Periodic Table of the Elements with the Gmelin System Numbers

1 H 2																1 H 2	2 He 1
3 Li 20	4 Be 26											5 B 13	6 C 14	7 N 4	8 O 3	9 F 5	10 Ne 1
11 Na 21	12 Mg 27											13 Al 35	14 Si 15	15 P 16	16 S 9	17 Cl 6	18 Ar 1
19 * K 22	20 Ca 28	21 Sc 39	22 Ti 41	23 V 48	24 Cr 52	25 Mn 56	26 Fe 59	27 Co 58	28 Ni 57	29 Cu 60	30 Zn 32	31 Ga 36	32 Ge 45	33 As 17	34 Se 10	35 Br 7	36 Kr 1
37 Rb 24	38 Sr 29	39 Y 39	40 Zr 42	41 Nb 49	42 Mo 53	43 Tc 69	44 Ru 63	45 Rh 64	46 Pd 65	47 Ag 61	48 Cd 33	49 In 37	50 Sn 46	51 Sb 18	52 Te 11	53 I 8	54 Xe 1
55 Cs 25	56 Ba 30	57** La 39	72 Hf 43	73 Ta 50	74 W 54	75 Re 70	76 Os 66	77 Ir 67	78 Pt 68	79 Au 62	80 Hg 34	81 Tl 38	82 Pb 47	83 Bi 19	84 Po 12	85 At	86 Rn 1
87 Fr	88 Ra 31	89*** Ac 40	104 71	105 71													* NH_4 23

**Lanthanides 39	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
***Actinides	90 Th 44	91 Pa 51	92 U 55	93 Np 71	94 Pu 71	95 Am 71	96 Cm 71	97 Bk 71	98 Cf 71	99 Es 71	100 Fm 71	101 Md 71	102 No 71	103 Lr 71

A Key to the Gmelin System is given on the Inside Back Cover

Gmelin Handbook of Inorganic Chemistry

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Volumes on "Fluorine" (Syst. No. 5) and "Carbon" (Syst. No. 14)

The perfluorohalogenoorgano compounds of main group elements are described in the following volumes and are a part of Syst. No. 5 "Fluorine". — On account of the close connection to carbon, the volumes of Syst. No. 14 "Carbon", are also listed.

F Fluorine

Perfluorohalogenoorgano Compounds of Main Group Elements

Tl. 1 (Erg.-Werk, Bd. 9): Verbindungen von Schwefel — 1973

Tl. 2 (Erg.-Werk, Bd. 12): Verbindungen von Schwefel (Fortsetzung), Selen, Tellur — 1973

Tl. 3 (Erg.-Werk, Bd. 24): Verbindungen von Phosphor, Arsen, Antimon und Wismut — 1975

Tl. 4 (Erg.-Werk, Bd. 25): Verbindungen mit Elementen der 1. bis 4. Hauptgruppe (außer Kohlenstoff) — 1975

Tl. 5: Verbindungen mit Stickstoff (Heterocyclische Verbindungen) — 1978

Tl. 6: Verbindungen mit Stickstoff (Heterocyclische Verbindungen) (Fortsetzung). Formelregister für Tl. 5 und 6 — 1978

Tl. 7: Aliphatische und aromatische Stickstoff-Verbindungen — 1979

Tl. 8: Aliphatische und aromatische Stickstoff-Verbindungen (Fortsetzung) — 1980

Pt. 9: Aliphatic and Aromatic Nitrogen Compounds (Conclusion) — 1981

Suppl. Vol. 1: Compounds with Elements of Main Groups 1 to 5 (excluding N) and with S (partially) — 1984 (present volume)

"Fluor" Hauptband — 1926

"Fluor" Ergänzungsband 1 — 1959

"Fluorine" Suppl. Vol. 2 (Element) — 1980

"Fluorine" Suppl. Vol. 3 (Compounds with Hydrogen) — 1982

C Carbon

Tl. B1: Isotope. Atom. Molekel. Einstoffsystem. Dampf. Diamant — 1967

Tl. B2: Graphit — 1968

Tl. B3: Chemisches Verhalten von Graphit. Graphitverbindungen. Kolloider Kohlenstoff — 1968

Tl. C1: Verbindungen mit Edelgasen, Wasserstoff und Sauerstoff — 1970

Tl. C2: Chemisches Verhalten von CO und CO_2 — 1972

Tl. C3: Gleichgewicht CO_2/CO. Wasserhaltige Lösungen von Kohlensäure. Carbonat-Ionen. Peroxokohlensäuren — 1973

Tl. C4: Ausgewählte C-H-O Radikale. HCOOH. CH_3COOH. $H_2C_2O_4$ — 1975

Tl. D1: Kohlenstoff-Stickstoff-Verbindungen — 1971

Tl. D2 und D3: Kohlenstoff-Halogen-Verbindungen — 1974 bzw. 1976

Tl. D4 und D5: Kohlenstoff-Schwefel-Verbindungen — 1977

Tl. D6: Kohlenstoff-Schwefel-Verbindungen (Fortsetzung). Kohlenstoff-Selen- und Kohlenstoff-Tellur-Verbindungen — 1978

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Gmelin Handbook of Inorganic Chemistry

8th Edition

F

Perfluorohalogenoorgano Compounds of Main Group Elements

Supplement Volume 1

Compounds with Elements of Main Groups 1 to 5 (excluding N) and with S (partially)

with 3 illustrations

By Alois Haas

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Preface

This is the first of three Supplement Volumes which complete (up to the end of 1981) the series „Perfluorohalogenoorgano Compounds of Main Group Elements", Part 1 to 9.

Supplement Volume 1 describes the compounds of the Main Group Elements 1 to 4, as well as the compounds of phosphorus, arsenic, antimony, and bismuth, and is concluded by chapters on sulfur(II) compounds (thiocarbonyls). Supplement Volume 2 continues the coverage of the sulfur(II) compounds followed by the description of sulfur(IV), sulfur(VI), selenium, tellurium and halogen compounds (in an oxidation state higher than 1) as well as a formula index for the Supplement Volumes 1 and 2. The third volume surveys the nitrogen compounds and contains a formula index for this volume.

Concept, organization, and selection as to the coverage of the material are the same as in the Main Volumes. Title compounds are newly synthesized ones as well as those compounds already referenced in the Main Volumes and for which new facts have been published. These Main Volume compounds are always cited in the chapters on preparation. If no new preparation is mentioned, a reference is given concerning the Main Volume citation and to the chapters on physical and chemical properties in the Supplement Volume.

Conventions as to the presentation of the data are given in the prefaces of the Main Volumes. In contrast to the convention for NMR chemical shifts used previously, the sign of the chemical shift is now designated as positive downfield from the reference standard according to: IUPAC Commission on Molecular Structure and Spectroscopy, Pure and Applied Chemistry **29** [1972] 625/8, **45** [1976] 217/9.

I wish to thank Prof. Dr. Dr. h.c. E. Fluck and his coworkers for their excellent cooperation. I also wish to take the opportunity to express my appreciation to colleagues who assisted me by providing reprints and patents.

Bochum, December 1983 A. Haas

Table of Contents

1 Perfluorohalogenoorgano Compounds of Main Group 1 Elements

1.1 Preliminary Remarks

The compounds of the Main Group 1 elements are covered to the end of 1973 in "Perfluorhalogenorgano-Verbindungen der Hauptgruppenelemente" Part 4, 1975 (cited here as Part 4), for further details see the preface of this Supplement Volume.

1.2 Perfluorohalogenoorgano Compounds of Lithium and Sodium

1.2.1 Preparation and Physical Properties

Difluorodilithiomethane CF_2Li_2

Trifluoromethyllithium CF_3Li

Chlorodifluoromethyllithium $ClCF_2Li$

Trifluorovinyllithium $F_2C=CFLi$

Difluorodilithiumethylene $F_2C=CLi_2$

Chlorodifluorovinyllithium $F_2C=CClLi$ and $ClFC=CFLi$

The molecular energies for planar and tetrahedral geometries of a number of molecules with a tetracoordinated carbon atom, among them CF_2Li_2, have been surveyed by ab initio MO calculations. It was shown that in the case of CF_2Li_2, the energy of the form with C_2 symmetry, obtained by rotating the FCF plane in the cis planar form by 20° about the angle bisector, is 0.7 kcal/mol lower than the energy of the planar structure, for details see [1].

For CF_3Li and $F_2C=CFLi$ no new preparations are reported (see Part 4, p. 2), for chemical reactions see Chapter 1.2.2, p. 9.

$ClCF_2Li$ is formed in the reaction of $ClCF_2C(O)OCH_3$ with LiCl in the solvent hexamethylphosphoric triamide and is stabilized by the interaction with the solvent forming a complex [2, 3].

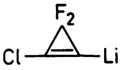
$F_2C=CFLi$ is obtained in almost quantitative yield reacting $F_2C=CFCl$ and n-C_4H_9Li in a mixture of tetrahydrofuran, ether and pentane (5:3:3) at −135°C [4]. It also forms in more than 90% yield on adding CH_3Li to a solution of $F_2C=CFBr$ in tetrahydrofuran, ether and pentane at −110°C [5].

When n-C_4H_9Li in ether is added to a solution of $F_2C=CCl_2$ in tetrahydrofuran (−120°C, 10 min) and the temperature is then raised to −90°C (5 min), $F_2C=CClLi$ is formed in more than 85% yield [6]. In ether as the only solvent the yield lowers to 40% [7], for the dependance of the yield from the ratio of both solvents see [6]. In an ether solution $F_2C=CCl_2$ reacts with n-C_4H_9Li at −70°C (0.5 h) to form $F_2C=CClLi$ [8]. $FClC=CFLi$ is prepared by the reaction of $ClFC=CFCl$ with n-C_4H_9Li at −115°C in ether/tetrahydrofuran [7].

The barriers of rotation around carbon-carbon double bonds and the relative stability of planar and perpendicular olefins, among them $F_2C=CLi_2$, were analysed within the framework of the ab initio unrestricted Hartree-Fock theory in terms of electrostatic, exchange repulsion, polarization, charge transfer, and their coupling interactions [54].

References p. 14

1-Lithium-2-chlorodifluorocyclopropene



1-Lithiumperfluoro(2,2-dimethylpropane) $(CF_3)_3CCF_2Li$

1-Lithiumperfluoro(3-oxa-4-methylpentane) $(CF_3)_2CFOCF_2CF_2Li$

1,6-Dilithiumdodecafluorohexane $Li(CF_2)_6Li$

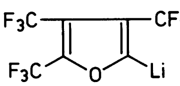
CNDO/2 calculations with a partial-geometry optimation were carried out on 1-lithium-2-chlorodifluorocyclopropene [9].

The metalation of $(CF_3)_3CCF_2H$ with RLi [R = CH_3, n-C_4H_9, $(CH_3)_3C$] gives $(CF_3)_3CCF_2Li$. The reaction is carried out with CH_3Li in ether and with n-C_4H_9Li or $(CH_3)_3CLi$ in alkane solvents [10].

n-C_4H_9Li in ether reacts with $(CF_3)_2CFOCF_2CF_2I$ at −78°C (1 h) to give $(CF_3)_2CFOCF_2CF_2Li$ [11]; replacing n-C_4H_9Li by C_6F_5Li increases the yield [12].

$Li(CF_2)_6Li$ forms on reacting $Br(CF_2)_6Br$ or $(CH_3)_2SiH(CF_2)_6SiH(CH_3)_2$ in tetrahydrofuran with C_2H_5Li or $(CH_3)_3CLi$ at −190 to −78°C (15 min) or −95°C (12 min), respectively [13].

5-Lithium-2,3,4-tris(trifluoromethyl)furan



On adding an ether solution of C_4H_9Li at −35°C (1 h, N_2 atmosphere) to a stirred ether solution of 2,3,4-tris(trifluoromethyl)furan the Li-substituted furan forms with further stirring (1 h) [14].

Pentafluorophenyllithium C_6F_5Li

C_6F_5Li is prepared by adding a hexane solution of n-C_4H_9Li to an ether solution of C_6F_5Br or C_6F_5H at −78°C (1 h) [15].

The ion-pair equilibrium between 9-t-butylfluorene (R) and C_6F_5H in cyclohexylamine according

$$R^-Li^+ + C_6F_5H \rightleftharpoons RH + C_6F_5^-Li^+$$

is covered in [16].

Perfluoro(4-methylphenyl)lithium $4\text{-}CF_3\text{-}C_6F_4Li$

1,2-, 1,3- and 1,4-Dilithiumtetrafluorobenzene $1,2\text{-}Li_2\text{-}C_6F_4$, $1,3\text{-}Li_2\text{-}C_6F_4$, $1,4\text{-}Li_2\text{-}C_6F_4$

1,3,5-Trilithiumtrifluorobenzene $1,3,5\text{-}Li_3\text{-}C_6F_3$

At −30°C (0.5 h) C_4H_9Li reacts with $4\text{-}Br\text{-}C_6F_4CF_3$ to form $4\text{-}CF_3\text{-}C_6F_5Li$ [17]. On adding an ether solution of $1,2\text{-}Br_2\text{-}C_6F_4$ to a stirred hexane solution of C_4H_9Li over 50 min, followed by stirring for further 35 min, $1,4\text{-}Li_2\text{-}C_6F_4$ is formed. $1,2\text{-}Li_2\text{-}C_6F_4$ is obtained on adding n-C_4H_9Li in hexane over 23 min to $1,2\text{-}Br_2\text{-}C_6F_4$ in ether, with further stirring (70 min) [18]. Similar reactions between n-C_4H_9Li and $1,3\text{-}H_2\text{-}C_6F_4$, $1,3\text{-}Br_2\text{-}C_6F_4$ or $1,4\text{-}Br_2\text{-}C_6F_4$ in ether at −70°C (about 2 h, stirring) form the corresponding title compounds [19].

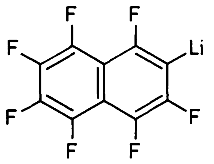
1,3,5-Trifluorobenzene was metalated with n-C_4H_9Li in ether forming $1,3,5\text{-}Li_3\text{-}C_6F_3$ [20].

4-Lithiumtetrafluorophenylperfluoropolyether $4\text{-Li-}C_6F_4CF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$

4-Lithiumtetrafluorobenzoylperfluoropolyethers $4\text{-Li-}C_6F_4C(O)R_f$,
$R_f = CF(CF_3)OC_3F_7$, $CF(CF_3)OCF_2CF(CF_3)OC_3F_7$, $CF(CF_3)[OCF_2CF(CF_3)]_4OC_3F_7$,
$CF_2(OC_2F_4)_2OC_2F_5$, $CF_2(OCF_2)_3OCF_3$

The first compound forms by the reaction of a tetrahydrofuran/ether solution of $4\text{-Br-}C_6F_4CF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ with a hexane solution of C_4H_9Li. The other compounds are obtained by similar reactions with 4-Br-benzoyl compounds as starting materials [21].

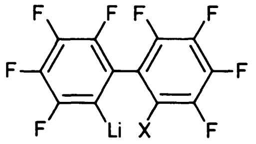
Heptafluoro-2-naphthyllithium



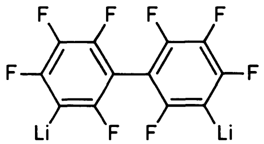
2-Lithiumnonafluorobiphenyl X = F

2-Lithium-2′-bromooctafluorobiphenyl X = Br

2,2′-Dilithiumoctafluorobiphenyl X = Li

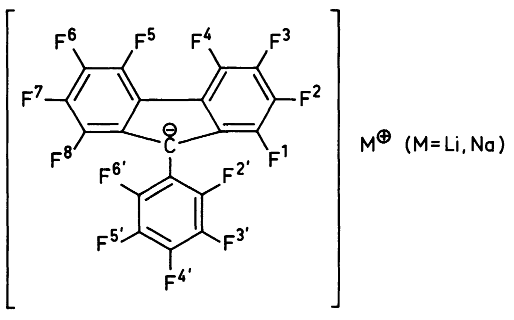


3,3′-Dilithiumoctafluorobiphenyl $3,3'\text{-}Li_2\text{-}C_6F_4\text{-}C_6F_4$

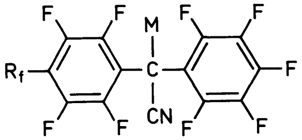


In an ether-hexane mixture, 2-H-heptafluoronaphthalene was reacted with C_4H_9Li at −75 °C (2 h) under N_2 to yield heptafluoro-2-naphthyllithium [22, 23]. Lithiation of 2,2′-dibromooctafluorobiphenyl took place in ether at −78 °C by adding a hexane solution of $n\text{-}C_4H_9Li$ with stirring over a period of 40 min. After additional stirring for 1.5 h 2-lithium-2′-bromooctafluorobiphenyl is obtained. Similarly 2-lithiumnonafluorobiphenyl was prepared from 2-bromononafluorobiphenyl and $n\text{-}C_4H_9Li$, and 2,2′-dilithiumoctafluorobiphenyl by the reaction of 2,2′-dibromooctafluorobiphenyl and $n\text{-}C_4H_9Li$ [24]. In tetrahydrofuran $3,3'\text{-}H_2\text{-}C_6F_4\text{-}C_6F_4$ and $n\text{-}C_4H_9Li$, dissolved in hexane, reacted at −76 °C (2.0 h) to give $3,3'\text{-}Li_2\text{-}C_6F_4\text{-}C_6F_4$ [19].

Perfluoro(9-phenylfluorenyl)lithium and -sodium

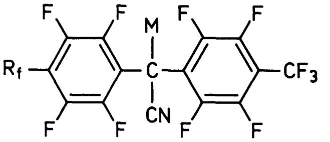


Perfluoro(4-alkylphenyl)pentafluorophenylcyanomethyllithium and -sodium



M = Li, Na, R_f = CF_3, C_2F_5, $CF(CF_3)_2$, $C(CF_3)_3$

Perfluoro(4-alkylphenyl)perfluoro(4-methylphenyl)cyanomethyllithium and -sodium



M = Li, Na, R_f = CF_3, C_2F_5, $CF(CF_3)_2$, $C(CF_3)_3$

9-Hydroperfluoro(9-phenylfluorene) reacts with LiH or NaH in 1,2-dimethylether at 20 to 25°C (1 h) to form the lithium and sodium salts. In the following is given the ^{19}F NMR spectrum of the lithium salt, which is almost identical with that of the sodium compound (chemical shifts δ in ppm have a positive sign downfield from the internal standard C_6F_6, dimethylether as solvent): $\delta(F^3,F^6) = -17.3$, $\delta(F^2,F^7) = -6.6$, $\delta(F^{3'},F^{5'}) = -3.8$, $\delta(F^{4'}) = 0.0$, $\delta(F^1,F^8) = 2.9$, $\delta(F^4,F^5) = 19.8$, $\delta(F^{2'},F^{6'}) = 23.2$, $J(F^1\text{-}F^2) = 20.5$ Hz, $J(F^1\text{-}F^3) = 9$ Hz, $J(F^1\text{-}F^4) \approx 9$ Hz, $J(F^2\text{-}F^3) = 20.5$ Hz, $J(F^3\text{-}F^4) = 19$ Hz, $J(F^1\text{-}F^{2'}) \approx 4$ Hz, $J(F^{3'}\text{-}F^{4'}) = 21.5$ Hz [25]. The difference of the chemical shifts of the perfluoro(9-phenylfluorenyl)ion and of 9-hydroperfluoro-(9-phenylfluorene) is given and discussed in [26].

The metal compounds of the perfluoro(diaryl)cyanomethanes were prepared [27] in dimethylformamide according to

$4\text{-}R_f\text{-}C_6F_4\text{-}CH(CN)\text{-}C_6F_5 + MH \rightarrow 4\text{-}R_f\text{-}C_6F_4\text{-}CM(CN)\text{-}C_6F_5$

and

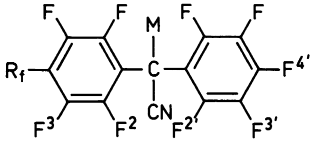
$4\text{-}R_f\text{-}C_6F_4\text{-}CH(CN)\text{-}C_6F_4\text{-}CF_3\text{-}4' + MH \rightarrow 4\text{-}R_f\text{-}C_6F_4\text{-}CM(CN)\text{-}C_6F_4\text{-}CF_3\text{-}4'$

$R_f = CF_3$, M = Li, Na; $R_f = C_2F_5$, M = Li, Na; $R_f = (CF_3)_2CF$, M = Li, Na; $R_f = (CF_3)_3C$, M = Li, Na

The ^{19}F NMR data of the compounds are compiled in **Table 1**, p. 5, and **Table 2**, p. 5.

Table 1

^{19}F NMR Spectra of the Lithium and Sodium Compounds of the Following Perfluoro(diaryl)cyanomethanes [27]:

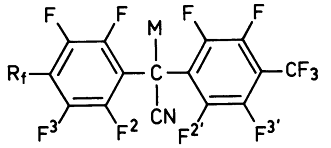


Chemical shift δ in ppm (positive sign means lowfield from the internal standard C_6F_6), spin-spin coupling constant J in Hz, 10 mol% solution in 1,2-dimethoxyethane, [a] ±0.7 ppm, [b] ±0.2 ppm, [c] ±0.5 ppm.

M	R_f	δ(F^2)	δ($F^{2'}$)	δ(F^3)	δ($F^{3'}$)	δ($F^{4'}$)	δ(CF_3)	δ(CF_n)	Absolute J(F-F) coupling constants in Hz
Na	CF_3	15.0[c]	21.5	15.0	−4.3[b]	−4.3[b]	110.2	–	–
Li	CF_3	15.5[c]	21.2	15.5	−3.6[b]	−3.6[b]	110.3	–	–
Na	CF_3CF_2	15.2	21.6	16.1	−3.8[a]	−3.8[a]	77.2	55.4	$J(CF_2\text{-}F^3) = 29$
Li	CF_3CF_2	15.6	21.4	16.6	−3.5[a]	−3.5[a]	77.1	55.1	$J(CF_2\text{-}F^3) = 29$, $J(CF_3\text{-}CF_2) = 3.3$, $J(CF_3\text{-}F^3) = 7$
Na	$(CF_3)_2CF$	15.8	21.6	20.0	−4.0[a]	−4.0[a]	87.9	−11.4	–
Na	$(CF_3)_3C$	16.2	21.6	27.1	−3.6[a]	−3.6	101.5	–	–
Li	$(CF_3)_3C$	16.9	21.8	27.7	−3.3[a]	−3.3	102.0	–	$J(CF_3\text{-}F^3) = 25.7$, $J(F^2\text{-}F^3) = 14.5$

Table 2

^{19}F NMR Spectra of the Lithium and Sodium Compounds of the Following Perfluoro(diaryl)cyanomethanes [27]:



For definitions see Table 1; [a] ±0.6 ppm, [b] 0.6 ppm, [c]: because of poor resolution of the signals the chemical shift value could not be determined exactly.

