
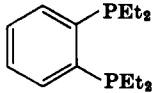
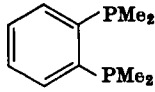
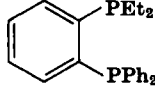
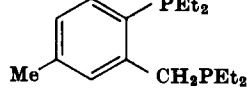
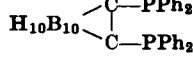
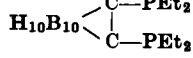
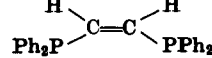
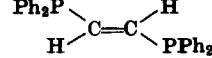
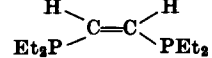
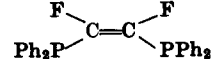
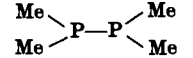
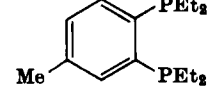
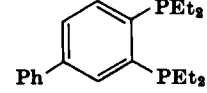
VII. Appendix: Ligand Abbreviations

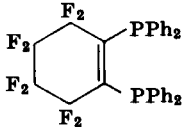
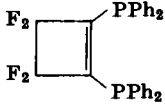
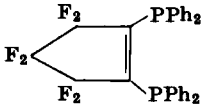
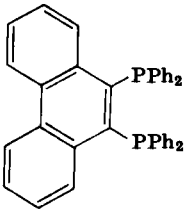
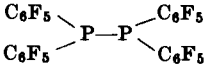
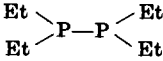
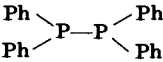
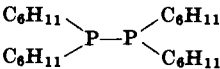
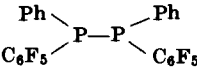
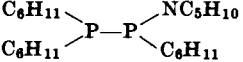
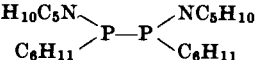
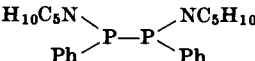
A. DITERTIARY PHOSPHINES

The system of abbreviations is a simple one, name y, *di(substituent-phosphino)backbone*. For example, bis(diphenylphosphino)ethane is dPe. Aryl substituents on the phosphorus atom are represented by capital letters (e.g., phenyl = P), alkyl substituents by lower-case letters (e.g., methyl = m). The references refer to the preparations of the ligands.

Compound	Abbrev.	Ref.
$(C_6H_{11})_2PCH_2P(C_6H_{11})_2$	dCym	(180)
$Ph_2PCH_2PPh_2$	dPm	(152, 180)
$Me_2PC_2H_4PMe_2$	dme	(68)
$Et_2PC_2H_4PEt_2$	dee	(64, 152, 263)
$Ph_2PC_2H_4PPh_2$	dPe	(64, 180)
$(C_6H_{11})_2PC_2H_4P(C_6H_{11})_2$	dCye	(180)
$(PhCH_2)_2PC_2H_4P(CH_2Ph)_2$	dBze	(164)
$(NCC_2H_4)_2PC_2H_4P(C_2H_4CN)_2$	dne	(130)
$(F_3C)_2PC_2H_4P(CF_3)_2$	dmre	(37, 129)
$(F_3C)_2PC_2F_4P(CF_3)_2$	dmref	(129)
$Et_2PC_4H_8PEt_2$	deb	(180)
$Ph_2PC_4H_8PPh_2$	dPb	(166, 180, 237)
$(C_6H_{11})_2PC_4H_8P(C_6H_{11})_2$	dCyb	(180)
$Et_2PC_5H_{10}PEt_2$	def	(180)
$Ph_2PC_5H_{10}PPh_2$	dPf	(166, 180, 237)
$(C_6H_{11})_2PC_5H_{10}P(C_6H_{11})_2$	dCyf	(180)
$Et_2PC_6H_{12}PEt_2$	deh	(180)
$Ph_2PC_6H_{12}PPh_2$	dPh	(166, 180, 237)
$(C_6H_{11})_2PC_6H_{12}P(C_6H_{11})_2$	dCyh	(180)
$Et_2PC_3H_6PEt_2$	dep	(180)
$Ph_2PC_3H_6PPh_2$	dPp	(166, 180, 237)
$(C_6H_{11})_2PC_3H_6P(C_6H_{11})_2$	dCyp	(180)
$(NCC_2H_4)_2PC_3H_6P(C_2H_4CN)_2$	dnp	(130)
	HMP	(164)
PhP  PPh	DMPP	(164)
$PhCH_2P$  PCH_2Ph	DMBP	(164)
	BPEP	(8)
	BPPP	(83)
$Ph_2PC\equiv CPh_2$	DPPA	(142)
$Ph_2PCH_2C\equiv CCH_2PPh_2$	DPPB	(193)
$Et_2PC\equiv CPEt_2$	DEEA	(64)
$Ph_2PCH_2OCH_2PPh_2$	POP	(6)
$Ph_2PC_2H_4OC_2H_4PPh_2$	POPO	(237)

(continued)

Compound	Abbrev.	Ref.
	PPP	(140)
	PEE	(140)
	PMM	(140)
	PEP	(140)
	BzEE	(107)
	dPC	(7)
	deC	(230)
	VPP	(5)
	TVPP	(5)
	VPE	(65)
	V _F PP	(84)
	MP-P	(37, 202, 223)
	4-MePEE	(107, 141)
	4-PPEE	(107, 141)

Compound	Abbrev.	Ref.
	f ₈ fos	(100)
	ffos	(98)
	f ₆ fos	(103)
	PPPhen	(84)
	P _t P-P	(11)
	EP-P	(152, 202)
	PP-P	(79, 249)
	CyP-P	(183)
	P _t PP-P	(117)
	NP-P	(243-245)
	NNP-P	(243-245)
	NNPP-P	(243-245)

B. DISECONDARY PHOSPHINES

Quite a number of these have been prepared, but very few have been used in complexation reactions. The following examples serve to illustrate the type of abbreviation used in the text.

Compound	Abbrev.	Ref.
PhP(H)C ₂ H ₄ P(H)Ph	dP _{se}	(172-174, 177, 179, 184)
EtP(H)C ₂ H ₄ P(H)Et	de _{se}	
(C ₆ H ₁₁)P(H)C ₄ H ₈ P(H)(C ₆ H ₁₁)	dCy _{sb}	

C. DIPRIMARY PHOSPHINES

Compound	Abbrev.	Ref.
H ₂ PC ₂ H ₄ PH ₂	dHe	(204)

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BERYLLIUM HALIDES AND PSEUDOHALIDES

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I. Introduction

The recent interest in the chemistry of beryllium and its compounds perhaps stems from its wide applications currently being developed, having moved from the nuclear power orientation, prevalent in 1961, to one which now explores aerospace and instrument applications. Beryllium possesses a generous supply of unique chemical and physical properties. It and the beryllides have great scientific and practical interest owing to the low neutron capture cross section of beryllium, their high melting points, relatively low specific gravities, hardness, high strengths at high temperature (ten times that of ceramics) and resistance to corrosion, these properties making them useful in aviation, rocket,

and nuclear technology. This area of beryllium chemistry has recently been reviewed (127, 413, 416, 461), as also has the beryllium oxide system (55, 99, 127). Several articles (25, 29, 31, 142, 347, 498) cover various aspects of the organic chemistry of beryllium, and two books (122, 139) contain sections devoted to this topic. While Russian work on beryllium fluoride and the fluoroberyllates has been reviewed up to 1959 (330), these and the other halides have only been the subject, in recent years, of sections in Everest's book (139), covering many aspects of beryllium chemistry, and in a book devoted almost entirely to the analytical chemistry of beryllium (333). This present review deals with all the major aspects of the halide and pseudohalide chemistry of beryllium; the literature has been covered up to the middle of 1970. Beryllium fluorides and chlorides are important industrially, as intermediates in the preparations of metallic beryllium. Beryllium chloride has also been used in diagnosing tuberculosis; sodium beryllium fluoride has been used in the manufacture of glass having high ultraviolet permeability, as a flux in certain porcelain enamels, and in coating special welding rods.

Beryllium is normally divalent in its compounds, the first ionization potential ($\text{Be}^0 \rightarrow \text{Be}^+$) being 9.32 eV, the second ($\text{Be}^+ \rightarrow \text{Be}^{2+}$), 18.21 eV, and its standard electrode potential $E_{\text{Be}^{2+}/\text{Be}}^\ominus$, -1.70 volts. Although the atomic radius of beryllium is 0.93 Å, its ionic radius is only 0.31 Å; because of its high ionic potential of 6.45 (cf. 1.05 for the sodium ion), beryllium has a tendency to form covalent rather than ionic compounds. The ability of the group II elements to form complex ions is greatest with beryllium and thus it resembles aluminum in its chemistry rather than magnesium. Using the Pauling relationship, the percentage ionic character of the Be-X bond (where X = F, Cl, Br, I) is 80, 42, 35, and 25%, respectively (264). Thus the fluoride has considerable ionic character and forms no stable complexes with neutral ligands (L) of the type L_xBeF_2 , but forms many stable anionic fluoride complexes. In contrast, the other three halides behave as though they are essentially covalent and form numerous stable complexes with neutral ligands. The Be-F bond is thermodynamically stable in aqueous solution because the bond energy is greater than that of Be-O, whereas the Be-X (X = Cl, Br, I) bond energies are less than for Be-O, hence thermodynamic instability. Because of these differences, beryllium fluoride is discussed separately from the other three halides.

Compounds containing beryllium-halogen bonds are extremely sensitive to moisture. Thus, some difficulty in handling these compounds exists and it is perhaps for this reason that variable melting points have been reported for some compounds and the authenticity of some compounds must be in doubt.

II. Beryllium Fluorides

A. ANHYDROUS BERYLLIUM FLUORIDE

1. Preparation

Beryllium fluoride cannot be isolated from aqueous solution since as for the other halides, hydrolysis takes place during dehydration with the formation of a thick syrupy liquid which continues to hydrolyze with the elimination of HF. A spongy mass of an oxyfluoride of indefinite composition is finally produced (46, 221, 276). The process discovered by Lebeau (272) as early as 1898, involving the thermal decomposition of ammonium tetrafluoroberyllate, is used most widely for the production of the anhydrous fluoride. Although decomposition takes place slowly at 125°,* in practice it is normally carried out at 900°–1100°, glassy BeF₂ being produced (422). The fluoride may also be obtained from Be(OH)₂ and HF (4, 272) or from NH₄HF₂ and BeO, Be(OH)₂, or basic beryllium acetate (2, 237, 314, 315, 390, 518). Fluorination of BeO with F₂ or ClF₃ gives poor results (221). The fluorination of beryllium sheet with F₂ follows a parabolic rate law and a protective coating of BeF₂ is produced (357); however, the equipment problem involved in the fluorination of BeO with HF makes this process unattractive (3, 221, 237). The product obtained from the digestion of BeO in 40% HF is low in fluorine content (221), further confirming that hydrolysis of BeF₂ readily takes place.

Sublimation at 1038° of BeF₂ at 1 mm pressure in the presence of 2% beryllium metal has been used for purification on a small scale, but this has not been so effective in large-scale preparations [experiments undertaken by the Brush Beryllium Co., quoted in (313)].

2. Properties and Polymorphism

Much of the work on beryllium fluoride has been carried out by the Russians Novoselova and co-workers in Moscow, and Toropov and Grebenshchikov in Leningrad.

Beryllium fluoride is a hygroscopic solid (276) existing in several crystalline forms and has low conductivity in the fused state (269, 324), indicating that although more ionic in nature than the other halides, it still has considerable covalent character. Addition of alkali metal fluorides produces conducting materials which on electrolysis yield beryllium metal (269, 536). It oxidizes when heated in an oxygen current,

* Temperatures are in °C except where otherwise stated.

forming the volatile compound $2\text{BeO} \cdot 5\text{BeF}_2$, and with water vapor, BeO and HF are formed; the pyrohydrolysis commences at 420° with a maximum reaction rate at 800° – 1000° (363). Though slightly soluble in absolute ethanol, it is very soluble in ethanol–water solutions of high water content, but the solution process is slow (276). Further, it is only sparingly soluble in liquid HF (225), indicating that BeF_2 is a stronger base in HF than is $\text{Be}(\text{OH})_2$ in water.

A variety of melting points have been ascribed to BeF_2 , $542^\circ \pm 3^\circ$ (185), $543^\circ \pm 5^\circ$ (408), 545° (87, 112, 447), 821° (341), ca. 800° (337, 446), 590° (337), 545° – 550° (324), 555° (503); boiling point, 1327° (238). The most recently quoted value of 555° (503) was obtained using very pure distilled BeF_2 and the melting behavior was confirmed by several methods. An inflection (341, 446) in the vapor pressure/temperature curve at ca. 800° was believed to be due to fusion of BeF_2 , since it had earlier been noted that although BeF_2 softens at about 560° , it does not become free-flowing until ca. 800° (87, 334, 350). It has since been suggested that this inflection is indicative of depolymerization of BeF_2 to form a free-flowing liquid and that the true melting temperature is 555° (503).

The vapor pressure (vp) of BeF_2 has been measured by the flow (185, 341, 446, 447), torsion (185, 210), gravimetric (185), and manometric methods and by a differential variant of the Knudsen method (53, 239); the available data are somewhat discordant. At 627° , the vp is 0.0155 (53), 0.013 (239), and 0.019 mm (210); at 827° , 3.3 (447), 3.45 (446), ca. 5.0 (185), and 3.7 mm (341); and the partial pressure of Be_2F_4 in equilibrium with liquid beryllium fluoride at 627° is 8.8×10^{-6} mm (53). The constants in the vapor pressure equation $\log p_{\text{mm}} = A - B/T$ (T in $^\circ$ abs.) for BeF_2 are shown in Table I and for Be_2F_4 in the range 617° – 704° , $A = 11.532$, $B = 14927$ (53).

The composition of the vapor has been determined qualitatively by mass spectrometry (53, 58, 210). Associated molecules are only minor constituents of the saturated vapor and the ion of highest molecular weight Be_2F_3^+ , found in low abundance, indicates the presence of Be_2F_4 molecules. The saturated vapor at molecular effusion pressures has been estimated to contain less than 1 mole % Be_2F_4 (210).

The "model principle" has been used by Goldschmidt (180) to compare members of an isomorphous series in which structures are of the same type, even though the charge on corresponding ions or the ionic radii or both, are different. A common type of "model structure" is that in which the radii and polarizing properties of the ions in one structure are nearly the same as those in the second, but the charges on the ions in the two structures are not the same. The structure having the lower

TABLE I

VAPOR PRESSURE DATA FOR BeF_2 $\log p_{\text{mm}} = A - B/T$ (T in $^\circ\text{abs.}$)

A	B	Temperature range ($^\circ\text{C}$)	Ref.
11.596	12134	573–676	(239)
10.466	10943	802–1025	(447)
11.822	12385	740–803	(446)
10.651	11121	803–968	(446)
10.622	11189	542–704	(53)
11.125	11555	547–667	(210)
13.041	13762	767–821	(341)
9.904	10268	821–1002	(341)

charges is referred to as the weakened model and the other the reinforced model. As the fluoride ion has a radius nearly identical with that of the oxide ion but one-half the charge and similarly for the Be^{2+} and Si^{4+} ions, beryllium fluoride and silica, the fluoroberyllates and silicates show remarkable structural similarities. Beryllium fluoride thus behaves as a weakened model of silica, as demonstrated by the lower melting point, solubility, and hardness, and greater reactivity relative to SiO_2 . Likewise, the fluoroberyllates behave as weakened models of the silicates, provided that the cations have similar ionic radii and polarizability and that the charge numbers on the cation in the fluoroberyllate is one-half that on the cation in the silicate; e.g., the NaF-BeF_2 system behaves as a weakened model of the CaO-SiO_2 system. The weakened character of the beryllium systems is due to the smaller electrostatic attractions resulting from the lower charge numbers of the ions relative to those in the silicate systems.

Like both silica and germania, BeF_2 has a radius ratio of about 0.3, a figure which Goldschmidt (180) believes will allow compounds of the AX_2 type to form glasses. Beryllium fluoride like silica has a tendency to supercool and is difficult to crystallize; rapid cooling of the melt produces vitreous BeF_2 (for further discussion, see Section II, C).

Silica exists in three crystalline forms: quartz (stable to 870°), tridymite (stable from 870° – 1470°), and cristobalite (stable from 1470° to the melting point 1710°). Each of the polymorphic forms exists in two subsidiary forms, low (α) and high (β) temperature modifications with transition points at 573° for quartz, 120° – 160° for tridymite, and 200° – 275° for cristobalite. The structure of silica consists of a three-dimensional network of SiO_4 tetrahedra, joined so that each oxygen is common

to two tetrahedra. The relationship between cristobalite and tridymite corresponds to that between zinc blende and wurtzite, although neither has a close-packed structure. In quartz, the tetrahedra are so linked that they acquire a spiral formation and this form is optically active. In each case, the α and β forms differ only by slight alteration in the disposition of the SiO_4 tetrahedra, and there is no difference in the way the tetrahedra are linked together. These alterations are thus easy to effect and are readily reversible.

By analogy with silica, the structures of the three crystalline forms of BeF_2 are presumably composed of BeF_4 tetrahedra. The quartz- and cristobalite-like polymorphs are well established and there is evidence for low and high temperature modifications. Our present knowledge of the stability ranges and transition points of the different forms leaves something to be desired, partly since the BeF_2 system is more difficult to study than the SiO_2 system owing to the sensitivity of the fluoride to moisture. Conversions between the crystalline forms are sluggish since they require bond rupture, followed by rearrangement, before the re-linking of the BeF_4 units; such processes in the solid state are always slow. Russian workers, whose results up to 1959 are summarized in ref. (330), consider that the β -quartz form is the stable form at room temperature (corresponding to the α -quartz form of SiO_2) and this is transformed into the α -quartz form at ca. 220° (334, 409). The α -quartz form when slowly heated is transformed at 420° – 450° into what is possibly a tridymite form. At ca. 680° , this phase is converted to the α -cristobalite form of BeF_2 (corresponding to the β -cristobalite form of SiO_2), the β -to α -transformation of the cristobalite forms occurring at 130° (334). Decomposition of $(\text{NH}_4)_2\text{BeF}_4$ *in vacuo* below 450° produces the cristobalite modification (89, 94), which is also obtained by crystallization from glasses of high BeF_2 content at temperatures of 450° or lower and is converted into the quartz form by heating to high temperature (410). The quartz form is also obtained if $(\text{NH}_4)_2\text{BeF}_4$ is decomposed in a quartz crucible or when the decomposing mixture is fused toward the completion of the removal of NH_4F (334). The cristobalite form is partly inverted to the quartz form in 3 weeks at 340° or 430° , but persists in cristobalite form at 516° or above (408). The high temperature quartz form exists in equilibrium with liquid in binary fluoride systems up to the melting point of BeF_2 , and the cristobalite form appears to have a metastable existence (409). During a study of the kinetics of the fluorination of beryllium sheet, it was noted that the α -quartz form is produced below 525° , but above this temperature the film has the rhombic tridymite structure (357). Further evidence for the existence of the tridymite form was obtained by heating BeF_2 in the presence of 4% ZrF_4 to 590° – 600°

for several hours, and powder data indicate a close analogy between this and the tridymite form of SiO_2 (253). The quartz form of BeF_2 is hexagonal (350) and the cristobalite form has a tetragonal unit cell (89), like the low temperature form of cristobalite SiO_2 . At 130° , this is transformed into a cubic structure, corresponding to the high temperature form of cristobalite SiO_2 (240).

In view of the above inconsistencies, the beryllium fluoride system requires further investigation before firm conclusions concerning the stability relations of the different crystalline forms can be safely drawn.

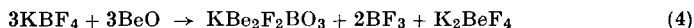
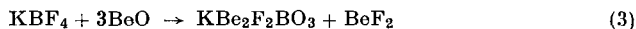
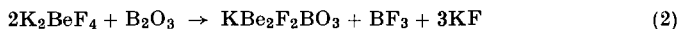
3. Reactions

In contrast to the other halides, complexes of beryllium fluoride with only one neutral ligand, namely, ammonia, are known. In 1927 Biltz and Rahlfs (68) obtained at -78.5° BeF_2NH_3 which decomposed at higher temperatures. The BeF_2 used in this preparation was probably contaminated with oxyfluoride as it was obtained from aqueous solution. However, BeF_2 prepared by a more reliable method, though sparingly soluble in liquid ammonia, forms the complex $\text{BeF}_2\cdot 2\text{NH}_3$, formulated as $[\text{Be}(\text{NH}_3)_4]^{2+}[\text{BeF}_4]^{2-}$ from spectroscopic data. Thermal decomposition proceeds at lower temperature than for the adduct of the corresponding chloride, but is not accompanied by appreciable ammonolysis. The first ammonia molecule is lost at 80° – 130° and the second at 130° – 150° (191).

Heating BeF_2 with B_2O_3 (40) produces Be_2FBO_3 , isostructural with



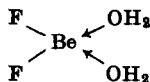
the mineral hambergite Be_2OHBO_3 , whose structure (560) consists of BO_3 triangles and deformed BeO_4 tetrahedra involving three oxygen atoms and an OH group. The OH groups are bonded only to two beryllium atoms, while each of the oxygens surrounding a boron atom also belongs to two BeO_4 tetrahedra. Fusion of K_2BeF_4 with B_2O_3 at 600° – 800° or KBF_4 and BeO at 550° – 700° produces the water-insoluble double salt $\text{KBe}_2\text{F}_2\text{BO}_3$ (40).



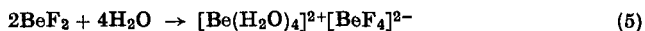
The solubility of BeF_2 in methanol increases with increasing HF concentration. At 25.15% HF, a solid phase, formulated as $[\text{MeOH}_2]^+[\text{BeF}_3]^-$, is obtained (107), but this compound has not been studied in detail. The complex molecule Be_2OF_2 has been identified by mass spectrometry in the BeO – BeF_2 system above 1327° (137).

B. AQUEOUS CHEMISTRY OF BERYLLIUM FLUORIDE

The anhydrous fluoride is hygroscopic and very soluble in water (cf. SiO_2). Solutions of beryllium fluoride may also be obtained by dissolving the metal in hydrofluoric acid; the dissolution rate decreases linearly with decreasing acid concentration (199). Evaporation of these solutions leads to the elimination of HF with consequent formation of basic residues (276). The limiting solubility is ca. 18 moles/liter at 25° corresponding to a ratio of 2 moles of water per mole of BeF_2 , hence the suggestion for the formation of the complex



in *saturated* solution (256, 276). The existence of this complex is also supported by ^9Be magnetic resonance studies of *saturated* aqueous solutions of BeF_2 ; solutions at saturation are clear and viscous (276). Since aqueous solutions do not form a precipitate with calcium chloride, the low concentration of F^- in solution is demonstrated (ionization of BeF_2 in 1 and $2 \times 10^{-4} M$ solutions has been estimated as 2 and 6%, respectively (276)). On addition of BaCl_2 solution, 50% of the beryllium is precipitated as BaBeF_4 and, thus, autocomplex formation is believed to take place in aqueous solution (32). However, ^{19}F NMR spectroscopy

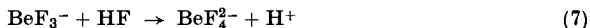
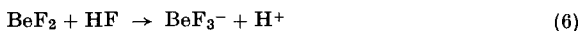


indicates that *dilute* solutions containing fluoride and beryllium in the ratio 2:1 contain BeF^+ and BeF_3^- , as well as the predominant (60%) species BeF_2 (108), all presumably solvated. Conductivity and emf data also support the presence of such species in *dilute* solutions of BeF_2 (389). Addition of ethylenediamine or triethanolamine to beryllium fluoride solutions precipitates beryllium hydroxide, leaving solutions from which the tetrafluoroberyllates $(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_3)_2\text{BeF}_4$ or $[\text{HN}(\text{CH}_2\text{CH}_2\text{OH})_3]_2\text{BeF}_4$ may be isolated (32). Passage of a beryllium fluoride solution through a hydrogen ion-exchange column produces a solution containing fluoroberyllic acid, H_2BeF_4 (32).

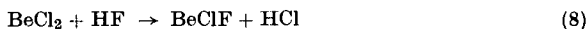
Beryllium fluoride (276), in contrast to the chloride (32, 200), is a weak electrolyte in aqueous solution. Although all the aforementioned species are probably present in equilibrium in aqueous solutions of beryllium fluoride, if the autocomplex predominates, the weak electrolytic nature suggests the existence of hydrogen bonds between $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ and $[\text{BeF}_4]^{2-}$ ions (32).

Conductometric measurements on $\text{NH}_4\text{F}/\text{BeSO}_4$ solutions have indicated the presence of the ions $[\text{BeF}_3]^-$, $[\text{BeF}_4]^{2-}$, $[\text{BeF}_5]^{3-}$, and $[\text{BeF}_6]^{4-}$ (390). Not surprisingly, later workers (443) have been unable to find evidence for the existence of these last two ions. The species $[\text{BeF}]^+$, BeF_2 , $[\text{BeF}_3]^-$, and BeF_4^{2-} are present in solutions containing both beryllium and fluoride and the relative concentration of the ions depends on the F:Be ratio and on the pH (443, 490); these ions are probably hydrated, e.g., $[\text{BeF}(\text{H}_2\text{O})_3]^+$ (489) and $[\text{BeF}_3\text{H}_2\text{O}]^-$ (140). The particularly stable ion $[\text{BeF}_4]^{2-}$ is produced in the presence of excess fluoride (396) and evidence that the beryllium is present in the form of the complex anion has been obtained from the failure of $\text{Be}(\text{OH})_2$ to precipitate on the addition of ammonia and by the concentration of beryllium at the anode on electrolysis (414). The formation of the stable tetrafluoroberyllates accounts for the ability of beryllium salts to solubilize sparingly soluble fluorides, e.g., Ca and Li, and to demask reaction systems which are masked by fluoride (367, 492). No stable entity containing BeF^+ has yet been isolated.

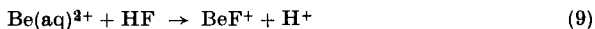
The pH of a solution of HF increases in the presence of BeF_2 due to the formation of the fluoroberyllate ions (488). However, the pH of



an HF solution of beryllium chloride is lower than that of beryllium fluoride of the same concentration and the plot of pH against the ratio of HF to BeCl_2 shows a distinct bend at an HF: BeCl_2 ratio of 1:1 corresponding to either



or



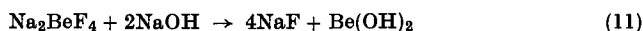
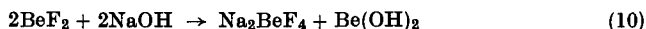
Stepwise formation constants (k) together with their method of determination for the beryllium-fluoride species are shown in Table II. Recent results obtained by measurements of the redox potential in the $\text{Fe}^{3+}/\text{Fe}^{2+}$ - $\text{Be}^{2+}/\text{F}^-$ system and of the pH in the $[\text{BeF}_4]^{2-}$ - H^+ system at ionic strength 0.5 (106) and by a potentiometric method using a lanthanum fluoride solid state electrode (297) show substantial agreement. No evidence has been found for the presence of polynuclear species in solution, nor of species of composition $[\text{Be}_x\text{F}_y(\text{OH})_z]^{(2x-y-z)+}$ (297). By a distribution procedure, the consecutive reaction constants K_n , defined as $[\text{BeF}_n][\text{H}^+]/[\text{BeF}_{n-1}][\text{HF}]$, have been determined: $\log K_1 = 1.99$, $\log K_2 = 1.12$, $\log K_3 = 0.32$ (198).

TABLE II
STEPWISE FORMATION CONSTANTS FOR BERYLLIUM SPECIES

$\log k_1$ (BeF ⁺)	Ref.	$\log k_2$ (BeF ₂)	Ref.	$\log k_3$ (BeF ₃ ⁻)	Ref.	$\log k_4$ (BeF ₄ ²⁻)	Ref.
3.64 ^d	(386)	2.29 ^d	(386)	1.83 ^d	(386)	1.1 ^f	(140)
4.29 ^a	(489)	2.40 ^a	(493)	2.788 ^c	(297)	1.426 ^c	(297)
4.71 ^c	(106)	3.61 ^c	(106)	2.80 ^c	(106)	1.86 ^d	(386)
4.90 ^c	(297)	3.762 ^c	(297)	2.97 ^c	(70)	1.99 ^e	(243)
5.06 ^c	(70)	3.78 ^c	(70)	3.56 ^e	(243)	2.27 ^c	(106)
5.40 ^b	(23)	4.94 ^e	(243)				
5.64 ^a	(493)						
5.89 ^b	(243)						

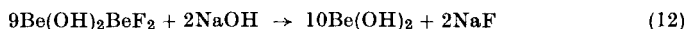
^a Solubility.^b Spectrophotometrically.^c Potentiometrically.^d Ion exchange.^e Calculated.^f NMR.

Beryllium fluoride dissociates only slightly in solution (243, 276, 488, 489, 490, 493) and not surprisingly behaves differently from other beryllium salts in solution. Hydrolysis in the BeF₂-NaOH system proceeds in two stages:



The formation of Na₂BeF₄ was confirmed by chemical analysis (441, 444). This work invalidates Prytz's comments that the addition of NaOH lowers the solubility of BeF₂, but does not precipitate Be(OH)₂ (388, 389). When the hydrolysis is carried out with carbonate or bicarbonate solutions, basic beryllium carbonates appear to be formed (443). Novoselova (329) has shown that Be(OH)₂, containing variable amounts of fluoride, begins to precipitate with NaOH from 0.1 *M* beryllium fluoride solution at pH 6 and is complete at pH 11.6–11.9 after 1.8 equivalents of alkali have been added, whereas precipitation from Na₂BeF₄ and (NH₄)₂BeF₄ begins only at pH 7.5–8.0. Precipitation of Be(OH)₂ from solutions of the fluoride takes place at higher pH than from solutions of other salts such as the chloride and sulfate (329). For sulfate solutions, precipitate begins to form at *n*(= NaOH : Be) > 1, but with dilute BeF₂ solutions, hydroxide appears at *n* = 0.2. At *n* = 1, 50%

of the beryllium is precipitated and as with the sulfate, precipitation is complete at $n = 1.8$. This suggests that at $n < 0.2$, the soluble basic salt $\text{Be}(\text{OH})_x\text{F}_{2-x}$ is formed and from $n = 0.2$ – 1.8 , the insoluble basic salt $9\text{Be}(\text{OH})_2\text{BeF}_2$ is formed, and then with further addition of NaOH , a reaction occurs in the solid phase. This reaction is slightly reversible and



a slight excess of NaOH is necessary for complete formation of $\text{Be}(\text{OH})_2$, which dissolves to form beryllate as more NaOH is added. When an excess of fluoride is present in solution, much more than two equivalents of NaOH are necessary for complete precipitation (491). If a stoichiometric amount of ammonia is added to a BeF_2 solution, only 65% of the beryllium is precipitated. Complete precipitation of beryllium, even by 30% excess of NH_4OH , can only be attained if the $\text{F}:\text{Be}$ ratio is at most 2. When this ratio is greater than 2, the amount of hydroxide precipitated decreases and when the $\text{F}:\text{Be}$ ratio in the initial mixture is 6, no hydroxide is deposited. The quantity of beryllium precipitated by NH_4OH depends not only on the relative proportions of beryllium and fluoride in solution, but also on the absolute fluoride concentration (329, 451).

C. BERYLLIUM FLUORIDE AND FLUOROBERYLLATE GLASSES

From X-ray diffraction studies (547), satisfactory agreement has been obtained between calculated and experimental scattering curves on the assumption of a random network structure for vitreous BeF_2 in which each beryllium is tetrahedrally surrounded by four fluorines and each fluorine in turn, is bonded to two beryllium atoms. Such a three-dimensional network is analogous to those found for vitreous silica and germania. Beryllium hydride is also amorphous (27, 204) and it doubtless consists of a three-dimensional network similar to that of vitreous BeF_2 , although in the case of the hydride, the bonding is likely to be electron-deficient in nature. Infrared spectroscopic measurements indicate the weakened structure of glassy BeF_2 relative to SiO_2 (562). The formation of halide glasses is uncommon and Zachariassen (559) has discussed the criteria for glass formation and Turnbull and Cohen (513) have explained, on the basis of kinetic considerations, the failure of some pure liquids to crystallize. The latter workers have shown that for a free-flowing liquid, free of nucleating singularities, crystallization will not take place if the kinetic barrier to nucleation exceeds, in the case of BeF_2 , 48 $\text{kcal} \cdot \text{mole}^{-1}$. In a network liquid, interatomic bonding must be ruptured for flow to occur and in this case, the free energy of activation, estimated

from viscosity data is ca. $50 \text{ kcal} \cdot \text{mole}^{-1}$; thus glass formation is easily explained (513). The network structure is further supported by the high specific resistance and viscosity and the magnitude of the corresponding energies of activation of the liquid. Liquid BeF_2 , like liquid SiO_2 and GeO_2 , is highly associated, even at elevated temperatures. At a temperature 200° above the melting point, the energy of activation for viscous flow (E_z) is greater than the heat of vaporization. The extrapolated viscosity at the melting point is at least 10^6 poise and the extrapolated E_z at least $100 \text{ kcal} \cdot \text{mole}^{-1}$ (278). For most metal halides, at temperatures not far above the melting point, the viscosity is of the order 10^{-2} poise and E_z seldom exceeds $10 \text{ kcal} \cdot \text{mole}^{-1}$ (201). The specific resistance is many orders of magnitude smaller than for most ionic halides (278) and this further demonstrates the structural differences between BeF_2 and the other halides. The low conductivity is somewhat surprising in view of the high ionic character of the Be-F bond.

Addition of alkali metal fluorides to molten BeF_2 causes a reduction in the viscosity, due to breaking of fluoride bridges, and therefore the degree of polymerization decreases. The stoichiometric end point for this process is at the composition M_2BeF_4 (284). There is also a corresponding increase in the electrical conductivity due to breaking down the network structure which also accounts for the positive enthalpies of mixing in $\text{LiF}-\text{BeF}_2$ mixtures (216).

On long standing in air, beryllium fluoride glasses become covered with a thin, cloudy film, as also do glasses containing only KF and BeF_2 , but the addition of bivalent metal fluorides remarkably decreases the hygroscopicity of the glasses (42, 224). Whereas the $\text{BaF}_2-\text{BeF}_2$ system is characterized by an immediate crystallization of all its melts, the other alkaline earth fluoride systems show a tendency to form homogeneous glasses in the concentration range 0–30% for CaF_2 and MgF_2 and 0–10% for SrF_2 (538).

The fluoride glasses have a wide range of transmission without absorption (408), but contamination with BeO makes the glasses turbid (537). Beryllium fluoride is nontransparent for short wavelengths 30–220 $\text{m}\mu$; with an increase in the wavelength the transparence of the glasses increases. Glass samples with a complex composition BeF_2-KF , $\text{BeF}_2-\text{KF}-\text{AlF}_3$, $\text{BeF}_2-\text{KF}-\text{MF}_2$ ($\text{M} = \text{Mg}, \text{Ca}, \text{Sr}, \text{or Ba}$), and $\text{BeF}_2-\text{KF}-\text{CaF}_2-\text{MgF}_2$ are transparent for all the wavelength regions mentioned. In the infrared, glassy BeF_2 is characterized by a region of transparency up to 5.5μ , but is nontransparent from 5.5 to 15μ (42). Fluoride glasses have low refractive indices, commonly lower than that of water (1.33), e.g., BeF_2 1.2747 (378), and the index increases for $\text{MF}-\text{BeF}_2$ glasses along the series $\text{Na} < \text{Li} < \text{K} < \text{Rb}$ (224, 537). Although

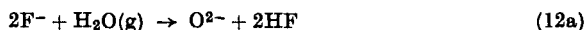
BeF_2 is structurally and crystal chemically a complete analog of SiO_2 , glasses on its basis have a higher percentage of ionic bonds than in silicate glasses and show a greater degree of ordering on solidification. In spectra of fluoroberyllate glasses, activated with rare-earths, more detailed resolution than for silicate glasses, similarly activated, may be the result of a more even ionic matrix or lower crystalline field strengths. The use of a beryllium fluoride glass matrix shows up a higher luminescence level (5D_1), owing to the higher optical clarity and low dissipation of light on irradiation (564, 565). The ESR spectra of some transition metal ions in fluoroberyllate glasses have been recorded (1).