M	R_f	δ(F^2)	δ($F^{2'}$)	δ(F^3)	δ($F^{3'}$)	δ($4'\text{-}CF_3$)	δ(CF_3)	δ(CF_n)	Absolute J(F-F) coupling constants in Hz
Na	CF_3	19.5	19.5	16.1	16.1	108.8	108.8	–	$J(CF_3\text{-}F^3) = 21.2$
Li	CF_3	19.9	19.9	16.5	16.5	108.6	108.6	–	$J(CF_3\text{-}F^3) = 21.5$
Na	CF_3CF_2	19.9[a]	19.9	17.5	16.8	108.9	77.3	54.7	–
Li	CF_3CF_2	20.0[a]	20.0	18.0	16.7	108.2	77.2	54.7	$J(CF_3\text{-}F^3) = 29.5$, $J(4'\text{-}CF_3\text{-}F^{3'}) = 20.5$
Na	$(CF_3)_2CF$	20.1[b]	20.1	20.1	16.5	109.0	87.9	−12.5	–
Li	$(CF_3)_2CF$	20.2[b]	20.2	21.1	16.8	109.1	88.0	−12.8	$J(4'\text{-}CF_3\text{-}F^{3'}) = 21.0$, $J(CF\text{-}F^3) = 39.5$, $J(CF_3\text{-}F^3) = 12.5$, $J(CF_3\text{-}CF) = 6$

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Table 2 (continued)

M	R_f	$\delta(F^2)$	$\delta(F^{2'})$	$\delta(F^3)$	$\delta(F^{3'})$	$\delta(4'\text{-}CF_3)$	$\delta(CF_3)$	$\delta(CF_n)$	Absolute J(F-F) coupling constants in Hz
Na	$(CF_3)_3C$	20.4[c]	20.4	28.2	16.3	108.9	101.8	–	–
Li	$(CF_3)_3C$	20.9	20.6	28.9	16.8	109.0	102.4	–	$J(4'\text{-}CF_3\text{-}F^{3'}) = 21.5$, $J(CF_3\text{-}F^3) = 25.9$, $J(F^2\text{-}F^3) = 11.0$

Tris(pentafluorophenyl)methylsodium $(C_6F_5)_3CNa$ and **-lithium** $(C_6F_5)_3CLi$

Bis(pentafluorophenyl)-4-chlorotetrafluorophenylmethylsodium
M = Na, X = Cl

Bis(pentafluorophenyl)-4-bromotetrafluorophenylmethylsodium
M = Na, X = Br

Bis(pentafluorophenyl)-4-trifluoromethyltetrafluorophenylmethyllithium
and **-sodium** M = Li, Na; X = CF_3

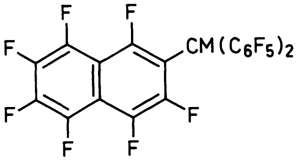
$(C_6F_5)_2(4\text{-}X\text{-}C_6F_4)CM$

Bis(pentafluorophenyl)-3-chlorotetrafluorophenylmethyllithium and **-sodium**
$(C_6F_5)_2(3\text{-}Cl\text{-}C_6F_4)CM$ (M = Li, Na)

Bis(pentafluorophenyl)-3,5-dichlorotrifluorophenylmethylsodium $(C_6F_5)_2(3,5\text{-}Cl_2\text{-}C_6F_3)CNa$

Bis(pentafluorophenyl)pentachlorophenylmethylsodium $(C_6F_5)_2(C_6Cl_5)CNa$

Bis(pentafluorophenyl)heptafluoro-2-naphthylmethyllithium and **-sodium** (M = Li, Na)



To a solution of $(C_6F_5)_2CHR$ in hexamethylphosphoric triamide, NaH was added and the solution stirred at 20 to 25°C (5 to 10 h). The replacement of H by Na takes place according to:

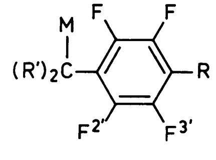
$$(C_6F_5)_2CHR + NaH \rightarrow (C_6F_5)_2CNaR + H_2$$

R = C_6F_5, $4\text{-}Cl\text{-}C_6F_4$, $4\text{-}Br\text{-}C_6F_4$, $4\text{-}CF_3\text{-}C_6F_4$, $3\text{-}Cl\text{-}C_6F_4$, $3,5\text{-}Cl_2\text{-}C_6F_3$, C_6Cl_5, heptafluoro-2-naphthyl ($C_{10}F_7$).

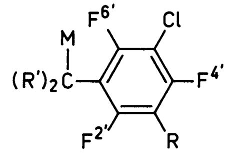
In a similar way, lithium compounds were prepared using $(C_6F_5)_2CHR$ with R = C_6F_5, $4\text{-}CF_3\text{-}C_6F_4$, $3\text{-}Cl\text{-}C_6F_4$, heptafluoro-2-naphthyl [17]. The ^{19}F NMR data of these compounds are given in **Table 3**, p. 7.

Table 3

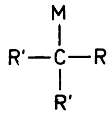
^{19}F NMR Spectra of the Compounds A, B, and C [17].



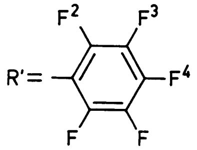
A



B



C



Chemical shift δ in ppm, positive sign lowfield from the internal standard C_6F_6, spin-spin coupling constant J in Hz, concentration of the compounds 10 mol% in hexamethylphosphoric triamide.

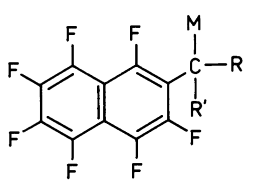
Compound	M	R	δ(R)	δ(F^2)	δ($F^{2'}$)	δ(F^3)	δ($F^{3'}$)	δ(F^4)	δ($F^{4'}$)
A	Na	F	14.6	−17.5	−17.5	6.1	6.1	14.6	δ(R)
A[a)]	Li	F	15.0	−17.3	−17.3	6.4	6.4	15.0	δ(R)
A	Na	Cl	—	−17.9	−17.9	6.0	−13.7	12.9	—
A	Na	Br	—	−18.3	−18.3	6.1	−21.0	12.9	—
A	Na	CF_3	−111.2	−19.8	−13.9	5.2	−13.9	8.2	δ(R)
A[b]	Li	CF_3	−111.8	−19.3	−14.0	5.2	−14.0	8.2	δ(R)
B	Na	F	4.8	−17.3	−23.3 −41.6($F^{6'}$)	6.1	δ(R)	14.7	− 6.7
B[c)]	Li	F	4.8	−17.3	−23.3 −41.5($F^{6'}$)	6.0	δ(R)	14.7	− 6.8
B[d)]	Na	Cl	—	−16.8	−46.6	6.6	—	15.4	−28.5
C	Na	C_6Cl_5	—	−17.5	—	6.4	—	15.4	—
C	Na	$C_{10}F_7$	—	−18.6	—	5.8	—	10.9	—
C	Li	$C_{10}F_7$	—	−19.1	—	5.5	—	10.8	—

[a)] J(F^3-F^4) = 21.8, J(F^2-F^4) = 7.0, J(F^2-F^3) = 19.0 Hz. — [b)] J(F^3-F^4) = 22.0, J(CF_3-$F^{3'}$) = 3.8 Hz. — [c)] J(F^3-F^4) = 22.5, J(R-$F^{6'}$) = 6.0, J($F^{2'}$-$F^{4'}$) = 10, J($F^{2'}$-$F^{6'}$) = 4.0, J(F^2-$F^{2'}$) = J($F^{4'}$-$F^{6'}$) = 0, J(R-$F^{2'}$) = J(R-$F^{4'}$) = 23.8 Hz. — [d)] J(F^3-F^4) = 22.5, J($F^{2'}$-$F^{4'}$) = 4.5, J(F^2-F^4) = 7.5, J(F^2-$F^{2'}$) = 0 Hz.

Heptafluoro-2-naphthyldicyanomethylsodium R = R′ = CN; M = Na

Heptafluoro-2-naphthylpentafluorophenylcyanomethyllithium and **-sodium**
R = C_6F_5, R′ = CN; M = Li, Na

Heptafluoro-2-naphthyl-4-tetrafluoropyridylcyanomethyllithium and **-sodium**
R = 4-C_5F_4N, R′ = CN; M = Li, Na



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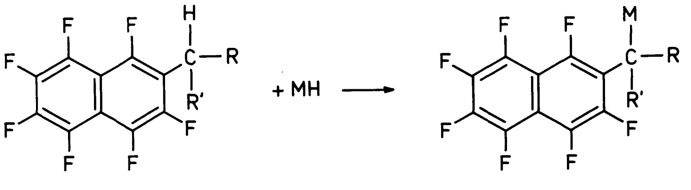
Bis(heptafluoro-2-naphthyl)cyanomethylsodium
R = β-heptafluoronaphthyl, R′ = CN; M = Na

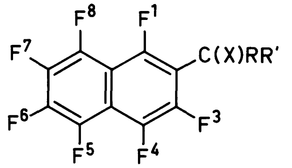
Heptafluoro-2-naphthylbis(pentafluorophenyl)methylsodium and **-lithium**
R = R′ = C_6F_5; M = Li, Na

Heptafluoro-2-naphthylmethanes react in 1,2-dimethoxyethane or hexamethylphosphoric triamide under dry nitrogen with LiH or NaH at 20 to 25°C (4 h) to form the corresponding metalated compounds [28] according to



The ^{19}F NMR spectra are shown in **Table 4**.

Table 4
^{19}F NMR Spectra of the Lithium and Sodium Compounds of the β-Heptafluoronaphthylmethanes [28].

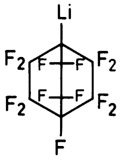


Chemical shift δ in ppm, positive sign lowfield from the internal standard C_6F_6, spin-spin coupling constant J in Hz, HPMA = hexaphosphoric triamide, DME = 1,2-dimethoxyethane, 10 mol% solution in HPMA or DME.

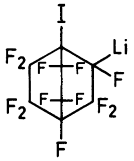
M	R	R′	Solvent	δ(F^1)	δ(F^3)	δ(F^4)	δ(F^5)	δ(F^6)	δ(F^7)	δ(F^8)
Na	CN	CN	HMPA	−34.8	−26.9	− 9.0	−12.4	3.2	−2.5	−12.4
Na	C_6F_5	CN	DME	−36.0	−27.0	− 9.3	−12.8	3.1	−2.3	−12.8
Li[a]	C_6F_5	CN	DME	−36.9	−27.1	− 9.8	−13.6	2.0	−2.9	−13.6
Na	C_6F_5	CN	HMPA	−34.9	−28.0	− 9.0	−12.9	4.6	−2.1	−12.9
Li[b]	C_6F_5	CN	HMPA	−35.1	−28.3	− 9.1	−13.2	4.6	−2.3	−13.2
Na	4-C_6F_4N	CN	DME	−41.8	−28.4	−10.1	−14.3	−2.3	−3.5	−15.3
Li[c]	4-C_6F_4N	CN	DME	−43.0	−29.2	−10.6	−14.9	−2.8	−4.0	−15.8
Na[d]	$C_{10}F_7$	CN	DME	−39.1	−28.3	− 9.7	−14.1	1.1	−2.9	−14.1
Na	$C_{10}F_7$	CN	HMPA	−39.2	−29.6	− 9.6	−14.1	1.6	−3.0	−14.1
Na	C_6F_5	C_6F_5	HMPA	−34.2	−27.5	− 8.3	−12.3	5.7	−1.2	−13.0
Li	C_6F_5	C_6F_5	HMPA	−34.6	−27.9	− 8.3	−12.9	5.5	−1.6	−12.9

[a] J(F^1-F^8) = 68, J(F^4-F^5) = 60 Hz. – [b] J(F^1-F^8) = 65, J(F^4-F^5) = 56 Hz. – [c] J(F^1-F^8) = 67, J(F^4-F^5) = 56 Hz. – [d] J(F^1-F^8) = 65, J(F^4-F^5) = 54 Hz.

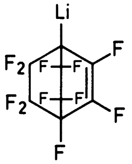
1-Lithiumtridecafluorobicyclo[2.2.2]octane



1-Iodo-2-lithiumdodecafluorobicyclo[2.2.2]octane



1-Lithium-undecafluoro-bicyclo[2.2.2]octa-2-ene



A stirred ether solution of 1-hydrododecafluorobicyclo[2.2.2]octane reacted with CH_3Li at 18°C to give 1-lithiumtridecafluorobicyclo[2.2.2]octane. Refluxing for 70 h leads to a slow loss of LiF to give the transient dodecafluorobicyclo[2.2.2]octa-2-ene. Back addition of LiI affords 1-iodo-2-lithiumdodecafluorobicyclo[2.2.2]octane. 1-Lithiumtridecafluorobicyclo[2.2.2]octane is, at reflux temperature, in equilibrium with 1-lithiumundecafluorobicyclo[2.2.2]octa-2-ene and 1-iodotridecafluorobicyclo[2.2.2]octane [29].

1.2.2 Chemical Reactions

1.2.2.1 Hydrolysis, Carboxylation and Reactions with SO_2

Perfluorohalogenoorgano compounds of the Main Group 1 elements are sensitive to H_2O, acids and bases. They hydrolyse to the corresponding hydrogenated perfluorochlorohydrocarbons and M^+ according to:

$$R_fM + H^+ \rightarrow HR_f + M^+ \ (M = Li, Na)$$

Another typical reaction is CO_2 insertion forming $R_fC(O)OM$; e.g., heptafluoro-2-naphthyllithium reacts with CO_2 at −75°C (0.5 h) to yield the corresponding lithium salt which on treatment with 4 M HCl gives heptafluoro-2-naphthoic acid (melting point 188 to 189°C) [22]. In a similar way 5-lithium-2,3,4-tris(trifluoromethyl)furan gave 2,3,4-tris(trifluoromethyl)-5-furancarboxylic acid in 72.8% yield (melting point 81°C) [14].

For the preparation of octafluoro-9-fluorenone and 2,2'-octafluorodiphenic acid using this method, see [24].

Perfluorohalogenoorganolithium compounds are very reactive intermediates and are used in situ for further reactions. They are often used for the preparation of the title compounds, e.g. [30]:

$$F_2C{=}CFLi + SO_2 \rightarrow F_2C{=}CFSO_2Li \xrightarrow{H^+} F_2C{=}CFSO_2H$$

Therefore, these types of reactions are not recorded here.

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1.2.2.2 Thermal Stability. Reactions with Br_2 and I_2

The enthalpy of the decomposition of $LiCF_3$ according to

$$LiCF_3 \rightarrow LiF + CF_2$$

has been calculated by thermodynamic data to be 2 kcal/mol. MINDO/3 and MINDO/2 calculations resulted in 2 and 0 kcal/mol, respectively [31].

$(CF_3)_3CCF_2Li$ decomposes in ether on standing overnight at −78°C. Under the same conditions it is much more stable in alkane solutions, which are the solvents of choice for the investigation of the reaction of the carbene species generated by α elimination of LiF [10].

Significant decomposition of $Li(CF_2)_6Li$ occurs at −78°C [13].

At −78°C $(CF_3)_2CFOCF_2CF_2Li$ formed from n-C_4H_9Li is at least stable for 20 h. When the temperature is raised to −30°C (2 h) decomposition with the formation of $(CF_3)_2CFOCF{=}CF_2$ is observed. When C_6F_5Li was used as starting material $(CF_3)_2CFOCF_2CF_2Li$ was found to be unstable even at −78°C providing $(CF_3)_2CFOCF{=}CF_2$ [12].

Heptafluoro-2-naphthyllithium eliminates LiF on warming from −78 to 20°C to give hexafluoro-1,2-naphthalene, for condensation with excess furan or heptafluoro-2-naphthyllithium see the original paper [23].

1-Iodo-2-lithiumdodecafluorobicyclo[2.2.2]octane decomposes to give 1-iodoundecafluorobicyclo[2.2.2]oct-2-ene. Refluxing 1-lithiumtridecafluorobicyclo[2.2.2]octane results in the formation of dodecafluorobicyclo[2.2.2]octa-2-ene [29].

Iodation of 1-lithiotridecafluorobicyclo[2.2.2]octane with I_2 leads to the corresponding iodo compound [29]. Heptafluoro-2-naphthyllithium reacts with Br_2 to yield 2-bromoheptafluoronaphthalene (melting point 73 to 74°C) [22].

1.2.2.3 Reactions with Organohalogenosilanes, -phosphines, -phosphineoxides, Benzene and Halogenobenzenes

Reactions of C_6F_5Li with the reagents C_6F_5X (X = H, F, Cl, Br, I), $C_6F_4X'_2$ (X′ = H, Cl), $C_6F_3Cl_3$, C_6H_6, $(C_6Y_5)_3P$, $(C_6Y_5)_3PO$, $(C_6Y_5)Si(CH_3)_3$ (Y = H, F) and $(CH_3)_{4-n}SiCl_n$ (n = 1, 2) in ether or in ether/n-hexane solution were investigated by GC/MS techniques. For details and results see original paper [15].

An ether solution of C_6F_5Li condenses with $(CH_3)_2(CHCl_2)SiCl$ at −70°C then warming to 20°C forming $C_6F_5Si(CH_3)_2CHCl_2$ (45% yield, boiling point 122°C/50 Torr). IR bands and ^1H NMR chemical shifts are presented. Five more compounds containing a $C_6F_5Si(CH_3)_2$ group were prepared and used as protecting groups for steroid alcohols forming volatile ethers, detectable at picogram levels in gas chromatography [32]. 1,3,5-Trifluorobenzene is metalated by C_6F_5Li in tetrahydrofuran at −70°C and gives 2-lithium-1,3,5-trifluorobenzene, which reacts with $(CH_3)_3SiCl$ to form 2-$(CH_3)_3Si$-1,3,5-$C_6F_3H_2$ (16.1% yield) and $(CH_3)_3SiC_6F_5$ (52%) [20].

C_6F_5Li with $(C_6H_5)_3B$ in a N_2 atmosphere at −78°C (3 h) and then at 20°C (12 h) forms the complex $Li[B(C_6H_5)_3C_6F_5]$. In a similar reaction $Li[B(4\text{-}CH_3\text{-}C_6H_4)_3C_6F_5]$ is prepared [33].

$Li(CF_2)_6Li$ reacts with $(CH_3)_3SiCl$ at −95°C yielding 72% $(CH_3)_3Si(CF_2)_6Si(CH_3)_3$ [13].

Lithiumtridecafluorobicyclo[2.2.2]octane forms with $(CH_3)_3SiCl$ in ether at 18°C (16 h) 1-(trimethylsilyl)tridecafluorobicyclo[2.2.2]octane (melting point 97°C) [29].

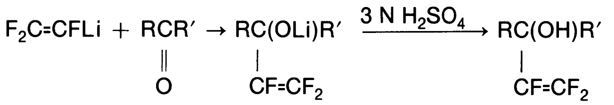
1.2.2.4 Reactions with Alcohol, Ketones and Aldehydes

The decomposition of $ClCF_2Li$ in hexamethylphosphoric triamide in the presence of CF_3CH_2OH at reflux temperature (12 h) gives 100% CHF_2Cl. The lithium compound reacts with ketones under similar conditions according to:

$$ClCF_2Li + RC(O)R' \rightarrow RR'C(OLi)CF_2Cl \xrightarrow{H^+} RR'C(OH)CF_2Cl$$

R, R′, boiling point °C/Torr, yield (%): C_6H_5, CF_3, 68 to 70/8; 63%; n-C_4H_9, CF_3, 52 to 53/18, 39%; C_6H_5, CF_2Cl, —, 18%; additional product 50% $C_6H_5CCl{=}CF_2$ [2, 3]. The reaction mechanisms and further reactions are described in [2].

When C_6H_5CHO is added to $F_2C{=}CFLi$ dissolved in a mixture of tetrahydrofuran, ether and pentane (4:1:1) at −60°C (0.5 h), $C_6H_5CH(OH)CF{=}CF_2$ (96% yield) is formed after treatment with 2 N HCl; ^1H NMR data are presented [5]. In a mixture of tetrahydrofuran, ether and pentane (5:3:3), $F_2C{=}CFLi$ reacts with ketones and aldehydes dissolved in ether at −13°C (for acetophenone at −30°C) according to:



$$F_2C{=}CFLi + \underset{\underset{O}{\|}}{RCR'} \rightarrow \underset{\underset{CF{=}CF_2}{|}}{RC(OLi)R'} \xrightarrow{3\,N\,H_2SO_4} \underset{\underset{CF{=}CF_2}{|}}{RC(OH)R'}$$

R, R′, boiling point in °C/Torr, n_D^{20}, yield: C_6H_5, CH_3, 40/0.1, 1.4875, 88%; -$(CH_2)_5$-, 36/0.05, 1.4320, 88%; C_6H_5, H, 51/0.1, 1.4865, 83%; C_5H_{11}, H, 37/0.5, 1.3985, 88%. IR bands [ν(C=C)], ^1H and ^{19}F NMR spectra are presented [4].

Cyclohexanone adds $ClCF{=}CFLi$ (at −110°C, then warmed to −80°C, 10 min) to yield after hydrolysis with 6 N H_2SO_4 85% 1-(2-chloro-1,2-difluoroethenyl)-1-cyclohexanol (boiling point 45°C/0.05 Torr). IR bands and ^{19}F NMR data are provided. Similarly $F_2C{=}CClLi$ reacts with n-C_3H_7CHO to give 40% n-$C_3H_7CH(OH)CCl{=}CF_2$ (boiling point 60 to 62°C/13 Torr, $n_D^{20} = 1.4185$). IR bands and ^{19}F NMR data are given [7]. $F_2C{=}CClLi$ adds ketones and aldehydes according to:

$$CF_2{=}CClLi + R^1R^2C{=}O \rightarrow R_1R_2C(OLi)C(Cl){=}CF_2 \xrightarrow{H^+} R_1R_2C(OH)CCl{=}CF_2$$

R^1, R^2, boiling point in °C/Torr, n_D^{20} and yields are as following: C_6H_5, H, 63 to 64/0.05, 1.5110, 82%; CH_3, CH_3, 37 to 40/13, 1.4160, 70%; -$(CH_2)_5$-, 44 to 45/0.05, 1.4630, 86%. IR[ν(C=C)], ^1H and ^{19}F NMR values are recorded [6]. With cyclohexanone dissolved in ether, $F_2C{=}CClLi$ forms on warming from −70 to 17°C (1.7 h) 62% 1-(1-chloro-2,2-difluorovinyl)cyclohexanol (boiling point 68 to 72°C/8 Torr) [8].