D. ANHYDROUS FLUORBERYLLATES

In the early work, great emphasis was given to general comparisons of fluoride and silicate systems, with principal interest in the structures of the intermediate compounds, rather than to precise determination of liquid-solid phase transitions, i.e., interest centered around the relationship of the fluoroberyllate systems to the silicate systems. As mentioned earlier, the fluoroberyllates and silicates show structural similarities, although there is considerable difference in melting points and hardness. The tetrafluoroberyllates (BeF_4^{2-}), analogous to the orthosilicates (SiO_4^{4-}), are the most stable fluoroberyllates, but neither sheet nor framework models are known. Beryllium fluorides cannot be handled in silica containers and special techniques and container materials are required for handling these materials (216, 240); under an SiF_4 pressure, attack on silica by beryllium fluorides is considerably reduced (26).

For use in thermal breeder reactors, materials must satisfy stringent requirements with respect to their nuclear, physical, and chemical properties (192). Consequently, choice of useful solvents for fissile and fertile species is restricted to a very small number of inorganic fluorides of which $^7\text{LiF}-\text{BeF}_2$ mixtures provide chemically stable fluids with excellent physical properties, low viscosity, vapor pressure, cross section, and melting temperature, and this system has gained preeminence as a solvent for fissile and fertile materials in the development of the molten salt reactor (MSRE) in the United States (503). The $\text{LiF}-\text{BeF}_2$ system has attracted the attention of many workers, but the results are diverse with respect to the liquidus, the existence of intermediate compounds formed by the components, and the polymorphism exhibited by the crystalline phases. Utilization of this as an ingredient in the MSRE has necessitated a restudy of this system and Thoma *et al.* (503) have published an excellent article on this system. Their phase results are shown in Fig. 1. The diversity in this system has been attributed to

metastable nucleation or to exposure of the solutions to water vapor which causes hydrolysis.



The solubility of BeO in the melt is low (ca. 200 ppm) in the range 30–50 mole % BeF₂ at 600°–700° and the solubility increases with increasing BeF₂ content, but does not exceed 500 ppm (212, 450). The reverse reaction, in which oxide impurities are removed from the melt by

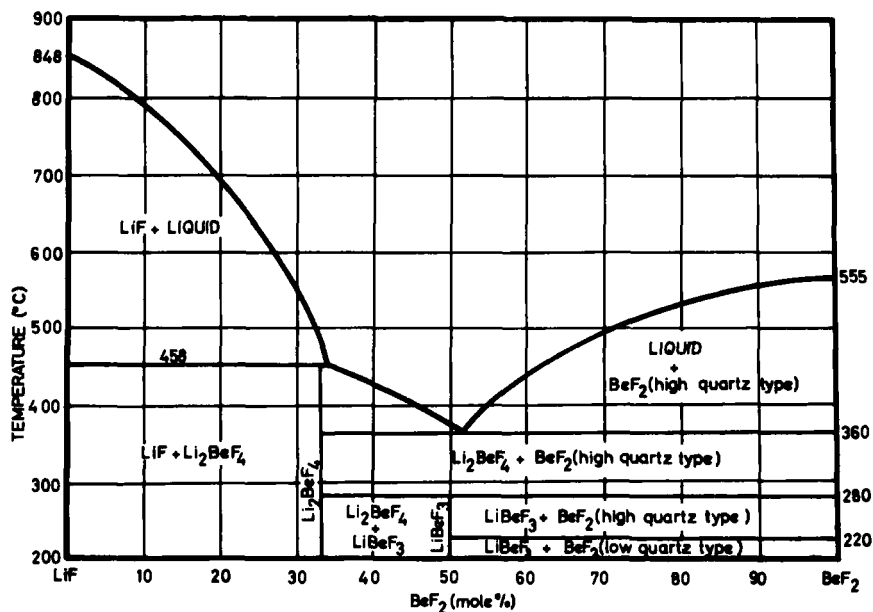


FIG. 1. The LiF-BeF₂ system [from (503), reproduced with permission].

sparging with HF, has been used as a standard purification treatment (448).

Early claims (348, 350, 500) for the existence of Li₃BeF₅, Li₃Be₂F₇, Li₄BeF₆, and Li₅BeF₇ have not been substantiated and only Li₂BeF₄, LiBeF₃, and possibly LiBe₂F₅ exist (410, 503). The trifluoroberyllate, m.p. 365° (500), is related to the pyroxene group (silicates in which SiO₄ tetrahedra share two corners to form long chains). Reports (348, 350) that Li₂BeF₄ exists in three polymorphic forms have not been corroborated, nor does it melt congruently [(410), cf. (408, 500)]. At 455°, a single crystal decomposes to a slurry of LiF and a liquid which coexist for the next 15°–20°; then above ca. 480°, the crystals dissolve in the

melt, and the sequence is reversed on cooling (503). The $\text{LiF}-\text{BeF}_2$ system has been likened to the $\text{MgO}-\text{SiO}_2$ (500) and $\text{ZnO}-\text{SiO}_2$ (408) systems. Although Li_2BeF_4 was believed to resemble the silicates phenacite (Be_2SiO_4) (197, 348, 410, 558), willemite (Zn_2SiO_4) (197, 408, 410, 558), and forsterite (Mg_2SiO_4) (408, 410), diffraction work clearly shows that the structure of Li_2BeF_4 is isotypic with that of Be_2SiO_4 (105). The structure (Fig. 2) consists of a chain of Li_2BeF_4 molecules, each metal ion being coordinated to four fluoride ions and these tetrahedra all share their corners to form a three-dimensional network (105). The average Be-F bond length is 1.55 Å, similar to the value of 1.57 Å found in $\text{Li}_6\text{BeF}_4\text{ZrF}_8$ (423). Owing to the difference in the Li-F and Be-F bond lengths, the tetrahedra are slightly distorted. The beryllium-containing ions BeF^+ , BeF_2^+ , Be_2F_3^+ , and LiBeF_2^+ have been observed

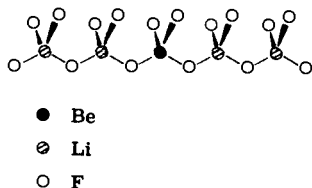
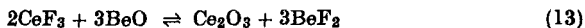


FIG. 2. Chain of tetrahedra along the C-axis of Li_2BeF_4 [from (105) reproduced with permission].

in the mass spectrum of an equimolar $\text{LiF}-\text{BeF}_2$ mixture; the binding energy of LiF to BeF_2 at ca. 630° is approximately $53 \text{ kcal} \cdot \text{mole}^{-1}$ (58).

Molten mixtures of UF_4 and ThF_4 , together with fluorides of alkali metals and BeF_2 or ZrF_4 , are potential fuels for a fluid-fueled nuclear reactor that can operate at high temperature in low pressure systems (504, 549), and certain molten fluoride mixtures are of value in the reprocessing of spent and therefore highly reactive elements for nuclear reactors (39). In connection with the utilization of such materials, equilibrium diagrams for the individual components and the binary and ternary mixtures have been obtained. In the $\text{BeF}_2\text{-MF}_4$ ($\text{M} = \text{Zr}, \text{Th}, \text{U}$) systems, compound formation has not been detected (233, 503, 548); eutectic points occur at 2 mole % ThF_4 and 0.5 mole % UF_4 , indicating the comparatively low solubility of BeF_2 in melts of these fluorides (233, 548) and the solubility of PuF_3 in fused alkali metal fluoride- BeF_2 mixtures is also quite low (38). Molten mixtures of BeF_2 and ThF_4 containing more than ca. 75% BeF_2 become very viscous at temperatures near the liquidus and equilibrium is reached only slowly, but the addition of small amounts of alkali metal fluorides reduces the viscosity, such

that equilibrium is attained more rapidly (504). The phase boundaries for the $\text{LiF}-\text{BeF}_2-\text{MF}_4$ ($\text{M} = \text{Th}, \text{U}$) systems have been determined; no evidence has been obtained for the formation of ternary compounds (504, 506) and in the $\text{NaF}-\text{BeF}_2-\text{MF}_4$ ($\text{M} = \text{Th}, \text{U}$) systems, the incongruently melting compounds $\text{NaFBeF}_2\text{MF}_4$ exist (505). The addition of BeO to fluoride melts causes precipitation of certain of the components as oxides, e.g., Pa , U , and Ce . Such reactions are of interest as a means of removing



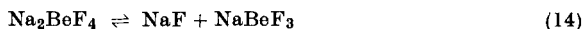
reactor poisons from molten fluoride fuels, although BeO is an undesirable impurity. In fluoride melts, the order of affinity for oxygen is $\text{UO}_2 \sim \text{ThO}_2 > \text{BeO} > 1$. Thus it is possible to remove uranium from fluoride melts by passing it down a BeO column, where UO_2 is precipitated and held on the column; use of 30 gm of BeO per kg of molten salt ($\text{LiF}-\text{BeF}_2-\text{ThF}_4$) reduces the uranium in solution from 1800 ppm to less than 1 ppm (449).

The present version of a molten salt reactor (279) operates with a mixture of ${}^7\text{LiF}-\text{BeF}_2-\text{ZrF}_4$ as solvent and diluent for ${}^{235}\text{UF}_4$. Successful operation of this reactor, development of chemical reprocessing methods, and specification of safety practices dictate the need for accurate and detailed knowledge concerning crystallization and phase behavior in the ${}^7\text{LiF}-\text{BeF}_2-\text{ZrF}_4$ and ${}^7\text{LiF}-\text{BeF}_2-\text{ZrF}_4-{}^{235}\text{UF}_4$ mixtures. In the former system (503, 506), in which the electrochemical oxidation of U(IV) has been studied (281), the complex compounds Li_2BeF_4 , Li_2ZrF_6 , Li_3ZrF_7 , $\text{Li}_3\text{Zr}_4\text{F}_{19}$, and $\text{Li}_6\text{BeF}_4\text{ZrF}_8$ exist. The crystalline ternary compound, $\text{Li}_6\text{BeF}_4\text{ZrF}_8$, stable at room temperature, exhibits a property, uncommon among complex fluorides, in that the unit cell contains two discrete anion groupings, a tetrafluoroberyllate and an octafluorozirconate ion (423). These discrete ions are connected by a shared lithium ion and the lithium ions share fluoride ligands in such a way as to achieve a set of fluorine neighbors, best described as distorted octahedral. The $\text{Be}-\text{F}$ distance is 1.57 Å and in the ZrF_6^{4-} dodecahedra, there are two independent $\text{Zr}-\text{F}$ bonds (2.05 and 2.16 Å) (423). This complex compound melts semicongruently at 470° and undergoes no polymorphic transitions. In the subsystem $\text{Li}_2\text{ZrF}_6-\text{BeF}_2-\text{ZrF}_4$, the existence of three-component liquid immiscibility, not previously described in fluoride systems, has been observed (503).

The salts NaBeF_3 , Na_2BeF_4 , NaBe_2F_5 , Na_3BeF_5 , and $\text{Na}_3\text{Be}_2\text{F}_7$ are believed to exist in the $\text{NaF}-\text{BeF}_2$ system (337, 338), which has been likened to the $\text{CaO}-\text{SiO}_2$ system (197, 409, 502), but the existence of NaBe_2F_5 has not been verified (408). There is little agreement about the melting behavior of these compounds (337, 338, 502). Only two modifica-

tions of NaBeF_3 have been identified, one having a structure similar to wollastonite ($\beta\text{-CaSiO}_3$) (348, 408) below 343° , with only a slight difference in structure above that temperature (409). The existence of several structural modifications of Na_2BeF_4 has been established (195, 228, 321, 349, 354, 409, 501, 502, 509, 563), but Thilo and co-workers (228, 501) prepared Na_2BeF_4 in HF solution and their product was doubtlessly contaminated with fluorosilicates, and indeed $2\text{Na}_2\text{BeF}_4 \cdot \text{Na}_2\text{SiF}_6$ has since been obtained from which SiF_4 is eliminated at 540° to form Na_3BeF_5 (499). The basic structure for Na_2BeF_4 consists of a two-layer close-packed array of fluorine atoms, in which half the octahedral holes are taken by sodium atoms and a quarter of the tetrahedral holes by beryllium atoms (195). Na_2BeF_4 reacts with SiO_2 at ca. 730° forming phenacite (332); in the $\text{NaF}\text{--}\text{Na}_2\text{BeF}_4\text{--}\text{Na}_3\text{ZrF}_7$ system, only simple eutectics are present (110).

The partial pressure of BeF_2 and NaF above Na_2BeF_4 , in the range $1008^\circ\text{--}1197^\circ$ is given by $\log p_{\text{mm}} = 8.6881 - 10939/T$ for BeF_2 and $\log p_{\text{mm}} = 8.4370 - 10623/T$ (T in $^\circ\text{Abs.}$) for NaF , i.e., over the range studied, Na_2BeF_4 dissociates in the melt (341) only to an insignificant degree according to



Vapors above $\text{NaF}\text{--}\text{BeF}_2$ contain the complex molecule $(\text{NaBeF}_3)_2$, as well as NaF and BeF_2 . The enthalpy of dissociation of the dimer is $51.1 \pm 5 \text{ kcal} \cdot \text{mole}^{-1}$ and the standard heat and free energy of dissociation at 811° for the gas phase reaction $\text{NaBeF}_3 \rightarrow \text{NaF} + \text{BeF}_2$ are 63.1 ± 4 and $32.4 \pm 2 \text{ kcal} \cdot \text{mole}^{-1}$, respectively (54, 447, 457).

When equimolar melts of Na_2BeF_4 and Li_2BeF_4 are allowed to cool slowly, LiF starts to crystallize at 460° , and below 320° $\text{Na}_2\text{LiBe}_2\text{F}_7$ is formed. When a similar mixture is rapidly cooled from $550^\circ\text{--}600^\circ$ to below 240° , NaLiBeF_4 is formed (226) existing in a single modification and melting at 350° (512). The structure of $\text{Na}_2\text{LiBe}_2\text{F}_7$, which may also be obtained by heating NaLiBeF_4 above 240° or from $\text{NaF}\text{--}\text{LiF}\text{--}\text{BeF}_2$ (226, 408), is similar to that of the melilite hardystonite, $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ (408). Also present in the $\text{Na}_2\text{BeF}_4\text{--}\text{Li}_2\text{BeF}_4$ system is $\text{Na}_3\text{Li}(\text{BeF}_4)_2$, isotypic with merwinite, $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$ (227, 512).

The existence of compounds MBeF_3 , M_2BeF_4 , MBe_2F_5 [$\text{M} = \text{K}$ (87, 336), Rb (182, 223, 322, 509, 510, 511), Cs (91, 92)], and M_3BeF_5 [$\text{M} = \text{K}$ (87, 336), Cs (91, 92)] have been established in the $\text{MF}\text{--}\text{BeF}_2$ systems, some existing in several polymorphic modifications. Potassium tetrafluoroberyllate is isotypic with K_2SO_4 and Be_2SiO_4 , having four molecules in the unit cell (355). The same basic structure persists for K_2BeF_4 , Rb_2BeF_4 , and Cs_2BeF_4 as for Na_2BeF_4 , all similar to larnite, $\gamma\text{-Ca}_2\text{SiO}_4$,

and olivine, (Fe, Mg)SiO₄, but slight deviations are found as the cation size increases (10, 164, 195, 321). The tendency for bond formation between the cation and the fluorine valence orbitals increases as the cation size increases, accounting for the rising thermal stability of the tetrafluoroberyllates with increasing size of the cation (10). The Be-F distances in the alkali tetrafluoroberyllates are ca. 1.45–1.53 Å, which is slightly longer than that found from an electron diffraction study of BeF₂ vapor (7), corresponding to the change from *sp* hybridization in BeF₂ vapor to *sp*³ hybridization in the tetrafluoroberyllate ion (182, 322, 434, 509, 510). The coordination numbers of the two cations (M₁ and M₂) in the tetrafluoroberyllates are shown in Table III (10, 164).

TABLE III
COORDINATION NUMBERS OF THE CATIONS
(M₁ AND M₂) IN M₂BeF₄

M	M ₁	M ₂
Na	6	6
K	8	8
Rb	6	8
Cs	10	8

A hindered motion of the BeF₄ group has been established in M₂BeF₄ (M = Na, K, Rb) in the range 10°–200° from ¹⁹F magnetic resonance spectra of polycrystalline samples (11). Above room temperature, there is a reorientation of BeF₄ tetrahedra around the 3-fold axis, perpendicular to the plane of densest packing. This kind of movement above 70° changes to isotropic reorientation of the tetrahedra around the center of gravity. However, only in the cesium compound is the region of reorientation of the tetrahedra around the 3-fold axis, separate from the region of isotropic reorientation by a noticeable temperature interval (ca. 30°). The potential barrier for each kind of motion is 12.7 ± 0.5 and 14.5 ± 0.5, kcal·mole⁻¹, respectively (9).

The dimetafluoroberyllates (MBe₂F₅; M = Li, Na, K) decompose before melting, whereas the rubidium and cesium salts are stable (330). The structure of RbBe₂F₅ consists of compressed RbF₆ octahedra with almost ideal hexagonal symmetry. Between the layers of octahedra is a double network of BeF₄ tetrahedra, infinite in two directions (Fig. 3), corresponding to the Si-O network in the dimetasilicates, e.g., talc and

micas, which have an infinite two-dimensional network of Si_2O_5 units (222, 223).

The $\text{K}_2\text{BeF}_4\text{--K}_2\text{SO}_4$ system consists of a continuous series of solid solutions and of the respective α and β states of the two salts (275); in the $\text{KF--K}_2\text{BeF}_4\text{--K}_3\text{ZrF}_7$ (280) and $\text{KF--K}_2\text{BeF}_4\text{--LaF}_3$ (112) systems, neither Be–Zr- nor Be–La-containing compounds exist.

The two salts are completely miscible in the $\text{MgF}_2\text{--BeF}_2$ system, which plays an important role in the industrial production of beryllium. The system is like the $\text{TiO}_2\text{--SiO}_2$ system, especially in the absence of compound formation (124, 535), quite surprising in view of the report that magnesium tetrafluoroberyllate can be isolated from aqueous solution (376).

Barium tetrafluoroberyllate exists in three modifications (241); the α -form has a rhombic lattice and is isostructural with the sulfate. The

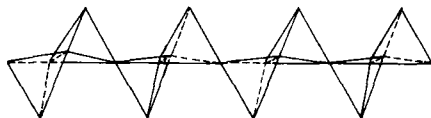
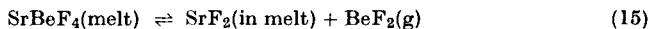


FIG. 3. x, z Projection of Be_2F_5 units in RbBe_2F_5 . The beryllium units lie at the centers of the tetrahedra and the fluorine units at the vertices.

cell parameters agree well with those obtained for BaBeF_4 prepared in aqueous solution, and this compound has been examined as a possible host lattice for RaBeF_4 as a reproducible, controllable source of neutrons (407).

Strontium tetrafluoroberyllate exists in several modifications and forms a eutectic with SrF_2 . When prepared by fusion of the components, the γ -modification is obtained, but when precipitated from aqueous solution, the β -form, which has high and low temperature forms, together with a small admixture of the γ -form is obtained (93). Evaporation of BeF_2 begins at 850° (93) and dissociation at $1010^\circ\text{--}1145^\circ$ occurs according to the equation:



$$\log K_p (\text{mm}) = 4.6970 - \frac{6392}{T} \quad (T \text{ in } ^\circ\text{abs.})$$

where the heat of dissociation is $29.0 \pm 3.0 \text{ kcal} \cdot \text{mole}^{-1}$ (340).

The $\text{CaF}_2\text{--BeF}_2$ system behaves as a weakened model of the $\text{MO}_2\text{--SiO}_2$ ($\text{M} = \text{Zr, Th}$) systems; the binary compound, CaBeF_4 , formed in this system being a model for zircon (ZrSiO_4) [see also ref. (197)]. This

tetrafluoroberyllate, which may also be obtained from aqueous solution (398), has a tetragonal lattice and melts incongruently as do the only compounds MSiO_4 ($\text{M} = \text{Zr}, \text{Th}$), formed in the above two systems (124).

Two compounds $3\text{PbF}_2 \cdot \text{BeF}_2$ and PbBeF_4 exist in the PbF_2 - BeF_2 system (410), but these have not been studied in detail.

E. AQUEOUS CHEMISTRY OF THE FLUOROBERYLLATES

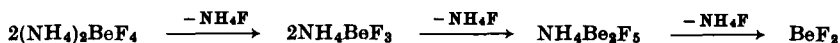
Contrary to chloroberyllates, many fluoroberyllates can be prepared in, and isolated from, aqueous solution. The tetrafluoroberyllates are the most stable and whereas the alkali metal and ammonium tetrafluoroberyllates may be obtained from aqueous solution, the dimetafluoroberyllates are generally only formed under anhydrous conditions. The ions BeF_4^{2-} and SO_4^{2-} are isoelectronic, isosteric, and similar in size; consequently, there is great similarity between sulfates and tetrafluoroberyllates (376, 396, 397). Barium tetrafluoroberyllate, isomorphous with the sulfate (397), is insoluble in water and is used for the gravimetric determination of beryllium (136, 173, 437, 439), and CaBeF_4 in its solubility behavior is like CaSO_4 (303). The sulfates and fluoroberyllates of Li, Rb, Cs, Tl, Ba, Ag, Pb, and NH_4 are known (397, 414) and the fluoroberyllates of K, Rb, Tl, and NH_4 are isomorphous among themselves, as well as with the corresponding sulfates (37, 318).

The acid, H_2BeF_4 , from which other tetrafluoroberyllates are readily obtained, is known only in aqueous solution. Such solutions, which are fairly stable, are obtained by passage of BeF_2 down an ion exchange column (32) or by the reaction of Ag_2BeF_4 with HCl (168). Conductometric and pH titrations of solutions of the acid reveal inflections at points corresponding to the formation of HBeF_4^- and BeF_4^{2-} (167).

The existence of $(\text{NH}_4)_2\text{BeF}_4$ and NH_4BeF_3 has been demonstrated in the NH_4F - BeF_2 - H_2O system; the former may be obtained by dissolution of BeO or $\text{Be}(\text{OH})_2$ in HF , followed by the addition of NH_4OH or $(\text{NH}_4)_2\text{CO}_3$ (242, 331) or by dissolving Be or BeO in NH_4F (199) or NH_4HF_2 (422). It is purified by recrystallization at low temperature, since it is very soluble in water at room temperature (331), although less soluble in propanol and butanol (405). The trifluoroberyllate is obtained from $(\text{NH}_4)_2\text{BeF}_4$ and BeF_2 and its solubility is greater than the tetrafluoroberyllate (496). Both ammonium fluoroberyllates exist in rhombic modifications, with four molecules in their unit cells; other modifications may exist as the diffraction data obtained for the rhombic modifications (462) differs from that of Thilo and Schröder (502). NMR studies (140, 146, 254) indicate that the fluoride ion is absent from aqueous solutions of $(\text{NH}_4)_2\text{BeF}_4$, that all the fluorine nuclei are equivalent,

and that the tetrafluoroberyllate ion has a tetrahedral structure which has also been suggested for the solid from infrared and Raman measurements (273, 297). However, the NMR spectrum of the solid indicates that there are four structurally nonequivalent fluorine nuclei, located at the corners of a nearly true tetrahedron in the $(\text{NH}_4)_2\text{BeF}_4$ unit cell (12).

Thermal decomposition of $(\text{NH}_4)_2\text{BeF}_4$ takes place in three stages:

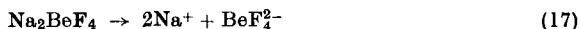


The intermediates have all been isolated and characterized (94, 496; cf. 502). The dimetafluoroberyllate may also be obtained in solution by the reaction (496):



The salt $(\text{NH}_4)_2\text{Mn}(\text{BeF}_4)_2 \cdot 6\text{H}_2\text{O}$ is formed when NH_4BeF_3 and NH_4MnF_3 solutions are mixed (43); using $(\text{NH}_4)_2\text{BeF}_4$ instead of NH_4BeF_3 , compound formation was not detected (41).

In the $\text{NaF}-\text{BeF}_2-\text{H}_2\text{O}$ system, the binary salts NaBeF_3 , Na_2BeF_4 , and $4\text{NaF} \cdot 3\text{BeF}_2 \cdot 2\text{H}_2\text{O}$ exist. The tetrafluoroberyllate may be recrystallized from water (353) in which it ionizes (540). The solubility of



Na_2BeF_4 (541) is considerably reduced by the presence of NaF , whereas the solubility of NaF is little affected by Na_2BeF_4 (328). Other salts, $2\text{Na}_2\text{BeF}_4 \cdot \text{NaHF}_2$ (102), $3\text{NaF} \cdot 2\text{BeF}_2$, $5\text{NaF} \cdot 4\text{BeF}_2 \cdot 2\text{H}_2\text{O}$, and $4\text{NaF} \cdot 3\text{BeF}_2 \cdot 2\text{H}_2\text{O}$ (100) have been prepared as well as the previously mentioned mixed salts, NaLiBeF_4 (512), which has a structure (226, 356) similar to monticellite (CaMgSiO_4), and $\text{Na}_3\text{Li}(\text{BeF}_4)_2$ (227). The hydrate, $\text{Li}_2\text{BeF}_4 \cdot \text{H}_2\text{O}$, can be readily dehydrated at 100° (397).

In the $\text{MF}-\text{BeF}_2-\text{H}_2\text{O}$ systems ($\text{M} = \text{K}, \text{Rb}$), the solid phases MBeF_3 , M_2BeF_4 , and MBe_2F_5 are present. The tetrafluoroberyllates dissolve in water without decomposition, but the tri- and dimetafluoroberyllates decompose in water (352, 397, 487). Cesium tetrafluoroberyllate is more soluble in water than the corresponding potassium and rubidium salts (397, 486).

Calcium tetrafluoroberyllate dissolves in both water and hydrochloric acid without decomposition, the solubility increasing as the acidity increases. The solubility polytherms and structures of CaSO_4 and CaBeF_4 are similar (303). The magnesium analog is obtained from a soluble metal salt and a hot, nearly saturated solution of $(\text{NH}_4)_2\text{BeF}_4$, provided that the salt is not kept too long in the boiling solution; it decomposes quantitatively into MgF_2 and BeF_2 (376).

Several other tetrafluoroberyllates (see below) have been obtained from aqueous solution, in most cases containing the same number of water molecules as the corresponding sulfates. It is not known whether these compounds exist in more than one polymorphic form— MBeF_4 [$\text{M} = \text{N}_2\text{H}_5$, Pb (397), $(\text{NH}_3\text{CH}_2-)_2$, $\text{NH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{NH}_3$, $(\text{NH}_3\text{C}_6\text{H}_4-)_2$ (168)], MHBef_4 [$\text{M} = \text{Me}_4\text{N}$ (397)], M_2BeF_4 [$\text{M} = \text{Me}_4\text{N}$, Ag, Tl (397), NH_3OH (34)], $\text{MBeF}_4 \cdot x\text{H}_2\text{O}$ [$\text{M} = \text{Ni}$, $x = 6, 7$ (398, 497); Co, $x = 4, 6, 7$ (398); Zn, $x = 7$ (398, 497); Fe, $x = 7$ (398), Cd, $x = 8/3$ (398), Cu, $x = 5$ (398, 497)], $\text{M}_2(\text{BeF}_4)_3$ [$\text{M} = \text{Al}$, Cr, $x = 18$ (33, 171); Fe, $x = 7$ (36)]. Many ammine complexes, e.g., $[\text{Zn}(\text{NH}_3)_4]\text{BeF}_4$, $[\text{Ag}(\text{NH}_3)_2]_2\text{BeF}_4$, and $[\text{Co}(\text{NH}_3)_4\text{BeF}_4]\text{BeF}_4$ have been prepared by Ray and his co-workers (33, 169, 172, 175, 395, 402).

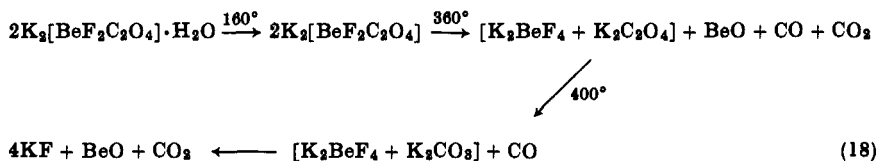
The alums, $\text{M}_2^1 \text{M}_2^2 (\text{BeF}_4)_4 \cdot 24\text{H}_2\text{O}$ [$\text{M}^2 = \text{Al}$, $\text{M}^1 = \text{NH}_4$, K, Rb, Cs, Tl, N_2H_5 , Me_4N , NH_3OH (33, 34); $\text{M}^2 = \text{Fe}$, $\text{M}^1 = \text{Rb}$, Cs (36); $\text{M}^2 = \text{Cr}$, $\text{M}^1 = \text{NH}_4$, H, K, Rb, Cs (35, 170, 174)] and schönite analogs, $\text{M}_2^1\text{BeF}_4\text{M}_2^2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ [$\text{M}^2 = \text{Ni}$, Co, Zn, Fe, Mg, Mn, Cd, $\text{M}^1 = \text{NH}_4$; $\text{M}^2 = \text{Ni}$, Co, Cu, Zn, $\text{M}^1 = \text{K}$ (414)] and $\text{M}_2^1\text{M}_2^2(\text{BeF}_4)_2 \cdot 6\text{H}_2\text{O}$ [$\text{M}^1 = \text{NH}_4$, $\text{M}^2 = \text{Cd}$, Co, Cu, Fe, Mn, Ni, Zn; $\text{M}^1 = \text{K}$, $\text{M}^2 = \text{Co}$, Ni; $\text{M}^1 = \text{Rb}$, $\text{M}^2 = \text{Cd}$, Co, Cu, Fe, Ni, Zn; $\text{M}^1 = \text{Cs}$, $\text{M}^2 = \text{Ni}$; $\text{M}^1 = \text{Tl}$, $\text{M}^2 = \text{Cd}$, Co, Cu, Ni, Zn (43, 318, 399, 400, 401, 495)] are obtained in aqueous solution and are isomorphous with the corresponding sulfates. A series of sulfato-fluoroberyllates, $(\text{NH}_4)_2\text{Cu}(\text{SO}_4)_{2-x}(\text{BeF}_4)_x \cdot 6\text{H}_2\text{O}$, $0 \leq x \leq 2$, have also been obtained (495) and in the $(\text{NH}_4)_2\text{BeF}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ system, evidence has been obtained for the existence of $(\text{NH}_4)_2\text{BeF}_4 \cdot \text{H}_2\text{SO}_4$, $3(\text{NH}_4)_2\text{BeF}_4 \cdot \text{H}_2\text{SO}_4$, and $(\text{NH}_4)_2\text{BeF}_4 \cdot 3\text{H}_2\text{SO}_4$ (135).

The close analogy between sulfates and fluoroberyllates is further exemplified by the similar ferroelectric behavior of some fluoroberyllates and sulfates. Ammonium tetrafluoroberyllate (374) and the sulfate (292), with which it is isomorphous at room temperature (318), become ferroelectric below the Curie points, -97° and -49.5° , respectively. At these temperatures, phase transitions appear, but the direction of the spontaneous polarization ferroelectric axis in the sulfate is at 90° to that in the fluoroberyllate (362) and the Curie-Weiss constants are very small compared to those of other ferroelectrics (358). Structural changes occurring in the vicinity of the ferroelectric transition points are accompanied by only small changes in proton magnetic absorption. The two compounds have similar absorption lines at room temperature, but entirely different ones at low temperature, and this may be due to the ferroelectric phases not being isomorphous (362). Above -180° , no line-width transition is found, showing that the hydrogen bonds, $\text{N--H} \cdots \text{F}$ are weak. Splitting of some bands in the infrared at temperatures below the Curie point indicates deformation of BeF_4^{2-} and NH_4^+ ions, but the

distortion is so small that it does not result in any significant redistribution of electron density in the Be-F bonds (77) and the phase transition is not accompanied by a change in the parameters of the $H \cdots F$ -Be bond (12). A necessary but not sufficient condition for a solid to be ferroelectric is the absence of a center of symmetry (77), and the presence of hydrogen bonds are essential in the polarization of some ferroelectrics.

Triglycine fluoroberyllate $(CH_2NH_2COOH)_3H_2BeF_4$ is also ferroelectric (375), like the sulfate and selenate (291). Substitution of BeF_4^{2-} for SO_4^{2-} in the triglycine salts raises the Curie temperature from 47° in the sulfate (22° in the selenate) to 73° (552) in the fluoroberyllate; the values of spontaneous polarization are of the same order of magnitude. The transition energies and entropy changes for transitions to the ferroelectric phase are, for the sulfate, $0.15 \text{ kcal} \cdot \text{mole}^{-1}$ and $0.48 \text{ cal} \cdot \text{mole}^{-1} \cdot \text{degree}^{-1}$, and for the fluoroberyllate, $0.40 \text{ kcal} \cdot \text{mole}^{-1}$ and $1.17 \text{ cal} \cdot \text{mole}^{-1} \cdot \text{degree}^{-1}$ (218). Triglycine fluoroberyllate has been doped with both Cs_2BeF_4 and Tl_2BeF_4 in order to prepare a habit-modified salt; but irrespective of crystalline habit, the Curie temperature is 73° . Crystalline imperfections, introduced during growth, are distributed anisotropically and have a marked effect upon the dielectric and ferroelectric polarization process (552).

The formation of complex fluoroberyllate oxalates has been indicated by the increased solubility of ammonium and alkali metal oxalates in beryllium fluoride solutions. From these solutions, hydrated salts $M_2[BeF_2C_2O_4] \cdot xH_2O$, which are also obtained from beryllium oxalate and alkali metal fluoride solutions, have been isolated. Analogous compounds containing malonate, salicylate, formate, acetate, or chloroacetate groups have not been obtained (440, 445). Thermal decomposition at ca. 400° of the alkali metal oxalatofluoroberyllates yields the tetrafluoroberyllate, the oxalate, and BeO [cf. (249)]. At higher temperatures, the oxalate decomposes too, and the resulting carbonate reacts with fluoroberyllate to form the alkali metal fluoride and BeO (101).

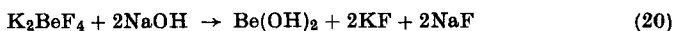


The formation of monohydroxytrifluoroberyllates and basic beryllium fluoroberyllates, described by Mitra and Ray (306-311), Sen-Gupta (442), and Pascal (370), has been the subject of some controversy. Sen-Gupta (438) has pointed out inherent discrepancies in this work and disputes the formation of some of these compounds. Kolditz and Bauer

(249) believe that the monohydroxytrifluoroberyllates are really tetrafluoroberyllates and that the preparative method described by Pascal (370) for the preparation of one of these compounds, utilizing KF, BeF₂, and Be(OH)₂ in the ratio 4:1:1, proceeds in the manner:



Although Mitra (306) interpreted his results from the thermometric titration of K₂BeF₄ with NaOH as indicating the formation of K₂BeF₃OH, Sen-Gupta (438) states that in the hydrolysis of BeF₄²⁻ with NaOH, Be(OH)₂ is precipitated according to

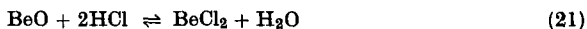


III. Beryllium Chlorides, Bromides, and Iodides

A. ANHYDROUS SYSTEMS

1. Preparation

Beryllium halides* are deliquescent and cannot be obtained from their hydrates, since on heating or on reaction with SOCl₂ or COCl₂, hydrolysis occurs with consequent formation of basic halides (17, 18, 205, 436, 544). A variety of methods are available for the preparation of the halides and the most convenient are by heating beryllium in a stream of dry halogen (5, 19, 24, 160, 219, 231, 302, 393, 555) or hydrogen halide (158, 181, 215, 219, 393, 430) at 400°–600°. Reductive halogenation procedures of the oxide have been extensively employed using carbon and halogen (56, 141, 214, 289, 298, 379, 380, 419, 474, 508, 553), carbonyl halide (84, 111, 285, 286, 418, 419), or carbon tetrachloride (160, 289, 300, 346, 474) and using beryllium carbide and halogen or hydrogen halide (215, 231, 271, 285, 298). Ether solutions containing mainly solvated beryllium halides are obtained by the reaction of beryllium metal with halogen or hydrogen halide in ether (17–19, 516, 521, 524). The equilibrium for the reversible reaction lies over to the left except

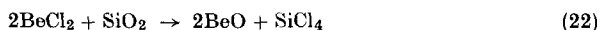


at very high temperatures (60, 473) and although beryllium chloride is also formed from BeO and sulfur (88, 289) or phosphorus chlorides (289), these reactions are less favorable; the halides have also been obtained by metathesis (109, 118, 271, 430).

* In Section III, the use of the word halide refers only to the chloride, bromide, and iodide.

2. Properties

The halides, which are insoluble in benzene (555) and usually only dissolve in solvents with which they react, may be isolated and purified by sublimation as colorless, crystalline needles, extremely sensitive to moisture and susceptible to oxidation on heating (144, 160, 393, 430, 553). Silicon tetrahalides and BeO are formed when beryllium halides are heated in glass apparatus (160, 187, 215, 219, 397, 465).



A variety of melting and boiling points have been ascribed to the halides (see tabulation below).

Halide	M.p. (°C)	B.p. (°C)	d_4^{25} (gm/ml)
BeCl ₂	399.2 ^a (160), 404 (418), 405 (144, 393), 410 (432), 416 (244), 425 (264), 440 (271)	482.3 ^b (160), 488 (393), 510 (264), 520 (473)	(α' -modification), 1.899 (214, 264), 1.901 (298)
BeBr ₂	487 (144), 488 (393), 490 (271), 506–509 (430)		(α -modification), 3.465 (285, 430)
BeI ₂	480 (144, 393), 510 (271)		(α -modification), 4.325 (298, 430)

^a Average of 20 results spread over an 8° range. Numbers underlined are considered most reliable.

^b Average of 12 results spread over a 3° range.

Data on the density and thermal coefficient of cubic expansion of BeCl₂ have been summarized by Klemm *et al.* (244–246). The fused chloride is a poor conductor of electricity (66, 69, 282, 539); the specific conductance at 451° is about one-thousandth that of sodium chloride (539).

The chloride, which is isomorphous with SiS₂ and Me₂Be, has four BeCl₂ molecules in the orthorhombic unit cell. Its structure (Fig. 4)

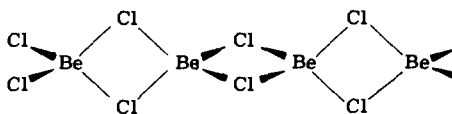


FIG. 4. The structure of solid BeCl₂.

consists of continuous chains with essentially tetrahedral configuration about each beryllium atom (411). The Cl-Be-Cl bond angle is 98.2° , which is less than the tetrahedral bond angle, as is also found for SiS_2 (104), instead of more (114°) as in Me_2Be (472), indicating all the bonds in BeCl_2 contain electron pairs with each chlorine atom using nearly pure p orbitals, i.e., BeCl_2 is not electron deficient. The Be-Cl distance is 2.02 Å [sum of covalent radii, 1.84 Å (371)]. The chains pack rather like circular cylinders with the Cl-Cl distance between chains about 3.85 Å (411).

Electron diffraction studies (7, 8) on BeX_2 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) showed two radial distribution peaks which were interpreted as Be-X and X-X distances in the monomeric species (Table IV). No evidence for the

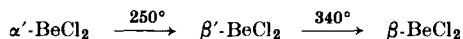
TABLE IV
INTERATOMIC DISTANCES IN BeX_2

X	Be-X (Å)	X-X (Å)	$\Sigma_{\text{covalent radii}}$ (Å)	$\Sigma_{\text{ionic radii}}$ (Å)
F	1.40	2.80	1.61	1.71
Cl	1.75	3.51	1.84	2.16
Br	1.91	3.84	1.99	2.30
I	2.18	4.22	2.23	2.51

presence of Be_2X_4 or BeX was found. The monomeric species are linear and, as expected, there is a shortening of the Be-Cl distance in going from the solid to the vapor, corresponding to the change from sp^3 to sp hybridization [see also (434)]. The Be-X distance is considerably less than the sum of the ionic radii, but approximates to the sum of the covalent radii; hence this must be regarded as direct confirmation that the Be-X bonds have a low degree of ionic character. Interatomic distances for MX_2 ($\text{M} = \text{Group II metal}, \text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) are given in references (7, 8).

BeCl_2 exhibits several polymorphic transitions (264), but only the fibrous (α') modification, formed on sublimation, has been studied to any appreciable extent [see (411)]. The BeCl_4 tetrahedra can be packed in ways other than linear chains to form different polymorphic modifications with small heat changes and, consequently, with very small rates of mutual conversion. On heating freshly sublimed BeCl_2 , the exothermic effects at 250° and 340° correspond to monotropic polymorphic transitions and the endothermic effect at 405° to an enantiotropic transition. During cooling of the melt, only one exothermic effect, corresponding

to solidification of the liquid, was observed. When previously fused BeCl_2 is repeatedly heated, only one enantiotropic transition is detected at 405° , besides the fusion effect. On rapid cooling of the melt or on crystallization of the gaseous phase, a metastable α' -modification arises which on subsequent heating, is converted at 250° into a cubic β' -modification and at 340° into a β -form which is orthorhombic, like the α' -modification:

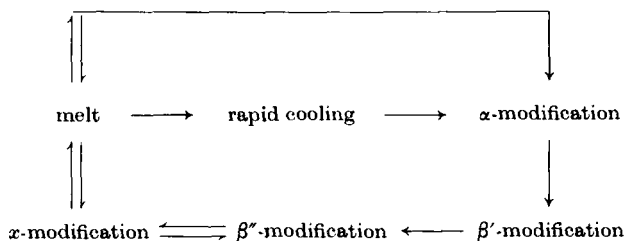


On slow cooling of the melt,



It is possible that the structure of the α - and α' -modifications are identical (264).

Freshly sublimed bromide (α -modification) does not undergo any polymorphic conversion up to the melting point. This modification, like the α -modification of the iodide, is isostructural with the α' -form of BeCl_2 (430). Several forms of BeI_2 are known (231, 430) which are stable in different temperature intervals.



The presence of these modifications of the beryllium halides may well account for the variety of melting points which have been found for them.

There is ample evidence for association in the vapor phase. The vapor of the iodide contains dimeric molecules; the equilibrium constants for the dimer-monomer equilibrium are 53.3 at 766° and 19.5 at 636° and the heat of dissociation is $14.8 \text{ kcal} \cdot \text{mole}^{-1}$ (252). The bromide is also associated in the vapor (393), but accurate data regarding its composition are not known. The data on the vapor composition of the chloride are somewhat confusing and should be treated with caution. The vapor is calculated to contain 23% dimer at 562° (393), whereas at 500° , it is presumed to consist largely of dimer, and calculations from Brewer's data (95) show only monomer is present at 1000° . Büchler and Klemperer have found evidence for associated species, which they have suggested are dimers (Fig. 5), from spectroscopic studies of

the vapor (103). Mass spectra studies (412) of the vapor composition, over the narrow temperature range 223°–305°, indicate dimer as well as monomer to be present. The dimer fraction under these conditions is

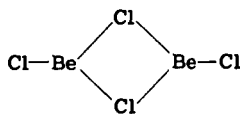


FIG. 5. Beryllium chloride dimer.

0.5–1.5% of the total number of molecules and increases with temperature, but it has since been pointed out that the possible contribution to the BeCl_2^+ peak, due to fragmentation of the dimer, was neglected (247). Transpiration studies combined with torsion-effusion experiments show the composition of the vapor over solid BeCl_2 contains 65% dimer at 198° and 90% at 410°, although a correction had to be applied in this work owing to the presence of water in the solid which was weighed out in air (247). A statistical analysis of torsion-effusion data indicates essentially monomeric species are present at effusion pressures at 197°–237° (187). Vapor pressure data for the halides are shown in Table V.

TABLE V
VAPOR PRESSURE DATA FOR BERYLLIUM HALIDES
 $\log p_{\text{mm}} = A - B/T$ (T in °abs.)

Halide	A	B	Temperature range (°C)	Ref.
BeCl_2	11.61	6564	340–405	(393)
	10.64	5908	405–460	(393)
	11.83	7200	167–327	(187)
	11.83	7260	197–237	(187)
	11.559	7093	187–231	(211)
BeBr_2	11.68	6564	351–422	(393)
BeI_2	10.64	5908	305–430	(393)

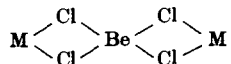
The anhydrous halides may be reduced to the metal in varying degrees of purity by Li, Na, K, Mg, or Ca (237, 271, 419), but only the fluoride reduction by magnesium (236, 316, 422, 534) and, less widely, electrolysis of chloride melts (419, 553, 554) are of industrial importance. Reduction of BeI_2 with hydrogen (215), its thermal decomposition (252, 299, 465, 533), and electrodeposition from a variety of solutions of beryllium halides are not satisfactory sources of the metal (83–86, 220,

555). Electrolysis of BeCl_2 -alkali metal chloride systems proceeds in two stages: (1) primary deposition of Be on the cathode, and (2) secondary deposition of the metal by electrically produced alkali metal (261, 262). The introduction of fluoride anions into chloride melts displaces the beryllium equilibrium potential by 0.6–0.8 volts compared with that in chloride electrolytes. This suggests a considerable strengthening of the bond between beryllium and the anion on going from $\text{Be}^{2+}\text{-Cl}^-$ to $\text{Be}^{2+}\text{-F}^-$ (469).

3. Halide Complexes

The relative strength of halide complexes is as expected if the complex formation were due to essentially electrostatic forces. In such cases, strong bonds should be formed by ligands combining slight polarizability with small ionic radii. These factors decrease monotonically from I^- to F^- and, therefore, the sequence of halide complexes is shown to be $\text{F}^- \gg \text{Cl}^- > \text{Br}^- > \text{I}^-$ (6). Whereas fluoroberyllates are known both in aqueous solution and in the solid state, owing to hydrolysis, chloroberyllates are formed only under anhydrous conditions, while neither bromo- nor iodoberyllates are known, perhaps for steric reasons.

The phase diagram of $\text{NaCl}\text{-BeCl}_2$ indicates the existence of Na_2BeCl_4 , isostructural with the sulfate, like one of the modifications of Na_2BeF_4 (427, 563). The tetrachloroberyllate undergoes a polymorphic transformation at 221° , marked by a sharp volume change, but without evident change of crystal structure; the existence of a metastable phase, NaBeCl_3 , has been established (160, 418, 432). The ion BeCl_4^{2-} is believed to be present in fused $\text{MCl}\text{-BeCl}_2$ ($\text{M} = \text{K}, \text{Cs}$) mixtures (263, 468), but evidence has been obtained for the presence of both anionic and cationic beryllium complexes in the fused $\text{NaCl}\text{-BeCl}_2$ system (129). Lithium and sodium tetrachloroberyllates differ from the potassium analog in crystal structure and thermal stability. Potassium tetrachloroberyllate crystallizes with the ionic type of lattice of K_2SO_4 , whereas the structure of Na_2BeCl_4 can be regarded as intermediate between the predominantly ionic structure of K_2BeCl_4 and the molecular lattice containing bridging units of the type



There is some distortion of the BeCl_4^{2-} tetrahedra in the tetrachloroberyllates on going from the sodium to the lithium salt (260, 433), although the symmetry of BeCl_4^{2-} differs little from tetrahedral (427, 428). The Be-Cl stretching force constant is 1.81×10^5 dynes $\cdot\text{cm}^{-1}$ and the bond length (1.89 Å) in the isolated BeCl_4^{2-} ion (427) is considerably less

than the bond length (2.02 Å) in crystalline BeCl_2 (411), in which all the chlorine atoms form bridge bonds and are essentially divalent.

TABLE VI
BeCl₂-METAL HALIDE PHASE SYSTEMS

Metal halide	Eutectic temperature	Composition of eutectic	Complex formed in system
LiCl	300	56	Li_2BeCl_4
NaCl	215	51	Na_2BeCl_4
AgCl	235	40	None
TlCl	370	18	Tl_2BeCl_4 and TlBe_2Cl_5
	ca. 300	55	
	ca. 350	85	
MgCl ₂	—	—	Solid solution formed with possible isodimorphism
CdCl ₂	327	85	None
CaCl ₂	355	85	Inconclusive
BaCl ₂	372	87	BaBeCl_4
PbCl ₂	292	47	None

A summary of BeCl_2 -anhydrous metal chloride phase systems (418) is given in Table VI. Vapor over BeCl_2 - AlCl_3 mixtures contain the species BeAlCl_5 (Fig. 6) and $\text{Be}_2\text{Al}_2\text{Cl}_{10}$ (Fig. 7) (431).

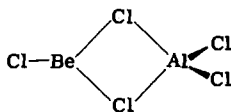


FIG. 6. The BeAlCl_5 structure.

The addition of hydrogen halide to ethereal beryllium chloride solutions produces the liquid complexes $\text{HBeCl}_2\text{X} \cdot 2\text{Et}_2\text{O}$ ($\text{X} = \text{Cl}, \text{Br}$);

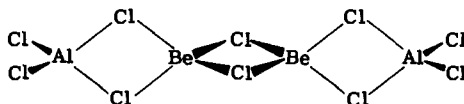


FIG. 7. The $\text{Be}_2\text{Al}_2\text{Cl}_{10}$ structure.

pyridine displaces the ether molecules yielding the corresponding pyridine complexes. The compounds are formulated as $[\text{D} \cdots \text{H} \cdots \text{D}]^+$ -

$[\text{BeCl}_2\text{X}]^-$ (D = pyridine, ether; X = Cl, Br) (304), like the similar compounds formed by the halides of Zn, Cd, Hg, Al, Ga, In, Tl, and Sb (161–163).

B. AQUEOUS CHEMISTRY OF THE HALIDES

All the anhydrous halides dissolve in water with considerable heat evolution, forming solutions containing the hydrated beryllium ion, which may also be obtained from Be or BeO and dilute acids (81, 248). Viscosity, freezing point, and conductivity data show the beryllium ion is more strongly hydrated than ions of other bivalent metals, which is in accordance with the large heat of solution of BeCl_2 and its small volume contraction when dissolved (155, 208, 456). The strong hydration of the beryllium ion can be partly explained by its formation of coordinate links with water molecules, the coordinate links being formed

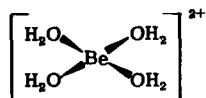


FIG. 8. The $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ ion.

by donation of the electrons of the oxygen lone-pairs into vacant sp^3 beryllium orbitals (Fig. 8). Ions such as Ba^{2+} do not form such bonds; the solvation forces here are ion–dipole and electrostatic in origin.

The solubility of BeCl_2 in water increases with temperature (72, 274), but decreases in solutions of HCl and LiCl (351), whereas the presence of NH_4Cl does not appreciably affect its solubility (343). NaCl, KCl, and AlCl_3 are readily salted out of aqueous solution by BeCl_2 (73, 74). The coordination number of the beryllium ion in solution is about 4; the lifetime of water molecules in the first coordination sphere of the Be^{2+} ion at room temperature is approximately 3×10^{-4} sec (143). The structure of beryllium chloride and bromide in concentrated aqueous solutions are thought to consist of polymeric chains of varying complexity (78, 79). However, because BeCl_2 , unlike BeF_2 , is a strong electrolyte in solution (200, 265, 391), it is therefore likely that such solutions will also contain ionic species of the type $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$, as described earlier.

The solid hydrate, $\text{BeCl}_2 \cdot 4\text{H}_2\text{O}$, which is extremely hygroscopic and stable up to 70° , is obtained by concentration of aqueous beryllium chloride solutions. Partial hydrolysis of the hydrated salt or an aqueous solution of the salt, takes place with HCl evolution (20, 125, 274, 301,

368, 556). Other workers (436), who were only able to obtain $\text{BeCl}_2 \cdot 4.5\text{H}_2\text{O}$, suggested that as a greater number of ligands were attached to beryllium than corresponds to its coordination capacity, such compounds must be formed as a result of inclusion of excess ligand into the cavities in the crystal lattice of the 1:2 compound, analogous to the inclusion compounds formed by urea with hydrocarbons. In view of the difficulty in obtaining $\text{BeCl}_2 \cdot 2\text{H}_2\text{O}$ (274), it is quite likely that the tetrahydrate can be formed containing the tetraaquoberyllium(II) ion which is present in the structure of $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ (45, 126, 459). The ease of hydrolysis increases from the fluoride to the iodide; consequently, although $\text{BeBr}_2 \cdot 4\text{H}_2\text{O}$ has been isolated, the corresponding iodide could not be obtained (125).

Basic chlorides, e.g., $\text{BeCl}_2 \cdot \text{Be}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ and $\text{BeO} \cdot \text{BeCl}_2 \cdot 5\text{H}_2\text{O}$, are formed by heating $\text{BeCl}_2 \cdot 4\text{H}_2\text{O}$, by dissolving $\text{Be}(\text{OH})_2$ in concentrated HCl solution, and by evaporation of aqueous solutions of beryllium chloride containing excess beryllium ions (369, 392, 544). Compounds in which ether molecules replace water molecules in the beryllium halide hydrates and the basic hydrates have also been reported, e.g., $[\text{Be}(\text{H}_2\text{O})_3\text{Et}_2\text{O}]\text{Cl}_2$, $[\text{Be}(\text{H}_2\text{O})_2(\text{Et}_2\text{O})_2]\text{I}_2$, and $5\text{Be}(\text{H}_2\text{O})_3(\text{dioxane})\text{Cl}_2 \cdot \text{Be}(\text{OH})_2$ (125, 368, 435, 545), but these have not been investigated in detail.

Hydrolysis of the $\text{Be}(\text{II})$ ion has been extensively studied, polynuclear species being formed. The addition of alkali to beryllium solutions causes precipitation to begin when $\text{OH}:\text{Be} > 1$, for the halides, precipitation is complete when $\text{OH}:\text{Be}$ is 2, and for the sulfate and nitrate when the ratio is ca. 1.8–1.9, i.e., the deposit contains some of the oxoanion. The formulas of the soluble complex ions, several having the general formula $[\text{Be}_n(\text{OH})_n]^{n+}$ (293), formed on hydrolysis, are in some doubt. Be_2O^{2+} (176, 387, 388), $\text{Be}(\text{OH})^+$ (359, 387), $\text{Be}_2(\text{OH})_2^{2+}$ (359, 387), $\text{Be}_3(\text{OH})_3^{3+}$ (59, 234, 290, 296, 359, 360, 417, 455), $\text{Be}_2\text{OH}^{3+}$ (59, 234, 296, 359, 455), $\text{Be}_5(\text{OH})_7^{3+}$ (296), $\text{Be}(\text{OH})_2$ (59, 234, 359, 455), and $\text{Be}_4\text{O}_2^{4+}$ or $\text{Be}_4(\text{OH})_4^{4+}$ (415) have all been suggested and, in some cases, formation constants have been derived. The main hydrolysis product in aqueous (59) and dioxane–water (359, 360) solutions is $\text{Be}_3(\text{OH})_3^{3+}$, doubtlessly solvated (Fig. 9) (234), together with $\text{Be}_2(\text{OH})^{3+}$; but there is disagreement over the contribution due to $\text{Be}(\text{OH})_2$.

There is no evidence for the existence of anionic chloroberyllate complexes in aqueous solution, analogous to fluoroberyllates, from electrochemical measurements (389) or from solubility isotherms of BeCl_2 –metal halide–water systems (72–76, 84, 335, 343, 351, 391). However, from anion exchange experiments in chloride media, it has been proposed that the beryllium exists in the form of BeCl_3^- in such solutions

and from both the elution behavior on cation exchange resins and the distribution of beryllium between HCl and phosphoric acid esters, it has also been suggested that polynuclear cationic chloroberyllium complexes are also formed in solution (82, 132, 198, 251, 257, 361).

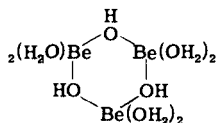


FIG. 9. The solvated $[\text{Be}_3(\text{OH})_3]^{3+}$ ion.

In the compounds $\text{BeX}_2 \cdot \text{HgX}_2 \cdot 5\text{H}_2\text{O}$, $\text{Be}(\text{OH}) \cdot \text{HgX}_3 \cdot 2\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{Br}$), $3\text{Be}(\text{OH}) \cdot 12\text{HgI}_2 \cdot 6\text{H}_2\text{O}$ (475), $2\text{BeCl}_2 \cdot \text{M}_2\text{Cl}_6 \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Fe}, \text{Cr}$), and $3\text{BeCl}_2 \cdot 2\text{TlCl}_3$ (325), the beryllium is more likely to be in the form of a cationic species than an anionic halide complex.

C. COORDINATION COMPLEXES

The beryllium halides are Lewis acids and form many coordination compounds with oxygen-, sulfur-, and nitrogen-containing donor molecules. Usually only two ligands coordinate to beryllium, the beryllium-halogen covalent bond remaining intact, but with strong donors having small steric requirements, ionization of the beryllium-halogen bond takes place and the tetracoordinated $\text{Be}(\text{II})$ ion is formed. The known complexes of the halides are listed in Table VII, together with some of their properties.

1. Oxygen and Sulfur Complexes

The hydrate, ether-hydrate, and dioxane-hydrate complexes have been discussed earlier (Section III, B). Beryllium halide-diethyletherate systems have been extensively studied and have been the subject of several publications by the Russian workers Turova, Novoselova, and Semenenko. Beryllium chloride reacts exothermically with anhydrous ether, forming a two-phase solution from which colorless crystalline prisms of the bisetherate are deposited on cooling or evaporation of the solvent (460). This compound (521) and the analogous dimethyletherate

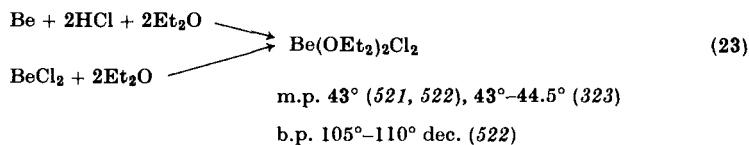


TABLE VII
BERYLLIUM HALIDE AND PSEUDOHALIDE COORDINATION COMPLEXES^a

Complex	M.p. (°C)	Properties	Solubility	Ref.
Dichloro adducts				
Be(H ₂ O) ₄ Cl ₂	96	Colorless hygroscopic prisms	s(a)	(125, 274)
Be(H ₂ O) _{4.5} Cl ₂	—	Orthorhombic tablets evolving HCl on heating	s(a)	(402)
Be(H ₂ O) ₃ (Et ₂ O)Cl	—	Colorless needles	—	(125)
Be(H ₂ O) ₄ (Et ₂ O)- Cl ₂ ·0.25HCl	—	Deliquescent acicular crystals	—	(435)
5Be(H ₂ O) ₃ (dioxane)- Cl ₂ ·Be(OH) ₂	—	Colorless hygroscopic crystals	s(a)	(545)
Be(Me ₂ O) ₂ Cl ₂	63–64 dec.	Colorless hygroscopic crystals	s(b)(c)(d)	(524)
[Be(Et ₂ O)Cl ₂] ₂	116–118	Colorless needles	s(c)	(97)
Be(Et ₂ O) ₂ Cl ₂	43–44.5	Colorless crystalline prisms	s(c)(e)	(21, 149, 323, 460, 521, 522, 555)
Be(Et ₂ O) ₃ Cl ₂	—	Colorless acicular crystals stable in Et ₂ O solution below –2°	s(e)	(522)
Be(THF) ₂ Cl ₂	150	Colorless needles	s(c)(f)	(425, 520)
Be(THF) ₃ Cl ₂	—	Solid, stable below –2°	—	(520)
Be(THP) ₂ Cl ₂	161	White needles	s(c)(f)	(524)
Be(dioxane)Cl ₂	—	White deliquescent crystalline solid	s(g); ss(c)(e)(h)	(342, 524)
Be(PhOMe) ₂ Cl ₂	—	White hygroscopic needles	s(a)(c)(e)	(153)
Be(Cl(CH ₂) ₄ OMe) ₂ Cl ₂	—	Colorless rods	s(e)	(24)
Be(MeOC ₂ H ₄ OMe)Cl ₂ ^b	237–244 dec.	White crystalline hygroscopic solid	i(c)(e)(j)	(118, 524)
Be(Me ₂ CO) ₂ Cl ₂	—	Colorless crystals	—	(154)

Be(Me ₂ CO) ₂ Cl ₂ ·4C ₆ H ₆	—	Colorless crystals	s(g)	(154)
Be(Ph ₂ CO) ₂ Cl ₂	—	Colorless needles	s(e)	(153)
Be(PhCHO) ₂ Cl ₂	—	White microcrystalline hygroscopic solid	s(g)(k); ss(c)(e)(l)(m)	(149)
Be(PhCH:CHCHO) ₂ Cl ₂	—	White hygroscopic needles, μ = 7.33 D	s(c)	(153, 229)
Be(HCOOEt) ₂ Cl ₂	—	Viscous liquid	—	(295)
Be(MeCOOMe) ₂ Cl ₂	—	White crystalline solid	—	(295)
Be(MeCOOEt) ₂ Cl ₂	—	White solid	—	(295)
Be(MeCOOPr ⁿ) ₂ Cl ₂	—	Colorless viscous liquid	—	(295)
Be(MeCOOPr ^t) ₂ Cl ₂	—	White crystalline solid	—	(295)
Be(MeCOOBu ⁿ) ₂ Cl ₂	—	Light brown viscous liquid	—	(295)
Be(MeCOOBu ^s) ₂ Cl ₂	—	Brown viscous liquid	—	(295)
HBeCl ₃ (Et ₂ O) ₂	—	Green liquid, fumes in air	—	(304)
HBeCl ₂ Br(Et ₂ O) ₂	—	Green liquid, fumes in air	—	(304)
BeCl ₂ ·3POCl ₃	58–58.5	White prisms	s(c)(e)(n)	(527)
Be(S ₂ N ₂ O)Cl ₂	288–301	Yellow solid	—	(28)
BeCl ₂ ·GaCl ₃ ·3Et ₂ O	61	White solid	s(e)	(426)
BeCl ₂ ·AlCl ₃ ·3Et ₂ O	55	White solid, μ = 6.29 D	s(e)	(514, 515)
[Be(Me ₂ S)Cl ₂] ₂	135	Colorless prisms	s(c)	(118)
Be(Me ₂ S) ₂ Cl ₂	55, 117–119	White hygroscopic crystalline solid	s(c)(e)(f)(p)	(118, 464)
Be(Me ₂ S) ₃ Cl ₂	—	White needles, stable below 5°	—	(464)
Be(MeSC ₂ H ₄ SMe)Cl ₂	—	Colorless needles	ss(c)	(118)
Be(Et ₂ S) ₃ Cl ₂	—	White needles at low temp., liquid at room temp.	—	(464)
Be(Bu ^t ₃ S) ₃ Cl ₂	—	White needles at low temp., liquid at room temp.	—	(464)
Be(quinoline) ₂ (H ₂ O)Cl ₂	—	Colorless hygroscopic needles	—	(404)
Be[CO(NH ₂) ₂] ₄ Cl ₂	213–214	White solid	—	(385)
Be(PhCONH ₂) ₂ Cl ₂	107–109	White solid	—	(385)

(continued)

TABLE VII—*continued*

Complex	M.p. (°C)	Properties	Solubility	Ref.
Be[<i>o</i> -C ₆ H ₄ (OH)NH ₂] ₂ Cl ₂	—	Dark brown solid	i(c)(d)(e)	(384)
Be[<i>m</i> -C ₆ H ₄ (OH)NH ₂] ₂ Cl ₂	—	Ash-colored solid	i(c)(d)(e)	(384)
Be[<i>o</i> -C ₆ H ₄ (COOH)NH ₂] ₂ Cl ₂	—	Light pink solid	i(c)(d)(e)	(384)
Be[<i>m</i> -C ₆ H ₄ (COOH)NH ₂] ₂ Cl ₂	—	Brown solid	s(a); i(c)(d)(e)	(384)
Be[<i>p</i> -C ₆ H ₄ (NO ₂)NH ₂] ₂ Cl ₂	—	Yellow solid	s(g)	(384)
Be[<i>o</i> -C ₆ H ₄ (OMe)NH ₂] ₂ Cl ₂	—	Light gray solid	—	(381)
Be[<i>p</i> -C ₆ H ₄ (OMe)NH ₂] ₂ Cl ₂	—	Light gray solid	—	(381)
Be[<i>o</i> -C ₆ H ₄ (OEt)NH ₂] ₂ Cl ₂	—	Light gray solid	—	(381)
Be[<i>p</i> -C ₆ H ₄ (OEt)NH ₂] ₂ Cl ₂	—	Light gray solid	—	(381)
Be[—C ₆ H ₃ (OMe)NH ₂] ₂ Cl ₂	—	Ash solid	—	(381)
Be(cocaine) ₂ Cl ₂	—	Colorless crystals	s(a)	(364)
Be[CS(NH ₂) ₂] ₂ Cl ₂	—	Yellow hygroscopic solid	—	(385)
Be(PhNHCSNH ₂)Cl ₂	—	Light yellow solid	—	(385)
Be(<i>o</i> -tolyl-NHCSNH ₂)Cl ₂	—	Light pink solid	—	(385)
Be(<i>m</i> -tolyl-NHCSNH ₂)Cl ₂	—	Light pink solid	—	(385)
Be(<i>p</i> -tolyl-NHCSNH ₂)Cl ₂	—	Light pink solid	—	(385)
Be(PhNHCSNHPh)Cl ₂	—	Light yellow solid	—	(385)
Be(<i>o</i> -tolyl-NHCSNH- <i>o</i> -tolyl)Cl ₂	—	Pink solid	—	(385)
Be(<i>m</i> -tolyl-NHCSNH- <i>m</i> -tolyl)Cl ₂	—	Pink solid	—	(385)
Be(<i>p</i> -tolyl-NHCSNH- <i>p</i> -tolyl)Cl ₂	—	Pink solid	—	(385)
Be(NH ₃) ₄ Cl ₂	—	Colorless hygroscopic crystals	—	(57, 67, 149, 301)
Be(NH ₃) _x Cl ₂	—	$x = 12, 6, \text{ and } 2$	—	(57, 67, 301)
BeCl ₂ ·Be(NH ₂) ₂ · x NH ₃	—	Colorless solid	ss(q)	(57)

BeCl ₂ ·2NH ₃ ·Me ₂ CO	—	Solid, poor analysis	—	(149)
Be(MeNH ₂) ₄ Cl ₂	—	White powder	—	(149)
Be(Me ₃ N) ₂ Cl ₂	—	White solid	—	(381)
Be(Me ₃ N) _{1.5} Cl ₂	171-174	White solid	—	(97)
Be(Et ₂ NH) ₂ Cl ₂	—	White crystalline needles	—	(153)
Be(Bu ⁿ NH ₂) ₂ Cl ₂	—	Colorless microscopic crystals	s(c)(e)(l)	(153)
Be(en) ₂ Cl ₂	—	White powder	—	(150)
Be(PhNH ₂) ₂ Cl ₂	—	Crystalline needles	s(k)	(149)
Be(PhNMe ₂) ₂ Cl ₂	—	Green solid	—	(281)
Be(PhNEt ₂) ₂ Cl ₂	—	Pink solid	—	(281)
2BeCl ₂ ·3Ph ₂ NH	—	Pink crystals	—	(281)
Be(PhNH ₂ Et) ₂ Cl ₂	—	Light yellow solid	—	(281)
Be(α-C ₁₀ H ₇ NH ₂) ₂ Cl ₂	—	Light ash solid	—	(281)
Be(β-C ₁₀ H ₇ NH ₂) ₂ Cl ₂	—	Light ash solid	—	(281)
Be(<i>p</i> -CH ₃ C ₆ H ₄ NH ₂) ₂ Cl ₂	—	Yellow needles	s(a)(g)(k); ss(c)(e)	(153)
Be(<i>m</i> -CH ₃ C ₆ H ₄ NH ₂) ₂ Cl ₂	—	Light gray solid	—	(281)
Be(<i>o</i> -CH ₃ C ₆ H ₄ NH ₂) ₂ Cl ₂	—	Light red needles	s(g)(k)	(151)
Be(PhCH ₂ NH ₂) ₂ Cl ₂	—	White solid	—	(381)
Be[Ph(PhCH ₂)NH] ₂ Cl ₂	—	Gray solid	—	(381)
Be[Ph(Et)(PhCH ₂)N] ₂ Cl ₂	—	Brown solid	—	(381)
Be[(CH ₂) ₆ N ₄] ₂ Cl ₂	—	Colorless acicular crystals, $d_4^{20} = 1.23$	—	(196)
Be[<i>p</i> -C ₆ H ₄ (NH ₂) ₂] ₂ Cl ₂	—	Dark red solid	—	(381)
Be[1,2-C ₁₀ H ₆ (NH ₂) ₂] ₂ Cl ₂	—	Violet solid	—	(381)
Be[<i>p</i> -C ₆ H ₄ (NEt ₂)NH ₂] ₂ Cl ₂	—	Black solid	—	(381)
Be[<i>p</i> -C ₆ H ₄ (NEt ₂)NH ₂] ₂ Cl ₂	—	Black solid	—	(381)
Be(PhNHNH ₂) ₃ Cl ₂	—	White hygroscopic solid	s(g)(k)	(149)
Be(PhNHNH ₂) ₄ Cl ₂	—	Yellowish solid	—	(150)
Be(pyridine) ₂ Cl ₂	152	White crystals	—	(97, 153, 154)
Be(piperidine) ₂ Cl ₂	—	Microcrystalline white solid	—	(148)
Be(α-picoline) ₂ Cl ₂	—	White crystals	ss(c)(g)	(148)

(continued)

TABLE VII—continued

Complex	M.p. (°C)	Properties	Solubility	Ref.
Be(lepiline) ₂ Cl ₂	—	White hygroscopic solid	s(g); ss(c)(e)	(153)
Be(quinoline) ₂ Cl ₂	—	Yellow solid	s(g); ss(c)(e)	(151)
Be(quinaldine) ₂ Cl ₂	—	White microcrystalline solid	s(g)(l); ss(e)(h)(l)	(148)
Be(2,2'-bipyridyl)Cl ₂	—	Colorless needles, dec. > 330°	ss(e)	(117, 118)
HBeCl ₃ (pyridine) ₂	108	White crystals	—	(304)
HBeCl ₂ Br(pyridine) ₂	115	White crystals	—	(304)
Be(1-phenyl-3-methyl- pyrazolone) ₂ •(Et ₂ O) ₂ Cl ₂	—	White microcrystals; little evidence this is a pure compound	—	(148)
Be(HCN) ₄ Cl ₂	—	White prisms	s(a)(g)	(151)
Be(C ₂ H ₄ (CN) ₂) ₂ Cl ₂	—	White hygroscopic solid	s(c)(e)	(151)
Be(MeCN) ₂ Cl ₂	—	Colorless crystals	—	(154)
Be(EtCN) ₂ Cl ₂	—	Colorless hygroscopic prisms	s(c)(e)	(151)
Be(EtCN) _x Cl ₂	—	$x = 2, 3, 4, 5, 7$	—	(152)
Be(Me ₂ CHCH ₂ CH ₂ CN) _x Cl ₂	—	Silvery lustrous flakes	s(c)(e)(g)	(151)
Be(Me ₂ CHCH ₂ CH ₂ CN) _x Cl ₂	—	$x = 2, 3, 4$	—	(152)
Be(PhCN) ₂ Cl ₂	—	Colorless needles	s(e)(g)(k)	(154)
Be(PhCH ₂ CN) ₂ Cl ₂	151.5	White needles	s(c)(e)	(151, 153)
Be(<i>p</i> -MeC ₆ H ₄ CN) ₂ Cl ₂	—	Colorless crystals	s(e)(g); ss(c)	(151)
Be(<i>p</i> -MeC ₆ H ₄ CN) _x Cl ₂	—	$x = 2, 3, 4, 5, 7$	—	(152)
Be(α -C ₁₀ H ₇ CN) ₂ Cl ₂	—	Yellow crystals	s(e)(g)	(151)
Be(PhNO ₂) ₂ Cl ₂	—	Colorless crystals	s(g)(k); ss(c)(e)(l)	(149)
Be(8-nitronaphthylamine) ₂ Cl ₂	—	Orange solid	ss(d)(g)(h)(l)	(148)
Be(2,4-dinitrophenyl- hydrazine)Cl ₂	—	Chocolate solid prepared at 100°	—	(384)
Be(2,4-dinitrophenyl- hydrazine) ₂ Cl ₂	—	Chocolate solid prepared at 0°	—	(384)