In ether 4-CF_3-C_6F_4Li reacts with $(C_6F_5)_2CO$ to yield after hydrolysis with concentrated HCl 4-trifluoromethyl-2,3,5,6-tetrafluorophenylbis(pentafluorophenyl)carbinol which sublimes at 170°C/5 Torr. IR and ^{19}F NMR spectra are given [17]. Addition of $(CF_3)_2CFOCF_2CF_2Li$ to $(CF_3)_2CO$ at −78°C (3 h) in hexane gives 94% $(CF_3)_2CFOCF_2CF_2C(CF_3)_2OLi$ (boiling point 155 to 157/0.3 Torr) [11].

1.2.2.5 Reactions with Olefins, Cyclopentadiene and $C_6H_5ICl_2$

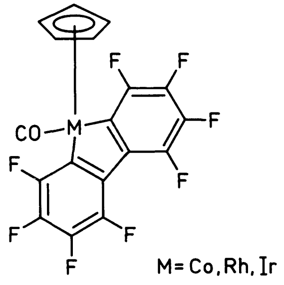
Adding $CF_3CF{=}CF_2$ in the form of a gas to an ether solution of C_6F_5Li in a stream of dry argon between −80 and 50°C, keeping the mixture at −70°C (3 h) and, afterwards acidifying with 10% HCl at 10°C, gives 8% cis-1-perfluoro(phenylpropylene), 40% trans-1-perfluoro(phenylpropylene), 10% trans-perfluoro[α-(4-biphenyl)propylene] and 5% pentafluorobrombenzene [34]. With excess n-C_4H_9Li dissolved in ether $F_2C{=}CCl_2$ forms at −40°C (0.5 h) 1-hexyne via $F_2C{=}CClLi$ [8]. An etheral solution of C_6F_5Li reacts at −78°C (1 h) with $C_6H_5ICl_2$ to give 23% $C_6F_5(C_6H_5)ICl$ (decomposition point 174°C) [35].

C_6F_5Li reacts with cyclopentadiene in hexane on refluxing (2 h) to yield 5,6,7,8-tetrafluoro-1,4-dihydro-1,4-methanonaphthalene (boiling point 93 to 94°C/18 Torr, melting point 44 to 44.5°C) [36].

1.2.2.6 Reactions with Transition Metal Compounds

When 1,3-$Li_2C_6F_4$ is treated with C_2H_5HgCl in ether at −70°C (2 h) and then at −40°C (3 h), low yields of 1,3-$(C_2H_5Hg)_2$-C_6F_4 are obtained (melting point 75 to 76°C). Treatment of 1,3-Li_2-C_6F_4 with C_2H_5HgCl gave impure 1-C_2H_5Hg-3-Br-C_6F_4 in low yields. In tetrahydrofuran 1,4-Li_2-C_6F_4 reacted with $(CF_3)_2CFHgCl$ at −70°C (0.3 h), then at −40°C (3.5 h) to give 9% 1,4-$[(CF_3)_2CFHg]_2$-C_6F_4 (melting point about 142°C). Condensation of 3,3′-Li_2-C_6F_4-C_6F_4 with C_2H_5HgCl in tetrahydrofuran/hexane at −70°C (2.75 h) gave 39% 3,3′-$(C_2H_5Hg)_2$-C_6F_4-C_6F_4 [19]. The preparation of perfluorobiphenylmercury can be achieved either by the reaction of 2,2′-Li_2-C_6F_4-C_6F_4 and $HgCl_2$ in ether or heating 2,2′-Li_2-C_6F_4-C_6F_4 with Hg at 300°C (melting point >370°C) [37].

In ether $(\pi\text{-}C_5H_5)Co(CO)I_2$ and 2,2′-Li_2-$C_6F_4\cdot C_6F_4$ are mixed at −78°C. The solution is warmed to 20°C (24 h) giving 49% 5-(π-cyclopentadienyl)-5-carbonyl-1,2,3,4,6,7,8,8-octafluorodibenzocobaltole. The Rh and Ir complex are made similarly [38].



Norbornadieneplatinum dichloride and 2,2′-Li_2-C_6F_4-C_6F_4 form 3.6% 5,5-norbornadiene-1,2,3,4,6,7,8,9-octafluorodibenzoplatinole. Similar 5,5-di(π-cyclopentadienyl)-1,2,3,4,6,7,8,9-octafluorodibenzozirconole in 4% yield is obtained [38].

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Reactions of C_6F_5Li

An ether solution of C_6F_5Li reacts with $ZrCl_4$ at −78°C to yield $Zr(C_6F_5)_4 \cdot C_2H_5OC_2H_5$ (73%) [39]. In an inert atmosphere C_6F_5Li and $[\pi\text{-}Cp_2TiCl]_2$ (Cp = cyclopentadienyl) react at −78°C (4 h) to yield 75% $\pi\text{-}Cp_2Ti(C_6F_5)$, melting point 111 to 113°C, decomposition [40].

A solution of VCl_4 in tetrahydrofuran was added under stirring at −80°C to a hexane solution of C_6F_5Li. The mixture was allowed to warm slowly to 20°C. In this procedure 70% $(C_6F_5)_3VCl$ is formed as tetrahydrofuran adduct (melting point 10 to 15°C) [41]. Treatment of $VCl_3 \cdot$(tetrahydrofuran)$_3$ with C_6F_5Li, dissolved in tetrahydrofuran, at −78°C followed by raising the temperature gradually to 20°C, gives 85% $(C_6F_5)_3V \cdot$(tetrahydrofuran) (melting point 10°C) [42]. C_6F_5Li reacts with $(\pi\text{-}C_5H_5)_3UCl$ to form $(\pi\text{-}C_5H_5)_3UC_6F_5$ [43] and with CuI at −78°C to give CuC_6F_5 which reacts with I_2 in tetrahydrofuran/hexane to yield 75% C_6F_5I and 7% $C_6F_5C_6F_5$ [44].

The salt $Li[(CO)_4FeC(O)C_6F_5]$ was prepared in ether at −78°C from C_6F_5Li and $Fe(CO)_5$ [45].

In an ether solution C_6F_5Li reacts with trichlorogermaniumcyclopentadienyldicarbonyliron to form $(C_6F_5)_3GeFe(CO)_2Cp$. Additional compounds were prepared analogously [46] according to:

$$(C_6H_5)_{3-n}X_nMM' + nC_6F_5Li \rightarrow (C_6H_5)_{3-n}(C_6F_5)_nMM' + nLiCl$$

X = Cl or Br, n = 1, 2, M = Si, M′ = $Mn(CO)_5^-$
X = Cl, Br, n = 1 to 3, M = Ge, M′ = $Mn(CO)_5^-$
X = Cl, Br, n = 1 to 3, M = Sn, M′ = $Fe(CO)_2Cp$
X = Cl, Br, n = 3, M = Si or Ge, M′ = $Fe(CO)_2Cp$.

In ether C_6F_5Li reacts with ClAu(tht) at −40°C to yield 84% C_6F_5Au(tht). The tht ligand (tht = tetrahydrothiophene) can be replaced by adding more C_6F_5Li (4:1 excess). After hydrolysis of the intermediate, treatment with $[(n\text{-}C_4H_9)_4N]Br$ gives 60% of $[(n\text{-}C_4H_9)_4N][Au(C_6F_5)_2]$ which is also obtained as a by-product in 44% yield from C_6F_5Li, $K[AuCl_4]$ and $[(n\text{-}C_4H_9)_4N]Br$. The desired product, $[(n\text{-}C_4H_9)_4N][Au(C_6F_5)_4]$, is formed in 12% yield. A higher yield (47%) of $[(n\text{-}C_4H_9)_4N][Au(C_6F_5)_4]$ is obtained from Cl_3Au(tht) and C_6F_5Li in ether at −78°C. In this reaction 30% $[(n\text{-}C_4H_9)_4N][Au(C_6F_5)_2]$ are produced [47, 48].

The complexes trans-$Ir(CO)(C_6F_5)L_2$ were prepared in 65% yield [49] via

$$trans\text{-}Ir(CO)ClL_2 + C_6F_5Li \xrightarrow{-78\,°C} trans\text{-}Ir(CO)(C_6F_5)L_2$$

L = $(C_6H_5)_3P$, $(C_6H_5)_2PCH_3$, $(4\text{-}CH_3\text{-}C_6H_4)_3P$

C_6F_5-substituted complexes of Pd and Pt were made [50] according to:

$$L_2MCl_2 + 2\,C_6F_5Li \rightarrow L_2M(C_6F_5)_2 + 2\,LiCl$$

M = Pd, L_2 = $2C_5H_5N$, $H_2NCH_2CH_2NH_2$, 1,10-phenanthroline, 1,2-bis(diphenylphosphino)-ethane, N,N,N′,N′-tetramethylenediamine

M = Pt, L_2 = 2 C_5H_5N(*cis*), 2 C_5H_5N (*trans*), 2,2′-bipyridine, 1,10-phenanthroline

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The C_6F_5 substitution of *cis* and *trans* isomers of Cl_2PtL_2 was carried out with C_6F_5Li in ether at −78 °C. The solution was stirred (12 h) while allowing it to warm to room temperature. Reaction takes place according to

$$Cl_2PtL_2 + 2\,LiC_6F_5 \rightarrow (C_6F_5)_2PtL_2 + 2\,LiCl$$

$$L = (C_6H_5)_2AsCH_2CH_2As(C_6H_5)_2,\ P(C_4H_9)_3,\ As(C_6H_5)_3$$

If $L = P(C_4H_9)_3$ no isomerization was observed, where as both the *cis*- and the *trans*-$Cl_2Pt[As(C_6H_5)_3]_2$ led only to cis-$(C_6F_5)_2Pt[As(C_6H_5)_3]_2$ [51].

When trans-$PdCl_2L_2$ [$L = As(C_6H_5)_3$, $H_2NCH_2C_6H_5$] was added to a stirred solution of C_6F_5Li dissolved in ether at −78°C during 15 min and the mixture was allowed to warm to 20°C after 3 h, 70% of *cis*-, *trans*-$Pd(C_6F_5)_2[As(C_6H_5)_3]_2$ and 75% *trans*-$Pd(C_6F_5)_2(NH_2CH_2C_6H_5)_2$ are produced [52].

To a solution of C_6F_5Li in ether, $K_2[PdCl_4]$ was added at −78 °C and the solution was stirred at 20°C (21 h) to give 26% $[(C_4H_9)_4N]_2[Pd(C_6F_5)_4]$ after addition of $[(C_4H_9)_4N]Br$. The reactions of $[MCl_2(tht)_2]$ (tht = tetrahydrothiophene) with C_6F_5Li is dependent on the ratio C_6F_5Li : dichloro complex and the reaction time. Reaction takes place according to

$$[MCl_2(tht)_2] + C_6F_5Li \rightarrow [M(C_6F_5)_2(tht)_2] \xrightarrow{C_6F_5Li} [M(C_6F_5)_3(tht)]^- \xrightarrow{C_6F_5Li} [M(C_6F_5)_4]^{2-}$$

If the ratio is 2:2:1 the neutral compounds are obtained in about 60% yield. For M = Pt both the *cis*- and *trans*-$[Pt(C_6F_5)_2(tht)_2]$ are formed, while with M = Pd only *trans*-$[Pd(C_6F_5)_2(tht)_2]$ is available. The components were mixed at −78 °C in ether and stirred at +20 °C (4 h). If the ratio was increased to 3:1 and the reaction time extended to 12 h, after addition of $[(C_4H_9)_4N]Br$ the complex $[(C_4H_9)_4N][M(C_6F_5)_3(tht)]$ is formed. The yields are 24% for M = Pd and 56% for M = Pt. With a 6:1 ratio and 24 h of stirring 70% $[(C_4H_9)_4N]_2[Pd(C_6F_5)_4]$ is formed. In the case of Pt it was not possible to isolate $[Pt(C_6F_5)_4]^{2-}$ even with a larger excess of LiC_6F_5. At 0 °C a very exothermic reaction takes place between $PdCl_2$ and LiC_6F_5 giving 15% of $[(C_4H_9)_4N]_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_4]$. In the case of $PtCl_2$ the reaction with LiC_6F_5 is smooth and allows the isolation of 66% $[(C_4H_9)_4N]_2[Pt(C_6F_5)_4]$. Mixing C_6F_5Li and $[(C_4H_9)_4N][Pd_2(\mu\text{-}Br)_2Br_4]$ in ether at −78°C and stirring the solution at 20°C (20 h) leads to 64% $[(C_4H_9)_4N]_2[Pd(C_6F_5)_4]$ after addition of $[(C_4H_9)_4N]Br$ [53].

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1.3 Perfluorohalogenoorgano Compounds of Potassium and Caesium

Perfluoroisopropylpotassium $(CF_3)_2CFK$

1-Chloro-1,2,2,2-tetrafluoroethylpotassium CF_3CFClK

KF in tetramethylenesulfone reacts with $CF_3CF{=}CF_2$ or $F_2C{=}CFCl$ in the presence of small amounts of CsF at 100°C overnight to form $(CF_3)_2CFK$ or CF_3CFClK, respectively [1]. Both substances react with organothiocyanates [1] according to:

$$CF_3C(X)FK + RSCN \rightarrow CF_3C(X)FSR + KCN$$

In the following are presented X, R, yield in % and boiling point in °C/Torr:

CF_3, $C_6H_5CH_2$, 37%, 85/20
CF_3, CH_3, 51%, 53 to 55
CF_3, C_6H_5, 56%, 67 to 69/20
CF_3, 4-O_2N-C_6H_4, 57%, 120/3
Cl, $C_6H_5CH_2$, 50%, 75 to 80/1

^1H and ^{19}F NMR data for the sulfides are given in [1].

Perfluoro(t-butyl)caesium $(CF_3)_3CCs$

In aprotic dipolar solvents $(CF_3)_2C{=}CF_2$ reacts with CsF to form $(CF_3)_3CCs$ [2], ^{19}F NMR (external standard CF_3COOH, positive sign downfield): $\delta = 27$ ppm [3]. With 1-chloroacetylenes containing a sufficiently strong electron-acceptor substituent R the compound reacts [2] according to

$$(CF_3)_3CCs + ClC{\equiv}CR \rightarrow (CF_3)_3CC{\equiv}CR + CsCl$$

R = CF_3, 90% yield, boiling point 47 to 49°C, $\nu(C{\equiv}C) = 2310\ cm^{-1}$, ^{19}F NMR (external standard CF_3COOH): $\delta(CF_3) = 24$ ppm, $\delta[C(CF_3)_3] = 17$ ppm.

R = C_6H_5, 50% yield, boiling point 66 to 67°C/16 Torr, $\nu(C{\equiv}C) = 2245\ cm^{-1}$, $\delta[C(CF_3)_3] = 10$ ppm.

In diglyme at −15°C $(CF_3)_3CCs$ and arylsulfenylchlorides dissolved in CH_3CN were mixed, heated to 20°C (0.3 h) and then stirred at 40°C (2 h) to form $(CF_3)_3CSR$ ([a] IR and ^{19}F NMR spectrum is given) [9]:

R	C_6H_5[a]	4-Cl-C_6H_4	3-O_2N-C_6H_4	4-O_2N-C_6H_4
yield in %	75	84	78	86
Boiling point in °C/Torr	175 to	87 to	114 to	(63 to 64)
(melting point in °C)	176/750	88/16	115/10	—
n_D^{20}	1.4210	1.4430	1.4574	—

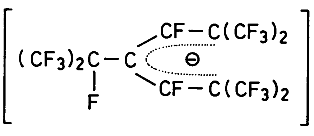
A chlorine replacement by the $(CF_3)_3C$ group is also observed with $ClCH_2OCH_2Cl$, Cl_2CHOCH_3 and $N(CH_2Cl)_3$. The reaction with $ClCH_2OCH_2Cl$ was carried out in diglyme at 35 to 40°C (0.5 h) to give 71% $(CF_3)_3CCH_2OCH_2C(CF_3)_3$ (boiling point 156 to 157°C, IR, ^1H and ^{19}F NMR data are given). Similarly Cl_2CHOCH_3 and $(CF_3)_3CCs$ reacted in a sealed tube at 180°C (16 h) to give 35% $(CF_3)_3CCHCl(OCH_3)$ (boiling point 112 to 113°C, $n_D^{20} = 1.3620$). Reacting $(CF_3)_3CCs$ in diglyme with a solution of $N(CH_2Cl)_3$ in CCl_4 at 60 to 70°C (1 h) forms $N[CH_2C(CF_3)_3]_3$ (32%), boiling point 65 to 66°C, ^1H and ^{19}F NMR data are given for the two compounds) [10]. In the reaction between $(CF_3)_2C{=}CF_2$ and CHX_3 (X = Cl, Br, I) in the presence of CsF in diglyme, giving 3,3-difluoro-2-halogeno-4,4,5,5-tetrakis(trifluoromethyl)cyclopent-1-ene, $(CF_3)_3CCs$ is postulated as an intermediate; for details, see [11]. For further reactions see [3].

[Bis(trifluoromethyl)heptafluoropropyl]methylcaesium $(CF_3)_2(C_3F_7)CCs$

$(CF_3)_2C{=}C(F)C_2F_5$ adds CsF in diglyme to form $(CF_3)_2(C_3F_7)CCs$. The compound reacts with $C_6H_5CH_2Br$ in diglyme at 50 to 60°C (2 h), then left overnight to give 90% $C_3F_7(CF_3)_2CCH_2C_6H_5$ (boiling point 66 to 68°C, ^1H and ^{19}F NMR data are given) [4].

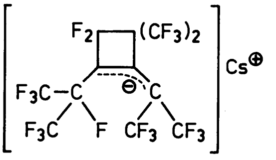
Caesium Compounds

$[(CF_3)_2\overset{\ominus}{C}CFC(CF_3)_2]\overset{\oplus}{Cs}$,



A

and



B

When a suspension of CsF and $(CF_3)_2C{=}C{=}C(CF_3)_2$ in absolute diglyme was stirred at 35°C (3 h) a homogeneous solution of $[(CF_3)_2\overset{\ominus}{C}CFC(CF_3)_2]\overset{\oplus}{Cs}$ was formed, IR: ν(C=C) = 1628 cm^{-1}, ^{19}F NMR (external standard CF_3COOH): $\delta(CF_3)$ = 24.7 (doublet), δ(CF) = 3.7 (multiplet) ppm, $J(CF_3\text{-}C\text{-}F)$ = 20 Hz. The compound is thermally very stable. No decomposition occurs upon standing for several days at 20°C or on heating to 150°C. Hydrolysis of the salt in diglyme with H_2O leads to $(CF_3)_2CHCF{=}C(CF_3)_2$ and traces of $(CF_3)_2CHC(O)CH(CF_3)_2$ [5, 6]. With C_6H_5COCl no substitution takes place, but C_6H_5COF, $(CF_3)_2C{=}C{=}C(CF_3)_2$ and CsCl are formed. At elevated temperatures $[(CF_3)_2\overset{\ominus}{C}CFC(CF_3)_2]\overset{\oplus}{Cs}$ is alkylated by compounds containing a mobile halogen atom [5], e.g.,

$[(CF_3)_2\overset{\ominus}{C}CFC(CF_3)_2]\overset{\oplus}{Cs} + RX \rightarrow (CF_3)_2CRCF{=}C(CF_3)_2 + CsX$ with

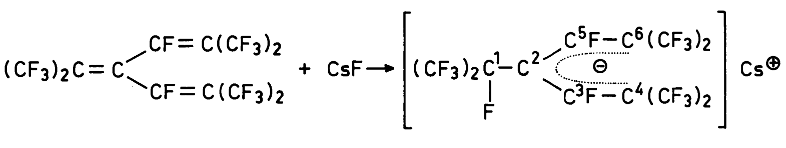
$R = CH_3$, X = I, 120°C (20 h), 44% yield, boiling point 95 to 100°C/752 Torr

$R = CH_2CH{=}CH_2$, X = Br, 160°C (40 h), 52% yield, boiling point 125°C/749 Torr, $n_D^{20} = 1.3270$

$R = CH_2OCH_3$, X = Cl, 55°C (15 h), 56% yield, boiling point 127 to 130°C/746 Torr, $n_D^{20} = 1.3205$

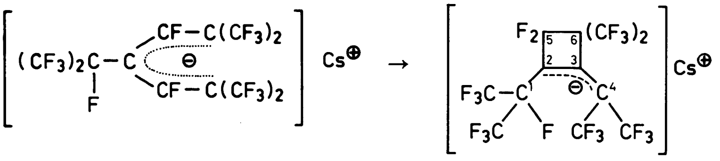
IR, ^{19}F NMR and mass spectroscopic data are provided in [5]. With HCl the compound gives $(CF_3)_2CHCF{=}C(CF_3)_2$ [6].

In absolute diglyme freshly calcinated CsF reacts with the perfluorinated α,α-bis(isobutenyl)isobutylene to form compound A according to



A

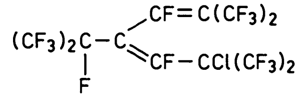
The ^{19}F NMR spectrum of the anion shows four unresolved signals with a 12:6:2:1 ratio of intensities. The chemical shifts (external standard CF_3COOH) are δ(1-CF_3) = 2.1 (m), δ(4-,6-CF_3) = 19.5 (m), δ(3-,5-CF) = 18.2 (m), δ(1-CF) = −91.0 (m) ppm. On standing at 20°C for 6 d the salt rearranges forming a cyclic anion (B) according to:



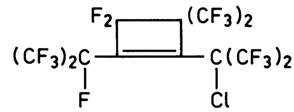
B

^{19}F NMR of the cyclic anion (external standard CF_3COOH): δ(1-CF_3) = 2.3 (m), δ(4-CF_3) = 26.5 (m), δ(6-CF_3) = 12.5 (m), δ(5-CF) = −10.0 (m); δ(1-CF) = −99.0 (m) ppm. At −50°C the signal δ(4-CF_3) is split into two signals appearing at −28.2 and −24.9 ppm due to retarded rotation around the C^3-C^4 bond and a partial double-bond character. The signal of one of the 4-CF_3 groups is close to the 1-CF signal and is split into a doublet with J(4-CF_3-1-CF) = 41.5 Hz. The 1-CF signal is split into a quartet also with J = 41.5 Hz [7].

Both compounds A and B react with Cl_2 at −78°C to yield compound C and D, respectively:



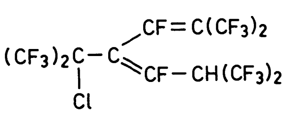
and



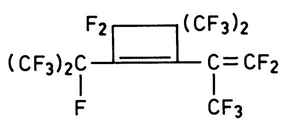
C
(boiling point 157 to 159°C)

D
(boiling point 54 to 55°C/20 Torr)

When the compound A is heated under vacuum or treated with H_2O, the original perfluorinated triene is regenerated. With HCl, compound A forms compound E. The compound B reacts with $BF_3 \cdot O(C_2H_5)_2$ to yield the cyclic compound F [7]:



E



F

IR, Raman, ^{19}F NMR, and mass spectroscopical data are provided [7].