Monochloro adducts

$[\text{Be}(\text{OBU}^t)\text{Cl}]_4$	—	White solid, decomp. from 170°	s(e)(c)	(14)
$[\text{Be}(\text{OBU}^t)(\text{Et}_2\text{O})\text{Cl}]_2$	88–90	Colorless crystals	s(c)	(14)
$[\text{Be}(\text{OBU}^t)(\text{THF})\text{Cl}]_2$	—	Colorless crystals	—	(14)
$\text{Be}(\text{OEt})\text{Cl} \cdot 0.7\text{CH}_3\text{COOEt}$	—	Viscous liquid	—	(295)
$\text{Be}(\text{OPr}^t)\text{Cl} \cdot 0.5\text{CH}_3\text{COOPr}^t$	—	Viscous liquid	—	(295)
$\text{EtBe}(2,2'\text{-bipyridyl})\text{Cl}$	—	Orange-yellow solid dec. 167°	ss(e)	(47)
$[\text{BU}^t\text{Be}(\text{Et}_2\text{O})\text{Cl}]_2$	79–80	Colorless needles	s(c)(e)	(204, 406)
$[(p\text{-tolyl})_2\text{C}:\text{NBeCl}]_2$	168–170	Colorless crystals	—	(484, 543)
$[(p\text{-tolyl}(\text{BU}^t)\text{C}:\text{NBeCl}]_2$	160–165 dec.	Colorless crystals	—	(484, 543)
$[\text{Ph}_2\text{C}:\text{NBeCl}]_2$	120–121	Crystalline solid	s(f)	(484, 543)
$\{\text{Be}[\text{o-C}_6\text{H}_4(\text{NH}_2)\text{O-}]\text{Cl}\}_2$	—	Black solid	—	(384)
$\{\text{Be}[\text{m-C}_6\text{H}_4(\text{NH}_2)\text{O-}]\text{Cl}\}_2$	—	Dark ash solid	—	(384)
$[\text{Be}(\text{o-C}_6\text{H}_4\text{NH}_2\text{COO-})\text{Cl}]_2$	—	Light ash solid	—	(384)
$[\text{Be}(\text{m-C}_6\text{H}_4\text{NH}_2\text{COO-})\text{Cl}]_2$	—	Light brown solid	—	(384)

Dibromo adducts

$\text{Be}(\text{H}_2\text{O})_4\text{Br}_2$	—	Prismatic hygroscopic crystals	—	(125)
$\text{Be}(\text{H}_2\text{O})_3(\text{Et}_2\text{O})\text{Br}_2$	—	Light yellow crystals	—	(125)
$\text{Be}(\text{Me}_2\text{O})_2\text{Br}_2$	70–72 dec.	Hygroscopic yellow crystals, sensitive to oxygen and light	—	(516)
$\text{Be}(\text{Et}_2\text{O})_2\text{Br}_2$	49, 53	Colorless rhomboidal crystals, four molecules in unit cell	—	(323, 425, 521, 523, 532)
$\text{Be}(\text{Et}_2\text{O})_3\text{Br}_2$	—	Stable below –4°	—	(523)
$\text{Be}(\text{THF})_2\text{Br}_2$	130 dec.	Flat crystalline tablets	—	(516)
$\text{Be}(\text{dioxane})\text{Br}_2$	—	Colorless solid	s(g); ss(c)(e)(h)	(342)
$\text{Be}(\text{CH}_3\text{COOEt})_2\text{Br}_2$	—	Brown viscous liquid	—	(295)
$\text{Be}(\text{H}_2\text{S})_2\text{Br}_2$	—	Dissociation pressure 24.5 mm at –20	—	(64)
$\text{Be}(\text{NH}_3)_4\text{Br}_2$	—	Colorless crystals	—	(57, 67)
$\text{Be}(\text{NH}_3)_x\text{Br}_2$	—	$x = 6, 10$	—	(67)

(continued)

TABLE VII—*continued*

Complex	M.p. (°C)	Properties	Solubility	Ref.
BeBr ₂ ·3Be(NH ₂) ₂ ·4NH ₃	—	White crystals	ss(q)	(57)
BeBr ₂ ·3Be(NH ₂) ₂ ·8NH ₃	—	White crystals	—	(57)
2BeBr ₂ ·Be(NH ₂) ₂ ·8NH ₃	—	White crystals	s(q)	(57)
Be(2,2'-bipyridyl)Br ₂	—	Pale cream solid	ss(e)	(117, 118)
Monobromo adducts				
HBeCl ₂ Br(Et ₂ O) ₂	—	Green liquid, fumes in air	—	(304)
HBeCl ₂ Br(pyridine) ₂	115	White crystalline solid	—	(304)
[Be(Obu ^t)(Et ₂ O)Br] ₂	—	Colorless crystals	s(c)(e)	(14)
[Be(Obu ^t)(THF)Br] ₂	—	Colorless crystals decomp. 230°	s(e)	(14)
Be(OEt)(CH ₃ COOEt)Br	—	Brown viscous liquid	—	(295)
[Bu ^t Be(Et ₂ O)Br] ₂	55–56	Colorless needles	s(c)(e)	(406)
Diiodo adducts				
Be(H ₂ O) ₂ (Et ₂ O) ₂ I ₂	—	Brown solid, poor analysis	—	(125)
Be(Me ₂ O) ₂ I ₂	—	Pale brown solid	—	(516)
Be(dioxane)I ₂	—	Pale yellow solid	—	(516)
Be(4-aminoantipyrine) ₂ I ₂	—	Light yellow solid	—	(133)
Be(H ₂ S) ₂ I ₂	—	Not fully characterized	—	(64)
Be(NH ₃) _x I ₂	—	$x = 4, 6, 13$	—	(67)
2BeI ₂ ·3NH ₃	—	Crystalline solid	s(q)	(271)
BeI ₂ ·3Be(NH ₂) ₂ ·4NH ₃	—	Crystalline solid	s(q)	(57)
BeI ₂ ·5Be(NH ₂) ₂ ·4NH ₃	—	Colorless crystals	s(q)	(57)
Be(2,2'-bipyridyl)I ₂	—	Yellow solid	ss(e)	(117, 118)

Monoiodo adducts

$[\text{Be}(\text{O}i\text{Bu})(\text{Et}_2\text{O})\text{I}]_2$	—	Colorless crystals, dec. from 120°	s(c)(e)	(14)
$[\text{Be}(\text{O}i\text{Bu})(\text{THF})\text{I}]_2$	167–168 dec.	Colorless crystals	s(c)	(14)

Pseudohalide adducts

$\text{Be}(4\text{-aminoantipyrine})_2(\text{SCN})_2$	—	Pale yellow solid	s(a)(k)	(133)
$\text{Be}(\text{Et}_2\text{O})_2(\text{SCN})_2$	37–38	White acicular crystals	s(c)(e)(g)(k)	(345)
$\text{Be}(\text{dioxane})_2(\text{SCN})_2$	—	Pale yellow crystals	—	(345)
$[\text{MeBeCN} \cdot \text{Me}_3\text{N}]_n$	—	Air-sensitive white solid	—	(120)

^a Key to abbreviations:

s = soluble

i = insoluble

ss = sparingly soluble

a = water

b = dimethyl ether

c = benzene

d = carbon tetrachloride

e = diethylether

f = toluene

g = ethanol

h = dioxane

j = xylene

k = acetone

l = chloroform

m = carbon disulfide

n = phosphorus oxychloride

p = dimethyl sulfide

q = ammonia

^b Incorrectly described in ref. (524) as $\text{Be}(\text{MeOC}_2\text{H}_4\text{OMe})_2\text{Cl}_2$, but analysis correct for $\text{Be}(\text{MeOC}_2\text{H}_4\text{OMe})\text{Cl}_2$.

(524) may also be prepared by reaction of the metal suspended in the ether with dry hydrogen chloride. Unlike beryllium chloride, the diethyl ether complex is appreciably soluble in C_6H_6 , CS_2 , and CCl_4 , although insoluble in petroleum ether (522). The hexagonal prisms are converted into a more stable modification on grinding, the properties of which differ from the former modification, being almost insoluble in ether and decomposing without melting. The melting point of the etherate crystals falls with time. Ether solutions, stored for a long time at room temperature, form a crystalline film or a flocculent precipitate whose composition is close to $Be(OEt_2)_2Cl_2$ and is structurally identical to the previously mentioned stable modification. The transformation is thought to be related to a change in configuration of the $Be(OEt_2)_2Cl_2$ molecule to form a more polar molecule which is less soluble in ether (522). After prolonged treatment of the dietherate *in vacuo* a crystalline dimeric monoetherate is formed, association occurring doubtless via chlorine bridges (97) (Fig. 10).

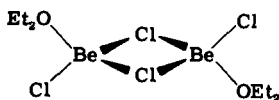


FIG. 10. The structure of $[Et_2OBeCl_2]_2$.

Anhydrous beryllium chloride dissolves in ether forming a two-phase system, the lower layer being a solution of ether in the complex and the upper layer being a solution of the etherate complex in ether. The composition of the top and bottom layers does not substantially change with temperatures between 15° and 80° . On cooling a dilute solution to about -70° , $BeCl_2 \cdot 3Et_2O$ crystallizes and this is stable below -2° ; between -2° and 15° , the dietherate, which melts under ether solution at 14.5° – 15.0° forming the lower immiscible layer, is the stable phase. The heats of solution of the di- and trietherates are -9.55 and -2.30 kcal·mole⁻¹, respectively, being slightly higher than those for the corresponding tetrahydrofuranates (520, 522).

The bromide dietherate may be obtained in similar fashion to the analogous chloride by crystallization from its ethereal solutions. Such solutions are prepared by dissolving anhydrous beryllium bromide in ether or by the reaction of beryllium metal with HBr or Br_2 in ether (425, 521). Brominated ethers are produced in the reaction of beryllium, bromine, and ether when carried out under refluxing conditions (17–19). The bromide dietherate has four molecules in the unit cell and is not isomorphous with the chloride (425). The melting point of $Be(OEt_2)_2Br_2$,

in contrast to the chloride, does not alter with time. The existence of a trietherate has been demonstrated and this reverts to the dietherate above -4° . The heats of solution for the di- and trietherates are -7.35 and -1.90 kcal \cdot mole $^{-1}$, respectively. Crystals of the bromide-dietherate melt under ether at 37° , when a lower layer of a solution of ether in the dietherate is formed; layering of the solution remains up to 160° (523).

Iodine also reacts with beryllium in ether, heat being required for the completion of the reaction, but a solid etherate could not be isolated (521).

Decomposition of the chloride dietherate begins at 55° – 60° and is complete at 220° – 240° , whereas the bromide analog starts to decompose at 70° and decomposition is complete by 160° – 170° (530). No definite intermediary thermal decomposition products are formed, but it may be inferred that decomposition takes place by the route



The bromide and chloride dietherates have dipole moments of 7.52 and 6.74 D [6.23 D quoted in ref. (514)], respectively, in benzene solution at 20° indicating the tetrahedral nature of the compounds (323, 532). Dielectric measurements on a number of molecular complexes of Be, Zn, Cd, and Hg halides have also been interpreted in terms of a tetrahedral configuration for undissociated complexes (229). Interaction between ether dipoles and the large dipoles of the beryllium halide bisetherates accounts for the existence of the weak trietherate complexes.

Beryllium halide etherates are poor conductors of electricity, the chloride being the best of the series. Electrolysis of an ethereal solution of the chloride yields 92% pure beryllium metal and electrolysis of a bromide solution yields a less pure metal (555). For ethereal solutions of beryllium chloride and bromide, the conductivity of the upper layer increases with concentration, but that of the lower layer decreases. There is a sharp increase in molar conductivity (100-fold) and viscosity in passing from the upper to the lower layer. The bromide and chloride dietherates are associated in benzene, but, since all the bonding orbitals are occupied, association must be weak, involving electrostatic or polarization forces. The degrees of association (α) increase linearly with concentration up to $\alpha = 2$ – 2.5 after which the increase is rather slow up to $\alpha \sim 3$ (525), whereas the ether addition compounds of aluminum chloride and bromide exist mainly as monomers up to very high concentrations (531). Isopiestic measurements in ether at concentrations bordering the heterogeneous region show the following degrees of association (525) as tabulated below.

Complex	Temp. (°C)	α
Be(OEt ₂) ₂ Cl ₂	20	3.0
Be(OEt ₂) ₂ Br ₂	20	2.9
Be(OEt ₂) ₂ Br ₂	37	3.0

The structure of the trimeric associate based on dipole-dipole interaction does not account for the large increase in conductivity and so it has been suggested that ion pairs of the type $[\text{Be}_3\text{Cl}_3(\text{Et}_2\text{O})_6]^{3\delta+}[\text{Cl}^{\delta-}]_3$ are present (526).

Although dimethyl ether, tetrahydrofuran, and tetrahydropyran complexes of beryllium chloride have been isolated as crystalline solids, a dibutyl ether complex could not be obtained (520, 524). The tetrahydrofuran complexes $\text{Be}(\text{THF})_2\text{Cl}_2$ and the corresponding bromide are isomorphous; an iodide complex could not be isolated (425, 516). Both "monoglyme" and dioxane readily replace diethyl ether; the dioxane complexes of the chloride and bromide are sparingly soluble in ether, dioxane, and benzene, indicating a polymeric structure for the adducts in which each of the two oxygen atoms in the dioxane molecule is coordinated to different metal atoms as in $\text{Mg}(\text{dioxane})\text{Br}_2$ (118, 342, 524).

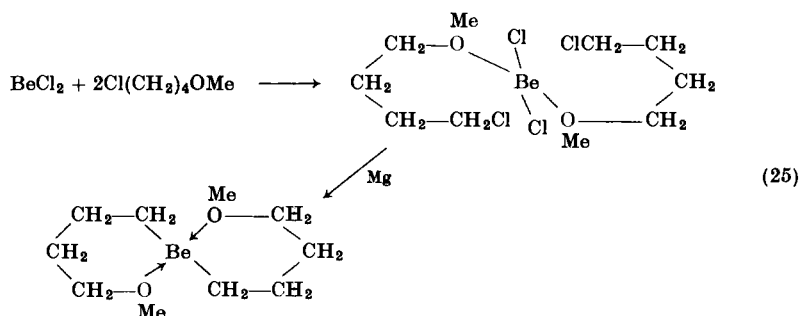
The thio analog of monoglyme, $\text{MeSC}_2\text{H}_4\text{SMe}$, will not replace ether in beryllium chloride-ether complexes, sulfur being a weaker donor than oxygen to beryllium, but it forms a 1:1 chelate complex with beryllium chloride in benzene solution (118).

The thermal stability of the chloride complexes with monoethers increases sharply from open chain to cyclic ethers. Melting points and thermal stability of dimethyl- and diethyletherates show some tendency to increase as the atomic weight of the halide increases. Beryllium bromide and iodide complexes with aliphatic ethers are light-sensitive (516, 524).

The structures of some of the "onium" compounds formed by beryllium halides have been discussed and estimates made for the interatomic distances and bond angles in these adducts. The infrared vibrations in these complexes have been tabulated, but beryllium-halogen vibrations have not been assigned (434, 517, 529), although beryllium-oxygen vibrational frequencies are well known (157).

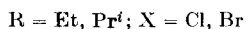
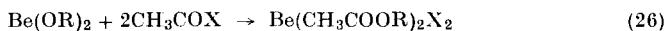
Beryllium chloride forms an interesting colorless crystalline 1:2 complex with 4-chlorobutylmethyl ether which is reduced by magnesium in ether forming the spiran-type compound beryllium bis-(δ -methoxy-

butyl) which may also be prepared directly from the Grignard reagent of the chloroether and BeCl_2 (24).



The rate of exchange of complexed and uncomplexed solvent, dimethylformamide, at 290°K varies from 2 sec^{-1} for AlCl_3 to 150 sec^{-1} for BeCl_2 . The primary solvation number for the $\text{Be}(\text{II})$ ion is four, oxygen being the donor atom and the activation energy for the exchange process is ca. $16 \text{ kcal} \cdot \text{mole}^{-1}$ (147, 294).

Beryllium halides form 1:2 complexes with aldehydes, ketones, and esters (149, 153, 154, 229, 295). The adducts are usually prepared from anhydrous beryllium halides and the Lewis base, although ester complexes have also been obtained from the reaction of beryllium alkoxides with excess acetyl halides (295).

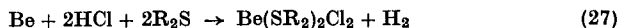


At 5° , solutions of BeCl_2 in $\text{Me}_2\text{CO}/\text{C}_6\text{H}_6$ deposit the unusual complex $\text{Be}(\text{Me}_2\text{CO})_2\text{Cl}_2 \cdot 4\text{C}_6\text{H}_6$, which readily loses benzene (154). Beryllium chloride also reacts with POCl_3 forming the crystalline complex $\text{BeCl}_2 \cdot 3\text{POCl}_3$ (527) and with S_4N_4 in thionyl chloride producing the yellow complex $\text{Be}(\text{S}_2\text{N}_2\text{O})\text{Cl}_2$ and thiodithiazyl dioxide ($\text{S}_3\text{N}_2\text{O}_2$) (28), but the structures of these chlorides are not clearly established.

The conductivity of $\text{BeCl}_2 \cdot \text{AlCl}_3 \cdot 3\text{Et}_2\text{O}$ is greater by three orders of magnitude than that of $\text{Be}(\text{OEt}_2)_2\text{Cl}_2$ and is three times that of $\text{Al}(\text{OEt}_2)_3$ in benzene solution. It shows no sign of dissociation into its components in organic solvents and forms a two-phase system in benzene and ether, even at high dilution, with the complex almost entirely concentrated in the lower phase. The complex which melts congruently at 55° , has been formulated with the ionic structure $[\text{Be}(\text{OEt}_2)_3\text{Cl}]^+[\text{AlCl}_4]^-$ on the basis of its infrared spectrum (514, 515). Phase studies of the $\text{Be}(\text{OEt}_2)_2\text{Cl}_2\text{-Ga}(\text{OEt}_2)\text{Cl}_3$ system over the whole range of concentration of components showed the existence of a 1:1

compound, melting congruently at 61° , isostructural with the corresponding aluminum compound and which may, therefore, be formulated as $[\text{Be}(\text{OEt}_2)_3\text{Cl}]^+[\text{GaCl}_4]^-$ (426).

Solutions containing adducts of beryllium halides with thioethers have been prepared by reaction of the halide with the donor and by reaction of beryllium metal in the donor solvent with hydrogen halide; reactions are less vigorous in thioethers than in ordinary ethers (118, 464).



$\text{R} = \text{Me}, \text{Et}, \text{Bu}^i$

$\text{R}_2\text{S} = \text{thiophene}$

Only the bisdimethyl sulfide complex of beryllium chloride has actually been isolated; Coates and Green (118) reported its melting point as 117° – 119° , while other authors (464) state that its vapor pressure is negligible up to its melting point (55°), but that it decomposes from 65° with the formation of alkyl halide. The complex di- μ -chlorodichlorobis(dimethylsulfide)diberyllium (Fig. 11) is obtained on evaporation *in vacuo* of a toluene solution of $\text{Be}(\text{SMe}_2)_2\text{Cl}_2$ (118).

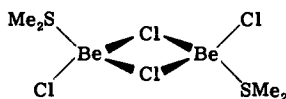


FIG. 11. The structure of $[\text{Me}_2\text{SBeCl}_2]_2$.

Trithioetherates, $\text{Be}(\text{SR}_2)_3\text{Cl}_2$ ($\text{R} = \text{Me}, \text{Et}, \text{Bu}^i$), have been obtained as white needles at low temperature, but these liquefy below room temperature (464). Although weak adducts of BeBr_2 and BeI_2 with H_2S have been obtained from which the H_2S may readily be recovered, the chloride does not dissolve in, nor react with, H_2S (64). BeI_2 reacts with H_2S on heating to form beryllium sulfide (270).

Amide and thioamide complexes of beryllium chloride have also been obtained (385). In the urea and thiourea complexes, oxygen and sulfur, respectively, are the donor atoms since the former forms an inner tetracoordinated beryllium complex and the latter a 2:1 complex in which the beryllium–halogen bond is retained; oxygen is a stronger donor to beryllium than sulfur and the presence of the NH_2 groups enhances the donor character of the oxygen and sulfur atoms, whereas the carbonyl and thiocarbonyl group decreases the basicity of the nitrogen atoms. Spectroscopic studies have shown that oxygen and sulfur, respectively, coordinate to the metals in urea and thiourea complexes of zinc and other metal halides (373, 557). Steric factors are believed to preclude the

formation of 2:1 complexes with symmetrical and asymmetrical substituted thioureas, although 1:1 complexes have been obtained in which sulfur rather than nitrogen is believed to be the donor atom, since these adducts are hygroscopic, unlike nitrogen coordinated complexes (385).

The Raman spectrum of the BeCl_2 -glycine system in aqueous solution is quite different from the spectra of the zinc- and cadmium-glycine systems. At low pH, a large shift in the C-C stretching frequency indicates strong coordination of the ligand to beryllium. Also, since the spectrum indicates that the amino group is protonated, it seems glycine binds only through the carboxyl oxygen and that Be(II) coordinates only two glycine molecules in solution. With increasing pH, hydrolysis of the Be(II) ion takes place with consequent breaking of the metal ligand bond (259).

2. Nitrogen Complexes

Beryllium halides form a series of ammonia complexes which increase in stability with increasing atomic weight of the halogen (65). The tetrammine, $\text{Be(NH}_3)_4\text{Cl}_2$, whose lattice parameters (424) differ little from those of K_2BeCl_4 , may be prepared by reaction of the anhydrous chloride with ammonia or by reaction of the metal in liquid ammonia with two equivalents of ammonium chloride (57, 67, 149, 301). On heating above about 250° , the tetrammine splits out NH_4Cl (138) but *in vacuo* at 210° – 255° the bisammine, melting at about 350° , is obtained (138). Experiments using a tensieudiometer have shown that beryllium chloride forms weak complexes with 12 and 6 molecules NH_3 at low temperatures, as well as the 4:1 and 2:1 complexes. Likewise the bromide and iodide have been shown to form adducts containing 10, 6, and 4 molecules NH_3 and 13, 6, and 4 molecules NH_3 per beryllium atom, respectively (67), and the unusual complex $2\text{BeI}_2 \cdot 3\text{NH}_3$ has also been reported (271). The tetrammines are the most stable and the adducts containing more than 4 molecules NH_3 are found only at low temperatures (57, 67). The dissociation pressures, total and partial heats of formation of the beryllium halide-ammine complexes, and the heats of solution in hydrochloric acid have been determined; $\text{Be(NH}_3)_4\text{Cl}$ has a slightly greater heat of formation than has $\text{Be(H}_2\text{O)}_4\text{Cl}_2$ (65, 67).

A solution of NH_4Cl in liquid ammonia dissolves beryllium to form BeCl_2 , which, in turn, reacts with excess metal to form a very slightly soluble ammonobasic beryllium chloride of approximate composition $\text{BeCl}_2 \cdot \text{Be(NH}_2)_2 \cdot x\text{NH}_3$. Similar reactions of BeBr_2 with NH_4Br yield $\text{BeBr}_2 \cdot 3\text{Be(NH}_2)_2 \cdot 4\text{NH}_3$, $2\text{BeBr}_2 \cdot \text{Be(NH}_2)_2 \cdot 8\text{NH}_3$, and $\text{BeBr}_2 \cdot 3\text{Be(NH}_2)_2 \cdot 8\text{NH}_3$, whereas the iodides produce $\text{BeI}_2 \cdot 3\text{Be(NH}_2)_2 \cdot 4\text{NH}_3$,

which gradually dissolves beryllium metal forming a colorless, crystalline complex $\text{BeI}_2 \cdot 5\text{Be}(\text{NH}_2)_2 \cdot 4\text{NH}_3$ (57).

Beryllium halides form a series of complexes with primary, secondary, and tertiary amines (97, 149, 151, 153, 381), diamines (150), and nitrogen-containing heterocycles (97, 117, 118, 148, 151, 153, 154). Aromatic amine complexes are normally colored and do not melt below 250° (149, 151, 153, 381). The diamines usually form 1:1 complexes in which ligands such as 1,2-naphthalenediamine act as chelating agents, whereas ligands like *p*-phenylenediamine probably act as catenating ligands. Ethylenediamine and benzidine produce complexes containing between 1 and 2 molecules of amine per beryllium (150), while 4-aminoantipyrine forms chelate complexes with beryllium bromide, iodide, and thiocyanate (133). Phenylhydrazine forms 4:1 and 3:1 complexes with BeCl_2 , the former being formed with a vast excess of donor and the latter when the ratio of BeCl_2 :ligand is 1:3 (149, 150). The hexamethylenetetramine- BeCl_2 complex is soluble in water and, on heating the aqueous solution, formaldehyde is produced (196).

American workers have observed some unusual reactions of beryllium chloride with amines. Tetramethylhydrazine and beryllium chloride react in ether yielding a white precipitate from which at 120° *in vacuo* $\text{Me}_2\text{NNMe}_2 \cdot 1.5\text{HCl}$ sublimes. In similar fashion, tribenzylamine and trimethylamine hydrochlorides have been obtained from the corresponding amines. In the absence of solvent, pyridine yielded $\text{C}_5\text{H}_5\text{N} \cdot \text{HCl}$, but in benzene solution $\text{Be}(\text{pyridine})_2\text{Cl}_2$ was obtained. The fate of the beryllium in these reactions, where amine hydrochloride is formed, has not been established. These same authors suggest that the 2:1 amine complexes of BeCl_2 have characteristics indicating their ionic nature and the ease with which the amine hydrochloride is formed supports their formulation as $[\text{L}_4\text{Be}]^{2+}[\text{BeCl}_4]^{2-}$. Further work is obviously necessary to establish the nature of the amine complexes of the beryllium halides.

Coates and Green (117, 118) have prepared a series of colored 2,2'-bipyridyl complexes of beryllium halides and organoberyllium compounds. All are chelate complexes with high intensity bands in the 220–300 $\text{m}\mu$ region, similar to those in free bipyridyl; the long-wavelength absorption bands only are given in Table VIII, together with the molar extinction coefficients. For absorptions giving visible color, there is a small decrease in λ_{max} , together with a marked decrease in extinction coefficient in passing from the less to the more electronegative halogen. For the organic derivatives the trend is in the same direction as the electronegativity of the organic group increases. The colors are due to electron transfer from one of the $\text{Be}-\text{X}$ bonds to the lowest unoccupied orbital of the bipyridyl. Thus, in the excited state of the complex, the

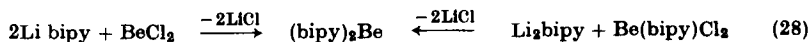
Be-X bond is acting as an electron donor. The donor character will be greater if the electrons in the bond are relatively loosely held, as in beryllium alkyls, than if bonding were strong, as is probable in the beryllium halides, although it is possible for the halide complexes that the electron source is one of the nonbonding orbitals of the halogen.

TABLE VIII
2,2'-BIPYRIDYL COMPLEXES OF BERYLLIUM COMPOUNDS^a

X in Be(bipy)X ₂	Color	λ_{\max} (m μ)	Molar extinction coefficient $\times 10^{-3}$
Cl	White	352 infl.	1.2
Br	Pale cream	364	2.4
I	Yellow	368	7.0
Ph	Yellow	353 infl.	0.5
Me	Yellow	395	2.7
Et	Red	461	3.7

^a From Coates (118), reproduced with permission.

Lithium bipyridyl reacts with beryllium chloride forming the green solid bisbipyridylberyllium which is also formed from dilithium bipyridyl and Be(bipy)₂Cl₂. This complex is formulated as (bipy⁻)₂Be²⁺ from magnetic and esr measurements (98, 118).



Many years ago, BeCl₂·2quinoline·H₂O was reported (404), but other workers (151) have not been able to substantiate the existence of this compound. Hydrazine hydrate gives complexes of the type 2BeCl₂·3N₂H₄·4H₂O and 2BeCl₂·5N₂H₄·2H₂O, which are probably mixtures of beryllium-aquo and beryllium-hydrazine complexes (150).

Nitrobenzene forms a bis complex with BeCl₂, but nitromethane reacts with the evolution of HCl (149). With nitriles, usually 2:1 adducts are formed. Succinonitrile forms a 1:1 chelate, whereas HCN forms a 4:1 complex, but cyanogen does not form a stable adduct (151, 154). In the BeCl₂(nitrile)₂-nitrile systems, the existence of adducts containing 3 and 4 moles of isocapronitrile and 3, 4, 5, and 7 moles of propionitrile and *p*-toluinitrile per beryllium atom has been demonstrated. Aceto- and naphthonitriles readily char in the presence of beryllium chloride (152). Complexes of metal halides with alkyl cyanides have been reviewed up to 1965 (546).

Aminophenols, aminobenzoic acids, nitroanilines, and 2,4-dinitrophenylhydrazine form 2 : 1 complexes which are usually insoluble in most

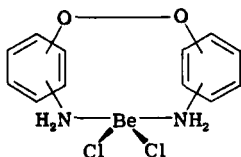


FIG. 12. Proposed structure of $\text{Be}_2[\text{C}_6\text{H}_4(\text{NH}_2)\text{O}]_2\text{Cl}_2$.

organic solvents. The latter also forms a 1 : 1 complex with BeCl_2 at 100° . Heating BeCl_2 with the aminophenol or aminobenzoic acid complexes in a 1 : 1 ratio results in the liberation of HCl and the proposed structures

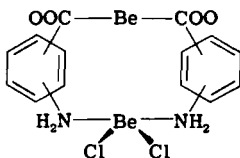


FIG. 13. Proposed structure of $\text{Be}_2[\text{C}_6\text{H}_4(\text{NH}_2)\text{COO}]_2\text{Cl}_2$.

for the products are shown in Figs. 12 and 13 (384). Evidence to substantiate these structures has not been presented.

D. HYDRIDO- AND ORGANOBERYLLIUM HALIDES

There are few references in the literature to the hydrido- and organoberyllium halides. Reactions between beryllium dialkyls and hydrogen halides, iodine, or beryllium halides and between the metal and alkyl halides, both in the presence and absence of ethers, produce the organoberyllium halides (114, 134, 177, 178, 420, 561). The ether-free products are insoluble in alkyl halides and are doubtless coordination polymers. The beryllium-alkyl groups in such compounds add across carbonyl bonds producing, after hydrolysis, alcohols (561) in similar fashion to the addition of beryllium dialkyls to carbonyl compounds (145).

t-Butylberyllium chloride monoetherate (Fig. 14), obtained from di-*t*-butylberyllium etherate and beryllium chloride, is dimeric in benzene solution, though monomeric in ether solution. The analogous bromide has also been obtained. It is surprising that a bisetherate has not been isolated, although it probably exists in ether solution, but steric crowding round the beryllium may preclude its formation (204, 406).

Ashby has provided conclusive evidence for the redistribution of BeX_2 ($\text{X} = \text{Cl}, \text{Br}$) with R_2Be ($\text{R} = \text{Me}, \text{Et}, \text{Ph}$) in ether (18, 19). The product is formulated as RBeX [cf. (130)], analogous to the Grignard reagent (16, 131). The degree of association of MeBeBr in ether is 1.0–1.1 in 0.05–0.10 M solution; Me_2Be , MeBeCl , and PhBeBr are also essentially monomeric in the same concentration range. The ^1H magnetic resonance spectrum of a 2:1 mixture of Me_2Be and BeBr_2 in ether at -78° indicates the presence of Me_2Be species, mixed with the redistribution product, MeBeBr (18, 19). Dimethyl sulfide solutions of BeCl_2 and excess Me_2Be at -45° are believed to contain the species $\text{MeBeCl}(\text{SMe}_2)_2$; whether BeCl_2 – Me_2S adducts are also present in such solutions has not been established (255). Coordination complexes of RBeX with dioxane and

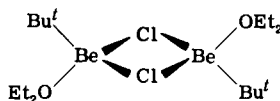


FIG. 14. The structure of $[\text{Bu}^t\text{Be}(\text{Et}_2\text{O})\text{Cl}]_2$.

2,2'-bipyridyl have been isolated from R_2Be – BeX_2 mixtures (18, 19, 47) and thus the Schlenk equilibrium (177) lies well to the right in ether



at room temperature. Beryllium reacts much faster with acid halides than with alkyl halides. The products of the former reaction have not been isolated in a pure state, but their structure as acylberyllium halides $[\text{RC}(\text{O})\text{--Be--X}]$ was established by the character of their chemical reactions. With water, acid halides, and ketones, these halides form aldehydes, α -diketones, and α -hydroxyketones, respectively (266, 267).

Strohmeier and co-workers have prepared a series of crystalline diethylberyllium salts, having the general formula $\text{MX}(\text{BeEt}_2)_n$ (Table IX), where MX is an alkali metal halide or pseudohalide or a quaternary ammonium halide and $n = 1, 2$, or 4. Complexes with LiF , NaCN , and CsCl could not be obtained (476–478, 481). The ease of complex formation is related to the lattice energy of MX and increases with increasing radius of the cation, but decreases with increasing size of the anion (478), as has been found for a similar series of salts of the aluminum alkyls (566). Ether-free diethylberyllium is liberated on heating most of the 2:1 complexes *in vacuo* or in hot benzene solution. In some cases 1:1 complexes are formed; $\text{RbF}(\text{BeEt}_2)_2$ on heating in benzene yields the 1:1 complex and an unusual complex $\text{RbF}(\text{BeEt}_2)_3$ (481). The structures

TABLE IX
COMPLEX DIETHYLBERYLLIUM SALTS $\text{MX}(\text{BeEt}_2)_n$

MX	<i>n</i>	M.p. (°C)	MX	<i>n</i>	M.p. (°C)
KF	2	83	Me_4NF	2	80–90 dec.
KF	1	46–48	Me_4NCl	2	Liquid
RbF	2	61–63	Et_4NCl	2	Liquid
CsF	2	29–31	$\text{PhCH}_2(\text{Me})_3\text{NF}$	2	Liquid
KCN	4	52–53	$\text{PhCH}_2(\text{Me})_3\text{NCl}$	2	Liquid

of the 2:1 complexes are probably similar to that of $\text{KF}(\text{AlEt}_3)_2$ (Fig. 15) (13). The specific conductivity of these salts lies in the range 10^{-2} – 10^{-3}

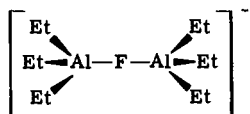
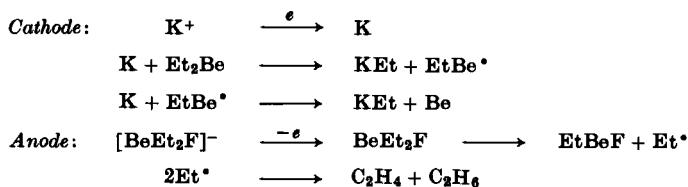


FIG. 15. The ion $[(\text{AlEt}_3)_2\text{F}]^-$ in $\text{KF}(\text{AlEt}_3)_2$; the fluorine atom is octahedrally surrounded by six potassium ions.

$\text{mhos} \cdot \text{cm}^{-1}$ at 80° and the decomposition potentials, which decrease with increasing temperature, are considerably larger than the polarization potentials (480, 481). Beryllium metal, containing 20–30% beryllium carbide, is electrically deposited from the 2:1 complexes at 60° – 100° (479, 483). The following mechanism has been proposed for the electrolysis of $\text{KF}(\text{BeEt}_2)_2$. The deposited beryllium contains both Be_2C and



polycrystalline K. Evidence for the radical intermediate EtBe^\bullet is provided from the fact that when the electrolysis is carried out in the presence of pyridine at 80° , the formation of the radical complex $(\text{pyBeEt})^\bullet$ is indicated by ESR (482).

Although the hydridoberyllium halides have not yet been formed, a recent disclosure (454) reveals the formation of their tertiary amine

complexes. These complexes, $\text{HBeX} \cdot \text{L}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{L} =$ tertiary amine), are essentially dimeric in benzene solution (where molecular weights have been measured). Thus, the structures of these compounds (Fig. 16) contain a double hydrogen bridge between two beryllium atoms

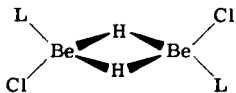
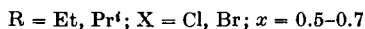


FIG. 16. Hydridoberyllium chloride-amine complexes ($\text{L} =$ tertiary amine).

like the similar complexes formed by the organoberyllium hydrides (48–50). The adducts are useful intermediates for the production of pure beryllium hydride, a useful component for propellants, and can be decomposed thermally to pure metallic beryllium. Reaction with olefins results in the formation of organoberyllium halide-amine complexes; reduction of aldehydes, ketones, nitriles, and esters can also be effected.

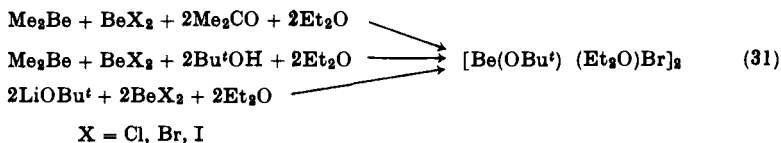
E. ALKOXY- AND KETIMINOBERYLLIUM HALIDES

The literature gives little information about the alkoxyberyllium halides. Acetyl halides react exothermically with beryllium alkoxides yielding ester complexes of the alkoxyberyllium halides.



With excess acetyl halide, ester complexes of the beryllium halides are produced (295).

Dimeric *t*-butoxyberyllium halide etherate complexes (14) have been obtained by similar routes used for the formation of dimeric alkoxy-magnesium halide etherates (119). Tetrahydrofuranates, prepared from



the etherates by displacement reactions, are also dimeric in benzene solution. $[\text{Be}(\text{OBu}^t)(\text{Et}_2\text{O})\text{Br}]_2$ is also dimeric in the solid state, its structure (453) being similar to that of the corresponding magnesium complex (317) with butoxy, rather than halogen bridges (Fig. 17) as expected, since beryllium- and magnesium-halogen bridge bonds do not often persist in the presence of ethers. The ether-free chloride (14) is

tetrameric in benzene solution like many alkylberyllium alkoxides (145) having probably a cubane-type structure like $(\text{MeZnOBu}^t)_4$ (452).

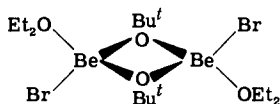


FIG. 17. The structure of $[\text{Be}(\text{OBu}^t)(\text{Et}_2\text{O})\text{Br}]_2$.

An unusual series of compounds, $\text{X}_2\text{Be}_3(\text{OBu}^t)_4$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{Me}, \text{Bu}^t, \text{PhC}\equiv\text{C}, \text{N}_3$, and BH_4), has recently been obtained (14). The structures of the chlorine member of this series (453) and $[(\text{Me}_2\text{N})_2\text{Be}]_3$ (22) are very similar (Fig. 18). In this latter compound, the terminal nitrogen

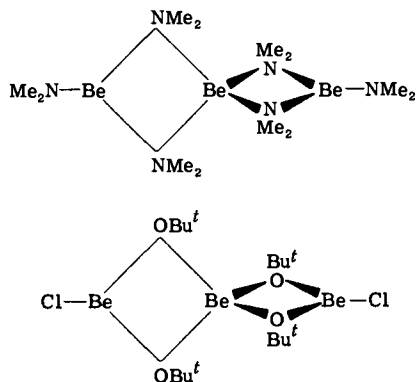


FIG. 18. Structures of $[(\text{Me}_2\text{N})_2\text{Be}]_3$ and $\text{Cl}_2\text{Be}_3(\text{OBu}^t)_4$.

and beryllium atoms are free to form a dative π bond. Beryllium-chlorine π bonding may be present in $\text{Cl}_2\text{Be}(\text{OBu}^t)_4$ and also in the ketiminoberyllium chloride dimers $(\text{R}_1\text{R}_2\text{C}=\text{NBeCl})_2$, which contain bridging ketimino groups (484, 543).

F. MISCELLANEOUS REACTIONS

Reactions of the halides, especially the chloride, with Grignard or lithium reagents or with organoaluminum compounds have been used for the preparation of beryllium alkyls and aryls (115, 116, 177, 179, 181, 258, 312, 377). With sodium hydridodiethylberyllate, or with R_2Be ($\text{R} = \text{alkyl, aryl}$) and LiH or NaBEt_3H in ether, solutions are obtained from which organoberyllium hydride complexes may be isolated (48-50, 121).

Beryllium bromide has been used as a catalyst for the bromination of several organic molecules (365, 366, 485). The chloride acts as a Friedel-Crafts catalyst and as a catalyst in the polymerization of olefins, but it is less effective than either AlCl_3 or ZrCl_4 (90, 123, 194).

Beryllium dialkyls usually react readily with donor molecules containing a reactive hydrogen atom, liberating alkane and forming associated compounds. The halides require more vigorous treatment before hydrogen halide is liberated in similar reactions. With organic acids and anhydrides, the normal or basic salts are formed (141, 158, 382, 429) and with alcohols or alkali metal alkoxides, beryllium alkoxides are produced (15, 30, 51, 149, 159, 383, 519, 528).

G. UNIVALENT BERYLLIUM HALIDES

Although beryllium usually exhibits a charge number of two, there is some evidence, especially spectroscopic evidence (Section V), for the existence of Be(I) halides.

The readily oxidizable intermediate, formed by the anodic dissolution of beryllium in halide solutions, is thought to be a Be(I) derivative (207, 268, 466-468), but the equilibrium concentration of Be^+ at 25° is very small and thus suggestions (80, 81, 166) that Be(I) may form at ordinary temperatures must be doubtful. Beryllium iodide reacts with beryllium at 400° , as shown by the disappearance of the metal, which is replaced by a fine white powder having a Be:I ratio of 1:1.4, but there is some doubt concerning the reliability of the beryllium analysis in this work (215).

In view of other unconfirmed reports of metals exhibiting unusual valency states, further work is necessary before the existence of Be(I) at ordinary temperatures can be substantiated.

IV. Beryllium Pseudohalides

A. CYANIDE

The product of the reaction between beryllium iodide and cyanogen at ca. 500° probably contains beryllium cyanide, since it dissolves in water forming a viscous solution which shows reactions characteristic of aqueous cyanide solutions (271). The anhydrous cyanide is precipitated from solution when ethereal dimethylberyllium is added to excess HCN in benzene. It does not react with trimethylamine nor dissolve in solvents with which it does not react since it, no doubt, has a cross-linked

polymeric structure (120, 283). Equimolar quantities of the above reactants form methylberyllium cyanide, which is associated like its trimethylamine complex (120).

B. AZIDE

Beryllium azide, $\text{Be}(\text{N}_3)_2$, is precipitated as a white, water-sensitive solid in the reaction of HN_3 with Me_2Be at low temperature. It is reasonably stable like the alkaline earth azides (551).

C. THIOCYANATE

An aqueous solution of $\text{Be}(\text{SCN})_2$ is obtained from the reaction of BeCO_3 and HSCN . From such solutions, a viscous or vitreous material is obtained, dissolving readily in donor solvents (339). Bisether, bisdioxane, and bis-4-aminoantipyrine complexes of $\text{Be}(\text{SCN})_2$ and the double salt $\text{Cs}_2\text{Be}(\text{SCN})_4 \cdot 2\text{H}_2\text{O}$ have been prepared and characterized (133, 339, 344, 345). The extraction of beryllium from aqueous ammonium thiocyanate solutions into organic solvents has been studied with a view to using this as a means of separating Be from other metal ions (61–63). The highest distribution coefficient ($\text{Be}_{\text{org}}^{2+}/\text{Be}_{\text{aq}}^{2+}$) was found when the organic phase was alcohol, ester, or ketone at pH 2–3; the beryllium extracts, as does Li^+ , Mn^{2+} , Al^{3+} , or Fe^{3+} , as the simple thiocyanate salt (61).

V. Spectroscopic Studies

Studies by Klemperer and co-workers (550), using electric quadrupole deflections of molecular beams to detect dipole moments, indicate that in the case of the gaseous group II dihalides, the linear form is found for light metal–heavy halogen, whereas the bent form is favored for light halogen–heavy metal combinations. The observed trends in the geometry of these halides has been explained on orbital energy considerations (203). The linear geometry of the beryllium halides has been confirmed by infrared spectroscopy (470).

Using the matrix isolation technique, the infrared spectra of the halides have been recorded by Snelson (470, 471); his assignments and calculated force constants, which are close to those found for the monohalides, are shown in Table X. Other bands at 1250 and 825 cm^{-1} in the fluoride and 570 and 750 cm^{-1} in the bromide are believed to be due to associated species [see also (103)]. A preliminary report (403) of the

emission spectrum of BeBr_2 has appeared in the literature. The force constant (1.1 mdynes/Å) in glassy BeF_2 is much smaller than for the gaseous linear molecule (562) and the main band at ca. 770 cm^{-1} in glassy BeF_2 is attributed to the Be-F stretching vibration in the BeF_4 tetrahedron (44, 52).

For the Be-Cl molecule, two electronic states, $X^2\Sigma$ and $A^2\Pi$, are known. Herzberg (206) applied new physical constants and conversion

TABLE X
INFRARED ASSIGNMENTS FOR THE BERYLLIUM HALIDES

Matrix	BeF_2		BeCl_2		BeBr_2		BeI_2
	ν_2	ν_3	ν_2	ν_3	ν_2	ν_3	ν_3
Neon	330	1542	238	1122	207	993	878, 872
Argon	309	1528		1108		985	877, 867
Estimated gas-phase frequency	345	1555	250	1135	220	1010	873
Stretching force constant (mdynes/Å)	5.15		3.28		2.53		1.96
Bending force constant (mdynes/Å)	0.12		0.08		0.06		0.04

factors to the spectral data of Friedrichson and Hogan (156) and obtained a value of 4.2 eV for the dissociation energy of BeCl. Gaydon (165) applied further corrections and obtained a value of 3.0 eV. In 1960, Novikov and Tunitskii (327) obtained a new set of spectral data for BeCl and derived a value of 5.9 eV for the dissociation energy. The doublet in the band spectrum of BeI in the 4100–4500 Å region is analogous to the $^2\Pi-^2\Sigma$ system of the other monohalides (320). The band spectrum of the BeF molecule was investigated in emission by Datta (128) and Jenkins (230), and only one band system in the UV region (3393–2812 Å) has been attributed to this molecule. The system, designated an A-X, has been attributed to arise from a $^2\Pi-^2\Sigma$ transition, for which the Franck-Condon factors, r -centroids, and vibrational constants have been evaluated (235, 305, 319, 494). A band in the visible region is also attributable to the $^2\Sigma-^2\Pi$ transition [cf. (394)]. In the emission spectrum in the vacuum ultraviolet (326), four band systems are ascribed to the Be-F radical. The rotational constants of BeF in the $C^2\Sigma$ state are close to the values found by Rao and Rao (394), who incorrectly assigned their band system to the $B^2\Sigma-A^2\Pi$ transition, instead of to a $C^2\Sigma-A^2\Pi$

transition (326). Several conflicting values [5.4 (319), 8.0 (494), 4.0 (463), 5.85 (209), and 6.4 eV (186)] for the dissociation energy of the BeF molecule have been reported, most having been obtained by a Birge-Sponer extrapolation from vibrational analysis of electronic spectra, but the results are inherently of a low order of accuracy as a result of this very long extrapolation. From mass spectrometric study of vapor species, produced by the fluorination of beryllium with CaF_2 and BF_3 in a Knudsen effusion cell, the value 5.85 ± 0.1 eV was derived for the BeF dissociation energy. This thermochemical value clearly establishes that the dissociation products of the $X^2\Sigma$ state of BeF are $\text{Be}(^1\text{S})$ and $\text{F}(^2\text{P})$, while those of the $A^2\Pi$ state are $\text{Be}(^3\text{P})$ and $\text{F}(^2\text{P})$ (209).

The vibrational spectrum of $\text{Be}(\text{NH}_3)_4\text{Cl}_2$ shows bands at 914, 493, and 290 cm^{-1} in the infrared, which are assigned to vibrations of the BeN_4 tetrahedron; the weak band at 493 cm^{-1} has been attributed to a slight distortion of the tetrahedron in the crystal lattice (188, 190). Bands assigned to Be-O vibrations lie in the region $860\text{--}930\text{ cm}^{-1}$ in a series of complexes of BeCl_2 with oxygen donors (529).

Two intense bands at ca. 386 and 800 cm^{-1} are observed in the absorption spectrum of K_2BeF_4 which are ascribed to the triply degenerate vibrations, the former due to deformation (ν_4) and the latter to the valence vibration (ν_3). In the Raman spectrum, the intense band at 560 cm^{-1} is due to the totally symmetrical vibration and another weak band at 388 cm^{-1} is ascribed to ν_4 ; repeated exposure yielded a weak band of the triply degenerate vibration at ca. 800 cm^{-1} , and the splitting of this band is explained by the lowering of the symmetry of the BeF_4^{2-} ion in the crystal field from T_d to C_{3v} . In accordance with this, a weak band in the infrared exactly corresponding to the total symmetrical band (ν_1) in the Raman spectrum is found at 560 cm^{-1} . A similar split of ν_3 also probably occurs in the spectra of rubidium and cesium fluoroberyllates, since these compounds also exhibit weak bands at 550 and 540 cm^{-1} , respectively (189, 372) (Table XI).

In the Raman spectrum of $(\text{NH}_4)_2\text{BeF}_4$, relatively weak peaks at 543 and 800 cm^{-1} are assigned to ν_1 and ν_3 , respectively, and very broad, low intensity peaks occur in the $300\text{--}400\text{ cm}^{-1}$ region. From the presence of peaks at 575 and about 420 cm^{-1} , it has been suggested (191) that $\text{BeF}_2 \cdot 2\text{NH}_3$ should be formulated as $[\text{Be}(\text{NH}_3)_4]^{2+}[\text{BeF}_4]^{2-}$.

The force constants for tetrahedral beryllium compounds of similar type increase regularly in the order Be-N, 2.38 (188, 190); Be-O, 3.04 (190); and Be-F, 3.50 md/\AA (189).

The band at 540 cm^{-1} in the absorption spectrum of K_2BeCl_4 corresponds to the triply degenerate stretching vibration of the BeCl_4^{2-} ion. The Raman band at 210 cm^{-1} is probably due to the triply degenerate

deformation vibration, while two equally intense maxima in the region of the triply degenerate stretching vibration in the absorption spectrum of Na_2BeCl_4 are ascribed to strong interion dipole-dipole interactions in the crystal lattice and not to slight distortion of the tetrahedra (427).

Although the literature contains reports of the ^9Be wide line spectra of the solids beryl (202), chrysoberyl (421), and beryllium oxide (217), there are only two reports (254, 256) of the NMR signal of the ^9Be nucleus in solution. The spectra of beryllium chloride in ether, the

TABLE XI
SPECTROSCOPIC ASSIGNMENTS FOR THE ALKALI METAL
TETRAFLUOROBERYLLATES

Metal	ν_1	ν_3	ν_4
Li	616	785, 809, 864	364, 330
Na	550, 567	767, 858	376
K	560	805, 835	386
Rb	550	797	379
Cs	540	780	372

acetylacetonate and 8-hydroxyquinaldinate in chloroform, and beryllium sulfate in water showed a single resonance line whose width at half-height was generally 5–10 Hz. No chemical shift from basic beryllium acetate standard was observed. Stronger bases in the adducts of beryllium species shift beryllium resonance signals to higher fields. The chemical shifts of beryllium chloride in the solvents Me_2S , Et_2O , and NH_3 occur at -5.5 , -3.1 , and -1.7 ppm, respectively, relative to $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ consistent with the known relative base strengths of these solvents. The adduct $\text{MeBeCl}(\text{SMe}_2)_2$ exhibits a resonance signal at -4.2 ppm. The only spin-spin coupling observed between ^9Be and other nuclei is for aqueous solutions of BeF_2 and $(\text{NH}_4)_2\text{BeF}_4$. The tetrafluoroberyllate ion gives a 5-line spectrum, $J_{^9\text{Be}-^{19}\text{F}} = 33 \pm 2$ Hz. All the compounds mentioned except BeF_2 are tetrahedral and thus the electric field surrounding the beryllium nucleus is relatively symmetrical and quadrupolar coupling is minimized and therefore narrow lines are observed. The beryllium-9 resonance of *saturated* aqueous beryllium fluoride solutions consists of a rather broad triplet centered at 0.8 ppm relative to $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ with $J_{^9\text{Be}-^{19}\text{F}} = 28$ Hz, favoring the presence of a tetrahedral species ($\text{BeF}_2 \cdot 2\text{H}_2\text{O}$) in such solutions (256) as proposed by Linnell and Haendler (276). However, conductivity emf and

TABLE XII: THERMODYNAMIC PROPERTIES OF BERYLLIUM MONO- AND DIHALIDES^a

Property ^b	BeF ₂	BeCl ₂	BeBr ₂	BeI ₂	BeF	BeCl	BeBr	BeI
$\Delta H^\ominus_{f(298^\circ\text{K})}$	-241.2 (a) (250) -244.3 (b) (113) -245.44 (c) (113)	-109.2 (458) -112.6 (302) -117.1 (f) (193) -117.5 (e) (193) -118.03 (232) -118.25 (507) -119.0 (d) (193) -155.0 (379)	-88.8 (96)	-50.6 (96)	-14 (542)	34 (542)	48 (542)	67 (542)
$\Delta H^\ominus_{f(298^\circ\text{K})\text{gaseous}}$	-183.8 (210) -184.4 (96) -187.0 (210) -191.2 (71) -191.3 (71)	-84.33 (247) -86.0 (96) -86.1 (211) -196.3 (g) (247) -197.18 (g) (247)	-58 (96)	-20.6 (96)	-40.0 (209) -48.3 (186) -52.6 (186)	2.0 (184) 3.7 (184) 13.1 (211)		
$\Delta H_{\text{SUB}}(298^\circ\text{K})$	55.3 (h) (210) 55.4 (h) (210) 56.0 (210) 56.8 (96) 58.1 (71)	32.0 (96) 32.1 (187) 32.5 (211) 33.0 (247) 33.1 (187) 35.1 (g) (247) 37.49 (g) (247) 38.38 (g) (247)	31 (96)	30 (96)				
ΔH_{SUB}	54.63 (137) (755°K) 55.20 (239) (0°K) 55.56 (137) (0°K) 56.6 (71) (750°K) 56.64 (446) (740°-803°K) 63.0 (341) (767°-821°K)	30 (393) (613°-733°K) 32.2 (247) (471°K) 32.9 (187) (440°-600°K) 34 (g) (412) (496°-578°K) 36.0 (g) (247) (663°K) 44 (412) (496°-578°K)	30 (393) (624°-695°K)	27 (393) (578°-703°K)				

$\Delta H_{\text{vap.}}$	40.38 (241) (1094°–1275°K) 50.1 (447) (1075°–1298°K) 50.88 (446) (1076°–1241°K) 53.22 (185) (823°–1223°K) 55.51 (239) (846°–950°K)			
ΔH_{fusion}	<2 (213)	2.07 (f) (277)		
ΔH_{diss}^a of dimer	32.9 (53) 34.5 (53)	24 (412)	14.8 (252)	
$\Delta H_{\text{solution}}$		–44.5 (379) –50.38 (260) –51.1 (288)		
S^\ominus (298°K)	52.3 (183) 52.4 (183)	18.12 (d) (277) 19.76 (e) (277) 92.51 (g) (247)	51.2 (186)	53.0 (184)
$\Delta H_{\text{SUB}(298^\circ\text{K})}$	47.8 (71)	43.2 (187) 52.99 (247)		
ΔH_{SUB}	44.9 (71) (750°K)	42.7 (187) (440°–600°K) 48.04 (247) (663°K)		
S	68.1 (471) (880°K) 69.0 (210) (880°K)	66.6 (470) (500°K)		
$\Delta S_{\text{vap.}}$	38.7 (185) (550°–950°K)			

^a Key to abbreviations: (a) β -cristobalite modification (b) amorphous modification (c) quartz modification (d) β -modification (e) α' -modification (f) α -modification (g) dimer (h) α -quartz modification

^b Entropy values in cal·mole^{–1}·degree^{–1}; enthalpy values in kcal·mole^{–1}.

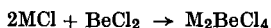
^{19}F magnetic resonance studies support the presence of other fluoro-beryllium species in *dilute* solution (108, 389).

The ^{19}F spectrum (146, 254) of aqueous ammonium tetrafluoroberyllate at 20° showed a single quartet, all four components equally intense and, therefore, all fluorine nuclei are equivalent; $J_{\text{Be-}^{19}\text{F}} = 33.2 \pm 1.2$ (254), 33.7 ± 0.2 (146), and 34.0 Hz (108). A quadruplet in the spectrum of commercial $(\text{NH}_4)_2\text{BeF}_4$ has been attributed (140) to BeF_3^- , consistent with the formulation $[\text{BeF}_3 \cdot \text{H}_2\text{O}]^-$. The spectra of aqueous beryllium solutions (108) containing variable amounts of fluoride show a quartet for each species present in solution. When $\text{F}:\text{Be} = 0.5$, only BeF^+ was detected; when $\text{F}:\text{Be} = 1.0$, both BeF^+ (65%) and BeF_2 (35%) were detected; when $\text{F}:\text{Be} = 2.0$, BeF^+ , BeF_2 (60%) and BeF_3^- [see also (140)] were present, and when $\text{F}:\text{Be} = 4.0$, BeF_3^- (22%) and BeF_4^{2-} (78%) were the only species in solution. The coupling constant increases with decrease in the number of fluorine atoms in the complex, but the line-widths in the multiplets do not substantially change from BeF_4^{2-} to BeF^+ .

VI. Thermodynamic Properties

The increasing interest in beryllium and its compounds in such fields as rocket propellants and nuclear reactors has dictated the necessity for obtaining accurate thermodynamic and physical data for its compounds. The known thermodynamic parameters for the beryllium di- and monohalides are listed in Table XII, and it is obvious that the monohalides are unstable with respect to disproportionation and could not exist in an ionic lattice. The evaluation of the enthalpies of formation and the entropies of metal dihalides is discussed by Brewer and co-workers (96).

The heat of solution of anhydrous BeF_2 is -24.17 kcal·mole $^{-1}$ (250), which may be compared with the heats of solution of Be and BeO in hydrofluoric acid of 94.25 and 23.3 kcal·mole $^{-1}$, respectively, (287). Values for the corresponding chloride systems are 13.65, 87.9 (287), and -89.2 kcal·mole $^{-1}$ (507), respectively. The standard heats of formation of some alkali metal tetrachloroberyllates, M_2BeCl_4 ($\text{M} = \text{Li}$, -315.50 ; Na , -316.54 ; K , -336.22 kcal·mole $^{-1}$), have been derived (260) via the enthalpies of reaction for



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SULFUR-NITROGEN-FLUORINE COMPOUNDS

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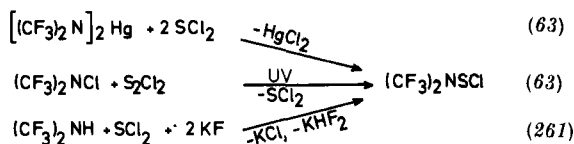
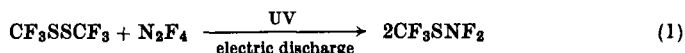
I. Introduction

Since the preparation of the first pure sulfur-nitrogen-fluorine compounds, NSF, NSF₃, and S₄N₄F₄, in 1955 (105-107) this field has developed very rapidly. The chemistry of these compounds has been the subject of several reviews (67-69, 72, 76) and has also been covered more or less fully in reviews on sulfur-fluorine (23, 134, 196, 236, 252, 276) and sulfur-nitrogen chemistry (12-15, 115, 207). The spate of recent publications has, however, rendered these earlier summaries incomplete. The present article covers developments up to the middle of 1970, with the main emphasis on recent work. Compounds with other halogens are considered only insofar as they are of interest in this context. The earlier division into acyclic and cyclic compounds has been retained, as has been the classification in terms of the various oxidation numbers of sulfur. An attempt has been made, starting from NSF and NSF₃, to point out the general relationships in the chemistry of sulfur-nitrogen-fluorine compounds.

II. Acyclic Compounds

A. SULFUR(+2)-NITROGEN-FLUORINE COMPOUNDS

Amino derivatives of sulfur difluoride (142, 245) are as yet unknown, but compounds of the type R₂N-S-X with X = Cl can be prepared (see Fig. 1). The only known sulfur(+2)-nitrogen-fluorine compound is trifluoromethyl thiodifluoramine, CF₃-S-NF₂ (256). It is quite unstable,

FIG. 1. Preparation of $(\text{CF}_3)_2\text{NSCl}$.

decomposing rapidly at room temperature. When the above reaction is carried out thermally, trifluoromethyl sulfur difluoride imide, CF_3NSF_2 , results (256):



B. SULFUR(+4)-NITROGEN-FLUORINE COMPOUNDS

In keeping with the higher coordination number of sulfur, the preparative possibilities in this case are much greater than for S(+2). Table I shows the types of compounds so far obtained, and also some types

TABLE I

TYPES OF COMPOUNDS WITH SULFUR IN THE +4 OXIDATION STATE

—	—	$\text{N}-\text{SF}_3$	—	—
—	$\text{—N}=\text{S} \begin{array}{l} \text{F} \\ \text{F} \end{array}$	$\left\{ \text{N}-\text{SF}_2-\text{C} \right\}$	—	—
$\text{—N}=\text{S}-\text{F}$	$\text{—N}=\text{S} \begin{array}{l} \text{F} \\ \text{N} \end{array}$		$\text{N}-\text{S} \begin{array}{l} \text{O} \\ \text{F} \end{array}$	$\text{F}-\text{N}=\text{S}=\text{O}$
	$\text{—N}=\text{S}=\text{N}-$			
	$\text{—N}=\text{S} \begin{array}{l} \text{N} \\ \text{N} \end{array}$		$\text{N}=\text{S}=\text{N}$	$\text{R}-\text{N}=\text{S}=\text{O}$

of fluorine-free derivatives which stem from N-S-F compounds. The chemistry of these compounds is shown in Fig. 2. Starting from NSF, almost all the above types may be synthesized. Whereas in the case of sulfur(+6) additions to the $\text{N}\equiv\text{S}$ triple bond of NSF_3 yield pentafluoro-sulfanylamines, R_2NSF_5 , with a single sulfur-nitrogen bond, as the stable end products (30, 34, 35), these additions with thiazyl fluoride

lead to sulfur difluoride imides, $R-N=SF_2$, with a sulfur-nitrogen double bond (238). So far it has not proved possible to bring about extensive

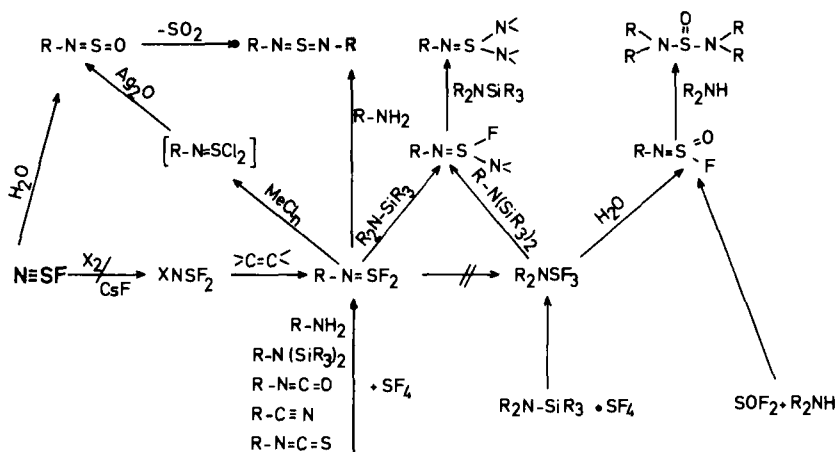


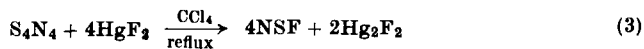
FIG. 2. Chemistry of S-N-F compounds.

addition to the aminosulfur trifluorides, R_2NSF_3 ; the corresponding reactions lead to cleavage of the N-S bond or to addition with simultaneous oxidation of the sulfur.

1. Thiazyl Fluoride, $\text{N}\equiv\text{S}-\text{F}$

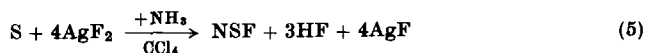
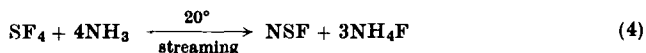
Several methods for preparing NSF are given in the literature.

(a) Fluorination of substances which contain S-N bonds. The starting material is S_4N_4 ; AgF_2 (97, 99), CoF_3 (97), and HgF_2 (93) may be used as fluorinating agents. Fluorination with SeF_4 , F_2 (37), and SF_4

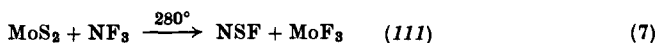


(37, 70) has also been described; IF_5 and SbF_5 first yield the adducts $(\text{NSF})_4 \cdot \text{S}_4\text{N}_4$ or $\text{S}_4\text{N}_4(\text{SbF}_5)_4$ which give NSF when they are decomposed thermally (37).

(b) Reaction of SF_4 with ammonia (37, 39, 70, 114)



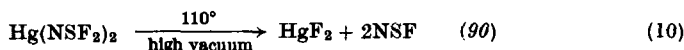
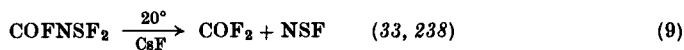
(c) Reaction of NF_3 with sulfur or metal sulfides.



The mechanism of the last two reactions has not been elucidated, but it may resemble the rearrangement of $\text{CF}_3\text{S}-\text{NF}_2$ to $\text{CF}_3-\text{N}=\text{SF}_2$. The compound $\text{S}=\text{N}-\text{F}$, which would be expected as an intermediate in this mechanism, has, however, not been observed so far. Formation of NSF in the flash photolysis of NF_3 with COS and CS_2 has also been reported (168).

These reactions yield NSF, mixed with many side products, which are often difficult to separate. Yields are small, reaching a maximum of 20%, except for reaction (6), for which 30% has been reported.

(d) Decomposition of compounds which already contain the N-S-F group has also been proposed for the preparation of thiazyl fluoride in addition to the methods described above.



The last route is particularly suitable for the preparation of larger quantities of NSF, as the reaction is almost quantitative and yields no other volatile products.

The structure of thiazyl fluoride (Fig. 3) has been determined from IR, NMR, and microwave spectra (146). The results do not agree with

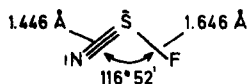
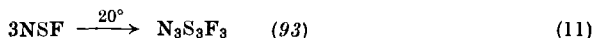


FIG. 3. Structure of thiazyl fluoride (146).

the structure proposed earlier on the basis of electron diffraction studies (99, 232). The N-S force constant f_{NS} , calculated from microwave and infrared data, has a value of 10.7 mdyne/Å (44, 176, 195), from which a bond order of 2.4 may be deduced (251). For NSCl, which has a similar structure, $f_{\text{NS}} = 10.0$ mdyne/Å, while the bond order $N_{\text{NS}} = 2.2$ (180). This dependence on the electronegativity of ligands bonded to sulfur supports the idea of $p_\pi-d_\pi$ bonding between nitrogen and sulfur.

Other data include enthalpy of formation: ΔH_f° (NSF, gas) = $+41 \pm 2$ kcal/mole (186); dissociation energy: $D(\text{N}=\text{S}) = 71 \pm 5$ kcal/mole (186); dipole moment: 1.902 D (44). The NMR (195) and electronic spectra (11) have also been recorded.

Thiazyl fluoride (m.p. -89°C ; b.p. 0.4°C) is a pale yellow liquid which is sensitive to moisture and cannot be stored at room temperature without decomposition. Trimerization occurs in the liquid state [Eq. (11)], while S_4N_4 and $\text{S}_3\text{N}_2\text{F}_2$ are formed in the gas phase at reduced



pressure (108, 112). The structure $\text{F}-\text{S}-\text{N}=\text{S}=\text{N}-\text{S}-\text{F}$ has been suggested for the last of these compounds. Since, however, X-ray investigations have shown the chlorine analog $\text{S}_3\text{N}_2\text{Cl}_2$ (e.g., 143) to have a ring structure (277), confirmation of the structure of $\text{S}_3\text{N}_2\text{F}_2$ would be of interest.

Because of its instability, NSF is somewhat difficult to handle, and accordingly only a few of its reactions are known. Its hydrolysis has been studied in detail (222) and yields thionyl imide, HNSO , in the first stage (97). This is cleaved hydrolytically to hydroxyl-amine and sulfoxylic acid, the latter then decomposing via $\text{S}_2\text{O}_3^{2-}$ to HSO_3^- and S. The HSO_3^- ion

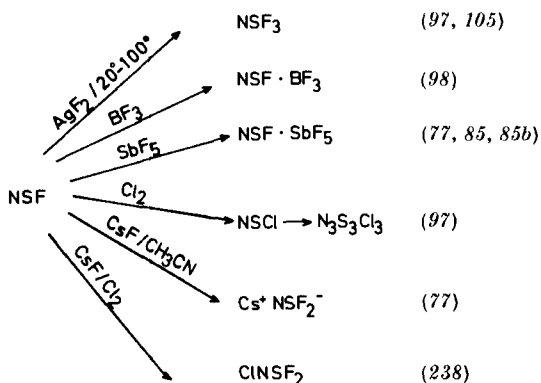
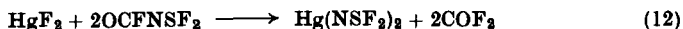


FIG. 4. Reactions of NSF.

reacts with residual sulfoxylic acid to form tri- and hexathionate, both of which may be isolated as their tetraphenylphosphonium salts. Other known reactions of NSF are shown in Fig. 4. The first reaction in Fig. 4 serves for making thiazyl trifluoride on a preparative scale. The last two reactions illustrate the transformation of thiazyl fluoride into the sulfur difluoride imides, which are discussed in the next section.

2. Sulfur Difluoride Imides $\text{RN}=\text{SF}_2$

a. Halosulfur Difluoride Imides. The simplest sulfur difluoride imides are the N-halogen compounds, XNSF_2 , where X may be F, Cl, Br, or I. They are best prepared by the reaction of $\text{Hg}(\text{NSF}_2)_2$ with halogens, while ClNSF_2 (238) is also formed from NSF, CsF, and chlorine. The mercurial is the first metallosulfur difluoride imide to be established and may be obtained from OCFNSF_2 and HgF_2 (90).