Pentafluorophenylcaesium C_6F_5Cs

The ion pair equilibrium between 9-t-butylfluorene (RH) and C_6F_5H in cyclohexylamine has an almost zero entropy for C_6F_5Cs [8].

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2 Perfluorohalogenoorgano Compounds of Main Group 2 Elements

2.1 Preliminary Remarks

The compounds of the Main Group 2 elements are covered to the end of 1973 in "Perfluorhalogenorgano-Verbindungen der Hauptgruppenelemente", Part 4, 1975 (cited here as Part 4), for further details see the preface of this Supplement Volume.

2.2 Perfluorohalogenoorgano Compounds of Magnesium

2.2.1 Preparation and Physical Properties

Trifluoromethylmagnesium bromide CF_3MgBr

Pentafluoroethylmagnesium bromide C_2F_5MgBr

Perfluoro-n-propylmagnesium bromide n-C_3F_7MgBr

Perfluorobutylmagnesium bromide n-C_4F_9MgBr

Perfluorohexylmagnesium bromide $C_6F_{13}MgBr$

Perfluorooctylmagnesium bromide $C_8F_{17}MgBr$

Perfluorodecylmagnesium bromide $C_{10}F_{21}MgBr$

Perfluoro(3-oxa-4-methylpentane)-1-magnesium bromide $(CF_3)_2CFOCF_2CF_2MgBr$

For the thermal decomposition of n-C_3F_7MgBr and $C_{10}F_{21}MgBr$ (Part 4, p. 61) see p. 22, for the reaction of a suspension of activated Mg in tetrahydrofuran with CF_3Br to give 1% CF_3MgBr [1] see also Part 4, p. 61. In ether solution C_6H_5MgBr reacts with $C_nF_{2n+1}I$ (n = 2, 6, 8) under N_2 atmosphere at −40°C with stirring to form $C_nF_{2n+1}MgBr$. The temperature of the reaction should not exceed −30°C. Replacement of C_6H_5MgBr by C_2H_5MgBr shows advantages on separating the products [2]. Under similar conditions n-C_4F_9I and C_2H_5MgBr form n-C_4F_9MgBr [3]. At −78°C (1 h, stirring) C_6H_5MgBr and $(CF_3)_2CFOCF_2CF_2I$ react to $(CF_3)_2CFOCF_2CF_2MgBr$ [4].

Perfluoro-1-octenylmagnesium bromide $C_6F_{13}CF{=}CFMgBr$

Perfluoro-1-octynylmagnesium bromide $C_6F_{13}C{\equiv}CMgBr$

Perfluoro-1-decynylmagnesium iodide $C_8F_{17}C{\equiv}CMgI$

1,6-Bis(bromomagnesium)perfluorohexane $BrMg(CF_2)_6MgBr$

1,11-Bis(bromomagnesium)perfluoro(3,9-dioxaundecane) $BrMg(CF_2)_2O(CF_2)_5O(CF_2)_2MgBr$

The reaction between magnesium and $C_6F_{13}CF{=}CFBr$ takes place at 20°C in tetrahydrofuran giving $C_6F_{13}CF{=}CFMgBr$ [5]. The following exchange reaction is carried out in ether under reflux conditions according to

$$R_fC{\equiv}CH + RMgX \rightarrow R_fC{\equiv}CMgX + RH$$

with $R_f = C_6F_{13}$, $R = C_2H_5$, $X = Br$ and with $R_f = C_8F_{17}$, $R = CH_3$, $X = I$ [6]. At −95°C in tetrahydrofuran $(CH_3)_2SiH(CF_2)_6SiH(CH_3)_2$ reacts with n-C_4H_9MgBr to form $BrMg(CF_2)_6MgBr$ in low yield [7]. Better yields (see also Part 4, p. 66) are obtained from C_2H_5MgBr and

References p. 26

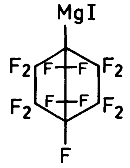
$Br(CF_2)_6Br$ in tetrahydrofuran at −70°C (0.5 h stirring) [21]. $BrMg(CF_2)_2O(CF_2)_5O(CF_2)_2MgBr$ can be prepared by the metal-halogen exchange reaction at −78°C in ether [4] according to:

$$I(CF_2)_2O(CF_2)_5O(CF_2)_2I + 2\ C_2H_5MgBr \rightarrow BrMg(CF_2)_2O(CF_2)_5O(CF_2)_2MgBr + 2\ C_2H_5I$$

Pentafluorophenylmagnesium bromide C_6F_5MgBr

4-Bromotetrafluorophenylmagnesium bromide 4-Br-C_6F_4MgBr

Tridecafluorobicyclo[2.2.2]octan-1-ylmagnesium iodide



A suspension of Mg in tetrahydrofuran reacts with C_6F_5Br at −30°C to give 80% C_6F_5MgBr [1], which is also formed on mixing ether solutions of Mg and of C_6F_5Br at −15°C and then allowing the resulting stirred mixture, in a dry N_2 atmosphere, to warm to 0°C during 2 h [9], and on refluxing the mixture for 1 h [32] and by an exchange reaction between C_2H_5MgBr and C_6F_5Br in ether at 0°C (0.5 h). Similarly 4-Br-C_6F_4MgBr was prepared from C_2H_5MgBr and 4-Br-C_6F_4Br [8]. Refluxing (2 h) a mixture of Mg and 1-iodotridecafluorobicyclo[2.2.2]octane in dry ether in the presence of a crystal of iodine, tridecafluorobicyclo[2.2.2]octan-1-ylmagnesium iodide is obtained [10]. ^{19}F NMR studies indicate that C_6F_5MgBr is the initially formed species in the reaction between C_6F_5Br and Mg. It is in an equilibrium with $(C_6F_5)_2Mg$ [18] according to:

$$2\ C_6F_5MgBr \rightleftharpoons (C_6F_5)_2Mg + MgBr_2$$

^{19}F NMR spectra are presented (see also Part 4, pp. 67/8) [18].

2.2.2 Chemical Reactions

2.2.2.1 General Remarks

Perfluorohalogenoorganomagnesium compounds are sensitive to moisture and should therefore be prepared in anhydrous solvents. Hydrolysis and acidolysis give the corresponding alkanes according to:

$$R_fMgX + HX' \rightarrow R_fH + MgXX'$$

with X = halogen and with X′ = OH or an acidic group, e.g., F, Cl, Br, I, HSO_4

The hydrolysis of $(CF_3)_2CFOCF_2CF_2MgBr$ or of $BrMg(CF_2)_2O(CF_2)_5O(CF_2)_2MgBr$ with 6 N HCl at −78°C gives $(CF_3)_2CFOCF_2CF_2H$ or $HCF_2CF_2O(CF_2)_5OCF_2CF_2H$, respectively [4]. Similarly, $C_6F_{13}CF{=}CFMgBr$ gives with hydrous acids $C_6F_3CF{=}CFH$. It could be shown that the *trans* configuration of the vinyl F atoms of the starting bromoolefin was maintained in $C_6F_3CF{=}CFH$ [5]. Dilute H_2SO_4 reacts with tridecafluorobicyclo[2.2.2]octan-1-ylmagnesium iodide to 1-H-tridecafluoro[2.2.2]octane and its 1-iodo analogue [10]. Another overall reaction is the reaction with CO_2 via

$$R_fMgBr + CO_2 \xrightarrow{H^+} R_fCOOH$$

References p. 26

At −78°C $(CF_3)_2CFO(CF_2)_2MgBr$ (16 h) or $BrMg(CF_2)_2O(CF_2)_5O(CF_2)_2MgBr$ (20 h) reacts with CO_2 to give after treatment with concentrated H_2SO_4 the acids $(CF_3)_2CFO(CF_2)_2COOH$ or $HOC(O)(CF_2)_2O(CF_2)_5O(CF_2)_2COOH$ [4]. In the analogous reaction $C_6F_{13}CF{=}CFMgBr$ forms with CO_2 the acid $C_6F_{13}CF{=}CFCOOH$ [5]. In ether, C_6F_5MgBr and PCl_3 react to form $(C_6F_5)_2PCl$ [9].

2.2.2.2 Thermal Decomposition

The decomposition of the compounds R_fMgBr (prepared from C_6H_5MgBr and R_fI) in ether on warming the mixture from −40 to +20°C leads to the formation of perhalogenated olefins, which are characterized by their ^{19}F NMR and mass spectroscopic data. The following decompositions have been investigated:

$C_2F_5MgBr \rightarrow F_2C{=}CFBr + F_2C{=}CFI + F_2C{=}CBr_2$
$n\text{-}C_3F_7MgBr \rightarrow CF_3CF{=}CFBr + C_3F_4Br_2$
$C_6F_{13}MgBr \rightarrow CF_3(CF_2)_3CF{=}CFBr + CF_3(CF_2)_3CF{=}CFI + C_{12}F_{24}$
$C_8F_{17}MgBr \rightarrow CF_3(CF_2)_5CF{=}CFBr + CF_3(CF_2)_5CF{=}CFI + C_{14}F_{32}$

For the discussion of the mechanism of the decomposition see the original paper [2].

In a similar investigation it is shown that the decomposition of $R_fCF_2CF_2MgX$ in ether, pentane or tetrahydrofuran at 20°C ($R_f = C_4F_{17}, C_6F_{13}, C_8F_{17}$, X = Cl, Br, I) yields the *trans*-1-haloperfluorinated olefins $R_fCF{=}CFX$. Coproducts are $R_fCF{=}CF_2$, an isomeric mixture of $R_fCF_2CF_2CF{=}CFR_f$, and unidentified compounds. In the presence of RMgX (R = CH_3, C_2H_5) the decomposition leads additionally to the formation of the *trans*-1-alkylperfluorovinyl compounds. For the physical data of the reaction products and for the discussion of the possible reaction mechanism see [12].

In presence of C_6H_5MgBr the Grignard $C_8F_{17}MgBr$ in ether decomposes forming a mixture of unsaturated perfluorinated compounds. The composition of this mixture depends strongly on the experimental conditions. The main products are $C_6F_{13}CF{=}CFBr$, $C_6F_{13}CF{=}CFC_6H_5$, and $C_6F_{13}C{\equiv}CC_6H_5$ [11].

A solution of $BrMg(CF_2)_6MgBr$ in tetrahydrofuran decomposes to 60% of its original concentration at −78°C during 2 h; for further details see [7]. Another investigation shows that this compound (formed at −70°C, see p. 20) decomposes after rapid warming to room temperature (0.15 min) to give 90% perfluorocyclohexene [21].

2.2.2.3 Reactions with Halogens, CuBr, CuI, $CdCl_2$, $(CH_3)_nSiCl_{4-n}$ (n = 1, 2), $RPCl_2$, Thiocyanates, Benzalacetophenones, Butene

The halogenation with Cl_2 converts $C_6F_{13}C{\equiv}CMgBr$ not to $C_6F_{13}C{\equiv}CCl$ but to $C_6F_{13}C{\equiv}CBr$ (55% yield, boiling point 123 to 126°C/760 Torr). $C_6F_{13}C{\equiv}CMgI$ reacts with Br_2 forming $C_6F_{13}C{\equiv}CCI$ (boiling point 48 to 53°C/15 Torr, IR and ^{19}F NMR data are provided) [6].

In etheral solution, C_6F_5MgBr reacts with CuBr at reflux temperature (1.5 h) under dry N_2 to give C_6F_5Cu, which is isolated as a $(C_6F_5Cu)_2\cdot$dioxane complex in 63 to 80% yield [13]. The reaction between C_6F_5MgCl and CuI at 0°C mainly gives C_6F_5I (72 to 84%) and some $C_6F_5C_6F_5$ (8 to 11%) [16].

As a reactive intermediate $(C_6F_5)_2Cd$ is formed from C_6F_5MgBr and $CdCl_2$ in refluxing ether during 75 min [15].

The reactions of C_6F_5MgBr with $(CH_3)_nSiCl_{4-n}$ (n = 1, 2) were studied by GC/MS techniques, for details see [32]. A solution of $BrMg(CF_2)_6MgBr$ in tetrahydrofuran reacted with an excess $(CH_3)_3SiCl$ at −70°C (72 h) to give $(CH_3)_3Si(CF_2)_6Si(CH_3)_3$ [21], see also [1].

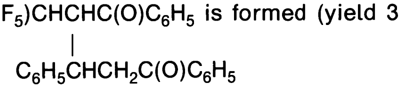
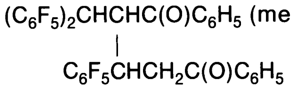
Below 20°C in ether, C_6F_5MgBr and $C_6H_5PCl_2$ form after 13 h a mixture of $C_6F_5(C_6H_5)PX$ (X = Cl, Br) (melting point 45 to 48°C) [9]. When a freshly prepared solution of C_6F_5MgBr in ether is added dropwise to an ether solution of $RPCl_2$ [R = CH_3, C_2H_5, $C(CH_3)_3$] at 20°C (2 h) and the mixture is stirred at 20°C for additional 2 h the following compounds [14] are formed:

$CH_3P(C_6F_5)_2$ (75% yield, boiling point 60 to 63°C/0.05 Torr), $C_2H_5P(C_6F_5)_2$ (77% yield, boiling point 86 to 89°C/0.05 Torr), $(CH_3)_3CP(C_6F_5)X$, X = Cl, Br (mixture of 20% chloride and 80% bromide, boiling point 55 to 70°C/1 Torr).

In a similar manner $(C_2H_5)_2NP(R)C_6F_5$ compounds are made from $(C_2H_5)_2NP(R)Cl$ and C_6F_5MgBr [14]:

$(C_2H_5)_2NP(C_6F_5)CH_3$ (80% yield, boiling point 64°C/0.1 Torr), $(C_2H_5)_2NP(C_6F_5)C_2H_5$ (81.5% yield, boiling point 75°C/0.1 Torr), $(C_2H_5)_2NP(C_6F_5)C(CH_3)_3$ (79% yield, boiling point 47°C/0.05 Torr). ^{19}F and ^{31}P NMR data are provided [14].

At −15°C C_4F_9MgBr reacts with $C_6H_5CH_2SCN$ in ether to 50% $C_4F_9SCH_2C_6H_5$ (boiling point 130 to 135°C/15 Torr) and with 4-Cl-C_6H_4-CH_2SCN to 45% 4-Cl-$C_6H_4CH_2SC_4F_9$ (boiling point 70 to 75°C/1 Torr). ^1H and ^{19}F NMR data are presented [3].

On dropping an ether solution of benzalacetophenone to an ether solution of C_6F_5MgBr at 20°C (18 h) under N_2  $\begin{array}{l} C_6H_5(C_6F_5)CHCHC(O)C_6H_5 \\ \quad | \\ C_6H_5CHCH_2C(O)C_6H_5 \end{array}$ is formed (yield 36%, melting point 183 to 184°C). A similar reaction took place with $C_6F_5CH{=}CHC(O)C_6H_5$ and C_6F_5MgBr giving 42%  $\begin{array}{l} (C_6F_5)_2CHCHC(O)C_6H_5 \\ \quad | \\ C_6F_5CHCH_2C(O)C_6H_5 \end{array}$ (melting point 158 to 159°C). The reaction of $C_6H_5CH{=}CHC(O)C_6F_5$ and C_6F_5MgBr gives 45% $C_6H_5(C_6F_5)CHCH_2C(O)C_6F_5$ (melting point 63 to 64.5°C). Similarly, $(C_6F_5)_2CHCH_2C(O)C_6F_5$ (melting point 63.5 to 64.5°C) can be made from $C_6F_5CH{=}CHC(O)C_6F_5$ and C_6F_5MgBr [15].

Trans-1,4-dibromo-2-butene and C_6F_5MgBr react in anhydrous ether at reflux temperature (28 h, stirring) to form 68% $C_6F_5CH_2CH{=}CHCH_2C_6F_5$ (melting point 94 to 94.5°C) [17].

2.2.2.4 Reactions with Aldehydes, Ketones, Carboxylic Acids, -Halides and -Anhydrides

In anhydrous ether C_2F_5MgBr condenses with $RCH{=}CHCHO$ at −40°C to form $RCH{=}CHCH(OH)C_2F_5$; R = CH_3, 60% yield, boiling point 116°C; R = C_6H_5, 70% yield, melting point 52°C. Similarly C_2F_5MgBr reacts with $H_2C{=}C(CH_3)CHO$ to yield 60% $H_2C{=}C(CH_3)CH(OH)C_2F_5$ (boiling point 110°C). With R_fMgBr and $C_6H_5CH{=}CHCHO$ 60% $C_6H_5CH{=}CHCH(OH)R_f$ are obtained: R_f = C_6F_{13} (melting point 56°C), R_f = C_8F_{17} (melting point 58°C). IR, ^1H and ^{19}F data are provided [2]. When dry CH_3CHO is added dropwise to a solution of tridecafluorobicyclo[2.2.2]octan-1-ylmagnesium iodide dissolved in ether 1-(1′-hydroxyethyl)tridecafluorobicyclo[2.2.2]octane is formed (melting point 89°C) [10]. Ferrocenecarboxaldehyde and C_6F_5MgBr react at 20°C in ether to form 98.5% (α pentafluorophenyl)ferrocenemethanol (melting point 110°C) [19]. With aldehydes and ketones $CF_2{=}CFMgI$ forms secondary [$RCH(OH)CF{=}CF_2$] and tertiary alcohols [$RR'C(OH)CF{=}CF_2$] which rearrange rapidly to

References p. 26

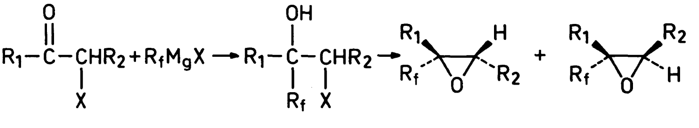
fluoroanhydrides of crotonic and cinnamic acids. The following compounds are made this way [20]:

Compound	Boiling point (in °C/Torr)	n_D	D (in g/cm^3)
$C_6H_5CH{=}CFC(O)F$	83.5 to 85/10	1.5588 (19.5°C)	1.255 (19.5°C)
$CH_3CH{=}C(CFH_2)C(O)F$	98 to 99	1.3931 (23°C)	1.112 (23°C)
$(CH_3)_2CHCH_2CH{=}CFC(O)F$	121 to 122	1.3932 (25°C)	1.036 (25°C)
$CH_3CH{=}CFCOOH$	74.5/741	1.3688 (20°C)	1.125 (20°C) [20]

In anhydrous tetrahydrofuran $(CF_3)_2CFOCF_2CF_2MgBr$ reacts with $(CF_3)_2CO$ at −78°C (16 h) and 20°C (4.5 h) to form 50% $(CF_3)_2CFO(CF_2)_2C(CF_3)_2OH$ (boiling point 123 to 124°C) [4]. Cyclohexanone and $BrMg(CF_2)_6MgBr$ react at −70°C (5 h, stirring) to give some 1-cyclo-$C_6H_{10}OH(CF_2)_6H$ and 43% 1,6-(cyclo-$C_6H_{10}OH)_2(CF_2)_6$ (melting point 151 to 152°C). Similarly $BrMg(CF_2)_6MgBr$ and $(CH_3)_2CO$ react at −70°C (18 h, stirring) to yield $H(CF_2)_6C(CH_3)_2OH$ (34% yield). The reaction of $BrMg(CF_2)_6MgBr$ with $(CF_3)_2CO$ gives $(CH_3)_2C(OH)(CF_2)_6C(CH_3)_2OH$ (28% yield, melting point 88 to 89°C) and $(CF_3)_2C(OH)(CF_2)_6C(CF_3)_2OH$, 62% yield [21].

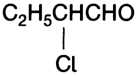
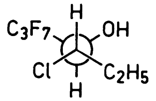
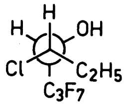
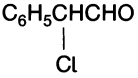
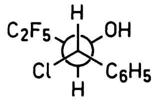
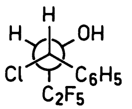
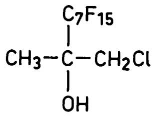
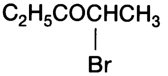
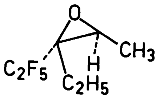
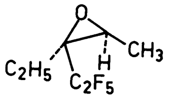
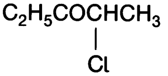
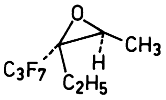
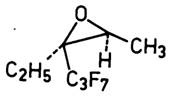
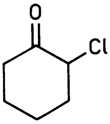
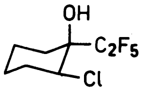
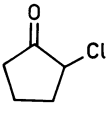
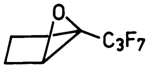
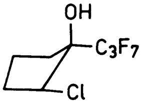
When $C_6F_{13}C{\equiv}CMgX$ is treated with $[CH_3C(O)]_2O$ at −30°C for X = Br 25% and for X = I 50% $CH_3C(O)CX{=}C(C_6F_{13})C(O)CH_3$ is isolated. If X = Br 17% of $CH_3C(O)C{\equiv}CC_6F_{13}$ is also obtained. Similarly $CF_3C(O)CH{=}C(OC_3H_7)C_6F_{13}$ is formed in refluxing ether from $C_6F_{13}C{\equiv}CMgX$ and $CF_3COOC_3H_7$. The yields are for X = I 30% and for X = Br 40%. IR, ^1H and ^{19}F NMR data are provided [6]. In ether, C_6F_5MgBr and $C_3F_7OCF(CF_3)C(O)F$ at 0°C (9 d) form 45% C_6F_5H (from hydrolysis of C_6F_5MgBr) and the products $C_6F_5C(O)CF(CF_3)OC_3F_7$ and 4-C_6F_5-$C_6F_4C(O)CF(CF_3)OC_3F_7$ in the ratio 121:3. After additional 7 d at 20°C only 12% C_6F_5H remained and the ratio was 80:10. The same reaction carried out in tetrahydrofuran gave after 4 h $C_6F_5C(O)CF(CF_3)OC_3F_7$ (boiling point 94°C/36 Torr) and 4-C_6F_5-$C_6F_4C(O)CF(CF_3)OC_3F_7$ (boiling point 145 to 146°C/10 Torr) in the ratio 41:55. In a competitive reaction between $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)F$ and $C_2F_5O(CF_2CF_2)_2CF_2C(O)F$ with C_6F_5MgBr at 0°C in ether after 3.5 h, only 25% of C_6F_5MgBr reacted. The reaction mixture, allowed to warm to 20°C and stirred for another 48 h, gave after hydrolysis 14.2% C_6F_5H, 71.7% $C_2F_5O(CF_2CF_2O)_2CF_2C(O)C_6F_5$ (boiling point 95 to 96°C), 5.4% $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)C_6F_5$ and 8.7% $(C_6F_5)_2C(OH)CF_2(OCF_2CF_2)_2$-$OC_2F_5$. Analogously 4-Br-$C_6F_4MgBr$ and $C_3F_7OCF(CF_3)C(O)F$ reacted in ether at −20°C (12 d) to form 36% 4-Br-C_6H_4H, 47.5% 4-Br-$C_6F_4C(O)CF(CF_3)OC_3F_7$ (boiling point 89°C/8.5 Torr), 8% 4-Br-C_6F_4Br and 7% 1,4-$[C_3F_7OCF(CF_3)C(O)]_2$-C_6F_4. When the same reaction is carried out in tetrahydrofuran at 0°C (2 h) the major products are 1,4-Br_2-C_6F_4 and 1,4-$[C_3F_7OCF(CF_3)C(O)]_2$-C_6F_4 in a 1:1 ratio [8].