As we mentioned above, $\text{Hg}(\text{NSF}_2)_2$ may be decomposed in vacuum to NSF and HgF_2 . The halides may be prepared under the conditions shown in Fig. 5. The chloro compound, ClNSF_2 is the most stable and does not

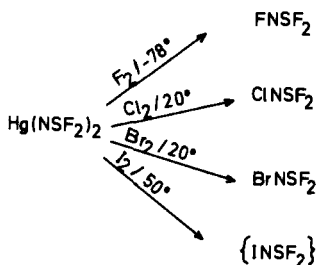
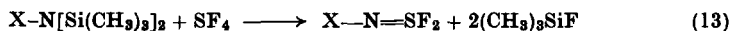


FIG. 5. N-Halogenosulfur difluoride imides (90, 91).

decompose below 100° . The iodine analog INSF_2 is much less stable, and its existence has been established only on the basis of the IR spectrum. FNSF_2 is the isomer of NSF_3 , which will be described later. Its yield in the reaction shown in Fig. 5 is small in contrast to ClNSF_2 and BrNSF_2 , for which the reactions are almost quantitative.

As was reported recently, ClNSF_2 and BrNSF_2 are formed from N-halogenohexamethyldisilazanes and SF_4 according to Eq. (13) (248).



Nothing can be said about the preparative value of this method as yields are not recorded, but the separation of N-halogenosulfur difluoride imides from the R_3SiF produced in the reaction is likely to be difficult, and indeed may be possible only by the use of gas chromatography. The structure of $\text{Hg}(\text{NSF}_2)_2$ has been determined by X-ray analysis (150); that of ClNSF_2 is based on electron diffraction (130) (Fig. 6). The short S-N distance of 1.439 Å in $\text{Hg}(\text{NSF}_2)_2$ is striking and is comparable with the corresponding distances of 1.416 Å in gaseous NSF_3 and 1.446 Å

in NSF. It corresponds with a bond order of 2.4. The marked involvement of the lone electron pair of the nitrogen atom in the S-N bond will explain the unusually large value of 131° for the angle at the nitrogen atom. The Hg-N distance corresponds with a single bond ($r_{\text{Hg}} = 1.30 \text{ \AA}$; $r_{\text{N}} = 0.70 \text{ \AA}$).

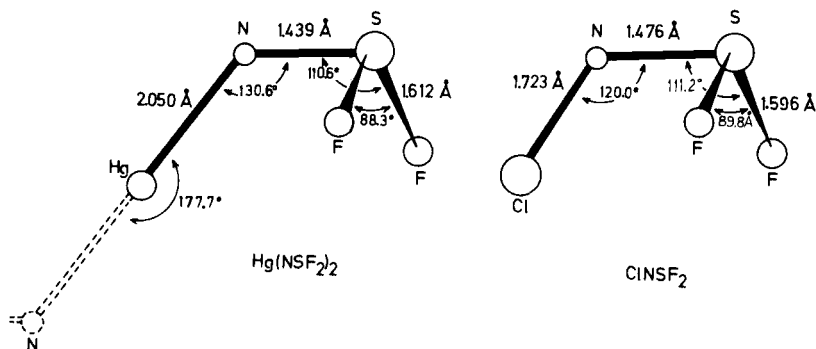


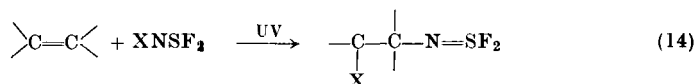
FIG. 6. Structures of $\text{Hg}(\text{NSF}_2)_2$ and ClNSF_2 .

The structure of ClNSF_2 resembles that of $\text{Hg}(\text{NSF}_2)_2$. The S-N distance (1.480 \AA) is somewhat greater and corresponds with a bond order of 2.0. The participation of the lone pair of electrons on nitrogen in the S-N bond must consequently be less and, as a result, the bond angle at nitrogen is smaller (120.3°). The bonding relationships may be represented by the two canonical structures shown, the bond being



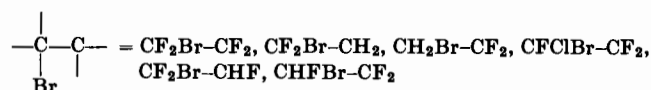
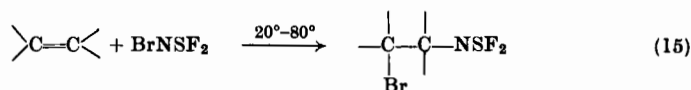
further strengthened by $p_{\pi}-d_{\pi}$ overlap. This weights structure (II) relative to (I) (178).

Organosulfur difluoride imides are accessible through the *N*-halogenosulfur difluoride imides. Addition to a C=C double bond takes place both by irradiation with ClNSF_2 or BrNSF_2 and also by thermal addition (in the case of BrNSF_2) (172-174).

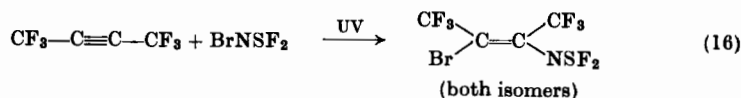


The reactions occur by a radical mechanism, the initial attack on the C=C bond being by the NSF_2 radical. The mechanism for the thermal addition has not yet been elucidated, although in this case the polarity

($\overset{\delta+}{\text{X}}-\overset{\delta-}{\text{NSF}_2}$) should be involved (172, 174) [the electronegativity of the NSF₂ group has been determined as 3.3 (101)].

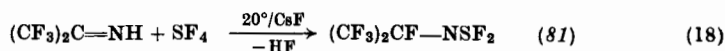
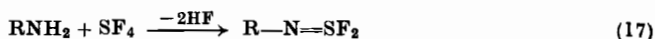


Addition to a triple bond has so far been observed in only one instance (174a).

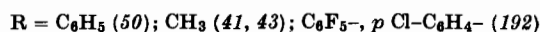
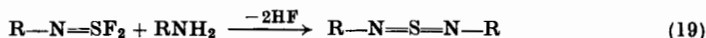


b. Further Sulfur Difluoride Imides R-N=SF₂. Almost all methods for preparing sulfur difluoride imides apart from those involving the halogen compounds depend on the reaction of sulfur tetrafluoride with nitrogen-containing compounds such as the following.

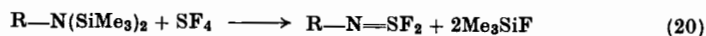
(1) Primary amines or perfluoroimines:



Substitution of all the fluorine atoms usually takes place with the strongly basic organic amines, whereas with inorganic amines the sulfur difluoride imide stage may be realized.

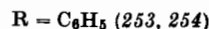


(2) *N*-silylated primary amines:

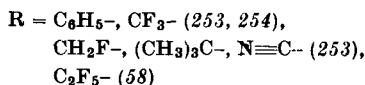
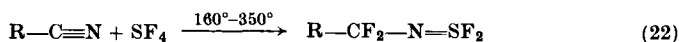


This reaction takes place less vigorously than that with the unsubstituted amines, so that the desired R-NSF₂ compounds are, in the main, obtained in good yields.

(3) Cyanates:

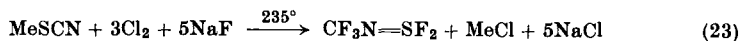


(4) Cyanides:



The last two reactions can only be used if the expected products are thermally stable.

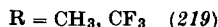
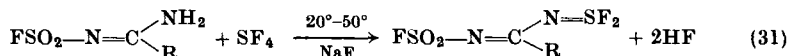
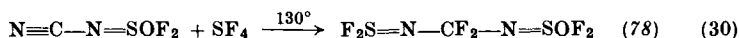
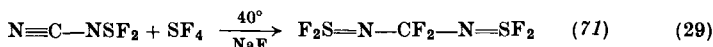
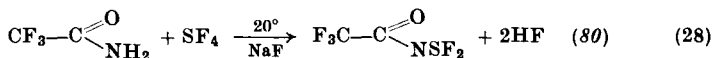
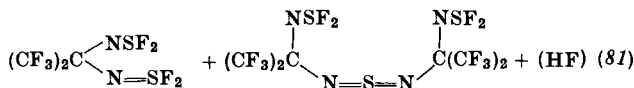
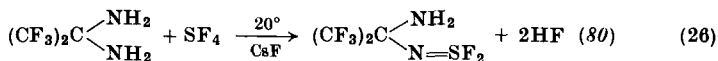
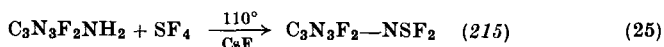
The compound CF_3NSF_2 is produced in the reaction of a large number of nitrogen-containing organic compounds with SF_4 (71, 126, 166, 254). It was first made by fluorinating methyl isocyanate (6), although the structure was not correctly assigned. It can now be obtained on a preparative scale by a method which does not involve the use of SF_4 (254, 260).



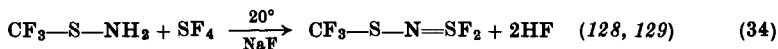
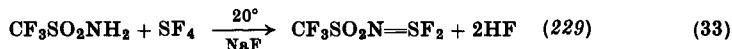
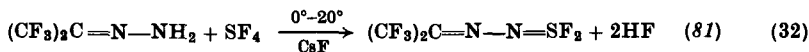
Me = alkali metal

It is not known if this reaction also takes place through SF_4 formed in the chlorination and subsequent fluorination of sulfur.

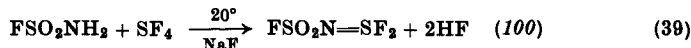
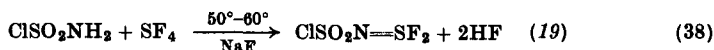
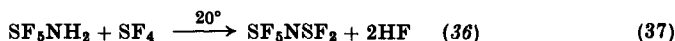
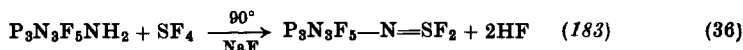
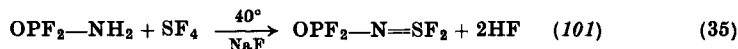
A series of interesting organosulfur difluoride imides has been synthesized with the aid of reactions (17)–(22).



Examples are also known where the sulfur difluoride imide group is bonded to the organic residue through a nitrogen or sulfur bridge.

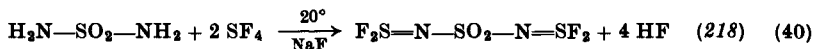


Purely inorganic members of the series, other than the *N*-halogeno- and metallocsulfur difluoride imides, are:

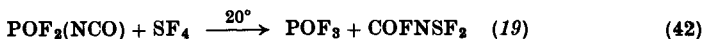
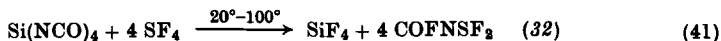


SF_5NSF_2 was also observed in the fluorination of S_4N_4 with elemental fluorine (38).

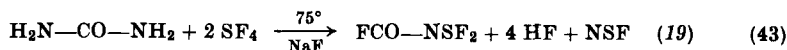
The compound FSO_2NSF_2 is further formed in the reaction of SF_4 with $\text{FSO}_2\text{N}=\text{C}=\text{O}$ (19, 227), HOSO_2NH_2 , and $\text{SO}_2(\text{NH}_2)_2$ (19). When the reaction with sulfamide is carried out at room temperature, *N,N'*-sulfonylbis(sulfur difluoride imide) may be isolated.



If the isocyanate group in reaction (21) is bonded to silicon or phosphorus, cleavage of the Si-N or P-N bond takes place with formation of *N*-fluoroformylsulfur difluoride imide, COFNSF_2 . Small quantities of



COFNSF_2 also result from the reaction of SF_4 with $\text{POF}(\text{NCO})_2$, $\text{PO}(\text{NCO})_3$ (32), and $\text{CH}_3\text{SO}_2\text{NCO}$ (32). The reaction with urea gives a 60% yield.



The next higher acyl sulfur difluoride imide, $\text{CF}_3\text{CONSF}_2$, is formed from trifluoroacetamide and SF_4 (80). *N*-Fluoroformylsulfur difluoride imide is, as the reactions in Fig. 7 show, an important starting material in sulfur-nitrogen-fluorine chemistry. Analogous reactions can be carried out with $\text{CF}_3\text{CONSF}_2$ (80).

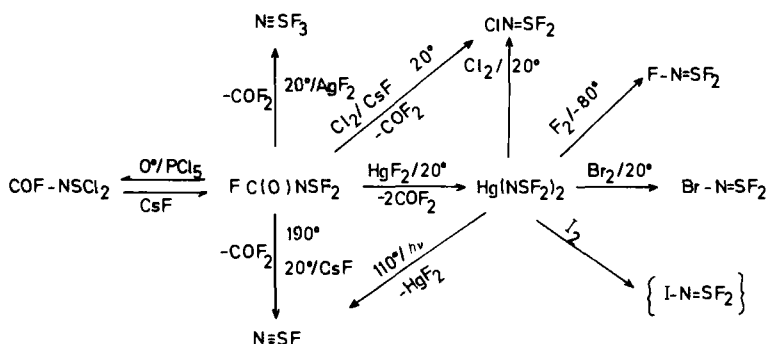


FIG. 7. Reactions of COFNSF_2 .

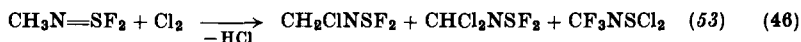
c. Pseudohalogenosulfur Difluoride Imides. The only known *N*-pseudohalogenosulfur difluoride imide is *N*-cyanosulfur difluoride imide,

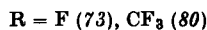
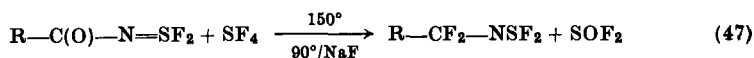


$\text{NC}-\text{NSF}_2$. In reaction (44) further interaction with SF_4 gives $\text{CF}_2(\text{NSF}_2)_2$.

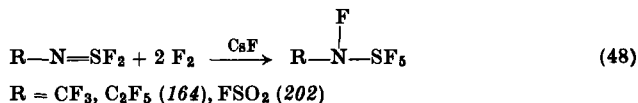
d. Reactions of the Sulfur Difluoride Imides. The following are the main reaction possibilities: (i) cleavage of the $\text{R}-\text{N}$ bond, (ii) addition to the $\text{N}=\text{S}$ bond, (iii) change in the oxidation number of sulfur, and (iv) replacement of the fluorine atoms of the $-\text{NSF}_2$ by other groups.

i. Reactions of this type have been described for the acyl- and *N*-halogenosulfur difluoride imides, but other reactions involving transfer of the $-\text{NSF}_2$ group are unknown. On the other hand, alkyl groups may be chlorinated and carbonyl groups converted to CF_2 groups by SF_4 .

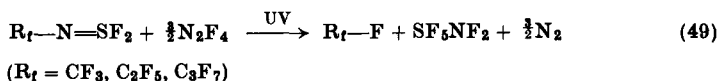




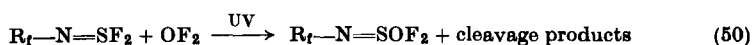
ii. Examples in the literature show that additions to the N=S bond



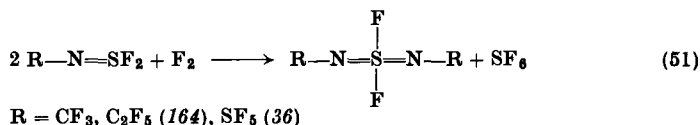
result in simultaneous oxidation of sulfur. Photochemical fluorination with N_2F_4 leads to cleavage of the C-N bond and oxidation of sulfur (59).



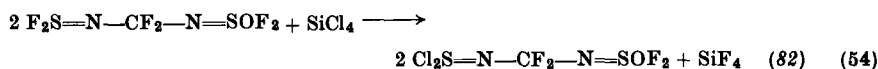
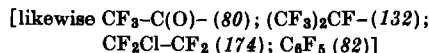
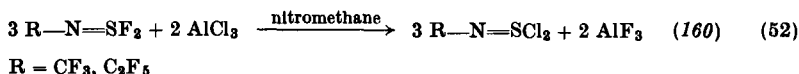
iii. Oxidation of sulfur with retention of the N=S double bond has so far been observed only in the irradiation of R_t-NSF_2 with OF_2 (174c).



The uncatalyzed reaction with fluorine results in oxidation of the sulfur and cleavage of the N=S double bond to form sulfur(VI) difluoride diimides.

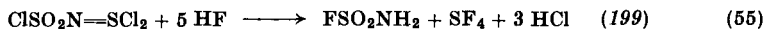


iv. Exchange of the fluorine atoms for other groups has been most fully studied. With AlCl_3 , PCl_5 , and SiCl_4 transformation to sulfur dichloride takes place.

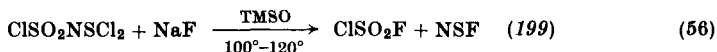


The reverse of the above reaction, involving the transformation of sulfur dichloride imides, which are often readily accessible in other ways

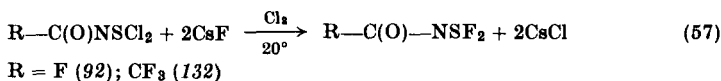
(reaction of amines with SOCl_2 [e.g., (199)] or SCl_2 or of sulfinylimides with PCl_5 [e.g. (175, 197)] has been successfully carried out in only a few instances. Hydrogen fluoride produces cleavage of the $\text{N}=\text{S}$ bond according to reaction (55).



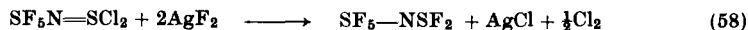
NaF leads to NSF .



Only in the reaction of $\text{R}-\text{C}(\text{O})\text{NSCl}_2$ with Cl_2 in presence of CsF did formation of the sulfur difluoride imide occur in place of the expected



formation of ClNSCl_2 . Fluorination of $\text{SF}_5\text{N}=\text{SCl}_2$, prepared from pentafluorosulfanylamine and SCl_2 , also gives the sulfur difluoride imide (31).



Other groups may also be introduced instead of chlorine (254), as shown in Fig. 8.

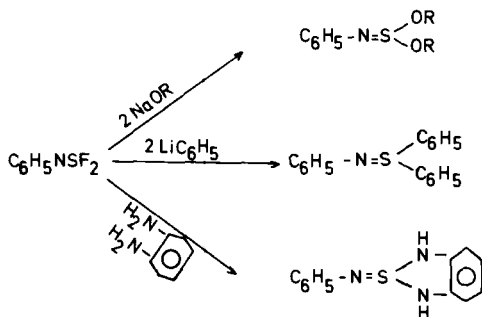
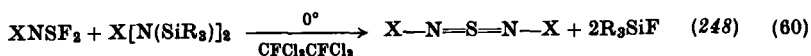
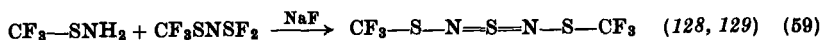
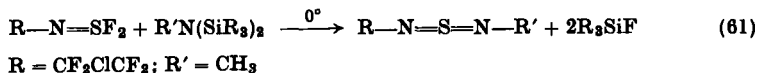


FIG. 8. Reactions of $\text{C}_6\text{H}_5\text{NSF}_2$ (254).

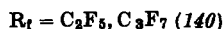
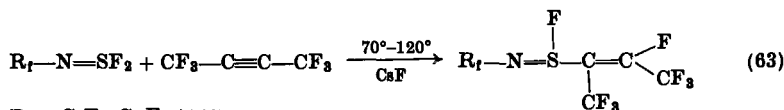
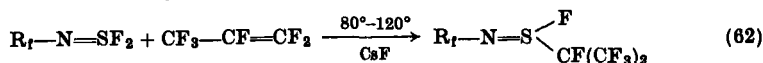
As has already been pointed out, reaction of sulfur difluoride imides with primary amines [cf. Eq. (17)] and sometimes also with *N*-silylated amines, gives sulfur diimides [for the chemistry of these compounds, see ref. (151)]. Sulfur diimides which are substituted by thio groups or halogens on the nitrogen atom can be prepared in this way.



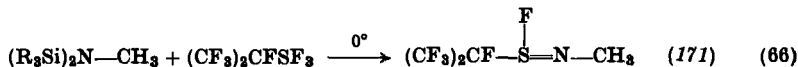
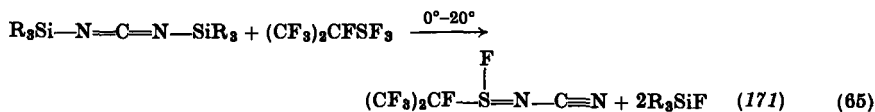
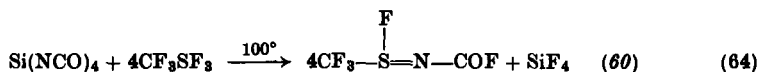
Using the reaction principle of Eq. (19), asymmetrically substituted products are also accessible (174b).



S-Perfluoroalkyl-substituted derivatives are formed by addition of $\text{R}_f\text{—N=SF}_2$ to the double bond of perfluoroalkenes and the triple bond of perfluoroalkynes in presence of CsF .



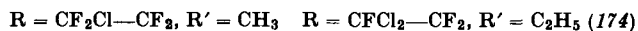
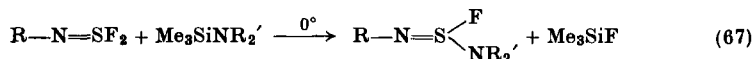
Cyclic products probably are also formed, although their structures have not as yet been fully established (57). A second route to *S*-perfluoroalkyl sulfur monofluoride imides is through perfluoroalkyl sulfur trifluorides, which can be transformed into the corresponding compounds as in the reaction with SF_4 .



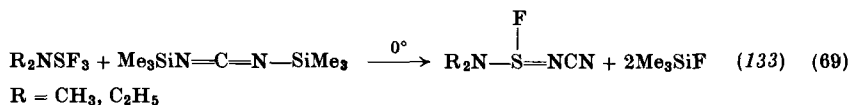
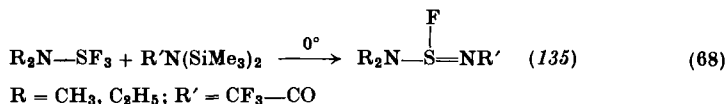
e. S-Dialkylaminomonofluoroimides, $\text{R—N=S} \begin{array}{l} \text{F} \\ \diagup \\ \text{N} \end{array}$. Representatives of

this class of compound, in which a nitrogen-sulfur single and double bond are adjacent, may be synthesized by the two following routes.

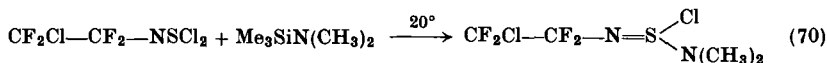
i. From sulfur difluoride imides and *N*-silylated secondary amines.



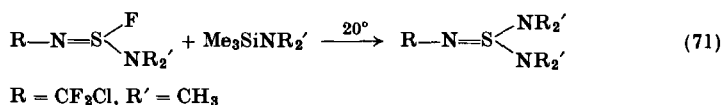
ii. From aminosulfur trifluorides and *N*-silylated primary amines.



Reactions of sulfur dichloride imides and sulfur difluoride imides are analogous (174b).

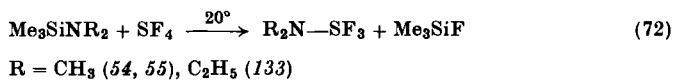


Whereas the fluorine derivatives are already quite unstable, the chlorine compounds may not be distilled without decomposition. With excess of $\text{Me}_3\text{SiNR}_2'$, two fluorine atoms are replaced [cf. Fig. 8] (174b):



3. Aminosulfur Trifluorides, R_2NSF_3

Aminosulfur trifluorides result from the cleavage of the Si-N bond in *N*-silylated primary amines by reaction with SF_4 .



Direct reaction of SF_4 with the unsilylated amines gives no definite products.

NMR investigations show that the structure of aminosulfur trifluoride is derived from that of SF_4 by replacement of one fluorine atom by the dialkylamino group. The compounds are as clear as water and are very highly reactive liquids which decompose rapidly in glass vessels

at room temperatures. They may be used as preparative reagents in much the same way as SF_4 [compare Eqs. (68) and (69)].

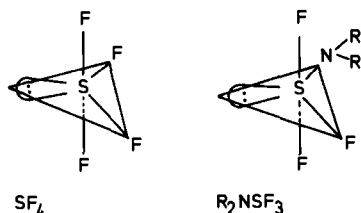
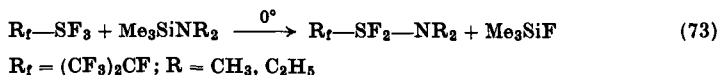


FIG. 9. Structures of SF_4 and R_2NSF_3 .

So far it has not proved possible to substitute a further fluorine atom by a simple, directly bonded nitrogen-containing radical, although by a reaction analogous to that in Eq. (72), and using perfluoroalkyl sulfur trifluorides, the first disubstituted nitrogen-containing derivatives of sulfur tetrafluoride have been made (170).



As with compounds of the type $(\text{R}_f)_2\text{SF}_2$ (233), NMR investigations gave no clear indication of the structure. The magnetic equivalence of the two CF_3 or R groups supports a trans configuration for the amino and R_f groups, but this could also arise from intramolecular exchange effects (233) (Fig. 10).

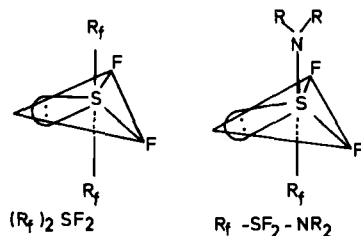


FIG. 10. Proposed structures of $(\text{R}_f)_2\text{SF}_2$ and $\text{R}_f\text{—SF}_2\text{—NR}_2$.

4. Fluorosulfinic Acid Amide $\text{R}_2\text{N—S}\begin{smallmatrix} \text{O} \\ \text{F} \end{smallmatrix}$

Fluorosulfinic acid amides, which are formed in the hydrolysis of aminosulfur trifluorides, also result from the reaction of SOF_2 with

secondary amines (119) or their *N*-silyl compounds (21a) according to Fig. 11.

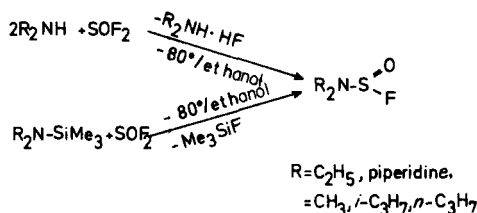
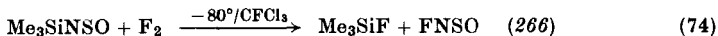


FIG. 11. Preparation of R_2NSOF (21a, 119, 174c).

These compounds are colorless and highly reactive liquids which decompose slowly at room temperature. With excess of amine and at higher temperatures exchange of the second fluorine atom also occurs, leading to $(R_2N)_2SO$.

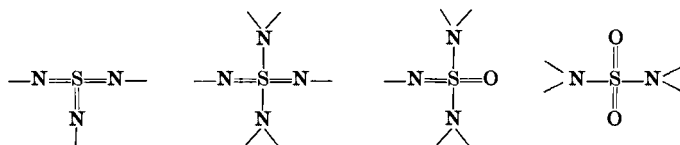
5. *N*-Fluorosulfinylimine, $F-N=SO$

The compound $F-NSO$ results in low yield in the reaction of trimethylsilyl sulfinylamine, Me_3SiNSO , with fluorine. It tends to explode and has not been closely investigated.



C. SULFUR(+6)-NITROGEN-FLUORINE COMPOUNDS

Table II summarizes the types of compound in which sulfur has the oxidation number +6. In addition, fluorine-free derivatives with the following groupings can be prepared.



The first nitrogen-sulfur(+6)-fluorine compound to be recognized was thiazyl trifluoride, $N \equiv SF_3$ (105); the first oxygen-sulfur(+6)-nitrogen-fluorine compound being FSO_2NR_2 (64, 137, 243a). The same role is played by NSF_3 for the sulfur(+6) compounds as by $N=SF$ for those of sulfur(+4). Starting from thiazyl trifluoride it is possible to synthesize almost every type of compound shown in Table II (see Fig. 12).

TABLE II
TYPES OF COMPOUNDS WITH SULFUR IN THE +6 OXIDATION STATE

—	—	>N-SF_5	—	—	—
—	—N=SF_4	$\left\{ \text{>N-SF}_4\text{—R} \right\}$	—	—	—
$\text{N}\equiv\text{SF}_3$	—			$\text{>N}=\overset{\text{O}}{\parallel}\text{SF}_3$	—
$\text{N}\equiv\text{SF}_2\text{—N} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix}$	$\text{—N=SF}_2\text{=N—}$		$\begin{smallmatrix} \text{F} \\ \\ \text{—N—S=O} \\ \\ \text{F} \end{smallmatrix}$		—
	$\begin{smallmatrix} \diagup \\ \text{N} \\ \\ \text{—N—S=N—} \\ \\ \text{F} \end{smallmatrix}$		$\begin{smallmatrix} \diagup \\ \text{N} \\ \\ \text{—N—S=O} \\ \\ \text{F} \end{smallmatrix}$	$\text{>N—SO}_2\text{F}$	

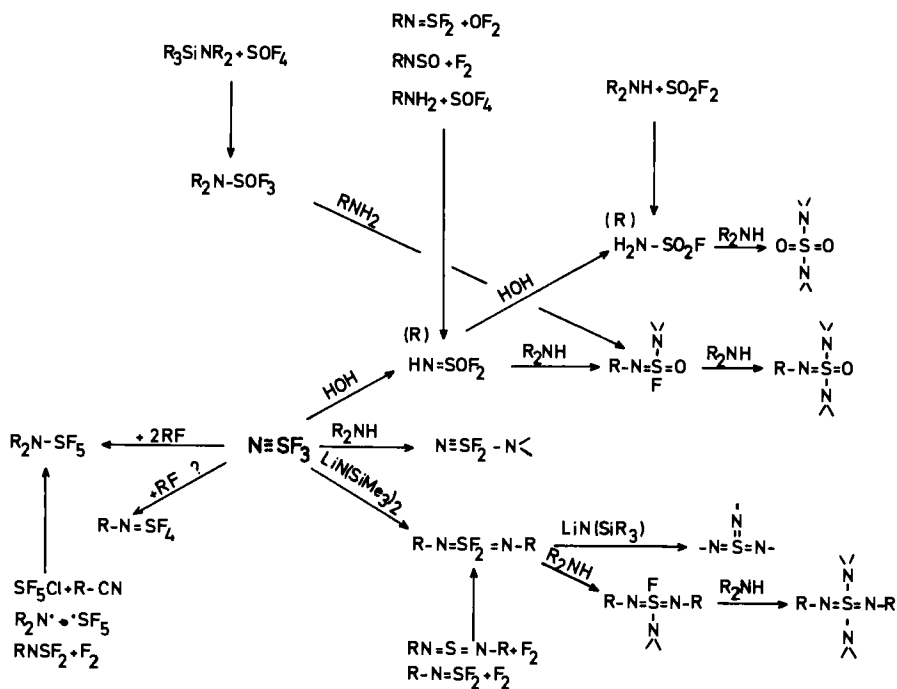


Fig. 12. Chemistry of N-S(+6)-F compounds.

1. Thiazyl Trifluoride, NSF₃

Two routes are available for the preparation of NSF₃: (a) fluorination of S-N compounds with sulfur in the +4 oxidation state (or lower), using AgF₂ (Fig. 13)

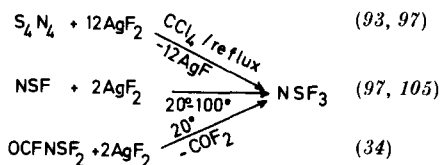


FIG. 13. Preparation of NSF₃.

and (b) reaction of S(+6)-F compounds with excess of ammonia:



The second method is not employed in preparative work because of the high toxicity of S₂F₁₀ and the low yield.

The structure of NSF₃ (Fig. 14) has been determined from the IR, NMR, and microwave spectra (145) and, as a first approximation, can be regarded as derived from that of SF₆ (*d*_{SF} = 1.56) by replacing three

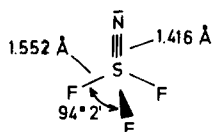


FIG. 14. Structure of NSF₃ (145).

fluorine atoms with one triply bonded nitrogen. The very short S≡N distance of 1.416 Å corresponds with a bond order of 2.7 (95), with the N-S bond strengthened as a result of *p_n*(N)-*d_n*(S) overlap (72). A calorimetric determination of the enthalpy of formation gave Δ*H*_f[°] (NSF₃, gas) = -85 kcal/mole. The dissociation energy *D*_{N=S} = 93 ± 2 kcal/mole [by combination with mass spectrometric appearance potentials (186)].

Force constants (181, 194, 195) and thermodynamic functions (181, 194) have been calculated from the IR (195) and Raman spectra (181). The NMR (195) and electronic spectra (181) have been recorded, as have critical data (93).

Thiazyl trifluoride (m.p. -72.6° ± 0.5°, b.p. -27.1° ± 0.1°), unlike NSF, is very stable both thermally and chemically. It resists hydrolysis

by dilute acids and reacts with metallic sodium only at 300°C. Decomposition in glass vessels sets in at 500° (97). Because of this stability the use of NSF₃ (mixed with SF₆) as a dielectric has been suggested (62).

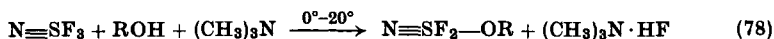
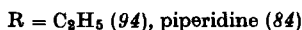
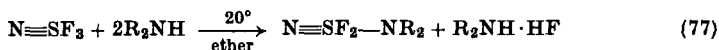
The reactions of NSF₃ may be divided into:

(a) Adduct formation with Lewis acids, e.g., BF₃. The product dissociates in the gas phase into its components. Support for the formation of an adduct comes from the IR spectrum (−180°). The sharp

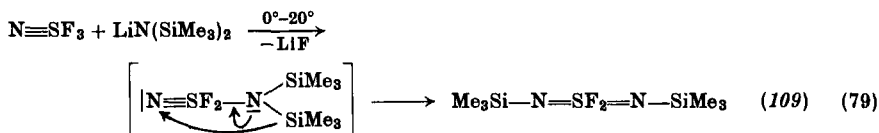


increase in the ν_{SN} frequency by about 200 cm^{−1} can be interpreted as due to a change in the N=S bond order from 2.7 in NSF₃ to 2.9 in the adduct. Antimony pentafluoride also forms the adduct, NSF₃·SbF₅ (85), although its structure has not yet been investigated.

(b) Exchange of the fluorine atoms while retaining the S=N bond.



(c) Exchange of the fluorine atoms and rearrangement of the products.



Reaction with a further molecule of LiN(SiMe₃)₂ results in the splitting off of the remaining two fluorine atoms and the formation of the aza analog of sulfur trioxide (109).



Tris(trimethylsilylimido)sulfur, S(=NSiMe₃)₃, is the first known derivative of sulfur triimide. It is also the only compound known to date in which sulfur has an oxidation number of +6 and a coordination number of 3 and which is also a monomer at room temperature.

The hydrolysis of $\text{N}\equiv\text{SF}_3$ is a reaction of the same type. In earlier investigations (97) only the end products (H_2NSO_3^- and F^-) could be identified, but now isolation of the intermediates has enabled the mechanism to be elucidated (Fig. 15).

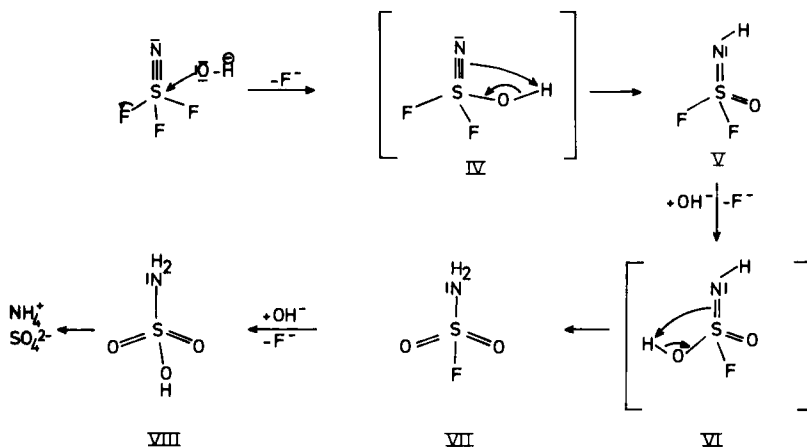
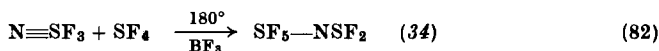
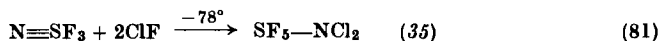
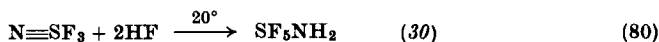


FIG. 15. Mechanism for the hydrolysis of NSF_3 (223).

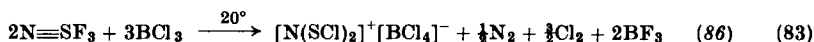
While the intermediates IV and VI rearrange rapidly, sulfur oxide difluoride imide can be isolated in the form of its tetraphenylphosphonium salt. It was not possible to detect fluorosulfonyl amide, but *N*-substituted derivatives have been observed in the hydrolysis of other sulfur oxide difluoride imides (210, 213, 228) [cf. Eq. (108)].

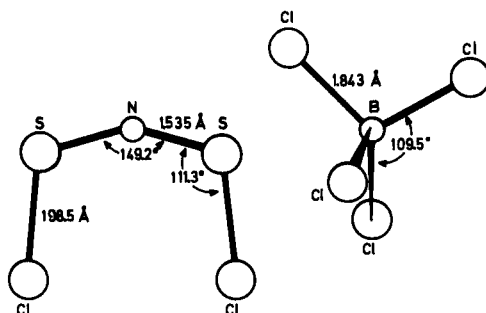
(d) Additions to the $\text{N}\equiv\text{S}$ triple bond.



The monoaddition products were not isolated; whether the IR bands also observed in the reaction represented by Eq. (81) can be assigned to a compound Cl—N=SF_4 has yet to be clarified (34).

Boron trichloride reacts with NSF_3 by a mechanism which is not yet understood, forming the interesting ionic compound $[\text{N}(\text{SCl})_2]^+[\text{BCl}_4]^-$



FIG. 16. Structure of $[N(SCl)_2]^+[BCl_4]^-$ (86).

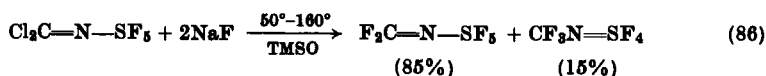
(86) Fig. 16. Reaction probably takes place through adduct formation followed by F-Cl exchange on sulfur and reduction of NSF_3 to $N\text{SCl}$. This is supported by other methods for the synthesis of this compound.



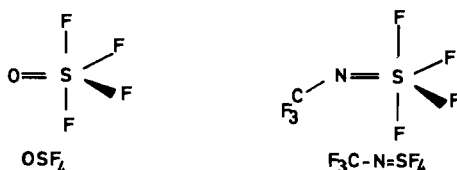
The corresponding salts with $[AlCl_4]^-$ and $[SbCl_6]^-$ also exist (110).

2. Sulfur Tetrafluoride Imides, $R-N=SF_4$

The only representative of this class of compounds is $CF_3N=SF_4$, a secondary product in the fluorination of $SF_5-N=CCl_2$ with NaF (263) or in the dehydrofluorination of SF_5-NHCF_3 with KF .



NMR investigations at -80°C indicate a trigonal bipyramidal structure (182) analogous to that of the isostructural $O=SF_4$ (Fig. 17).

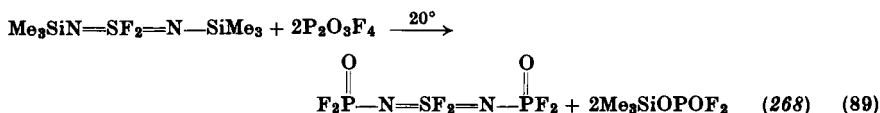
FIG. 17. Structures of OSF_4 and $CF_3-N=SF_4$.

3. Bisimidosulfur Difluorides, $R-N=SF_2=NR$

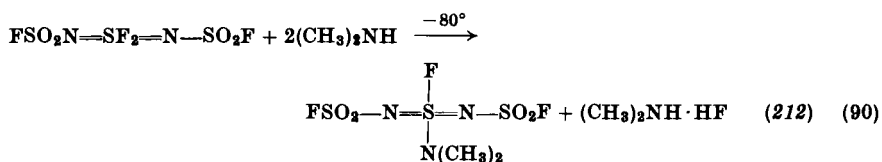
Two methods for preparing bisimidosulfur difluorides have already been given [Eqs. (51) and (79)]. A third possibility is the fluorination of



sulfur diimides. How general these methods are has not yet been tested, but $R_3Si-N=SF_2=N-SiR_3$ has proved to be a valuable starting material for the preparation of further bisimidosulfur difluorides, e.g.,



Only a single fluorine atom in bis(*N*-fluorosulfonyl)imido sulfur difluoride may be replaced by reaction with amines. At higher temperatures and



with excess of amines the aza analog of the sulfuric acid esters result (Fig. 18). Exchange of only one fluorine atom of the $-N=SF_2=N-$ group

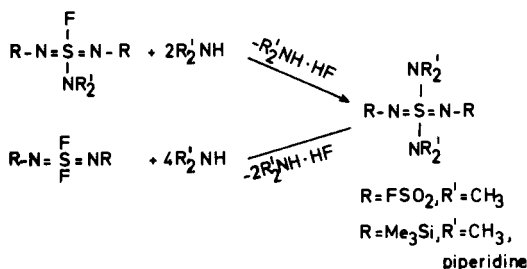
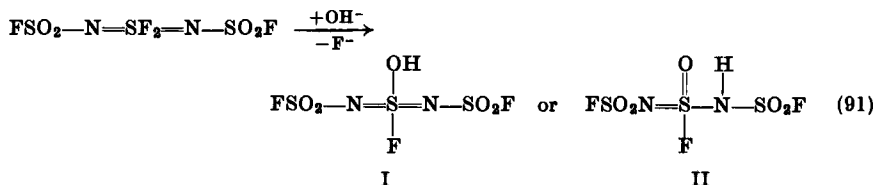


Fig. 18. Preparation of the aza analog of sulfuric acid ester.

can also be brought about by careful hydrolysis (228). The product is separated as the tetraphenylphosphonium salt, structure (II) being the most likely of the two possible tautomeric forms shown. There are no structural studies on bisimidosulfur difluorides, but NMR investigations on sulfur

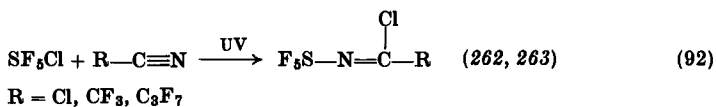


tetrafluoride imides in comparison with SOF_4 suggest a close relationship between the $\text{—N=SF}_2\text{=N—}$ group and SO_2F_2 . The chemistry of organic derivatives of the type $\text{—N=S(alk)}_2\text{=N—}$ and $\text{—N=S(alk)}_2\text{=O}$ has been discussed recently (255).

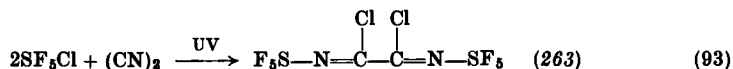
4. Pentafluorosulfanyl-Nitrogen Compounds, $\text{R}_2\text{N—SF}_5$

Synthetic routes to the pentafluorosulfanyl-nitrogen compounds are shown below.

(a) Addition of SF_5Cl to a $\text{C}\equiv\text{N}$ triple bond.



There is addition to both CN groups in dicyanogen.



As can be seen from Fig. 19, the pentafluorosulfanylazomethines are suitable starting materials for the preparation of a large number of further $\text{SF}_5\text{—N}$ derivatives (156, 262, 263).

(b) Addition of HF , SF_4 , and ClF to the triple bond in NSF_3 (30, 34, 35) according to Eqs. (80), (81), and (82). This route has already been described. It can be used in the preparation of SF_5NH_2 , from which further $\text{F}_5\text{S—N}$ -derivatives can be made (Fig. 20) (31, 36).

(c) Combination of SF_5 and NF_2 radicals gives pentafluorosulfanyl difluoramine, $\text{F}_5\text{S—NF}_2$ (Fig. 21). This also results from the reaction between sulfur and N_2F_4 (155, 157), and a very good yield is obtained when $\text{R}_f\text{—N=SF}_2$ is irradiated with N_2F_4 (59). It has a boiling point of -17.6° and is moderately stable chemically, being resistant to attack by dilute aqueous acids and bases at room temperature. Cleavage to SF_5Cl and HNF_2 occurs with HCl at 100°C and there is a reaction with SO_2 at 150°C in which FSO_2NF_2 and SF_4 are produced (20).

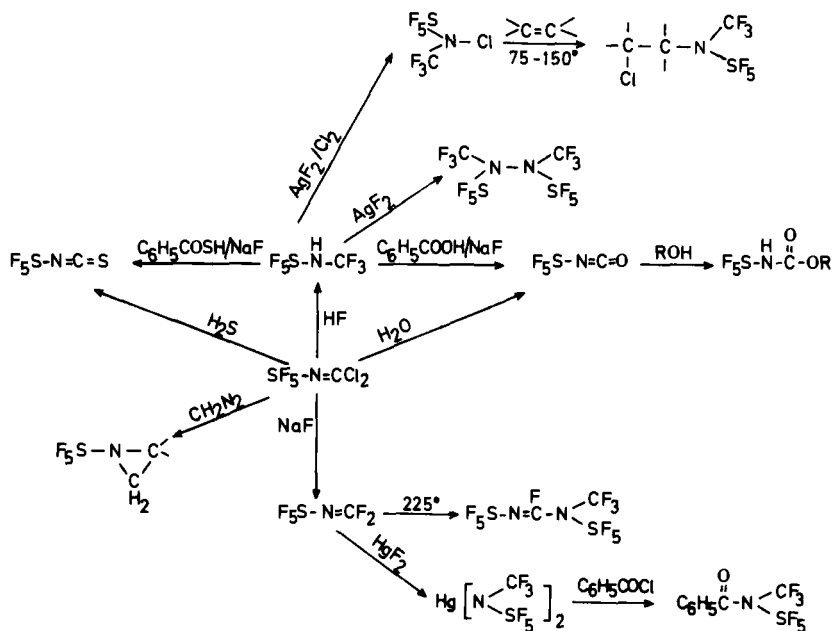
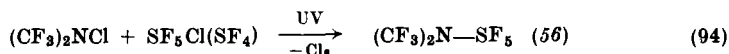
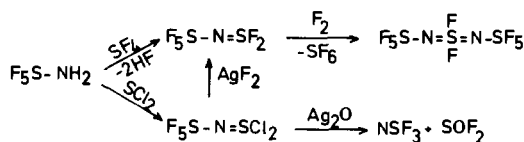
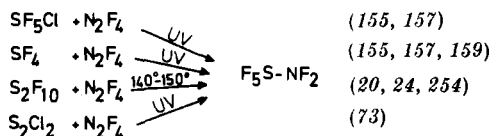


FIG. 19. Reactions of pentafluorosulfanylazomethines.

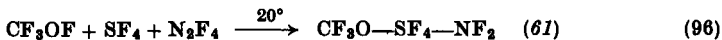
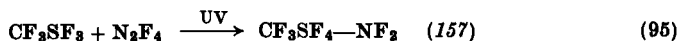
The compound $(\text{CF}_3)_2\text{N}-\text{SF}_5$ can be made in a reaction analogous to that used for SF_5NF_2 (56).



(d) *N*-Monosubstituted derivatives of SF_5-NF_2 are formed in low yields in the fluorination of sulfur difluoride imides (164, 202) [cf. Eq. (48)].

FIG. 20. Reactions of $\text{F}_5\text{S}-\text{NH}_2$.FIG. 21. Preparation of $\text{F}_5\text{S}-\text{NF}_2$.

The $\text{SF}_5\text{-N}$ groups is reasonably stable to chemical attack and attempts to substitute fluorine in these SF_5 compounds have so far been unsuccessful. Two tetrafluorosulfanylamino compounds are, however, known ($\text{CF}_3\text{OSF}_4\text{NF}_2$ and $\text{CF}_3\text{SF}_4\text{NF}_2$), and their preparation is similar to that of SF_5NF_2 .



NMR spectra show that the structure of the pentafluorosulfanyl amines is derived from that of SF_6 by replacing an axial fluorine atom by an amino group. In $\text{CF}_3\text{OSF}_4\text{NF}_2$ the two substituents are in the cis

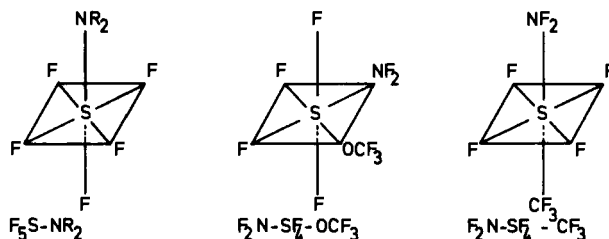
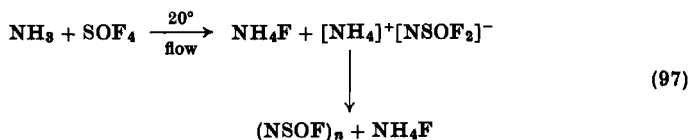


FIG. 22. Structures of pentafluorosulfanyl amines and tetrafluorosulfur(+6) amino derivatives.

position as in bisoxygen-substituted sulfur(+6) tetrafluorides, whereas in $\text{CF}_3\text{-SF}_4\text{-NF}_2$ they occupy axial trans sites, this arrangement being analogous to that in bisperfluoroalkyl-substituted derivatives (Fig. 22).

5. Sulfur Oxide Difluoride Imides, $\text{R-N}=\text{SOF}_2$

The free acid HNSOF_2 corresponding with the $[\text{NSOF}_2]^-$ ion, which is formed in the hydrolysis of NSF_3 , can be prepared by reaction of NH_3 with SOF_4 in ether (51, 188). Distillation gives an azeotrope from which ether is removed with BF_3 . Gaseous NH_3 and SOF_4 give a mixture of NH_4F and $[\text{NH}_4]^+[\text{NSOF}_2]^-$. Attempts to separate these two products by sublimation lead to polymerization to sulfur oxide fluoride imide $(\text{NSOF})_n$ (246).

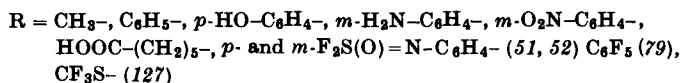
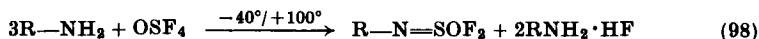


The same polymeric product is observed in the dehydrofluorination of HNSO_2F with CsF or in the reaction of NH_3 with SOF_4 in nonpolar solvents (188). The rubbery $(\text{NSOF})_n$ is comparable with the corresponding polymers of phosphonitrilic fluoride $(\text{PNF}_2)_n$ which is isoelectronic. The sulfur atoms, like those of phosphorus, have a tetrahedral environment. The sulfanuryl fluoride is more resistant to hydrolysis than the phosphorus compound.

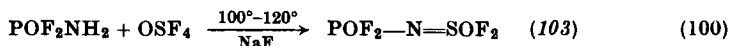
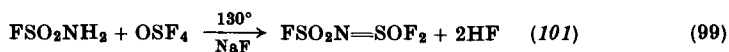
Known sulfur oxide difluoride imides are almost exclusively formed by reaction of OSF_4 with nitrogen-containing compounds. These reactions take place in a manner analogous to those of SF_4 , though, because of the lower reactivity of SOF_4 , higher temperatures are necessary. This is often a disadvantage when the products are easily decomposed by heat, but catalysts such as NaF , CsF , or BF_3 can sometimes be used to lower the reaction temperature. Some of the synthetic routes leading to sulfur difluoride imides cannot be applied here (e.g., the reaction with cyanates) or are successful only in isolated instances (e.g., with cyanides).

Sulfur oxide difluoride imides, RNSOF_2 , have up till now been made by the following methods.

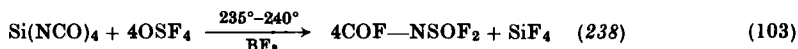
(a) Reaction of primary amines with OSF_4 .



Purely inorganic members of this family can also be made by this method

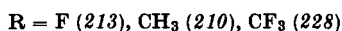


(b) By cleavage of Si-N compounds.



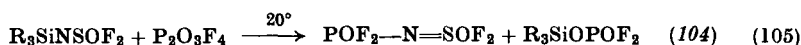
Two methods have also been published recently which avoid the use of OSF_4 .

(d) Fluorination of sulfinylimides.



(e) Oxidation of perhaloalkyl sulfur difluoride imides with OF_2 [cf. Equation (50)].

The compounds obtained by method (b) serve as starting materials for the preparation of further- NSOF_2 derivatives, the Si-N bond in $\text{R}_3\text{SiNSOF}_2$, for example, being cleaved by $\text{P}_2\text{O}_3\text{F}_4$.



N-Cyanosulfuroxide difluoride imide reacts with OSF_4 and SF_4 (Fig. 23). Just as in the case of COFNSF_2 , the corresponding *N*-halogeno

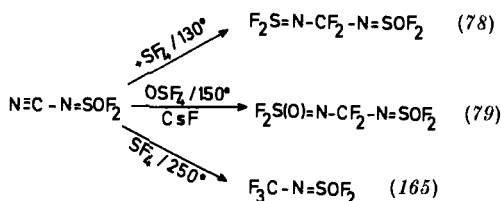


FIG. 23. Reactions of $\text{N}\equiv\text{C}-\text{NSOF}_2$.

compounds are made by starting from *N*-fluoroformylsulfur oxide difluoride imide (238) (Fig. 24). Reaction takes place in all probability

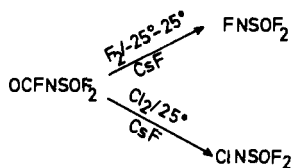
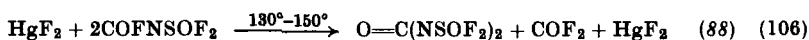


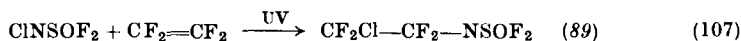
FIG. 24. Preparation of XNSOF_2 compounds (238).

via the ionic compound $\text{Cs}^+\text{NSOF}_2^-$ (238). At 130° – 150° HgF_2 gives $\text{O}=\text{C}(\text{NSOF}_2)_2$ (88):

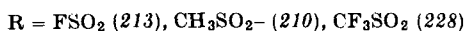
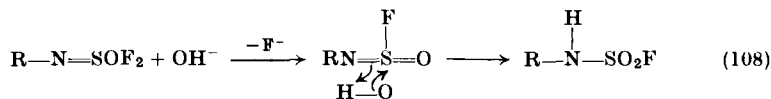


Chlorination of the residue of this reaction yields ClNSOF_2 , though the mercurial $\text{Hg}(\text{NSOF}_2)_2$, which would be expected from this reaction, has not yet been isolated in a pure form.

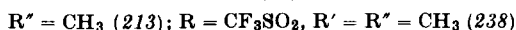
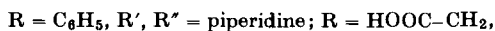
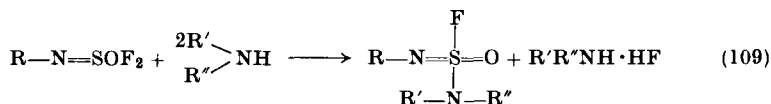
Addition to double bonds takes place with ClNSOF_2 as it does with N -halogenosulfur difluoride imides [Eq. (14)].



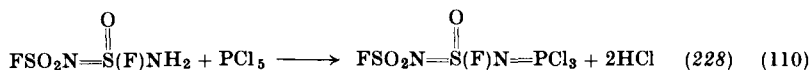
Organosulfur oxide difluoride imides are colorless compounds with considerable chemical stability. They are hydrolyzed only slowly by water or dilute acids, but attack is more rapid with dilute alkalis.



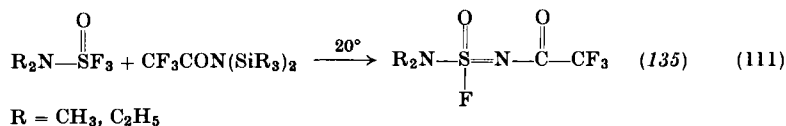
The N -substituted fluorosulfonylamines formed in this reaction can be isolated as their difficultly soluble tetraphenylphosphonium salts (cf. the reaction mechanism for the hydrolysis of NSF_3 , Fig. 15). Further hydrolysis leads to SO_4^{2-} and F^- ions and the corresponding amine. At low temperatures, amines bring about the exchange of a single fluorine atom, giving an S -dialkylaminosulfur oxide monofluorides.

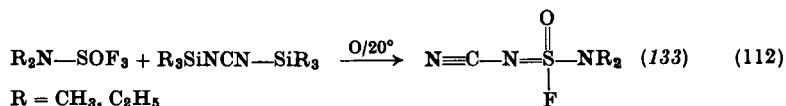


The NH_2 group of $\text{FSO}_2-\text{N}=\overset{\text{O}}{\text{S}}(\text{F})\text{NH}_2$ is a site for further reactions.



It is possible to get S -dialkylaminosulfur oxide monofluoride imides by reaction of dialkylaminosulfur oxide trifluorides with primary amines or their N -silylated derivatives.





In some cases exchange of the last fluorine atom is possible at higher temperatures (Fig. 25). So far sulfur oxide dichloride imides have not

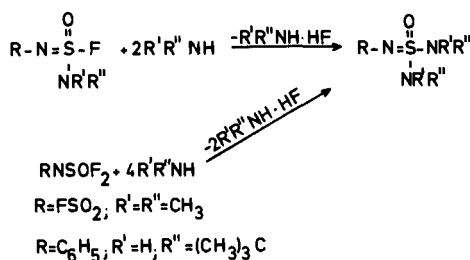
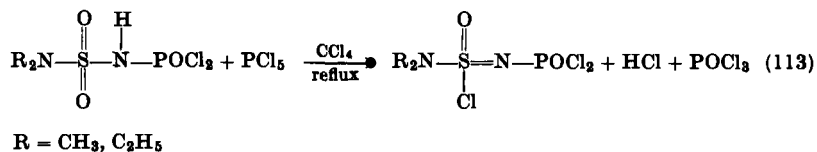


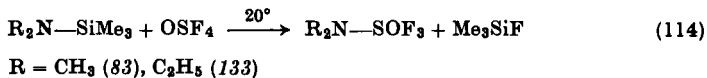
FIG. 25. Preparation of *S,S*-(dialkylamino)sulfur(+6) oxide imides (52, 212).

been made. The first two amino derivatives of this class of compounds were synthesized in the interesting reaction shown below (208).

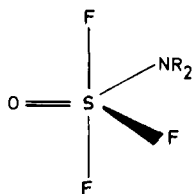


6. Aminosulfur Oxide Trifluorides, $\text{R}_2\text{N}-\text{SOF}_3$

As with the corresponding $\text{R}_2\text{N}-\text{SF}_3$ compounds, the aminosulfur oxide trifluorides are obtainable only by reaction of *N*-silylated secondary amines with OSF_4 .



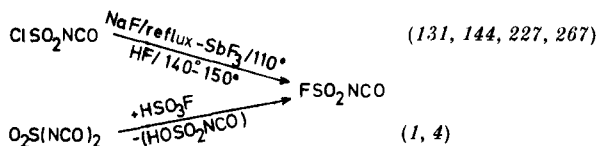
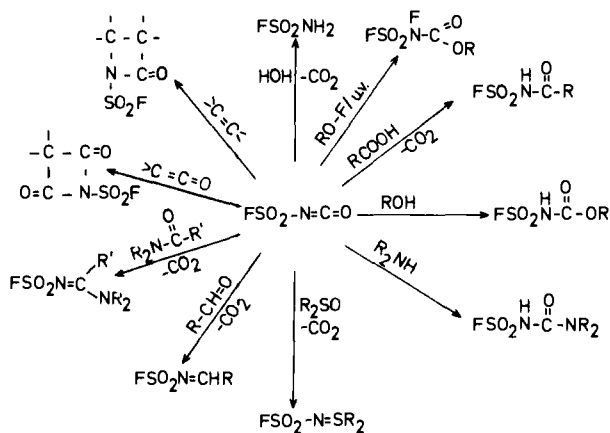
These are extraordinarily reactive colorless liquids and the structure can be shown by NMR investigations to be derived from that of OSF_4 by substitution of one equatorial fluorine atom by an dialkylamino group (Fig. 26). Their reactions have already been discussed [Eqs. (111) and (112)].

FIG. 26. Proposed structure of R_2NSOF_3 .

7. Fluorosulfonyl-Nitrogen Compounds, FSO_2-NR_2

Starting from fluorosulfonyl isocyanate, FSO_2NCO , fluorosulfonyl amide, FSO_2NH_2 , and imido disulfuryl fluoride, $HN(SO_2F)_2$, an almost bewildering number of fluorosulfonyl-nitrogen compounds may be derived.

a. Preparation and Reactions of FSO_2NCO . Several methods have been developed for this synthesis. It is best to start from the technical product $ClSO_2NCO$, which is fluorinated as shown in Fig. 27. Characteristic of the chemistry of fluorosulfonyl isocyanate (Fig. 28) is the high

FIG. 27. Preparation of $FSO_2N=C=O$.FIG. 28. Chemistry of FSO_2NCO .

reactivity of the -N=C=O group. The S-F bond is cleaved only with some difficulty and survives most reactions.

Reactions of FSO_2NCO with olefins (122), ketenes (125), amides (124), aldehydes (121, 123), ortho esters (17), and CH-acidic compounds (18) have been reviewed recently (120) and will not be considered here in detail.

Addition of alcohols and primary or secondary amines to the C=N double bond takes place as shown in Fig. 29, the products being formed

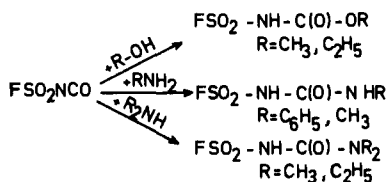
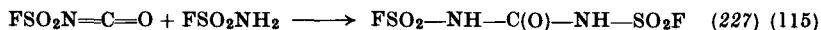


FIG. 29. Addition reactions of FSO_2NCO (227, 231).

in good yield. With fluorosulfonylamide, bisfluorosulfonylamidourea results (227).



Recently the addition of fluorine and hypofluorites to the double bond has also been reported (184) (Fig. 30). When acids are added to the

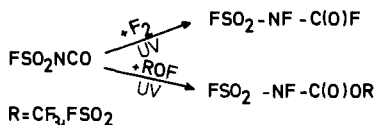
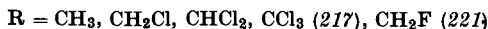
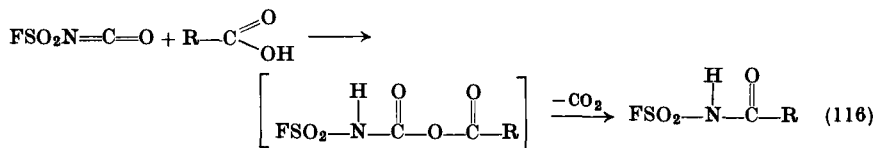
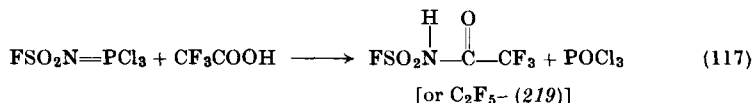


FIG. 30. Photolytic additions to FSO_2NCO (184).

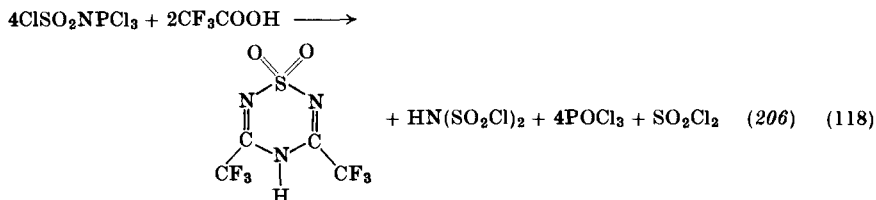
isocyanate group, decarboxylation takes place and *N*-fluorosulfonyl-substituted acid amides result.



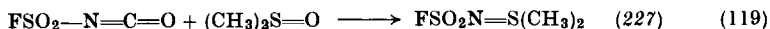
Reaction depends on the pK value of the acid. There is no reaction with CF_3COOH even after boiling for days, though the desired CF_3 derivative can be prepared by cleavage of trichlorophosphazonesulfonyl fluoride (221).



A parallel reaction with $ClSO_2NPCl_3$ gives a cyclic product (206).



In the reaction of dimethylsulfoxide with FSO_2NCO , CO_2 is split off:



If the addition product of FSO_2NCO having the formula $FSO_2\overset{\overset{H}{|}}{N}-C(O)R$ (OR , NR_2) is treated with PCl_5 , $POCl_3$ is eliminated and the corresponding *N*-methylenesulfonyl fluoride amide is formed (Fig. 31). Exchange

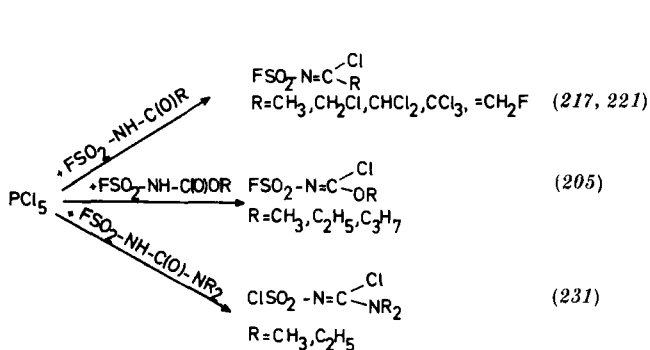


FIG. 31. Preparation of *N*-methylenesulfonyl fluoride amides.

of chlorine atoms bonded to carbon gives rise to a further series of fluorosulfonyl-nitrogen compounds (219, 221, 231). Figure 32 shows as

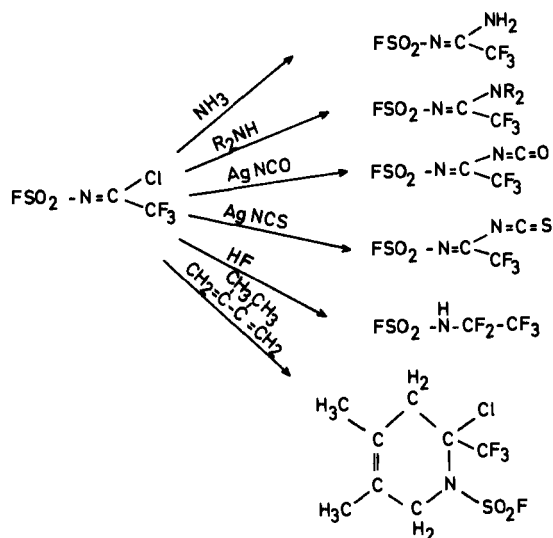
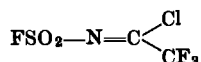
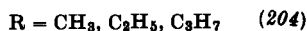
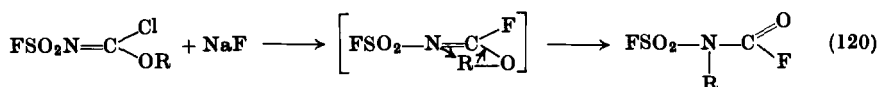


FIG. 32. Reactions of $\text{FSO}_2\text{-N}=\text{C} \begin{smallmatrix} \text{Cl} \\ \text{CF}_3 \end{smallmatrix}$ (219, 221).

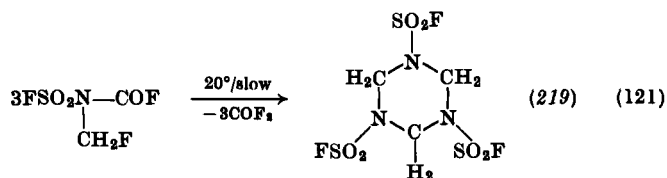
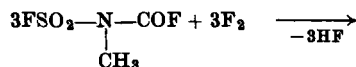
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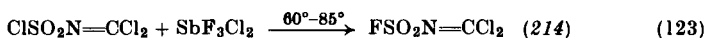
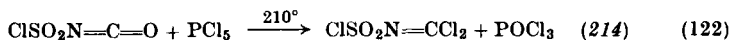
Rearrangements are found to occur when fluorosulfonyl isocyanide alkoxides are fluorinated with NaF.



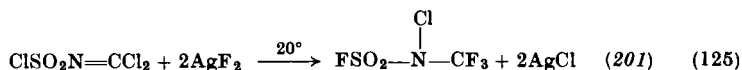
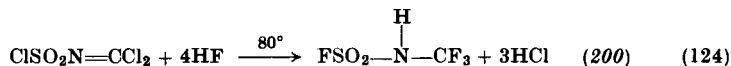
Reaction of the methyl compound with elementary fluorine gives the trifluorosulfonyltriazine (219).



N-Dichloromethylenesulfonyl fluoride amide is produced when PCl_5 reacts with ClSO_2NCO and the product is then fluorinated with SbF_3Cl_2 .



Either HF or AgF_2 will also fluorinate the CCl_2 group.



b. Preparation and Reactions of FSO_2NH_2 and FSO_2NR_2 . Apart from the preparation of FSO_2NH_2 by hydrolysis of FSO_2NCO (Fig. 33), the methods shown in Fig. 34 are also available.

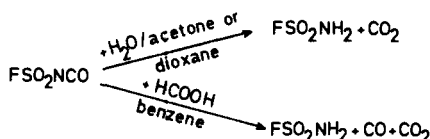


FIG. 33. Preparation of FSO_2NH_2 by hydrolysis of FSO_2NCO (144, 197).

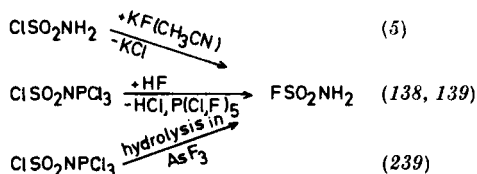


FIG. 34. Preparation of FSO_2NH_2 .

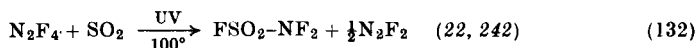
Direct reaction of SO_2F_2 or SO_2FCl with ammonia gives sulfamide in good yield (149), but when secondary amines are used, *N,N*-dialkyl- or diarylfluorosulfonyl amides result.



R = alkyl (64, 226), aryl (193)

The *N,N*-disubstituted derivatives of FSO_2NH_2 are also produced by the following reactions.

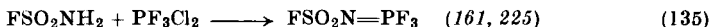
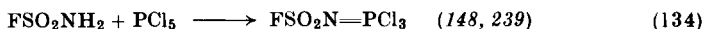
The latter of these two compounds is already known as a product of the photochemical or thermal reaction between N_2F_4 and SO_2 .



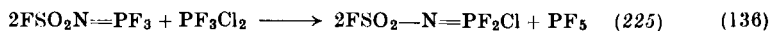
Whereas FSO_2NF_2 is very stable, $\text{H}_2\text{N-SO}_2\text{-NF}_2$, which results in the fluorination of sulfamide in aqueous solution, cannot be isolated in a pure state.



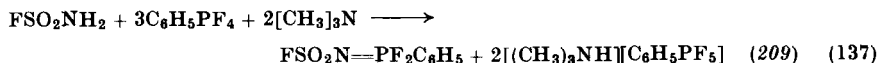
Fluorosulfonyl amide reacts with halides of phosphorus and sulfur forming P=N- or $\text{S=N-SO}_2\text{F}$ derivatives.