Perfluoroalkylmagnesium halides react with α-halogenocarbonyl compounds in ether to form diastereoisomeric halohydrins which cyclisize to the corresponding perfluoroalkyl epoxides according to:



The configuration of the epoxides RS and RR could be determined by the value of the ^4J(H-F)spin-spin coupling constant between the proton of the epoxide and the R_f group. Since the cyclization of the halohydrines to form the epoxides is stereospecific, the configuration of the halohydrines could be determined from the configuration of the epoxides. The synthesized compounds are given in **Table 5**, for spectroscopic data see the original paper [22].

Table 5
Reactions of Perfluoroalkylmagnesium Halides with α-Halogenocarbonyl Compounds [22].

Carbonyl compounds	R_fMgX	Relative amounts of halohydrine and of epoxide			
		RS		RR	
 $C_2H_5\underset{\underset{\displaystyle Cl}{\vert}}{C}HCHO$	C_3F_7MgBr		63%		37%
 $C_6H_5\underset{\underset{\displaystyle Cl}{\vert}}{C}HCHO$	C_2F_5MgBr		50%		50%
CH_3COCH_2Cl	$C_7F_{15}MgBr$	 $CH_3-\underset{\underset{\displaystyle OH}{\vert}}{\overset{\overset{\displaystyle C_7F_{15}}{\vert}}{C}}-CH_2Cl$			
 $C_2H_5CO\underset{\underset{\displaystyle Br}{\vert}}{C}HCH_3$	C_2F_5MgBr		44%		56%
 $C_2H_5CO\underset{\underset{\displaystyle Cl}{\vert}}{C}HCH_3$	C_3F_7MgBr		31%		69%
	C_2F_5MgBr		17%		83%
	C_3F_7MgBr		30%		70%

2.2.2.5 Reactions with Transition Metal Compounds

Titanocenedichloride reacts with C_6F_5MgBr to form $CpTi(C'_p)(C_6F_5)Cl$ (C_p = cyclopentadienyl, C'_p = π-2-$(CH_3)_2CH$-$C_5H_3CH_3$-, $\pi(C_6H_5)_2CH$-$C_5H_3CH_3$ [23] and Cp = cyclopentadienyl, Cp′ = π-t-butylcyclopentadienyl) [24]. In a similar reaction cyclopentadienyl-(1-phenylethylcyclopentadienyl)titanium dichloride and C_6F_5MgBr gave the corresponding diastereomers $CpCp'Ti(C_6F_5)Cl$ [25]. The reaction of $ZrCl_4$ with C_6F_5MgBr (ratio 1:4) in ether at −15°C and then at 20°C gave 94% $Zr(C_6F_5)_4$ [26]. Similar $Ni(C_6F_5)_2$ is made from $NiBr_2$ and C_6F_5MgBr [27]. A C_6F_5/Br exchange takes place between C_6F_5MgBr and $BrCo(acac)(en)P(C_6H_5)_3$. After acid hydrolyses the complex $C_6F_5Co(acac)(en) \cdot H_2O$ is obtained [28]. When $MCl(CS)[P(C_6H_5)_3]_2$ is added to a solution of C_6F_5MgBr in tetrahydrofuran and the mixture is left for 40 h at 20°C a yield of 60 to 62% $M(C_6F_5)(CS)[P(C_6H_5)_3]_2$ with M = Rh, Ir is produced [29]. A tetrahydrofuran solution of C_6F_5MgCl was slowly added to a suspension of $VCl_3 \cdot$(tetrahydrofuran)$_3$ in ether at −10°C. The products formed here are C_6F_5H and $VCl_2 \cdot 4\,C_5H_5N$ after treatment of the mixture with pyridine. If the molar ratio of the starting materials are changed from 1:1 to 1:2 at −15°C (1 h) and warming up to 20°C 43% $(C_6F_5)_4V \cdot$ 2 (tetrahydrofuran) were isolated besides 47% $VCl_2 \cdot 4\,C_5H_5N$ [30]. Treating $TiCl_4$ with four moles of C_6F_5MgBr in ether at −20°C leads to $(C_6F_5)_4Ti$. Partial substitution is obtained with two moles C_6F_5MgBr giving $(C_6F_5)_2TiCl_2$ [31]. For arylation of $K_2[PdCl_4]$, MCl_2, $MCl_2(tht)_2$, and $[(C_4H_9)_4N]_2[M_2(\text{-}Br)_2Br_4]$ (M = Pd, Pt; tht = tetrahydrothiophene) with C_6F_5MgBr, see [33] and p. 14.

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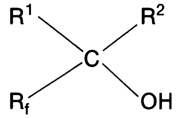
2.3 **Perfluoroalkylcalciumiodides** R_fCaI (R_f = C_2F_5, C_6F_{13})

Perfluoroalkyliodides react at 20°C with finely divided calcium in basic solvents such as tetrahydrofuran, dioxane or ether to form perfluoroalkylcalciumiodides as reactive intermediates. When pure calcium metal is used, the reaction starts vigorously at −20°C after an induction period of 0.5 h. Large proportions of undesired R_fH are produced, the proportion increasing with higher temperature. This disadvantage was partially overcome using calcium amalgam. The reaction starts immediately, proceeds smoothly, and is complete after 2 h at 20°C or 10 h at −20°C [1, 2]. In the presence of ketones or aldehydes at −20 to 40°C the reaction gives lower yields of R_fH and a higher yield of the corresponding alcohol. When the aldehyde or ketone is added after R_fCaI is formed, high yields of R_fH and lower yields of the alcohols are found. Reaction takes place in tetrahydrofuran [1, 2] according to:

$R_fI + Ca + R^1C(O)R^2 \rightarrow$



The alcohol is obtained after hydrolysis.

In the following are given R_f, R^1, R^2, reaction temperature in °C (time in h), yield, boiling point/Torr, (melting point)

C_2F_5, C_6H_5, H, −40 (20), 69%, 214°C;

C_6F_{13}, CH_3, CH_3, −40 (20), 37%, 47°C/15 Torr (38 to 40°C); [in addition $CH_3C(OH)(C_6F_{13})CH_2C(CH_3)_2OH$, boiling point 130°C/0.05 Torr is formed in 30% yield];

C_6F_{13}, CH_3, C_2H_5, −30 (18), 30%, 176°C [in addition 10% $CH_3C(OH)(C_2H_5)CH_2C(OH)(C_2H_5)C_6F_3$ is obtained];

C_6F_{13}, C_2H_5, C_2H_5, −40 (8), 66%, 198°C;

C_6F_{13}, $(CH_3)_2CH$, $(CH_3)_2CH$, −40 (18), 40%, 86 to 92°C/13 Torr;

C_6F_{13}, C_6H_5, H, −40 (20), 56%, (52 to 54°C);

C_6F_{13}, CH_3, C_6H_5, −35 (22), 30%, product not free from $C_6H_5C(O)CH_3$;

C_6F_{13}, -$(CH_2)_5$-, −20 (8), 58%, 222°C;

C_6F_{13}, 2-HO-C_6H_4, H, −40 (20), 21%, (75 to 79°C).

^1H, ^{19}F NMR and mass spectroscopic data are given in [2].

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[1] G. Santini, M. LeBlanc, J. G. Riess (J. Chem. Soc. Chem. Commun. **1975** 678/9). – [2] G. Santini, M. LeBlanc, J. G. Riess (J. Organometal. Chem. **140** [1977] 1/9).

3 Perfluorohalogenoorgano Compounds of Main Group 3 Elements

3.1 Preliminary Remarks

The compounds of the Main Group 3 elements are covered to the end of 1973 in "Perfluorhalogenorgano-Verbindungen der Hauptgruppenelemente", Part 4, 1975 (cited here as Part 4), for further details see the preface of this Supplement Volume.

3.2 Perfluorohalogenoorgano Compounds of Boron

Perfluorovinyldihalogenoboranes $F_2C{=}CFBX_2$ (X = F, Cl)

Tris(trifluorovinyl)boranes $(F_2C{=}CF)_3B$

No new syntheses and chemical reactions have been published (see Part 4, p. 117).

The IR spectra of gaseous and solid $F_2C{=}CFBF_2$ and of $F_2C{=}CFBCl_2$ have been recorded along with the Raman spectra of all three physical states. The wave numbers are given in [8]. The interpretation of the spectra, on assuming planar geometry for both molecules, gives the fundamental vibrations of the molecules in the gaseous state, see **Table 6**.

Table 6
Fundamental Vibrational Frequencies ν_i (in cm^{-1}) for Gaseous $F_2C{=}CFBF_2$ and $F_2C{=}CFBCl_2$ [8].

	$F_2C{=}CFBF_2$		$F_2C{=}CFBCl_2$		Approximate description
A′	ν_1	1725	ν_1	1694	C-C stretching
	ν_2	1410	ν_2	1290	C-F stretching
	ν_3	1390	ν_3	1392	antisymmetric CF_2 stretching
	ν_4	1323	ν_6	981	antisymmetric BX_2 stretching
	ν_5	1179	ν_4	1128	symmetric CF_2 stretching
	ν_6	1040	ν_5	1023	B-C stretching
	ν_7	709	ν_7	864	symmetric BX_2 stretching
	ν_8	679	ν_8	532	CF_2 rocking
	ν_9	584	ν_9	404	BX_2 scissoring
	ν_{10}	370	ν_{10}	329	CF_2 scissoring
	ν_{11}	351	ν_{12}	163	BX_2 rocking
	ν_{12}	248	ν_{11}	217	CF bending
	ν_{13}	138	ν_{13}	135	C-C-B bending
A″	ν_{14}	682	ν_{14}	632	CF_2 wagging
	ν_{15}	596	ν_{16}	245	BX_2 wagging
	ν_{16}	335	ν_{15}	323	CF bending
	ν_{17}	123	ν_{17}	90	CF_2 twisting
	ν_{18}	(69)	ν_{18}	(30)	BX_2 torsion

The IR spectra of gaseous and solid $(F_2C{=}CF)_3B$ and the Raman spectra of this compound in all three physical states have been recorded. Spectral changes that occur on solidification indicate the presence of two conformers in the fluid phases. A detailed vibrational assignment is proposed for the more stable form on the basis of C_3 molecular symmetry. The spectrum inclusive of assignment is given in the original paper [9].

Potassiumtrifluoromethyltrifluoroborate $K[CF_3BF_3]$, $CF_3BF_3^-$ Anion

Bis(trifluoromethyl)difluoroboric acid $H[(CF_3)_2BF_2]$

Bis(trifluoromethyl)difluoroborates $M[(CF_3)_2BF_2]$ (M = K, Cs), $(CF_3)_2BF_2^-$ Anion

The reaction between $(CH_3)_3SnCF_3$ and BF_3 (molar ratio 3:1) at 60°C (12 h) in CCl_4 yields as the main product $[(CF_3)_2BF_2]^-$ and $[CF_3BF_3]^-$. By addition of KF, the corresponding salts were isolated. $K[(CF_3)_2BF_2]$ is formed in 60% yield. The free acid $H[(CF_3)_2BF_2]$ is obtained by passing $K[(CF_3)_2BF_2]$ through the acidic ion exchange column (Riedel Permutit SC 102) and evaporation of the aqueous solution to dryness. By titration of $H[(CF_3)_2BF_2]$ with an aqueous solution of CsOH the slightly soluble $Cs[(CF_3)_2BF_2]$ is precipitated [1].

Physical Properties

$K[CF_3BF_3]$ crystallizes in the monoclinic system with space group $P2_1/c$-C_{2h}^5 (No. 14). The unit cell with dimensions a = 4.8453, b = 16.331, c = 6.348 ± 0.002 Å, β = 101° (±3°) contains four molecules. The X-ray density is 2.378, the pycnometric density (in CH_2Cl_2) is 2.5 ± 0.1 g/cm^3. The structure was refined to a R factor of 0.0058. The compound forms ionic crystals which impose no crystallographic symmetry on the ions. The $CF_3BF_3^-$ anion deviates somewhat from C_{3v} symmetry, the CF_3 and BF_3 groups being rotated about 8° from the staggered conformation. The average C-F, B-F and B-C bond distances are 1.343(8) Å (1.360 Å), 1.391(5) Å (1.409 Å) and 1.625(6) Å (1.640 Å), respectively. The values in parentheses are distances corrected for libration. The mean values of the angles are α(F-C-F) = 104.9(2)°, α(B-C-F) = 113.7(3)°, α(F-B-F) = 109.9(5)° and α(C-B-F) = 109.1(4)°.

The IR spectra of KF and polyethylene pellets of $K[CF_3BF_3]$ as well as Raman spectra of its aqueous solution, of crystal powder and of single crystals in the region of 50 to 2000 cm^{-1} were recorded and assigned for a staggered C_{3v} model of the $CF_3BF_3^-$ anion, see **Table 7** [7]. A normal-coordinate analysis yielded a harmonic force field. The following stretching force constants were obtained: f_{CF} = 4.85, f_{BF} = 4.19 and f_{BC} = 3.63 mdyn/Å. Bonding in CF_3B-compounds is discussed on the basis of X-ray and spectroscopic data [7].

^{19}F NMR (in aqueous solution, internal standard CF_3COONH_4, chemical shifts δ refer to the standard $CFCl_3$, negative values of δ means highfield) [1]:

$[CF_3BF_3]^-$: $\delta(CF_3)$ = −77.3 ppm, $\delta(BF_3)$ = −156.0 ppm, J(B-F) = 40.7 Hz, J(F-C-B) = 33.6 Hz.

Table 7
Vibrational Spectra of $K[CF_3BF_3]$ (in cm^{-1}) [7].

IR	Raman		Assignment and approximate description	
	crystal	solution		
80 w				
120 s				
189 m	190 vw	185 vw	$\nu_{11}(e)$	$\varrho(BF_3)$
308 315 } w	314 m	312 s, p	$\nu_5(a_1)$	$\delta(BF_3)$
331 w	331 334 342 } m	329 m, dp	$\nu_{10}(e)$	$\varrho(CF_3)$

Table 7 (continued)

IR	Raman crystal	Raman solution	Assignment and approximate description	
465 475 m	465 475 vw	466 vw	$\nu_9(e)$	$\delta(BF_3)$
560 vw	555 559 s	556 m, dp	$\nu_8(e)$	$\delta(CF_3)$
	625 vw	625 vw	$2\nu_5(A_1)$	
637.4 ^{11}B 640.5 ^{10}B s	639 ^{11}B 643 ^{10}B m	639 ^{11}B 643 ^{10}B w, p	$\nu_4(a_1)$	$\delta(CF_3)$
732.0 w	732 vs	731 vs, p	$\nu_3(a_1)$	$\nu(BF)$
963 ^{11}B 986 ^{10}B vs	962 ^{11}B 984 ^{10}B vw	961 ^{11}B 985 ^{10}B vw	$\nu_7(e)$	$\nu(BF)$
	1054 1080 ^{11}B 1070 1096 ^{10}B w	1063 ^{11}B 1076 ^{10}B w	$\nu_6(e)$	$\nu(CF)$
1066 ^{11}B 1094 ^{10}B vs	1023 ^{11}B 1054 ^{10}B vw		$\nu_2(a_1)$	$\nu(CF)$
1191 1203 w			$\nu_3 + \nu_9(E)$	
1342 ^{11}B 1358 ^{10}B w	1343 ^{11}B 1359 ^{10}B m	1339 ^{11}B 1356 ^{10}B m, p	$\nu_1(a_1)$	$\nu(BC)$
1518 ^{11}B 1541 ^{10}B vw			$\nu_7 + \nu_8(A_1 + A_2 + E)$	

$Cs[(CF_3)_2BF_2]$ crystallizes in the monoclinic system with space group $P2_1/m\text{-}C^2_{2h}$ (No. 11). The unit cell with dimensions 5.958(1), b = 7.628(1), c = 8.2997(9) Å, β = 100.50(1)° contains two molecules. The density is 2.863 g/cm^3. The structure was refined to a R factor of 0.028. The average C-F, B-F and B-C bond distances are 1.353, 1.391 and 1.618 Å, respectively. The mean values of the angles are α(F-C-F) = 104.5°, α(B-C-F) = 114.0°, α(F-B-F) = 108.1° and α(C-B-F) = 108.7°. Apparently because of Cs···F(B,C) interactions, one B-C bond has a staggered and the other an eclipsed conformation in the solid state. The IR (KF and polyethylene pellets) and Raman spectra (aqueous solution) were recorded and assigned assuming C_{2v} symmetry for the $(CF_3)_2BF_2^-$ anion in solution, see **Table 8** [6]. The analysis of

Table 8
Vibrational Spectra of the $(CF_3)_2BF_2^-$ Anion (in cm^{-1}) [6].
Assignment of the vibrations according to [14].

Raman (natural B)	IR ^{11}B/^{10}B	Assignment and approximate description	
	≈70(s)	lattice vibration	
	122(sh)	ν_8 (a_1)	$\delta(BC_2)$
	180(m)	ν_{26} (b_2)	$\delta(CBX)$
	234(m)	ν_{13}, ν_{21} (a_2, b_1)	$\delta(CBX)$

Table 8 (continued)

Raman (natural B)	IR $^{11}B/^{10}B$	Assignment and approximate description	
286(sp)	286(w)	ν_6 (a_1)	$\delta(BC_2)$
305(sh)		ν_{12} (a_2)	$\varrho(CF_3)$
311(m)	310(vw)	ν_{19} (b_1)	$\varrho(CF_3)$
334(mp)	334(m)	ν_5 (a_1)	$\varrho(CF_3)$
430(vw)	429(vw)	ν_{24} (b_2)	$\varrho(CF_3)$
515(mp)	514(m)	ν_4 (a_1)	$\delta_{as}(CF_3)$
553(sh)		ν_{18} (b_1)	$\delta_{as}(CF_3)$
	≈560(vw)		
564(m)		ν_{23} (b_2)	$\delta_{as}(CF_3)$
595(mp)	595(m)	ν_9 (a_1)	$\delta(BF_2)$
689(w)	689/691(s)	ν_{16} (b_1)	$\delta_s(CF_3)$
725(vsp)	725(w)	ν_2 (a_1)	$\delta_s(CF_3)$
	880/907(vs)	ν_{20}, ν_{25} (a_1, b_2)	$\nu(BC_2)$, $\nu(BF_2)$
1010(vw)	1011/1038(vs)	ν_7 (a_1)	$\nu(BF_2)$
~1055(w)	~1050(s)	ν_{17}, ν_{10} (b_1, a_2)	$\nu_{as}(CF_3)$
	~1090(vs)	ν_3 (a_1)	$\nu_{as}(CF_3)$
~1095(m)	~1100/1120(vs)	ν_{22} (b_2)	$\nu_{as}(CF_3)$
1319(mp)	1320/1334(s)	ν_{15} (b_1)	$\nu_s(CF_3)$

the vibrational spectra of $K[(CF_3)_2BF_2]$ yielded very similar wave numbers for the fundamentals of the anion [1]. A quadratic local symmetry force field via a normal coordinate analysis has been calculated. The most important force constants are f(B-C) = 3.68×10^2, f(B-F) = 417×10^2 and 4.85×10^2 N/m [6]. ^{19}F NMR of $[(CF_3)_2BF_2]^-$ (in aqueous solution, internal standard CF_3COONH_4, chemical shifts δ refer to the standard $CFCl_3$, negative values of δ means highfield): $\delta(CF_3) = -76.0$ ppm, $\delta(BF_2) = -181.3$ ppm, J(B-F) = 58.3 Hz, J(F-C-B) = 29.6 Hz [1].

Tris(pentafluorophenyl)borane $(C_6F_5)_3B$

Pentafluorophenyldichloroborane $C_6F_5BCl_2$

Lithiumtetrakis(pentafluorophenyl)borate $Li[B(C_6F_5)_4]$

No new syntheses are published for these compounds (see Part 4, p. 118).

During refluxing $(C_6F_5)_3B$ with $(C_6F_5NHBNC_6F_5)_3$ in toluene for 19 h no reaction is observed [10].

Reactions of $C_6F_5BCl_2$

The reaction between $C_6F_5BCl_2$ and $[(CH_3)_3Si]_2NH$ in n-hexane yields 67% $[(CH_3)_3Si]_2NB(C_6F_5)Cl$, boiling point 69 °C/0.001 Torr, ^{11}B NMR ($(C_2H_5)_2O \cdot BF_3$ external standard): $\delta(B) = 41.3$ ppm. Similarly $(CH_3)_3C[(CH_3)_3Si]NB(C_6F_5)Cl$ was obtained from $C_6F_5BCl_2$ and

$(CH_3)_3CNHSi(CH_3)_3$ in 68% yield, boiling point 64°C/0.001 Torr, ^{11}B NMR: $\delta = 38.8$ ppm. The substance 2,4,6-$(CH_3)_3$-$C_6H_2[(CH_3)_3Si]N$-$B(C_6F_5)Cl$ was made from $C_6F_5BCl_2$ and 2,4,6-$(CH_3)_3$-C_6H_2-$NHSi(CH_3)_3$ in 82% yield, boiling point 110 to 112°C/0.001 Torr, ^{11}B NMR: $\delta = 37.3$ ppm. ^1H, ^{19}F NMR and mass spectra were also provided [3].

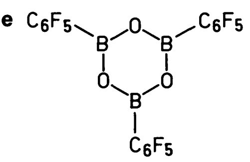
Specific electric resistance ϱ of $Li[B(C_6F_5)_4]$ in dioxalane [13]:

Molal concentration	1.39	0.91	0.69	0.45	0.23
ϱ (Ω·cm)	210	195	207	219	3215

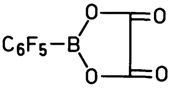
Refluxing a mixture of $C_6F_5BCl_2$ and bis[3-(3-thienyl)-2-thienylammonium]hexachlorostannate(IV) in dry benzene for 36 h gave 4-(pentafluorophenyl)-4,5-borazarobenzo[1,2-b; 4,3-b′]dithiophene [45%, melting point 194.0 to 194.5°C (sublimation)] [11]. On adding a solution of (E)-3-amino-2-[2-(2-thienyl)ethenyl]thiophene in C_6H_6 to a solution of $C_6F_5BCl_2$ in benzene with stirring and cooling the mixture reacted after refluxing for 32 h yielding about 61% 5-(pentafluorophenyl)-6-(2-thienyl)-5,4-borazarobenzo[b]thiophene melting range 161 to 165°C. Similarly methyl (E)-4-amino-5-[2-(2-thienyl)ethenyl]-2-thiophenecarboxylate and $C_6F_5BCl_2$ gave after 24 h an impure sample of methyl-5-(pentafluorophenyl)-6-(2-thienyl)-5,4-borazarobenzo[b]thiophene-2-carboxylate [12].