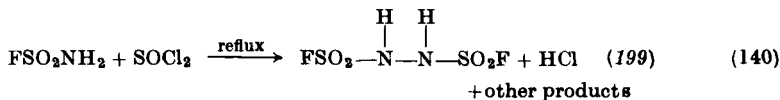
Chlorine-fluorine exchange in the -N=PF_3 group takes place in presence of excess of PF_3Cl_2 .

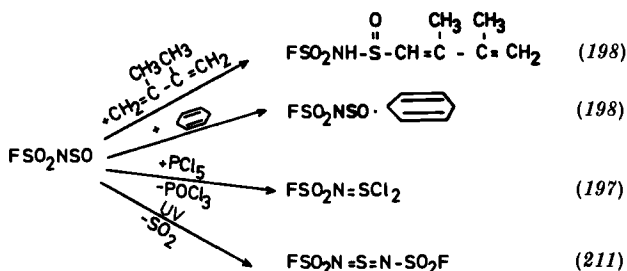


From the chlorine analog, ClSO_2NH_2 , chlorosulfonyl derivatives are isolated by reactions corresponding with those shown in Eqs. (135) and (136) (224). Organophosphorus-substituted fluorosulfonylphosphazo compounds can be made in the same way, although $\text{FSO}_2\text{N=PBr}_3$ is accessible only through FSO_2NSO .



Reaction of FSO_2NH_2 with SF_4 (100), SCl_2 (197), and SOF_4 (101) yields *N*-fluorosulfonylsulfur difluoride, dichloride or oxide difluoride imides, the reactions of which have already been discussed. The product with thionyl chloride is FSO_2NSO , but, if SOCl_2 and FSO_2NH_2 are heated under reflux, *N,N*-hydrazodisulfonyl difluoride is formed.



FIG. 36. Reactions of FSO_2NSO .

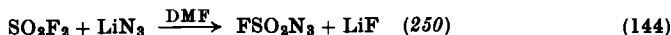
Some further reactions carried out with FSO_2NSO are shown in Fig. 36 [cf. also Eq. (104)]. One proton in FSO_2NH_2 can be replaced by a silyl group (198).



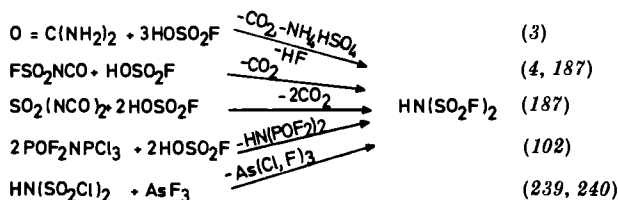
Cleavage of Kirsanov products with fluorosulfonic acid also leads to *N*-monosubstituted derivatives of FSO_2NH_2 , e.g.,



As might be expected, the azide FSO_2N_3 , the preparation of which is shown below, is explosive, and has so far found no use in preparative work.



c. Preparation and Reaction of Imidobissulfuric Acid Fluoride, $\text{HN}(\text{SO}_2\text{F})_2$. The various preparative routes to $\text{HN}(\text{SO}_2\text{F})_2$ are shown in Fig. 37. When $\text{FSO}_2\text{N}=\text{PCl}_3$ is cleaved with HOSO_2F , an azeotrope

FIG. 37. Preparation of $\text{HN}(\text{SO}_2\text{F})_2$.

with POCl_3 results (234), so that it is impossible to prepare pure $\text{HN}(\text{SO}_2\text{F})_2$ in this way. Its formation by hydrolyzing $\text{FSO}_2\text{NSOF}_2$ has

already been referred to in Eq. (108). Metal oxides or carbonates give the corresponding $\text{HN}(\text{SO}_2\text{F})_2$ salts (Fig. 38). The silver salt reacts with

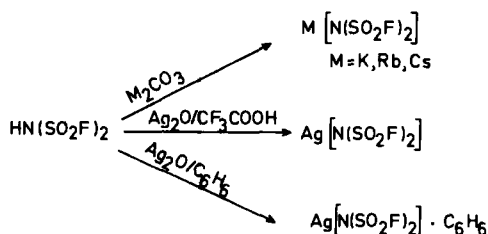
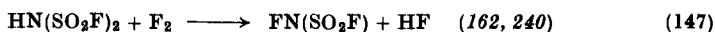
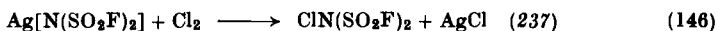
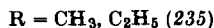
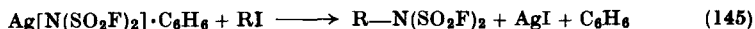


FIG. 38. Reactions of $\text{HN}(\text{SO}_2\text{F})_2$ (235).

alkyl iodides forming the corresponding *N*-alkyl derivatives, while chlorine gives $\text{ClN}(\text{SO}_2\text{F})_2$. The fluorine derivative is synthesized by



direct fluorination of imido bisulfuric acid fluoride. The N-Cl bond in the *N*-chloro compound is readily cleaved and this leads to the following reactions (Fig. 39).

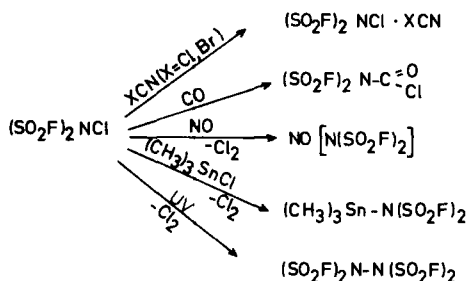
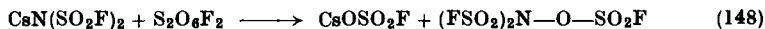
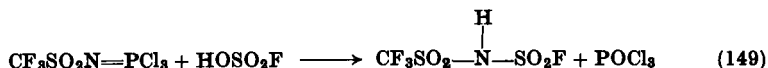


FIG. 39. Reactions of $\text{ClN}(\text{SO}_2\text{F})_2$ (237).

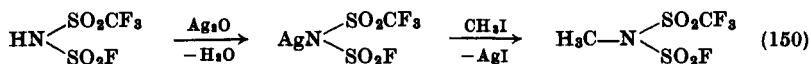
Finally, tris(fluorosulfonyl)hydroxylamine can be produced by the interesting cleavage of $\text{S}_2\text{O}_6\text{F}_2$ with $\text{CsN}(\text{SO}_2\text{F})_2$ (241).



S-Monoalkylated derivatives of $\text{HN}(\text{SO}_2\text{F})_2$ are obtained by either of two methods: (a) by hydrolysis of sulfur oxide difluoride imides [cf. Eq. (108)] or (b) from alkylsulfonylphosphazo compounds and fluorosulfonic acid (220a).



They undergo reactions analogous to those of $\text{HN}(\text{SO}_2\text{F})_2$ (220a).



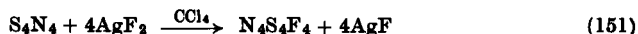
The interesting *O*-difluoramino-sulfur compounds FSO_2ONF_2 (163, 163a) and SF_5ONF_2 (135b, 235a) will not be discussed since they contain no S-N bond.

III. Cyclic Compounds

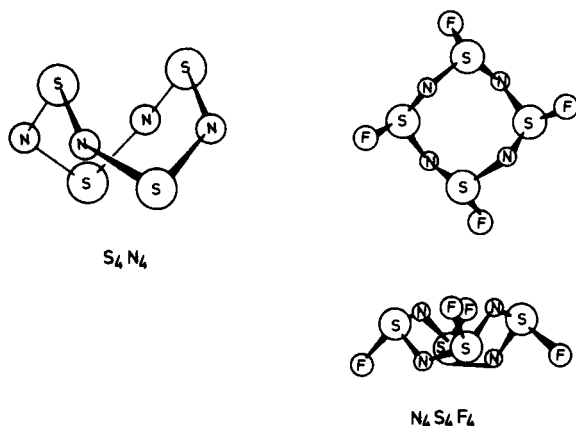
In contrast to the numerous acyclic sulfur-nitrogen-fluorine compounds already described, only a few cyclic compounds with 8-, 7-, or 6-membered rings are known.

1. Tetrathiazyl Tetrafluoride, $\text{S}_4\text{N}_4\text{F}_4$

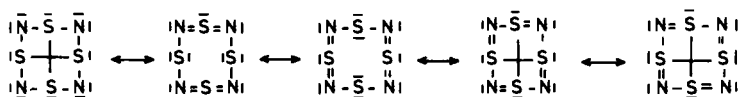
This is the only cyclic compound in this group to have an 8-membered ring structure. Attempts to synthesize it from simple molecules, e.g., by polymerization of NSF, have so far been in vain. This particular reaction always yields trithiazyl trifluoride, $\text{N}_3\text{S}_3\text{F}_3$, with a 6-membered ring. Synthesis of $\text{N}_4\text{S}_4\text{F}_4$ is successful only with the aid of S_4N_4 , which has a preformed 8-membered ring. When it is fluorinated in carbon tetrachloride solution with silver difluoride, colorless crystals of $\text{N}_4\text{S}_4\text{F}_4$ separate. The structure has been established by X-ray analysis (271, 273). Fluorine is bonded to sulfur and the conformation of the cage structure of the 8-membered ring of S_4N_4 changes to the compact wavy 8-membered ring of $\text{N}_4\text{S}_4\text{F}_4$ (Fig. 40). In order to understand this change in



structure it is first necessary to consider the geometrical and electronic structure of S_4N_4 (21, 46-49). X-Ray analysis (29, 158, 249) (Fig. 40) shows the molecule to have one direct S-N distance of 1.62 Å (1.60-1.63 Å), corresponding with a bond order of 1.2 (95). The distance between two sulfur atoms which are not bonded through nitrogen is 2.58 Å, which

FIG. 40. Structures of S_4N_4 and $N_4S_4F_4$.

is significantly less than the sum of the van der Waals radii of 3.7 Å (191) and somewhat greater than the distance of 2.04 Å for a single bond (259). The S-N-S, N-S-N, and N-N-S bond angles are 113°, 105°, and 90°, respectively. Several attempts have been made to explain these parameters as by the limiting mesomeric forms shown in Fig. 41.

FIG. 41. Limiting mesomeric forms of S_4N_4 .

According to Craig *et al.* (46-49), the single S-N distance justifies the assumption of $p_\pi-d_\pi$ bonds in the 8-membered ring of S_4N_4 . This is supported by measurements of the electron spin resonance in sulfur nitride ions (26, 27). It must not, however, be forgotten in this connection that the aromatic character of the ring is only poorly developed. This follows not only from the low S-N bond order of 1.2 (95), but also from HMO calculations (264, 265), which show that there is relatively little tendency for the d orbital of sulfur to participate in $p_\pi-d_\pi$ overlapping. It is assumed from geometrical considerations that interaction between the sulfur atoms is by means of a π bond (153). The same result comes from HMO calculations which also give a bond order value of 0.4 for the S-S bond (neglecting the d orbitals of the sulfur atom). The π bond is a direct consequence of the N-S...S angle of 90°.

Fluorination of S_4N_4 changes the geometrical structure of S_4N_4 (Fig. 40) as well as its electronic structure (Fig. 42). The ^{19}F NMR spectrum of $N_4S_4F_4$ (which melts at 153° and decomposes above 128°) shows a single peak at -35 ppm($CFCl_3$ as external standard), which indicates that the fluorine atoms in the molecule are structurally equivalent. Dielectric measurements show the dipole moment to be zero; the charges are uniformly distributed over the molecule. X-Ray analysis shows that

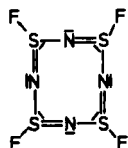


FIG. 42. Electronic structure of $N_4S_4F_4$.

the wavy $N_4S_4F_4$ ring has two different S-N distances of 1.660 and 1.540 Å (271, 273) with bond orders of 1.7 and 1.1, respectively, indicating localized π bonding. The strongly electronegative fluorine atoms favor promotion of electrons into sulfur d orbitals which become contracted. This makes a better overlap of the orbitals possible. Simultaneously the sulfur electrons become more firmly held, which operates against delocalization. The opening up of the S-N-S bond angle from 113° in S_4N_4 to 124° in $N_4S_4F_4$ indicates that the lone pair of electrons on nitrogen is contributing to the S-N bond of $N_4S_4F_4$.

The compound $N_4S_4F_4$ is somewhat soluble in carbon tetrachloride (3.448 gm/liter at 20°). It decomposes slowly in moist air and is hydrolyzed quantitatively by warm alkali according to the equation



Decomposition to NSF takes place when it is heated to 250° , but, as was mentioned in describing the reactions of NSF, polymerization of the latter yields $N_3S_3F_3$ and not $N_4S_4F_4$.

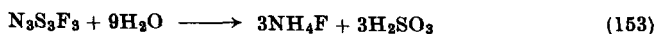
As a Lewis base, $N_4S_4F_4$ forms an adduct with BF_3 . The green solid $N_4S_4F_4 \cdot BF_3$ (87) is produced from gaseous BF_3 and solid, colorless $N_4S_4F_4$. It decomposes in dry nitrogen at room temperature after some hours. More prolonged reaction of BF_3 , for example, at 20° for 1 day, results in ring cleavage, the product being the unstable adduct $NSF \cdot BF_3$, which has already been described. In this instance, the behavior of $N_4S_4F_4$ differs from that of $N_3S_3F_3$, as will be seen later (85).

Attempts to replace fluorine atoms in $N_4S_4F_4$ by chlorine with the aid of chlorides such as $SiCl_4$, PCl_5 , or $(CH_3)_3SiCl$ were unsuccessful; in

each case $\text{N}_3\text{S}_3\text{Cl}_3$ was formed and not $\text{N}_4\text{S}_4\text{Cl}_4$ (85a). The latter probably occurs an intermediate of low stability during the chlorination of S_4N_4 . When a mixture of oxygen and nitrogen dioxide is passed over $\text{N}_4\text{S}_4\text{F}_4$ at 120° (85a), trisulfur dinitrogen dioxide, $\text{S}_3\text{N}_2\text{O}_2$, is formed in addition to SO_2 , SOF_2 , and a little SO_3 (116). A further oxide, trisulfur dinitrogen pentoxide, $\text{S}_3\text{N}_2\text{O}_5$ (117), is obtained by reaction of $\text{N}_4\text{S}_4\text{F}_4$ with SO_3 at 200° (85a).

2. Trithiazyl Trifluoride

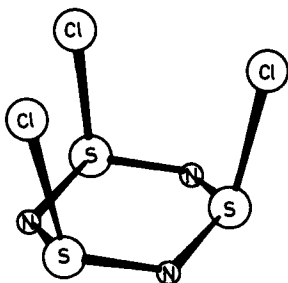
This may be prepared in two ways: (a) by polymerization of NSF or (b), directly by fluorination of a suspension of $\text{N}_3\text{S}_3\text{Cl}_3$ in carbon tetrachloride with AgF_2 at room temperature. The colorless, highly refractive crystals of $\text{N}_3\text{S}_3\text{F}_3$, which are appreciably volatile at room temperature, are readily soluble in carbon tetrachloride and benzene (244). They are stable in absence of air, although they decompose and become black in moist air. Hydrolysis by cold dilute sodium hydroxide



is quantitative. The oxidation number of sulfur is +4, as in $\text{N}_4\text{S}_4\text{F}_4$, and fluorine must be bonded to sulfur.

The structure of trithiazyl trifluoride has not yet been determined by X-ray analysis, so that the data for comparison with $\text{N}_4\text{S}_4\text{F}_4$ are lacking. In spite of this, however, some conclusions as to possible structures may be drawn. As in the case of $\text{N}_4\text{S}_4\text{F}_4$, the trimer shows only one signal in the ^{19}F NMR spectrum at -44.1 ppm [CFCl_3 external standard (220b)]. From this it can be concluded that all the fluorine atoms in $\text{N}_3\text{S}_3\text{F}_3$ are in equivalent positions. The value is close to that for $\text{N}_4\text{S}_4\text{F}_4$ (-35 ppm) and the electronic structures of the two compounds are likely to be similar.

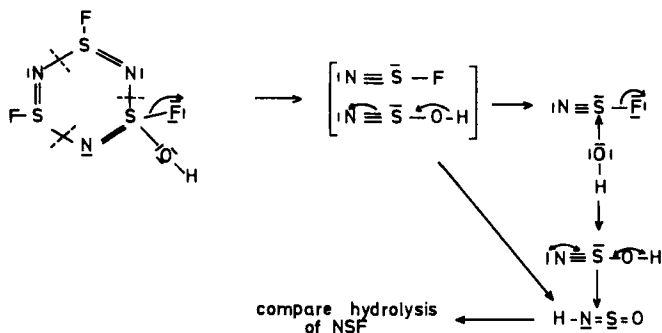
We can now consider the structure of $\text{N}_3\text{S}_3\text{Cl}_3$, from which $\text{N}_3\text{S}_3\text{F}_3$ is prepared (cf. Fig. 43), and which is itself prepared by chlorinating a suspension of S_4N_4 in carbon tetrachloride. X-Ray analysis (274) shows the $\text{N}_3\text{S}_3\text{Cl}_3$ molecule to have a chair form with the three chlorine atoms in axial positions. In contrast to $\text{N}_4\text{S}_4\text{F}_4$, there is only a single direct S-N distance of 1.605 \AA , corresponding with a bond order of 1.4 (95), and indicative of delocalized p_π - d_π bonding in the ring. The $\text{N}_3\text{S}_3\text{Cl}_3$ molecule is deformed; thus the distance of the nitrogen atoms from a plane containing the sulfur atoms is 0.225 \AA for N-1 and 0.126 \AA for N-2. The S-Cl distances of 2.084 and 2.150 \AA are also not equal. The relatively large S-N-S angle of 123.9° suggests that the lone pair of electrons on nitrogen is participating in the S-N bond.

FIG. 43. Structure of $N_3S_3Cl_3$.

It would be expected that the structure of $N_3S_3F_3$ would be similar to that of $N_3S_3Cl_3$. ^{19}F NMR measurements show all the fluorine atoms in $N_3S_3F_3$ to be equivalent. This, however, would be possible only if they were situated in an axial position on one side of the ring, as in $N_3S_3Cl_3$. It could also be concluded from the NMR data that, because of the similarity in the chemical shifts for $N_3S_3F_3$ and $N_4S_4F_4$, there would be different S-N distances in the N_3S_3 ring of $N_3S_3F_3$, i.e., localized π bonding.

Like $N_4S_4F_4$, the trimer also acts as a Lewis base and forms a colorless solid $N_3S_3F_3 \cdot BF_3$ with BF_3 , probably with electron donation by a single nitrogen atom in the ring. The adduct is unaffected by excess of BF_3 and is stable to about 60° . It thus differs considerably in stability from the corresponding derivative of $N_4S_4F_4$ (85).

The hydrolysis mechanism for $N_3S_3F_3$ may be closely related to that of NSF. If a little water is added to $N_3S_3F_3$ in a glass vessel, the gaseous compounds NSF, HNSO, SO_2 , and SiF_4 can be detected (96). The reaction scheme in Fig. 44 has been proposed. The first step may be

FIG. 44. Hydrolysis of $N_3S_3F_3$.

considered as involving nucleophilic attack by OH^- ions on the sulfur atom of $\text{N}_3\text{S}_3\text{F}_3$. Ring cleavage leads to NSF and HNSO , the latter being formed by further hydrolysis of NSF. Hydrolysis then follows the same route as was described for NSF, with formation of H_2NOH and $\text{S}(\text{OH})_2$, which interact through amidosulfinic acid, $\text{H}_2\text{NSO}_2\text{H}$, to give SO_2 and NH_3 . Subsequent reactions yield sulfur, $\text{S}_2\text{O}_3^{2-}$, and polythionate ions. Formation of SOF_2 may possibly be explained by a side reaction of NSF with HF and subsequent hydrolysis.

3. Trithiazyl Trifluoride Trioxide (Sulfanuric Fluoride), $\text{N}_3\text{S}_3\text{O}_3\text{F}_3$

This was first prepared by reaction of potassium fluoride with $\alpha\text{-N}_3\text{S}_3\text{O}_3\text{Cl}_3$ (147) in carbon tetrachloride at 145° (247). Direct synthesis from HNSOF_2 has not yet proved possible, although recently $\text{N}_3\text{S}_3\text{O}_3\text{F}_3$ was obtained in small amounts by a direct route involving heating OCFNSOF_2 with cesium fluoride (88). The product from the fluorination of $\text{N}_3\text{S}_3\text{O}_3\text{Cl}_3$ was separated into two isomers by gas chromatography. These were shown by their ^{19}F NMR spectra to be *cis*- and *trans*- $\text{N}_3\text{S}_3\text{O}_3\text{F}_3$. The *cis* compound (m.p. 17.4°) gave only one signal at -70.9 ppm (CFCl_3 as internal standard), whereas the *trans* isomer gave the multiplet characteristic of an AB_2 compound (-71.9 , -71.4 ppm: $J_{\text{AB}} = \pm 21.6$ Hz). Since the unique fluorine atom in *trans*- $\text{N}_3\text{S}_3\text{O}_3\text{F}_3$ is less shielded from the influence of solvents than the other two fluorine atoms, the sulfur-nitrogen ring of the molecule should be nonplanar, as in the case of $\text{N}_3\text{S}_3\text{O}_3\text{Cl}_3$ (9, 247). It may therefore be assumed that *cis*- $\text{N}_3\text{S}_3\text{O}_3\text{F}_3$ is structurally similar to $\alpha\text{-N}_3\text{S}_3\text{O}_3\text{Cl}_3$ (Fig. 45), the structure of which has been elucidated by X-ray analysis (9, 136, 272), and which is comparable with that of $\text{N}_3\text{S}_3\text{Cl}_3$ (cf. Fig. 7).

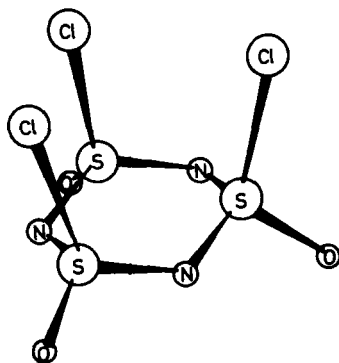


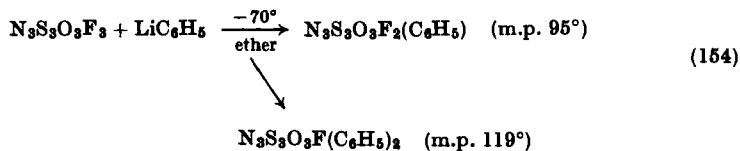
FIG. 45. Structure of $\alpha\text{-N}_3\text{S}_3\text{O}_3\text{Cl}_3$.

The $\text{N}_3\text{S}_3\text{O}_3\text{Cl}_3$ molecule forms a chair-shaped ring in which two nitrogen atoms lie 0.244 Å outside a plane containing the sulfur atoms, the distance for the third being 0.262 Å. There is only one direct S–N distance of 1.57 Å in the ring, corresponding with a bond order of 1.5 (95), so that delocalized p_π – d_π bonding can be assumed. The shorter S–N distance compared with that in $\text{N}_3\text{S}_3\text{Cl}_3$ results from polarization of sulfur by oxygen and from the absence of a lone pair of electrons on sulfur. The chlorine atoms are all on one side of the molecule in axial positions, with the oxygen atoms in equatorial positions. The S–O bond (1.407 Å) has some double-bond character; S_3O_6 , which is isosteric with $\text{N}_3\text{S}_3\text{O}_3\text{Cl}_3$, has a similar structure. Whether the fluorine analog $\text{N}_3\text{S}_3\text{O}_3\text{F}_3$ has localized or delocalized bond can only be determined by further experiments.

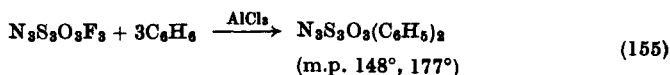
The chemical properties of $\text{N}_3\text{S}_3\text{O}_3\text{F}_3$ are noteworthy. The compound may be passed through a nickel tube at 350° almost without decomposition. Liquid hydrogen fluoride under pressure is without reaction at 150°; however, boiling caustic soda solution brings about hydrolysis to amidosulfonate and ammonia (247).

a. Substitution Products of $\text{N}_3\text{S}_3\text{O}_3\text{F}_3$. According to a preliminary communication (247), substitution of fluorine atoms in $\text{N}_3\text{S}_3\text{O}_3\text{F}_3$ is readily achieved by NH_3 and primary or secondary amines. Details, however, are not available. It has been shown recently (8) that diethylamine and *n*-octylamine react to give $\text{N}_3\text{S}_3\text{O}_3\text{F}[\text{N}(\text{C}_2\text{H}_5)_2]_2$ and $\text{N}_3\text{S}_3\text{O}_3\text{F}[n\text{-C}_8\text{H}_{17}\text{NH}]_2$.

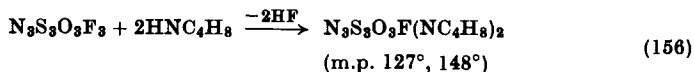
Various reactions give substitution products which occur as isomers (177). Thus, phenyllithium in ether at –70° reacts as follows:



The disubstituted product $\text{N}_3\text{S}_3\text{O}_3\text{F}(\text{C}_6\text{H}_5)_2$ can also be made by fluorinating $\text{N}_3\text{S}_3\text{O}_3\text{Cl}(\text{C}_6\text{H}_5)_2$ with NaF in acetonitrile (169). The m.p. (107°) is, however, different from that of the other preparation (119°) and isomers may be present. Complete substitution of the fluorine can be achieved only by a Friedel–Crafts reaction with benzene and aluminum chloride.



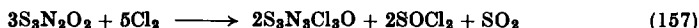
Further disubstituted compounds were prepared with morpholine, 2,6-dimethylmorpholine, piperidine, and pyrrolidine, e.g.,



The S-N rings in these compounds are nonplanar and an indication of possible structures comes from the ^{19}F NMR spectra (25). In the derivatives described above two different chemical shifts are found for the fluorine atoms, one at -72 to -73 , the other at -77 to -78 ppm (CFCl_3 as internal standard). The first value is attributed by the authors to an axial position of the fluorine atom (derived from the value of -72.8 ppm for *cis*- $\text{N}_3\text{S}_3\text{O}_3\text{F}_3$) and the other to an equatorial position. On this basis, $\text{N}_3\text{S}_3\text{O}_3\text{F}_2(\text{C}_6\text{H}_5)_2$ has both F atoms in the equatorial position (-77.2 ppm), while in $\text{N}_3\text{S}_3\text{O}_3\text{F}(\text{C}_6\text{H}_5)_2$ the F atom is in an axial position (-72 ppm). The infrared spectra of the compounds are similar to one another and correspond to those of α - and β - $\text{N}_3\text{S}_3\text{O}_3\text{Cl}_3$. Exact assignment of the observed frequencies to specific structural groups is, however, difficult, as no corresponding data are available for the sulfanuric chlorides or fluorides.

4. Trithiazyl Difluoride Chloride Oxide, $\text{N}_3\text{S}_3\text{F}_2\text{ClO}$

This is accessible through fluorination of $\text{N}_3\text{S}_3\text{Cl}_3\text{O}$ (243). The latter is a colorless crystalline solid, m.p. 110° , obtained from $\text{S}_3\text{N}_2\text{O}_2$ and liquid



chlorine with loss of SOCl_2 and SO_2 . A ring structure is assumed as it is oxidized by SO_3 to the cyclic compound $\text{N}_3\text{S}_3\text{Cl}_3\text{O}_3$. Only one peak is observed in the gas chromatogram, so that only a single compound is present. It is converted by silver difluoride in carbon tetrachloride to $\text{N}_3\text{S}_3\text{F}_2\text{ClO}$, for which a ring structure is also likely (Fig. 46). A single

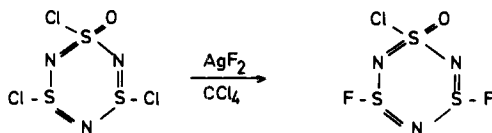


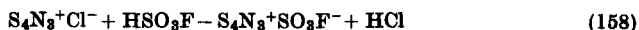
FIG. 46. Preparation of $\text{N}_3\text{S}_3\text{F}_2\text{ClO}$.

peak at -35.2 ppm is observed in the ^{19}F NMR spectrum (CFCl_3 as standard), and this corresponds with that of $\text{N}_4\text{S}_4\text{F}_4$. Nothing can be

said about the bonding relationships in $\text{N}_3\text{S}_3\text{F}_2\text{ClO}$, the first sulfur-nitrogen ring compound with different halogen substituents. The existence of this compound does, however, show that combinations between S-N ring systems in which sulfur has variable oxidation numbers is possible.

5. *Thiotrithiazyl Fluoride*, $[\text{N}_4\text{S}_3]^+\text{F}^-$, and *Fluorosulfonate*, $[\text{S}_4\text{N}_3]^+\text{SO}_3\text{F}^-$

Thiotrithiazyl fluoride is formed in the reaction of anhydrous hydrogen fluoride with $[\text{S}_4\text{N}_3]^+\text{Cl}^-$ at $80^\circ\text{--}100^\circ$ as yellow-brown crystals of the composition $[\text{S}_4\text{N}_3]^+\text{F}^- \cdot 1.5\text{HF}$ (113). The residual 1.5HF cannot be removed by heating without decomposing the compound. The infrared spectra of the fluoride and the starting material $[\text{S}_4\text{N}_3]^+\text{Cl}^-$ are very similar. Molecular weight determinations also show that both compounds dissociate into two univalent ions (16, 113), which is an indication of their saltlike character. This had previously been assumed for $[\text{S}_4\text{N}_3]^+\text{Cl}^-$ because of the ready exchange of chlorine for other anionic groups, e.g., NO_3^- or HSO_4^- . Thiotrithiazyl fluorosulfonate has also been prepared recently by reaction of $[\text{S}_4\text{N}_3]^+\text{Cl}^-$ with fluorosulfonic acid (189). The



structural formula proposed for the $[\text{S}_4\text{N}_3]^+$ ion (Fig. 47) (118) has been established by X-ray analysis of $[\text{S}_4\text{N}_3]^+\text{NO}_3^-$ (45, 152, 269, 270). In the

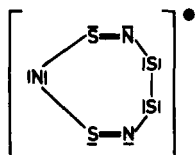
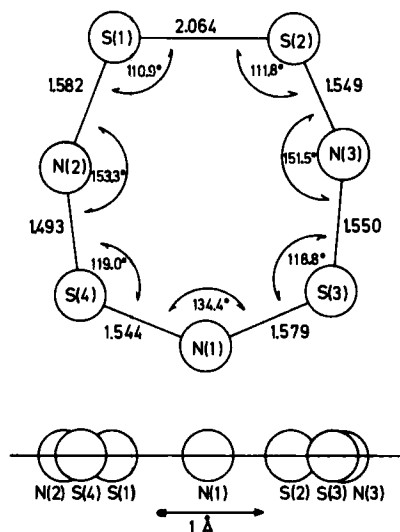


FIG. 47. Structural formula of S_4N_3^+ .

planar 7-membered ring there are alternating S-N bonds and one S-S bond (Fig. 48). The S-N distances are all almost equal, varying from 1.49 to 1.58 Å (45) and the average value of 1.55 Å leads to a bond order of 1.6. The S-S distance of 2.06 Å is very near to that for a single bond (2.08 Å). It is possible to suppose that there is very delocalized π bonding between the S-N bonds, but not between the two sulfur atoms. The bond angles at the nitrogen atoms are striking. They are controlled by the planar arrangement and have very high values (S(1)-N(2)-S(4), 153.3° ;

FIG. 48. Structure of the $[\text{S}_4\text{N}_3]^+$ ring (45).

$\text{S}(2)\text{--N}(3)\text{--S}(3)$, 151.5° ; $\text{S}(3)\text{--N}(1)\text{--S}(4)$, 134.4°). Some publications on the electronic structure of the $[\text{S}_4\text{N}_3]^+$ cation have also appeared (7, 28, 65, 141, 154).

IV. Bonding Relationships of the S-N Group

In order to characterize the S-N bond in sulfur-nitrogen compounds various attempts have been made to establish a relationship between the S-N bond distance (d_{SN}) and the bond order (N_{SN}). The resulting linear dependence (10, 28, 66, 67) of d_{SN} and N_{SN} can, however, only be considered as an approximation. The values of N_{SN} found for the larger S-N distances are certainly too high. Since reliable values for the force constant f_{SN} and for d_{SN} are available for some S-N compounds, including NSF and NSF_3 , a relationship between f_{NS} and d_{NS} has been established which takes the form $f_{\text{NS}} = 145d_{\text{NS}}^{-7.00}$ (cf. Fig. 48). Table III shows force constants and bond distances for some SN compounds. Here force constants have been deduced from measured bond distances or, conversely, bond distances from known force constants for the relationship given above. The values of the bond order calculated from force constants are also included. From the curve it is also possible to

TABLE III

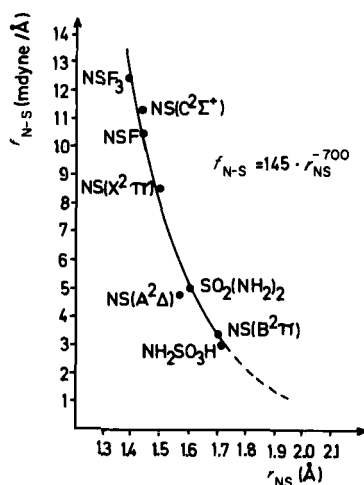
FORCE CONSTANTS, SN DISTANCES, AND BOND ORDER OF SULFUR-NITROGEN COMPOUNDS (95)^a

Compound	r_{NS} [Å]	f_{NS} [mdyne/Å]	N_{NS}
NSF ₃	1.416	12.55	2.7
NSF	1.446	10.71	2.4
NSCl	(1.46)	10.02	2.2
HNSO	(1.50)	8.3	1.9
S ₄ N ₄ F ₄	1.54	(6.9)	1.7
S ₄ N ₃ ⁺	1.55	(6.6)	1.6
α-S ₃ N ₃ O ₃ Cl ₃	1.564	(6.2)	1.5
S ₃ N ₃ Cl ₃	1.605	(5.3)	1.4
S ₄ N ₄	1.63	(4.6)	1.2
S ₄ N ₄ F ₄	1.66	(4.1)	1.1
S ₄ N ₄ H ₄	1.67	(3.9)	1.1
NH ₂ SO ₃ H	1.73	3.1	0.8

^a Numbers in parentheses are calculated values.

determine f_{SN} values and the corresponding bond orders for cyclic compounds for which d_{SN} values are known (Fig. 49).

The following example shows that the equation given above relating f_{NS} and d_{NS} is more satisfactory than the linear relationship. The ¹⁴N

FIG. 49. Force constant, f_{NS} , as a function of the SN distance, d_{NS} .

chemical shift for S_4N_4 has a value of 485 ± 20 ppm, which is near to the value for an S-N single bond (530 to 540 ppm), whereas the ^{14}N shift for $[S_4N_3]^+$ lies at 235 ppm (167). The measured value is too high if the S-N bond order of 1.5 is assumed for S_4N_4 based on the linear relationship (10, 28, 67). If, however, a value of 1.2 for S_4N_4 is taken from Table III, the ^{14}N shift compared with that of $S_4N_3^+$ falls into place. The bond orders determined here may be compared with bond energies determined experimentally. Some values are noted in Table IV. They do not show

TABLE IV
NS BOND ORDER, N_{SN} , AND NS BOND ENERGY, d_{NS}^a

	NSF ₃	NS ⁺	NSF	NCNSF ₂	(FSO ₂) ₂ NF	FSO ₂ NF ₂	F ₅ SNF ₂
$d_{(NS)}$	93 (186)	122.5 (185)	71 (186)	75 (95)	48 (190)	39 (190)	32 (190)
N_{SN}	2.7	2.6 (85b)	2.4	2.2	—	—	—

^a Numbers in parentheses are reference citations.

the expected trend and apparently the range of error in data obtained by the various methods is too large [cf. also (185)].

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