Lithium-tris(pentafluorophenyl)fluoroborate $Li[B(C_6F_5)_3F]$

Tris(pentafluorophenyl)boroxine



2-Pentafluorophenyl-1,3,2-dioxaborolan-4,5-dione



Poly-o- and Poly-m-carboranylene-perfluorophenylene $\left(CB_{10}H_{10}C\text{-}C_6F_4\right)_n$

A solution of $(C_6F_5)_3B$ in anhydrous dimethoxyethane reacts at reflux temperature (4 d) under an inert atmosphere to give $Li[B(C_6F_5)_3F]$. The specific electric resistance in a 1-molal solution in dimethoxyethane is 180 Ω·cm [13].

The dioxaborolandione is obtained in 95% yield on reacting $C_6F_5BCl_2$ in toluene with waterfree oxalic acid (molar ratio 1:1) at 20°C (66 h stirring). IR: $\nu_s(C{=}O) = 1635$, $\nu_{as}(C{=}O) = 1835\ cm^{-1}$ [2], ^{11}B NMR [external standard: $(C_2H_5)_2O \cdot BF_3$]: $\delta = 26$ ppm, MS: m/e = 266, M^+ (23); 194, $C_6F_5BO^+$ (100); 28, CO^+ (23) [4]. The compound decomposes before reaching sublimation temperature at 130°C. It reacts with pyridine forming an adduct which melts with decomposition at 139°C [2]. It also forms 1:1 adducts with 3,4-dihydroisoquinoline-N-oxide, N-methylbenzaldimine-N-oxide, pyridine-N-oxide and N-phenylsydnone. For physical data, see [4].

The decomposition of the dioxaborolandione (see below) at 130°C (1 h) in toluene yields 97% tris(pentafluorophenyl)boroxine (melting point 282°C). The compound can also be made from $C_6F_5BCl_2$ and H_2O in acetone at −78°C in 55% yield [2]. Reacting a mixture of $C_6F_5B{=}NC(CH_3)_3$ with $(C_6H_5)_2CO$ in $CHCl_3$ at −30°C (24 h) yields $(C_6F_5BO)_3$ [3].

Poly-o- and -m-carboranyleneperfluorophenylenes were prepared by reaction of o- or m-dilithiocarborane with C_6F_6 in refluxing xylene according to:

$$LiCB_{10}H_{10}CLi + C_6F_6 \rightarrow \left(CB_{10}H_{10}C\text{-}C_6F_4\right)_n + 2\,LiF$$

In both cases ether soluble and insoluble materials are obtained. The total yield for m$\left(\nu CB_{10}H_{10}C\text{-}C_6F_4\right)_n$ is 93%. The insoluble part does not melt before 300°C, the soluble between 180 to 240°C. The yield for the o isomer is 75% with the insoluble part not melting before 340°C and the soluble melting between 168 to 242°C. ν(B-H) = 2610; ν(C=C) = 1600 to 1400; ν(C-F) = 1400 to 1000; 723 cm^{-1} (BH skeletal vibration) [5].

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3.3 Perfluorohalogenoorgano Compounds of Aluminium

Pentafluorophenylalane-etherate $C_6F_5AlH_2 \cdot [O(C_2H_5)_2]_n$, n = 1, 2

Pentafluorophenylalane-trimethylamine $C_6F_5AlH_2 \cdot [N(CH_3)_3]_n$, n = 1, 2

Bis(pentafluorophenyl)alane-etherate $(C_6F_5)_2AlH \cdot [O(C_2H_5)_2]_n$, n = 1, 2

Bis(pentafluorophenyl)alane-trimethylamine $(C_6F_5)_2AlH \cdot [N(CH_3)_3]_n$, n = 1, 2

Pentafluorophenylbromoalane-etherate $C_6F_5Al(Br)H \cdot C_2H_5OC_2H_5$

Bis(pentafluorophenyl)chloroalane-etherate $(C_6F_5)_2AlCl \cdot O(C_2H_5)_2$

Bis(pentafluorophenyl)chloroalane-trimethylamine $(C_6F_5)_2AlCl \cdot N(CH_3)_3$

Tris(pentafluorophenyl)alane-etherate $(C_6F_5)_3Al \cdot O(C_2H_5)_2$

Tris(pentafluorophenyl)alane-trimethylamine $(C_6F_5)_3Al \cdot N(CH_3)_3$

Lithiumtetrakis(pentafluorophenyl)alanate-etherate $Li[Al(C_6F_5)_4] \cdot O(C_2H_5)_2$

Lithiumtetrakis(pentafluorophenyl)alanate-trimethylamine $Li[Al(C_6F_5)_4] \cdot N(CH_3)_3$

The preparation of $(C_6F_5)_nAlH_{3-n}$ occurs according to:

$$AlH_{3-n}Cl_n + nC_6F_5Li \rightarrow (C_6F_5)_nAlH_{3-n} + nLiCl$$

Stoichiometrical amounts of C_6F_5Li and $AlH_{3-n}Cl_n$ were reacted at −30°C in ether to yield $(C_6F_5)_nAlH_{3-n}\cdot[O(C_2H_5)_2]_x$ with n = 1, 2 and x = 1, 2. When treating the adducts with $(CH_3)_3N$, ether is replaced and $(C_6F_5)_nAlH_{3-n}\cdot x[N(CH_3)_3]$ is obtained. As a by-product $C_6F_5AlHBr\cdot O(C_2H_5)_2$ is formed from $C_6F_5AlH_2$ and C_4H_9Br (obtained from $C_6F_5Br + C_4H_9Li$) in ether solution [1]. Reacting stoichiometrical amounts of $AlCl_3$ in ether with C_6F_5Li gives $(C_6F_5)_2AlCl\cdot O(C_2H_5)_2$, $(C_6F_5)_3Al\cdot O(C_2H_5)_2$ and $Li[Al(C_6F_5)_4]\cdot O(C_2H_5)_2$. In all compounds ether can be replaced by $(CH_3)_3N$ [2]. No physical data are presented.

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3.4 Perfluorohalogenoorgano Compounds of Gallium

Since Part 4 (see p. 127) appeared, no new results on these gallium compounds were published.

3.5 Perfluorohalogenoorgano Compounds of Indium

Pentafluorodichloroindane-1,4-dioxane $C_6F_5InCl_2\cdot$1,4-dioxane

For preparation and physical properties see Part 4, p. 128/31.

Ether solutions of equimolar amounts of $C_6F_5InCl_2\cdot$1,4-dioxane and the appropriate ligand react at 20°C (5 to 10 min) to give in more than 80% yield the complexes according to the following ligand exchange reaction

$$C_6F_5InCl_2\cdot\text{1,4-dioxane} + L \rightarrow C_6F_5InCl_2L + \text{1,4-dioxane}$$

In the following are given the reactant L, the melting point and ν(In-Cl) (in cm^{-1}) of the reaction product: N,N,N′,N′-tetramethylethylenediamine, 128°C, 317 (m, br), 264 (m, br); 1,2-bis(diphenylphosphino)ethane, ~210°C, 313 (s, br), 304 (m, sh); 2,2′-bipyridyl, 166 to 167°C, 303 (m, br), 277 (m, br); 1,10-phenanthroline, ~145°C, 314 (m, br), 294 (s, br); 2,2′:6′,2″-terpyridyl, >200°C (decomposition), 311 (m, br), 265 (s, br), for the complete list of IR bands see the original paper [1].

Reactions of $C_6F_5InCl_2$-dioxane with pyridine, $(C_6H_5)_3P$ and $(CH_3)_2SO$ cause quantitative rearrangement into $InCl_3$ and $In(C_6F_5)_3$. Mixing solutions of $(C_6F_5)_3In$-1,4-dioxane and quinolin-8-ol in ether and keeping the mixture at 20°C (48 h) pentafluorophenylbisquinolin-8-olatoindium(III) (65%) is obtained. The same product can be made also from $C_6F_5InCl_2$-1,4-dioxane and thallous quinolin-8-olate in $CHCl_3$ at 20°C (2 h) in a quantitative yield. The decomposition temperature is about 240°C. A solution of equimolar amounts of $(C_6F_5)_3In\cdot$1,4-dioxane and quinolin-8-ol in ether gave impure bis(pentafluorophenyl)quinolin-8-olato-indium(III) with a decomposition temperature of ~240°C. IR absorptions are presented [1].

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[1] G. B. Deacon, J. C. Parrot (Australian J. Chem. **27** [1974] 2547/55).

3.6 Perfluorohalogenoorgano Compounds of Thallium

3.6.1 Preparation and Physical Properties

Bis(pentafluorophenyl)thallium hydroxide $(C_6F_5)_2TlOH$

Bis(pentafluorophenyl)thallium nitrate $(C_6F_5)_2TlNO_3$

No new syntheses have been published for these compounds (see Part 4, pp. 131/46). New details on chemical reactions are given in Chapter 3.6.2, p. 37.

Pentafluorophenylthallium(III)bis(trifluoromethanesulfonate) $C_6F_5Tl(OSO_2CF_3)_2$

Bis(pentafluorophenyl)thallium(III)pentafluorophenylbenzoate $(C_6F_5)_2TlOC(O)C_6F_5$

$C_6F_5Tl(OSO_2CF_3)_2$ has been obtained in 67% yield on adding C_6F_6 to a solution of $[CF_3C(O)O]_3Tl$ and CF_3SO_3H in CF_3COOH containing a small amount of water. The reaction mixture was heated under reflux (4 h), then cooled, evaporated to half volume and allowed to stand at 20°C for 12 h. The white precipitate was dried and recrystallized. ^{19}F NMR (negative shifts δ upfield from the internal standard $CFCl_3$): $\delta(CF_3SO_2) = -77.8$, $\delta(F^2,F^6) = -121.6$ (d of d), $\delta(F^3,F^5) = -157.2$ (d of tr), $\delta(F^4) = -147.6$ ppm (d of tr), $J(F^2,F^6\text{-}F^4) = 20$ Hz, $J(F^3,F^5\text{-}F^2) = 20$ Hz, $J(Tl\text{-}F^2,F^6) = 1385$ Hz, $J(Tl\text{-}F^3,F^5) = 787$ Hz, $J(Tl\text{-}F^4) = 179$ Hz [1].

For preparation of $(C_6F_5)_2TlOC(O)C_6F_5$ see Part 4, p. 131. The compound melts at 270 to 271°C (decomposition). ^{19}F NMR (internal standard $CFCl_3$, F atoms attached to the benzoate ring are designated by primes): $\delta(F^2,F^6) = -120.6$ (d of d), $\delta(F^3,F^5) = -160.2$ (d of tr), $\delta(F^4) = -151.7$ ppm (d of tr), $J(Tl\text{-}F^2,F^6) = 967$ Hz, $J(Tl\text{-}F^3,F^5) = 415$ Hz, $J(Tl\text{-}F^4) = 91$ Hz, $\delta(F^{2'},F^{6'}) = -140.7$ (d of d), $\delta(F^{3'},F^{5'}) = -163.1$ (m), $\delta(F^{4'}) = -154.4$ ppm (tr); mass spectrum: m/e = 583, $M^+ - C_6F_5$ (<1); 539, $(C_6F_5)_2Tl^+$ (100); 334, $C_{12}F_{10}^+$ (6) [2].

Bis(pentafluorophenyl)thallium chloride $(C_6F_5)_2TlCl$

Bis(pentafluorophenyl)thallium bromide $(C_6F_5)_2TlBr$

A solution of C_6F_5Li in ether was reacted with anhydrous $TlCl_3$ at −78°C (0.5 h, stirring) to yield 83% $(C_6F_5)_2TlCl$ (see Part 4, p. 131), melting point 220°C [3], 249 to 252°C; IR: $\nu(Tl\text{-}Cl) = 213$, $\delta(Tl\text{-}Cl) = 133\ cm^{-1}$ [10]. ^{19}F NMR [internal standard $CFCl_3$, solvent $(CD_3)_2CO$]: $\delta(F^2,F^6) = -119.4$ (d of d), $\delta(F^3,F^5) = -160.6$ (d of tr), $\delta(F^4) = -152.6$ (d of tr) ppm, $J(Tl\text{-}F^2,F^6) = 812$ Hz, $J(Tl\text{-}F^3,F^5) = 360$ Hz, $J(Tl\text{-}F^4) = 84$ Hz [10].

When a solution of C_2H_5MgBr in ether was filtered into a stirred ether solution of an equimolar amount of C_6F_5Br and heated under reflux for 1 h, C_6F_5MgBr is formed. It reacts with $TlCl_3$ (molar ratio $C_6F_5MgBr/TlCl_3 = 8:3$) to yield 74% $(C_6F_5)_2TlBr$ (see Part 4, p. 131) [2], melting point 224 to 228 [2, 10]; IR: $\nu(Tl\text{-}Br) = 150$, $\delta(Tl\text{-}Br) = 68\ cm^{-1}$ [10]; ^{19}F NMR [internal standard $CFCl_3$, solvent $(CD_3)_2CO$]: $\delta(F^2,F^6) = -119.7$, $\delta(F^3,F^5) = -160.4$, $\delta(F^4) = -152.5$ ppm, $J(Tl\text{-}F^2,F^6) = 780$ Hz, $J(Tl\text{-}F^3,F^5) = 339$ Hz, $J(Tl\text{-}F^4) = 82$ Hz. The change of the ^{19}F NMR spectrum of the bromide in the solvent sequence pyridine, perdeuteroacetone, methanol, and perdeuterodimethylsulfoxide has been discussed [4].

Tris(pentafluorophenyl)thallium $(C_6F_5)_3Tl$

A solution of $(C_6F_5)_2TlOC(O)C_6F_5$ in pyridine was heated in a stream of O_2-free N_2 under reflux (1 h) to give $(C_6F_5)_3Tl\cdot$pyridine as an intermediate. After heating, the pyridine was removed under vacuum and the residue was sublimed in vacuo at 100 to 150°C. Treatment of the sublimate with 1,4-dioxane and recrystallization from 1,4-dioxane gave 60% $(C_6F_5)_3Tl \cdot 1,4$-dioxane (melting point 269 to 276°C) [2]. The decomposition of neat $(C_6F_5)_2TlOC(O)C_6F_5$ under N_2 in absence of a solvent at 310°C (1 h) gave 40% $(C_6F_5)_3Tl \cdot 1,4$-dioxane after treatment as described above, melting range 258 to 263°C [2, 5]. In boiling dry pyridine, $(C_6F_5)_2TlBr$ and $(C_6F_5SO_2)_2Ba$ react after 50 min to give $(C_6F_5)_3Tl$ (66%) (see Part 4, p. 131) as a crude pyridine complex. After recrystallization from dioxane 38% $(C_6F_5)_3Tl \cdot 1,4$-dioxane is obtained [6, 9]. When $(C_6F_5)_2TlBr$ was heated with Cu powder in refluxing 1,4-dioxane (2 h) about 50% $(C_6F_5)_3Tl \cdot 1,4$-dioxane is formed, melting range 260 to 265°C (decomposition) [7, 8]. In boiling ether $(C_6F_5)_2TlBr$ and Cu powder react during 4 h, followed by after addition of dioxane, to 75% $(C_6F_5)_3Tl \cdot 1,4$-dioxane [8]; ^{19}F NMR [internal standard $CFCl_3$, solvent $(CD_3)_2CO$]: $\delta(F^2,F^6) = -118.1$ [4], -118.2 (d of d) [9], $\delta(F^3,F^5) = -159.3$ [4], -161.0 (d of tr) [9], $\delta(F^4) = -151.5$ [4], -154.1 (d of tr) ppm [9], $J(Tl\text{-}F^2,F^6) = 542$ Hz [9], 546 ± 8 Hz (in dioxane) [4], $J(Tl\text{-}F^3,F^5) = 223$ Hz [9], 217 ± 8 Hz (in dioxane) [4], $J(F^4\text{-}Tl) = 51$ Hz [9], 58 ± 1 Hz (in dioxane) [4]; IR: 2990 (w), 2922 (w), 2894 (sh), 2868 (w), 1638 (m), 1611 (w), 1512 (vs), 1471 (vs, br), 1443 (sh), 1376 (sh), 1368 (m), 1360 (m), 1296 (w), 1269 (m), 1259 (m), 1137 (sh), 1126 (sh), 1108 (s), 1087 (vs), 1076 (vs), 1070 (sh), 1055 (sh), 1044 (sh), 1007 (w, br), 960 (vs, br), 895 (m), 861 (vs), 779 (m), 740 (w, br), 718 (w), 610 (m), 606 (m), 581 (w), 485 (w) cm^{-1} [8]. Mass spectrum: m/e = 706, $(C_6F_5)_3Tl^+$; 539 $(C_6F_5)_2Tl^+$; 334, $(C_6F_5)_2^+$; 265, $C_{11}F_7^+$ [8].

Tetrakis(pentafluorophenyl)thalliate(III) $M[Tl(C_6F_5)_4]$

Bis(pentafluorophenyl)-bis(pentachlorophenyl)thalliate(III) $M[Tl(C_6F_5)_2(C_6Cl_5)_2]$

Pentafluorophenyltrichlorothalliate(III) $M[Tl(C_6F_5)Cl_3]$

Tris(pentafluorophenyl)chlorothalliate(III) $M[Tl(C_6F_5)_3Cl]$

Hexakis(pentafluorophenyl)thalliate(III) $M_3[Tl(C_6F_5)_6]$

Chloro-bis[chlorobis(pentafluorophenyl)]dithalliate(III) $M[Cl(C_6F_5)_2TlClTl(C_6F_5)_2Cl]$

Chloro-bis[tris(pentafluorophenyl)]dithalliate(III) $M[(C_6F_5)_3TlClTl(C_6F_5)_3]$

For M see Table 9 and the following paragraph.

In the presence of tetraalkylammoniumbromide, $(C_6F_5)_2TlBr$ or $TlCl_3$ reacts with C_6F_5Li in ether to give $[R_4N][Tl(C_6F_5)_4]$. The reaction is carried out at −78°C under dry N_2. While stirring for 4 h the solution is allowed to warm up to 20°C. The yields are 70 to 90%. On adding $(C_6F_5)_2TlBr$ to a stirred ether solution of C_6Cl_5Li at −15°C in dry N_2 followed by the addition of $[(n\text{-}C_4H_9)_4N]Br$, $[(n\text{-}C_4H_9)_4N][Tl(C_6F_5)_2(C_6Cl_5)_2]$ is produced. In ether solution $[(n\text{-}C_4H_9)_4N][Tl(C_6F_5)_4]$ reacts with $TlCl_3$ at 20°C (40 h, stirring) to form $[(n\text{-}C_4H_9)_4N][(C_6F_5)_3TlClTl(C_6F_5)_3]$ as a precipitate as well as $[(n\text{-}C_4H_9)_4N][Tl(C_6F_5)_3Cl]$ which was isolated from the filtrate [11, 12]. At −78°C $(C_6F_5)_2TlBr$, C_6F_5Li (molar ratio 1:6) and $(n\text{-}C_4H_9)_4NBr$ in ether react on stirring for 1 h, followed by slow warming to 0°C (2 h) to give $[(n\text{-}C_4H_9)_4N]_3[Tl(C_6F_5)_6]$ (44% yield). The reaction of an ether solution of $[(n\text{-}C_4H_9)_4N][Tl(C_6F_5)_4]$ and $(C_6F_5)_2TlCl$ (stirring at 20°C, 6 h) gave $[(n\text{-}C_4H_9)_4N][(C_6F_5)_3TlClTl(C_6F_5)_3]$ (73% yield) [12]. Physical Properties of the complexes are given in **Table 9**.

References p. 39

Table 9
Physical Properties of the Thallium(III) Complexes [11, 12].
Melting point (m.p., dec. = decomposition), molar conductivity Λ (in $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$, $5\cdot 10^{-4}$ M solutions, solvent acetone), IR stretching vibrations ν(Tl-C) and ν(Tl-Cl) (in cm^{-1}).

Compound	m.p. (in °C)	Λ	ν(Tl-C)	ν(Tl-Cl)
$[(n\text{-}C_4H_9)_4N][Tl(C_6F_5)_4]$	127 (dec.)	99	765(s)	–
$[(C_2H_5)_4N][Tl(C_6F_5)_4]$	132 (dec.)	117	762(vs)	–
$[(C_6H_5)_3(C_6H_5CH_2)N][Tl(C_6F_5)_4]$	128	100	765(s)	–
$[(n\text{-}C_4H_9)_4N][Tl(C_6F_5)_2(C_6Cl_5)_2]$	142 (dec.)	85	760(m), 754(m)	–
$[(n\text{-}C_4H_9)_4N][Tl(C_6F_5)_3Cl]$	83	97	790(m), 770(m)	250(m)
$[(C_6H_5)_3C_6H_5CH_2N][Tl(C_6F_5)Cl_3]$	127	127	–	295(s), 280(s)
$[(n\text{-}C_4H_9)_4N][Cl(C_6F_5)_2TlClTl(C_6F_5)_2Cl]$	152	114	790(s), 778(m)	255(m), 201(m)
$[(n\text{-}C_4H_9)_4N][(C_6F_5)_3TlClTl(C_6F_5)_3]$	107	83	775(s), 768(sh)	205(m)
$[(n\text{-}C_4H_9)_4N]_3[Tl(C_6F_5)_6]$	63	288 (in CH_3NO_2)	764(m)	–

3.6.2 Chemical Reactions

3.6.2.1 Reactions of $C_6F_5Tl(OSO_2CF_3)_2$, $(C_6F_5)_2TlOH$, $(C_6F_5)_3Tl$ and $(C_6F_5)_2TlNO_3$

In aqueous solution $(C_6F_5)_2Tl(OSO_2CF_3)_2$ reacts with NaI to yield 67% C_6F_5I. The reaction with $NaOC(O)CH_3$ gives 20% $(C_6F_5)_2TlOC(O)CH_3$, melting point 234°C (decomposition), ^{19}F NMR (negative shifts highfield from the internal standard $CFCl_3$, solvent $CDCl_3$): $\delta(F^2,F^6) = -119.9$ (d of m), $\delta(F^3,F^5) = -159.5$ (d of m), $\delta(F^4) = -151.8$ ppm (d of m), $J(Tl\text{-}F^2,F^6) = 1385$, $J(Tl\text{-}F^3,F^5) = 787$, $J(Tl\text{-}F^4) = 179$ Hz. For ^1H NMR, IR and mass spectra see the original paper [1].

An equimolar mixture of $(C_6F_5)_2TlOH$ and ascorbic acid in pyridine forms $[(C_6F_5)_2Tl]^+[\text{ascorbate}]^-$. The ESR spectrum of the complex is provided [25]. Using this method, two other radical anions are formed with o-benzoquinone and $3\text{-}[(CH_3)_3C]\text{-}5\text{-}[(C_6H_5)_3C]\text{-}1,2\text{-}(HO)_2\text{-}C_6H_2$. ESR data are provided [26].

Reactions of $(C_6F_5)_3Tl\cdot 1,4$-dioxane with 1,3-diphenyltriazene (Hdpt) or 1-phenyl-3-(2′-pyridyl)triazene (Hppt) in refluxing benzene under N_2 results in forming the corresponding tris(triazenido)thallium(III) derivatives $Tl(dpt)_3$ or $Tl(ppt)_3$, and C_6F_5H [27]. Formation constants for the compounds formed from $(C_6F_5)_2TlNO_3$ and the neutral ligands ethylenediamine, hexamethylphosphortriamide, pyridine, $(CH_3)_2SO$, $(CH_3)_2NC(O)H$ and CH_3CN are given [28].

3.6.2.2 Reactions of $(C_6F_5)_2TlX$ (X = Cl, Br)

3.6.2.2.1 Dimerization

The compounds $(C_6F_5)_2TlX$ (X = Cl, Br) are dimerized in benzene. The equilibrium constant K (in dm^3/mol) for the dimerization reaction

$$2\,(C_6F_5)_2TlX \rightleftharpoons [(C_6F_5)_2TlX]_2$$

is $K = 1.5\times10^4$ (concentration c = 0.0116 mol/dm^3, expressed in terms of the monomer concentration), $K = 6.1\times10^2$ (c = 0.0113). In acetone, the compounds are nonelectrolytes and monomeric or very slightly associated [10]. For further information see Part 4, p. 152.

3.6.2.2.2 Reactions with $(C_6H_5)_3PO$, $(C_6H_5)_3P$ and 2,2′-Bipyridyl

Stoichiometric amounts of $(C_6F_5)_2TlX$ and $(C_6H_5)_3PO$ (X = Cl, Br) react in a polar solvent to give the 1:1 complexes $[(C_6F_5)_2(C_6H_5)_3PO]TlCl$ (melting point 221 to 222°C, decomposition) and $[(C_6F_5)_2(C_6H_5)_3PO]TlBr$ (melting point 202 to 203°C, decomposition). $(C_6F_5)TlBr$ and $(C_6H_5)_3P$ (molar ratio 1:1) react in a methanol-water mixture to yield 87% $[(C_6F_5)_2(C_6H_5)_3P]TlBr$ (melting point 135 to 137°C, decomposition). Similarly $(C_6F_5)_2TlX$ and 2,2′-bipyridyl form 1:1 complexes. For X = Cl: 89% yield, melting point 160 to 166°C, single crystals melt at 167 to 168°C; for X = Br 92% yield melting range 174 to 176°C. For equilibrium constants and specific conductivity see the original paper [10].

3.6.2.2.3 Oxidative Addition Reactions

Reactions of $(C_6F_5)_2TlX$ (X = Cl, Br) with metals in low oxidation states give TlX and an organometallic compound containing the metal, in two oxidation states higher. The following examples illustrate this type of reaction. Refluxing of an acetone solution of $(C_6F_5)_2TlCl$ with $SnCl_2$ for 3 h leads to $(C_6F_5)_2SnCl_2$ (see p. 68) [3, 13]. Under similar conditions $Pt[P(C_6H_5)_3]_4$ gave *cis*-$(C_6F_5)_2Pt[P(C_6H_5)_3]_2$, and $ClRh[P(C_6H_5)_3]_2$ yielded $(C_6F_5)_2RhCl[P(C_6H_5)_3]_2$. As many as 15 pentafluorophenylmetal complexes were prepared in a similar manner [13]. Treating $(C_6H_5)_3PAuX$ with $(C_6F_5)_2TlX$ in benzene leads to $(C_6H_5)_2(C_6H_5)_3PAuX$. If X = Br the reaction is carried out at 20°C (2 h); for X = I refluxing for 3 h is necessary. Similarly $(C_6F_5)_2(C_6H_5)_3AsAuCl$ was prepared by refluxing $(C_6F_5)_2TlBr$ and $(C_6H_5)_3AsAuCl$ in benzene for 4 h [14]. Refluxing a solution of ClAu(dpe)AuCl[1] and $(C_6F_5)_2TlBr$ in benzene for 3 h leads to 53% $Cl(C_6F_5)_2Au(dpe)Au(C_6F_5)_2Cl$ [15]. Similarly XAuL and $(C_6F_5)_2TlY$ reacted in boiling benzene under stirring to give $XAu(C_6F_5)_2L$. In the following X, Y, L and reaction conditions are given: Br, Br, $As(C_6H_5)_3$, 2 h; I, I, $As(C_6H_5)_3$ 20°C (1 h); Cl, Br, $P(C_6H_5)_3$ [16]. When to a solution of $[(n\text{-}C_4H_9)_4N][(C_6F_5)AuBr]$ in benzene $(C_6F_5)_2TlBr$ was added and the mixture was stirred for 5 h at 20°C 90% $[(n\text{-}C_4H_9)_4N][(C_6F_5)_3AuBr]$ is obtained [17]. Nickel complexes were made [18] according to:

$$2\,XNiL_3 + (C_6F_5)_2TlBr \rightarrow 2\,XNi(C_6F_5)L_2 + TlBr + 2\,L,$$

$$X = Cl, Br, I;\ L = P(C_6H_5)_3 \text{ and } As(C_6H_5)_3$$

The same products can also be obtained from $XNi(CO)_2[P(C_6H_5)_3]_2$ (X = Cl, Br) [18].

Mixtures of bi- and mononuclear palladium(II) compounds were synthesized by

$$X_2PdL_2 + (C_6F_5)_2TlBr \rightarrow X_2Pd_2(C_6F_5)_2L_2 + XPd(C_6F_5)L_2,$$

$$X = Cl,\ L = P(C_6H_5)_3,\ P(C_6H_5)_2CH_3,\ As(C_6H_5)_3$$

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[1] dpe = 1,2-bis(diphenylphosphino)ethane

No Pd^{IV} complex is formed in this reaction [19]. The conversion of $[Co(diars)_2]Br_2$ into [*trans*-$C_6F_5(Br)Co(diars)_2]Br$ by $(C_6F_5)_2TlBr$ has been mentioned without further information [diars = o-phenylenebis(dimethylarsine)] [20, 21]. Cobalt(II)Schiff base complexes react with $(C_6F_5)_2TlBr$ according to:

$$2\,CoL + (C_6F_5)_2TlBr \rightarrow 2\,(C_6F_5)CoL + TlBr,$$

L = N,N′-ethylenebis(acetylacetonimine) [22, 24], N,N′-ethylenebis(salicylaldimine), N,N′-o-phenylenebis(salicylaldimine) [22].

Trans-$Cl_2Pt[P(C_2H_5)_3]_2$ and *cis*-$Cl(C_6F_5)Pt[P(C_2H_5)_3]_2$ react with $(C_6F_5)_2TlBr$ to give $[Cl_2Pt[P(C_2H_5)_3]_2Tl(C_6F_5)_2Br]$ and $[Cl(C_6F_5)Pt[P(C_2H_5)_3]Tl(C_6F_5)_2Br]$ [23].

3.6.2.2.4 Pentafluorophenylation Reactions

A type of reactions different from those in the preceeding chapter is observed on reacting $XAuP(C_6H_5)_3$ (X = C_6H_5, NO_3, CH_3COO, SCN) with $(C_6F_5)_2TlBr$. In all these cases no oxidative addition but only ligand exchange X for C_6F_5 takes place, according to:

$$XAuP(C_6H_5)_3 + (C_6F_5)_2TlBr \rightarrow C_6F_5AuP(C_6H_5)_3 + C_6F_5Tl(Br)X$$

Refluxing $XAuP(C_6H_5)_3$ and $(C_6F_5)_2TlBr$ in benzene for 3 h (X = C_6H_5), respectively, 1 h (X = NO_3, CH_3COO, SCN) gave $C_6F_5AuP(C_6H_5)_3$. In addition $(C_6F_5)_2TlX$ (X = NO_3, CH_3COO, SCN) and $(C_6H_5)_2TlBr$ were obtained. No reaction occurred between $C_6F_5AuP(C_6H_5)_3$ and $(C_6F_5)_2TlBr$. On refluxing $[(C_6H_5)_3P]_2AuClO_4$ with $(C_6F_5)_2TlBr$ in benzene for 2.5 h, $C_6F_5AuP(C_6H_5)_3$ and $TlClO_4$ are formed [16].

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4 Perfluorohalogenoorgano Compounds of Main Group 4 Elements

4.1 Preliminary Remarks

The compounds of the Main Group 4 elements are covered to the end of 1973 in "Perfluorhalogenorgano-Verbindungen der Hauptgruppenelemente", Part 4, 1975 (cited here as Part 4), for further details see the preface of this Supplement Volume.

4.2 Perfluorohalogenoorgano Compounds of Silicon

4.2.1 Preparation

(Trifluoromethyl)iododifluorosilane CF_3SiF_2I

(Pentafluoroethyl)trifluorosilane $C_2F_5SiF_3$

Tris(pentafluorophenyl)silane $(C_6F_5)_3SiH$

Tetrakis(pentafluorophenyl)silane $(C_6F_5)_4Si$

Hexakis(pentafluorophenyl)disilane $(C_6F_5)_3SiSi(C_6F_5)_3$

Hexakis(pentafluorophenyl)disilylmercury $(C_6F_5)_3SiHgSi(C_6F_5)_3$

Bis(octafluorobiphenyl)silane $(C_{12}F_8)_2Si$

No new syntheses are published for these compounds, for preparation see Part 4, pp. 146/65. New details on physical properties and on chemical reactions are given in the following sections.

2,2-Difluorosilaethylene $F_2C{=}SiH_2$

1,1,2,2-Tetrafluorosilaethylene $F_2C{=}SiF_2$

CNDO/2 calculations have been carried out on unknown compounds with a silicon-carbon double bond, among them $F_2C{=}SiH_2$ and $F_2C{=}SiF_2$. Geometries, charge densities, bond orders [1] and dipole moments are predicted [2].

3,3,3-Trifluoro-1-propynylsilane $CF_3C{\equiv}CSiH_3$

The reaction between $CF_3C{\equiv}CMgI$ and H_3SiBr at 20°C (0.5 h) gives $CF_3C{\equiv}CSiH_3$ in yields of 40 to 60% [18].

Bis(trifluoromethyl)tetrafluorodisiloxane $CF_3SiF_2OSiF_2CF_3$

At 20 °C (5 min) CF_3SiF_2I reacts with HgO in the presence of small amounts of $SbCl_5$ to give 38% $CF_3SiF_2OSiF_2CF_3$ [3].

(Trifluoromethyl)trifluorosilane CF_3SiF_3

(Heptafluoropropyl)trifluorosilane $CF_3CF_2CF_2SiF_3$

(2-Chloro-1,1,2,2-tetrafluoroethyl)trifluorosilane $ClCF_2CF_2SiF_3$

(Pentafluorophenyl)trifluorosilane $C_6F_5SiF_3$

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(Chlorotetrafluorophenyl)trifluorosilane $C_6F_4ClSiF_3$

The fluorination of CF_3SiF_2I with SbF_3 gives CF_3SiF_3 (see Part 4, p. 148). It is also a by-product in the reaction of CF_3SiF_2I with $SbCl_3$. Higher yields ($\gtrsim$90%) are obtained by use of CF_3SiF_2Br. In the presence of Sb_2O_3 or Ag_2CO_3 at 20 °C CF_3SiF_2I decomposes to substantial quantities of CF_3SiF_3 [3]. n-$C_3F_7SiF_3$ was synthesized from n-$C_3F_7SiF_2I$ [4].

Passing $ClCF_2CF_2SiCl_3$ (see Part 4, p. 149) repeatedly in vacuo through a column (20 cm) containing SbF_3 and $SbCl_5$ (5% by weight) gave $ClCF_2CF_2SiF_3$ in 92% yield. The chlorination of $HCF_2CF_2SiF_3$ with Cl_2 in a sealed silica ampule gives on irradiation at 20°C (24 h) the title compound in a quantitative yield [5].

The interaction of C_6F_6 or C_6F_5Cl with $HSiCl_3$, induced by accelerated electrons, at 130 to 150 °C gives a mixture of compounds from which $C_6F_5SiF_3$ or $C_6F_4ClSiF_3$ (unknown constitution) could be isolated [6].

(Trifluoromethyl)chlorodifluorosilane CF_3SiF_2Cl

(Trifluoromethyl)bromodifluorosilane CF_3SiF_2Br

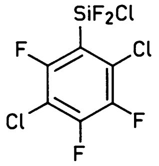
The reaction of CF_3SiF_2I and $SbCl_5$ produces CF_3SiF_2Cl in 52% yield. Similarly, $SbBr_3$ gives CF_3SiF_2Br in a somewhat lower yield [3].

(Pentafluorophenyl)chlorodifluorosilane $C_6F_5SiF_2Cl$

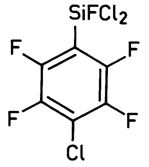
(Chlorotetrafluorophenyl)chlorodifluorosilane $C_6F_4ClSiF_2Cl$

(Pentafluorophenyl)dichlorofluorosilane $C_6F_5SiFCl_2$

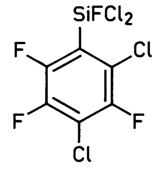
(2,5-Dichloro-3,4,6-trifluorophenyl)chlorodifluorosilane



(4-Chloro-2,3,5,6-tetrafluorophenyl)dichlorofluorosilane and Isomers



(2,4-Dichloro-3,5,6-trifluorophenyl)dichlorofluorosilane



(Tetrafluorophenyl)difluorochlorosilyldichlorofluorosilane $C_6F_4(SiF_2Cl)SiFCl_2$

(Tetrafluorophenyl)bis(dichlorofluorosilane) $C_6F_4(SiFCl_2)_2$

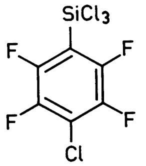
(Tetrafluorophenyl)dichlorofluorosilyltrichlorosilane $C_6F_4(SiFCl_2)SiCl_3$

(Chlorotrifluorophenyl)fluorodichlorosilyltrichlorosilane $C_6F_3Cl(SiFCl_2)SiCl_3$

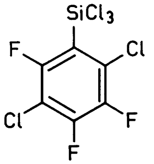
(Dichlorodifluorophenyl)bis(fluorodichlorosilane) $C_6F_2Cl_2(SiFCl_2)_2$

(Pentafluorophenyl)trichlorosilane $C_6F_5SiCl_3$

(4-Chloro-2,3,5,6-tetrafluorophenyl)trichlorosilane and Isomers



(2,5-Dichloro-3,6,6-trifluorophenyl)trichlorosilane



(Tetrafluorophenyl)bis(trichlorosilane) $C_6F_4(SiCl_3)_2$

The fluorochlorosilanes, containing a perfluorinated phenyl group (C_6F_5), are made at 130 to 150 °C in a reaction, induced by accelerated electrons, of C_6F_6 with $SiHCl_3$. The yield of the individual products depends on temperature, molar ratio of the reactants and absorbed dose. Diagrams are pointing out these dependences. Under similar conditions C_6F_5Cl reacts with $HSiCl_3$ to form a mixture from which $C_6F_4ClSiF_{3-n}Cl_n$ ($n = 0, 1, 2, 3$) could be isolated [6].

Silanes of known constitution and containing chlorofluorophenyl groups are synthesized by irradiating a mixture of 1,4-Cl_2-C_6F_4 and $HSiCl_3$ with electrons (1.5 MeV, 60 μA) in a flow system. The yield of 2,5-Cl_2-$C_6F_3SiCl_3$ is 7%. The compounds 4-Cl-$C_6F_4SiCl_3$ and 2,5-Cl_2-$C_6F_3SiCl_2F$ are obtained as a mixture in 40 to 44% yield and similarly 4-Cl-$C_6F_4SiFCl_2$ together with 2,5-Cl_2-$C_6F_3SiF_2Cl$ in 5% yield. An isomeric mixture of $C_6F_3Cl(SiFCl_2)SiCl_3$ plus $C_6F_2Cl_2(SiFCl_2)_2$ is formed in 10 to 13% yield. The yields of monosilyl- and disilyl products were 35 and 8%. The constitution of the disilylated compounds are in all cases unknown [4].

(Trifluoromethyl)pentafluorodisilane $CF_3SiF_2SiF_3$

(Hexafluorodisilyl)difluoromethane $SiF_3CF_2SiF_3$

Both compounds are obtained from iodosilane precursors which are formed in the reaction of SiF_2 with CF_3I (see Part 4, p. 149) [4].

4.2.2 Physical Properties

Physical data for the silanes are collected in **Table 10**, p. 44. Additional investigations are reported below.

Crystal Structure of $(C_6F_5)_4Si$

Single-crystal X-ray data show that the compound forms tetragonal crystals with space group $I4_1/a$-C_{4h}^6 (No. 88). The unit cell with the dimensions $a = 17.165 \pm 0.012$ Å, $c = 8.125 \pm 0.008$ Å contains four molecules, density $D_0 = 2.90$ g/cm^3. Bond distances and angles are presented in [8].

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Table 10

Physical Data for Perfluorohalogenoorganosilanes.

Boiling point (b.p.) in °C/pressure in Torr, melting point (m.p.) in °C, refractive index n_D, density D in g/cm^3, NMR spectrum: chemical shift δ (positive values lowfield from the standard), spin-spin coupling constant J (s = singlet, tr = triplet), IR spectrum in cm^{-1}.

Compound	b.p./Torr (m.p.) in °C	^{1}H and ^{19}F NMR (δ in ppm), IR spectrum (in cm^{-1}), n_D, D
$CF_3C{\equiv}CSiH_3$ [18]	21[5] (−127)	^{1}H NMR[6]: $\delta(SiH_3) = 3.91$; J(H-F) = 1.7 Hz ^{19}F NMR[7]: $\delta(CF_3) = -53.0$ IR (gas)[8]: 2202 (ms), 1268 (vs), 1260 (vs), 1219 (m), 1213 (m), 1176 (vs), 920 (m), 914 (s), 685 (m), 613 (w), 346 (mw), 312 (w), 235 (w)
$CF_3SiF_2OSiF_2CF_3$ [3]	–	^{19}F NMR[1]: $\delta(CF_3) = -66.9$, $\delta(SiF_2) = -148.7$, $J(CF_3\text{-}SiF_2) = 10.9$ Hz, J(^{29}Si-F) = 270.9 Hz IR: 1269 (m), 1224 (m), 1180 (vs), 1129 (vs), 1015 (s), 952 (m), 903 (m), 671 (w), 507 (m)
CF_3SiF_3 [3]	–	^{19}F NMR: $\delta(CF_3) = -66.30$, $\delta(SiF_3) = -150.7$, J(F-F) = 11.0 Hz, J(Si-F) = 273.2 IR: 1251 (w), 1133 (vs), 1023 (s), 866 (m), 730 (vw), 520 (vw), 495 (m), 354 (m)
$CF_3CF_2SiF_3$ [4]	–	^{19}F NMR[1]: $\delta(CF_3) = -86.5$, $\delta(CF_2) = -134.4$, $\delta(SiF_3) = -150.2$, $J(CF_3\text{-}CF_2) = -3.59$ Hz, $J(CF_3\text{-}SiF_3) = -2.81$ Hz, $J(CF_2\text{-}SiF_3) = +4.92$ Hz, J(Si-F) = +275.3 Hz
$CF_3CF_2^aCF_2^bSiF_3$ [4]	–	^{19}F NMR[1]: $\delta(CF_3) = -83.0$, $\delta(CF_2^a) = -127.2$, $\delta(CF_2^b) = -131.3$, $\delta(SiF_3) = -148.8$, $J(CF_3\text{-}CF_2^a) =$ (+0.1 to +0.5) Hz, $J(CF_3\text{-}CF_2^b) = +9.10$ Hz, $J(CF_3\text{-}SiF_3) = -1.76$ Hz, $J(CF_2^a\text{-}CF_2^b) = 0.62$ Hz, $J(CF_2^a\text{-}SiF_3) = -357$ Hz, $J(CF_2^b\text{-}SiF_3) = +4.82$ Hz, J(Si-F) = +275.7 Hz
CF_3SiF_2Cl [3]	–	^{19}F NMR[1]: $\delta(CF_3) = -67.9$, $\delta(SiF_2) = -134.3$, $J(CF_3\text{-}SiF_2) = 8.9$ Hz, J(Si-F) = 303.7 Hz IR: 1245 (m), 1132 (vs), 1007 (s), 919 (s), 748 (w), 624 (s), 443 (m)
CF_3SiF_2Br [3]	–	^{19}F NMR[1]: $\delta(CF_3) = -68.3$, $\delta(SiF_2) = -127.8$, $J(CF_3\text{-}SiF_2) = 8.2$ Hz, J(Si-F) = 321.7 Hz IR: 1234 (m), 1128 (vs), 997 (s), 906 (s), 740 (w), 558 (s), 520 (w), 410 (m)
CF_3SiF_2I [3]	–	^{19}F NMR[1]: $\delta(CF_3) = -69.9$, $\delta(SiF_2) = -120.1$, $J(CF_3\text{-}SiF_2) = 6.9$ Hz, J(Si-F) = 342.4 Hz IR: 1232 (s), 1127 (vs), 989 (m), 896 (s), 742 (w), 539 (m), 505 (m), 403 (m)
$ClCF_2CF_2SiF_3$ [5]	37	^{19}F NMR[2]: $\delta(CF_2Cl) = +7.5$ (tr), $\delta(CF_2) = -48.0$ (tr), $\delta(SiF_3) = -68.8$ (s), $J(CF_2Cl\text{-}CF_2) = 8.7$ Hz

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Table 10 (continued)

Compound	b.p./Torr (m.p.) in °C	^{1}H and ^{19}F NMR (δ in ppm), IR spectrum (in cm^{-1}), n_D, D
$C_6F_5SiF_3$ [6]	—	IR[3)]: 1650 (m), 1524 (s), 1486 (vs), 1400 (w), 1310 (s), 1250 (w), 1110 (vs), 995 (vs), 988 (vs), 912 (s), 518 (m), 444 (s), 408 (w) n_D^{20} = 1.3661, D_{20}^{20} = 1.6315
$C_6F_5SiF_2Cl$ [6]	—	IR[3)]: 1655 (m), 1529 (s), 1487 (vs), 1400 (w), 1310 (s), 1260 (w), 1110 (vs), 995 (s), 985 (vs), 920 (s), 635 (m), 602 (s), 580 (m), 520 (w), 455 (w), 445 (w), 413 (s) n_D^{20} = 1.3831, D_{20}^{20} = 1.6135
$C_6F_5SiFCl_2$ [6]	—	IR[3)]: 1651 (m), 1527 (s), 1487 (vs), 1398 (w), 1308 (w), 1256 (w), 1108 (vs), 986 (vs), 940 (s), 640 (s), 612 (m), 590 (m), 560 (s) n_D^{20} = 1.4168, D_{20}^{20} = 1.6251
$C_6F_5SiCl_3$ [6]	—	IR[3)]: 1650 (m), 1528 (s), 1480 (vs), 1390 (w), 1305 (m), 1250 (w), 1105 (vs), 985 (vs), 635 (s), 610 to 600 (vs, br), 540 (s), 475 (m) n_D^{20} = 1.4663, D_{20}^{20} = 1.6427
$C_6F_4ClSiF_3$[9)] [6]	—	IR[3)]: 1632 (m), 1517 (s), 1490 (s), 1475 (s), 1460 (vs), 1340 (w), 1270 (m), 1108 (s), 993 (vs), 967 (w), 930 (m), 915 (m), 874 (m), 518 (w), 475 (m), 445 (m), 423 (w) n_D^{20} = 1.4065, D_{20}^{20} = 1.6275
$C_6F_4ClSiF_2Cl$[9)] [6]	—	IR[3)]: 1632 (m), 1520 (w), 1490 (vs), 1475 (s), 1458 (vs), 1390 (w), 1360 (w), 1270 (m), 1110 (vs), 982 (vs), 930 (s), 920 (w), 902 (s), 882 (m), 620 (s), 597 (vs), 582 (m), 450 (w), 420 (m) n_D^{20} = 1.4223, D_{20}^{20} = 1.6685
$C_6F_4ClSiFCl_2$[9)] [6]	—	IR[3)]: 1632 (m), 1515 (w), 1490 (s), 1475 (vs), 1457 (vs), 1390 (w), 1367 (w), 1270 (m), 1105 (vs), 972 (s), 932 (s), 920 (s), 890 (m), 660 (w), 637 (vs), 615 (s), 572 (s), 552 (s) n_D^{20} = 1.4495, D_{20}^{20} = 1.6812
$C_6F_4ClSiCl_3$[9)] [6]	—	IR[3)]: 1630 (s), 1610 (w), 1510 (w), 1490 (s), 1470 (vs), 1455 (vs), 1390 (m), 1265 (s), 1100 (vs), 968 (s), 923 (s), 890 (m), 655 (w), 637 (m), 623 (m), 607 (vs, br), 550 (s), 523 (s) n_D^{20} = 1.4901, D_{20}^{20} = 1.7038
4-Cl-C_6F_4-$SiCl_3$ [7]	—	n_D^{20} = 1.4920, D_{20}^{20} = 1.7362
2,5-Cl_2-$C_6F_3SiCl_3$ [7]	—	n_D^{20} = 1.5221, D_{20}^{20} = 1.7603
4-Cl-$C_6F_4SiFCl_2$ [7]	—	n_D^{20} = 1.4690, D_{20}^{20} = 1.6534

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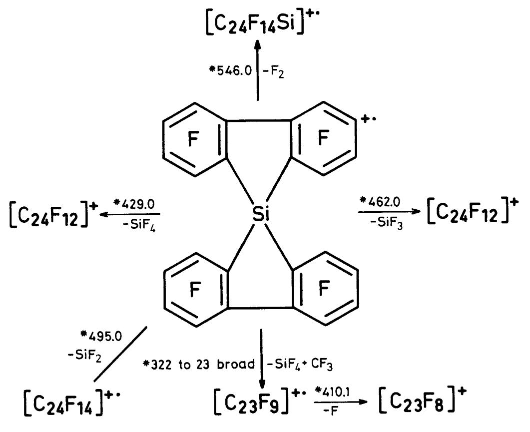
Table 10 (continued)

Compound	b.p./Torr (m.p.) in °C	^1H and ^{19}F NMR (δ in ppm), IR spectrum (in cm^{-1}), n_D, D
2,5-Cl_2-$C_6F_3SiFCl_2$ [7]	–	$n_D^{20} = 1.4987$, $D_{20}^{20} = 1.7289$
2,5-Cl_2-$C_6F_3SiF_2Cl$ [7]	–	$n_D^{20} = 1.4756$, $D_{20}^{20} = 1.6980$
$C_6F_3Cl(SiFCl_2)SiCl_3$ 4) [7]	–	$n_D^{20} = 1.5040$, $D_{20}^{20} = 1.7608$
$C_6F_2Cl_2(SiFCl_2)_2$ 4) [7]	–	$n_D^{20} = 1.5108$, $D_{20}^{20} = 1.7667$
$CF_3SiF_2SiF_3$ [4]	–	^{19}F NMR 1): $\delta(CF_3) = -69.8$, $\delta(SiF_2) = -142.4$, $\delta(SiF_3) = -123.3$, $J(CF_3\text{-}SiF_2) = +6.09$ Hz, $J(CF_3\text{-}SiF_3) = +1.91$ Hz, $J(SiF_2\text{-}SiF_3) = +13.27$ Hz
$SiF_3CF_2SiF_3$ [4]	–	^{19}F NMR: $\delta(SiF_3) = -150.5$, $\delta(CF_2) = -146.6$, $J(SiF_3\text{-}CF_2) = +2.97$ Hz, $J(SiF_3\text{-}SiF_3) = +1.66$ Hz

1) Negative values of chemical shifts upfield from $CFCl_3$. Values for CF_3SiF_2I are for a neat sample referenced to external $CFCl_3$. Values for the other compounds correspond to samples including some CF_3SiF_2I, which was used as an internal reference. — 2) External standard CF_3COOH. — 3) Tentative partial assignments are given in the original paper. — 4) Mixture of isomers. — 5) Extrapolated from log p(Torr) = 6.695 − 1320/T, $\Delta H_v = 25.2 \pm 0.4$ kJ · mol^{-1}, $\Delta H_v/T_s = 91.9$ J · mol^{-1} · K^{-1}. — 6) Internal standard $Si(CH_3)_4$. — 7) Internal standard $CFCl_3$. — 8) The IR spectrum in the solid state and assignments are also reported [18]. — 9) Constitution unknown.

Mass Spectrum of $(C_{12}F_8)_2Si$

The partial mass spectrum is presented as a percentage of total ion current with all isotopic contributions to a particular species. Extensive metastable peaks permit the assignment of the following partial fragmentation scheme [9].



Vibrational and Electronic Spectra. Molecular Constants

In the IR spectrum of $CF_3C{\equiv}CSiH_3$, the fine structure due to overall or unrestricted internal rotation in perpendicular bands associated with motions of the SiH_3 group has been investigated. The following vibrational bands are given: $\nu = 2206.8$ (Si-H stretching), $2\nu = 4342.4$, $\delta = 945.1$ (SiH_3 deformation), $\varrho = 680.5\ cm^{-1}$ (SiH_3 rocking). The rotational constants for the symmetric-top molecule are $A'' = 2.811$ and $B'' = 0.030\ cm^{-1}$. For details see the original paper [10].

From the integral intensity of the Si-H stretching band, the Si-H bond dipole moment for $(C_6F_5)_3SiH$ is calculated to be 0.75 D. With a Si-H bond distance of 1.47 Å a charge on the H atom of -0.11 is obtained. Similar results are found for further tris-substituted silanes and are discussed in respect to the Si-C bond [11]. Similarly, the relation between the integral intensity and the (p-d)π interaction of groups attached to Si with the silicon atom is investigated for a series of organosilicon compounds, among them $(C_6F_5)_3SiH$ [12], see also [13].

The integral intensities of the C-C vibrational bands were measured in the range of 1650 to 1580 cm^{-1} for 15 compounds $C_6F_5MX_3$ (M = Si, C; X = H, F, Cl, OC_2H_5) including $C_6F_5SiF_3$, $C_6F_5SiFCl_2$ and $C_6F_5SiCl_3$. The results indicated a higher polarity of the C_6F_5Si fragment compared with C_6F_5C [14].

UV absorption spectra [wavelength λ in nm (molar absorptivity $\varepsilon \cdot 10^{-3}$)]:

$C_6F_5SiF_3$: $\lambda_{max} = 206$ (6.20), 272 (1.70) [14]
$C_6F_5SiFCl_2$: $\lambda_{max} = 209$ (8.60), 274 (1.65) [14]
$C_6F_5SiCl_3$: $\lambda_{max} = 211$ (11.70), 274 (194) [14]
$(C_6F_5)_3SiH$: λ_{max} (in pentane) = 270; λ_{max} (in CH_2Cl_2) = 270 [15]
$(C_6F_5)_3SiSi(C_6F_5)_3$: λ_{max} (in pentane) = 239 (sh), 273; λ_{max} (in CH_2Cl_2) = 272 [15]
$(C_6F_5)_3SiHgSi(C_6F_5)_3$: λ_{max} (in pentane) = 250; λ_{max} (CH_2Cl_2) = 252 [15]

The longwave absorption bands are associated with the presence of the C_6F_5Si fragment and indicate for $(C_6F_5)_3SiHgSi(C_6F_5)_3$ the presence of intramolecular coordination of ortho-fluorine atoms to the Hg atom [15].

4.2.3 Chemical Reactions

Thermal Stability and Hydrolysis

Heating $ClCF_2CF_2SiF_3$ in a Carius tube at 175 °C (17 h) gives a 98% decomposition forming equimolar amounts of SiF_4 and $F_2C{=}CFCl$. The formation of the carbene $ClCF_2CF$ was demonstrated by heating $ClCF_2CF_2SiF_3$ at 175 °C (24 h) in the presence of excess $(CH_3)_3SiH$. The products obtained were: 99% SiF_4, 6.5% $F_2C{=}CFCl$ and 92% $ClCF_2CHFSi(CH_3)_3$ (boiling point 82 °C) [5]. Each of the compounds CF_3SiF_2X (X = F, Cl, Br) decomposes in the vapor phase at 100 °C rather rapidly with a half-life time less than 0.5 h to form a mixture of C_2F_4, cyclo-C_3F_6 and SiF_3X. No reaction was observed between CF_2 and SiF_3Cl or SiF_3Br. Pyrolysis of CF_3SiF_2I at 100 °C/250 Torr proceeds with a half-life time of 12 min. If the pyrolysis is terminated before complete destruction of CF_3SiF_2I, the colors of the solid products range from orange to brick red. In addition two liquid substances of low volatility colored ruby red and yellow are formed. Among the gaseous products, unreacted CF_3SiF_2I, CF_3SiF_3, Si_2F_6, SiF_3I, and CF_2I_2 in order of decreasing amounts were identified. Complete pyrolysis results in the formation of colored solids and a yellow liquid which were not characterized. Analysis of the gas phase shows the abundance of C_2F_4 and SiF_4 which are decomposition products of CF_3SiF_3 [3].

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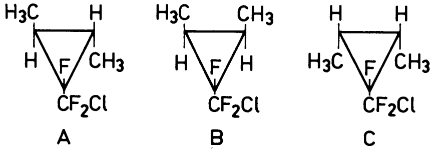
In the gas phase CF_3SiF_2I reacts with water vapor at 20 °C to form in the first step CF_3SiF_2OH and HI. In a secondary reaction CF_3SiF_2OH condenses to $CF_3SiF_2OSiF_2CF_3$ and H_2O. The disiloxane is attacked by water vapor somewhat less rapidly than CF_3SiF_2I forming CF_3SiF_3 and involatile polymeric materials. In the presence of excess HI, CF_3SiF_3 reacts with water vapor to give CF_2HI and SiF_4. Also, CF_3SiF_2Cl and CF_3SiF_2Br behave similarly to CF_3SiF_2I on exposure to water vapor. Hydrolytic attack occurs at the heavier halogen and generates CF_3SiF_3 through the intermediate $(CF_3SiF_2)_2O$. A secondary reaction of CF_2 and HBr leads to CF_2HBr. No CF_2HCl is formed at 25 °C. The hydrolytic reactions studied suggest the rate of attack of water vapor on Si-X bonds follow the order $I > Br > Cl, O > F$. The Si-F bond in CF_3SiF_3 is apparently not directly attacked [3].

Reactions of $(C_6F_5)_3SiH$ with CH_3ONa and CH_3Li

The product isotope effect (PIE), k_{SiH}/k_{SiD}, was measured for nine trisubstituted silanes. For the reaction $(C_6F_5)_3SiH$ plus CH_3ONa in CH_3OH/CH_3OD at 21 °C, PIE was 3.98. A value of 4.03 was obtained when CH_3ONa was replaced by pyridine and a value of 3.70 with a HCl/HDO/CH_3OH/CH_3OD medium was measured. For $(C_6F_5)_3SiH$ the PIE value is smaller than those found for the much less reactive $(p\text{-}Cl\text{-}C_6H_4)_3SiH$ and $(p\text{-}CF_3\text{-}C_6H_4)_3SiH$ [16]. In ether $(C_6F_5)_3SiH$ reacts with CH_3Li at −50°C (1 h) to give, after treatment of the reaction products with CO_2 in H_2O/H^+, 90% C_6F_5COOH [17].

Reactions of $ClCF_2CF_2SiF_3$ with Olefins

Pyrolyses of $ClCF_2CF_2SiF_3$ at 175°C (24 h) in the presence of *trans*-2-butene gave 99% SiF_4, 11% $F_2C{=}CFCl$ and 86% A. The latter is formed by stereospecific addition of the carbene $(CF_2Cl)CF$ to the olefin. However, under the same reaction conditions, reacting the silane with *cis*-2-butene did not result in a stereospecific addition. The products obtained were 99% SiF_4, 18% $F_2C{=}CFCl$, 19% A, 48% B, and 15% C.



A B C

The characterization of the three isomers were carried out by means of ^{19}F NMR spectroscopy. When the silane was heated with allene in a sealed tube at 180°C (17 h) 93% SiF_4, a trace of $F_2C{=}CFCl$ and 92% 1-chlorodifluoromethyl-1-fluoro-2-methylenecyclopropene (boiling point 71°C) are obtained. Heating with $F_2C{=}CF_2$ at 180°C (17 h), SiF_4 and $CF_2{=}CFCl$ (contaminated with a trace of tetrafluoroethylene) are formed quantitatively with some $(CF_2)_x$ also formed [5].

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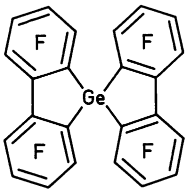
4.3 Perfluorohalogenoorgano Compounds of Germanium

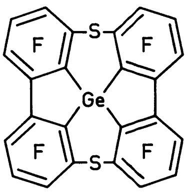
4.3.1 Preparation

Pentafluorophenylgermane $C_6F_5GeH_3$

Bis(octafluorobiphenyl)germane



Bis(2,2'-thiobis-3,4,5-tetrafluorophenyl)germane



Bis[tris(pentafluorophenyl)germanyl]cadmium $(C_6F_5)_3GeCdGe(C_6F_5)_3$

No new syntheses are published for these compounds, for preparation see Part 4, pp. 165/81. New details on physical and on chemical reactions are given in the following sections.

2,2-Difluorogermaethylene $F_2C{=}GeH_2$

1,1,2,2-Tetrafluorogermaethylene $F_2C{=}GeF_2$

CNDO/2 calculations have been carried out on the as yet unprepared compounds $F_2C{=}GeH_2$ and $F_2C{=}GeF_2$. Geometries, charge densities and bond orders are predicted [1]. In addition optimized bond lengths, electron densities, dipole moments, valence of atoms and bond indices are calculated [10].

Trifluoromethylgermane CF_3GeH_3

3,3,3-Trifluoropropynylgermane $CF_3C{\equiv}CGeH_3$

Bis(trifluoromethyl)germane $(CF_3)_2GeH_2$

Tris(trifluoromethyl)germane $(CF_3)_3GeH$

Bis(pentafluorophenyl)germane $(C_6F_5)_2GeH_2$

Tris(pentafluorophenyl)germane $(C_6F_5)_3GeH$

Bis(pentafluorophenyl)chlorogermane $(C_6F_5)_2GeHCl$

Bis(pentafluorophenyl)bromogermane $(C_6F_5)_2GeHBr$

1,1,2,2-Tetrakis(pentafluorophenyl)digermane $(C_6F_5)_2GeHGeH(C_6F_5)_2$

A twofold excess of CF_3Br was reacted with $KGeH_3$ in hexamethylphosphoramide at 0°C (2 min) to give 5% CF_3GeH_3 [20]. At 20°C (0.5 h) GeH_3Cl reacts with $CF_3C{\equiv}CMgI$ in diglyme to give 40 to 60% $CF_3C{\equiv}CGeH_3$ [41]. The reaction of $(CF_3)_3GeI$ and of $(CF_3)_2GeI_2$, dissolved in aqueous HBr, with a solution of $NaBH_4$ in H_2O at 0°C (0.5 h) in a N_2 atmosphere gave 93% $(CF_3)_3GeH$ and 85% $(CF_3)_2GeH_2$, respectively [2].

The reaction of $[(C_2H_5)_3Ge]_2Ge(C_6F_5)_2$ with H_2O at 100°C (1 h) in tetrahydrofuran gave quantitatively $(C_6F_5)_2GeH_2$, which was also obtained from the trigermane and HCl in tetrahydrofuran at 50°C (2 h) in 87% yield. Some $(C_6F_5)_2GeH_2$ is formed on heating the trigermane with CH_3OH in tetrahydrofuran at 50°C for 9 h [3]. In similar reactions, $(C_6F_5)_3GeGe(C_2H_5)_3$ hydrolyzed in tetrahydrofuran at 20°C (15 min) to give 82% $(C_6H_5)_3GeH$, which also is formed quantitatively in the reaction of the digermane with HCl at 20°C (20 min). Reaction of $(C_6F_5)_3GeGe(C_2H_5)_3$ with $CuCl_2$ at 50°C (0.5 h), with AgCl at 100°C (3 h) or with $AuCl_3$ at 100°C (0.75 h) in tetrahydrofuran gave 50, 56 or 46% yields of $(C_6F_5)_3GeH$, respectively [3]. UV irradiation of a degassed solution of $(C_6F_5)_3GeHgPt[P(C_6H_5)_3]_2Ge(C_6F_5)_3$ in toluene at 40 to 50°C (4 h) gave 50% $(C_6F_5)_3GeH$ [4], which is also obtained from this starting compound and HCl in C_6H_6 at 80°C (2 h) in 68% yield. When H_2 is bubbled through a solution of the complex in C_6H_6 at 80°C some $(C_6F_5)_3GeH$ is formed on standing at 20°C for 15 h [4]. $(C_6F_5)_3GeGe(C_6F_5)_3$ reacts in tetrahydrofuran with water, methanol, HCl, CH_3COOH, CF_3COOH at temperatures of 70 to 100°C (0.25 to 1 h) to give 70 to 98% $(C_6F_5)_3GeH$ [5, 8]. With $(C_2H_5)_3SnH$, the digermane forms 84% $(C_6F_5)_3GeH$ at 70°C (8 h) [8]. The compound $[(C_6F_5)_3Ge]_2Hg \cdot M(C_6F_5)_3$ ($M = Tl$, Pr) reacts with HCl in tetrahydrofuran forming $(C_6F_5)_3GeH$ quantitatively for $M = Tl$ [6] and for $M = Pr$ (20°C, 12 h). As a side product $(C_6F_5)_3GeH$ forms in 47% yield in the reaction of the complex with $(C_6F_5)_3GeBr$ in tetrahydrofuran at 20°C [7]. In boiling benzene (17 h), $(C_6F_5)_3GePt[P(C_6H_5)_3]_2H$ is cleaved by HCl to give 64% $(C_6F_5)_3GeH$ [9]. Dry HCl gas reacts with $[(C_6F_5)_3Ge]_2BiC_2H_5$ (dissolved in tetrahydrofuran) at 20°C (20 min) yielding 95% $(C_6F_5)_3GeH$ [17].

The heterocycle $[(C_6F_5)_2Ge]_3Bi_2$ is cleaved by HCl in tetrahydrofuran at 20°C (72 h) to give 95% $(C_6F_5)_2GeHCl$, which was also obtained by the following route [17]:

$$(C_6F_5)_2GeBr_2 + Mg/Hg \xrightarrow[-70\text{ to }+20\,°C]{\text{ether}} [(C_6F_5)_2Ge]_n \xrightarrow[50\,°C]{\text{HCl/THF}} (C_6F_5)_2GeHCl$$

A mixture of $(C_6F_5)_2GeBr_2$ and $(C_6F_5)_2GeH_2$ under Ar reacted at 160 to 165°C (6 h) to yield 74% $(C_6F_5)_2GeHBr$. In hexane $(C_6F_5)_2GeHBr$ and $(C_6F_5)_2Ge(H)Sn(C_2H_5)_3$ reacted at 20°C (30 to 40 h) to give 81% $[(C_6F_5)_2GeH]_2$ [10].

Tris(pentafluorophenyl)germanole $(C_6F_5)_3GeOH$

Hexakis(trifluoromethyl)digermoxane $(CF_3)_3GeOGe(CF_3)_3$

Hexakis(pentafluorophenyl)digermoxane $(C_6F_5)_3GeOGe(C_6F_5)_3$

Tris(pentafluorophenyl)trifluoroacetyloxygermane $(C_6F_5)_3GeOC(O)CF_3$

In a sealed tube $(CF_3)_3GeI$ reacts with excess HgO at 20°C (24 h) to yield $(CF_3)_3GeOGe(CF_3)_3$ quantitatively. Hydrolysis of $(CF_3)_3GeI$ with 3 M hydrochloric acid gave $(CF_3)_3GeOGe(CF_3)_3$ in good yields [2]. A mixture of $(C_6F_5)_3GeGe(C_6F_5)_3$ and H_2O in tetrahydrofuran react on heating to 70°C (0.25 h) to give 95% $(C_6F_5)_3GeOH$ [5, 8]. Heating of neat $(C_6F_5)_3GeOH$ at 140°C (11 h) forms 95% $(C_6F_5)_3GeOGe(C_6F_5)_3$ which is also obtained from $(C_6F_5)_3GeGe(C_6F_5)_3$ and $(CH_3)_3COOH$ at 40°C (23 h) in tetrahydrofuran in 47% yield [8]. The reaction between CF_3COOH and $(C_6F_5)_3GeGe(C_6F_5)_3$ in tetrahydrofuran at 100°C (1 h) gives 65% $(C_6F_5)_3GeOC(O)CF_3$ [5, 8].

Trifluoromethyltrihalogenogermane CF_3GeX_3 (X = Br, I)

Pentafluoroethyltrihalogenogermane $C_2F_5GeX_3$ (X = Br, I)

Bis(trifluoromethyl)dihalogenogermane $(CF_3)_2GeX_2$ (X = Br, I)

Tris(trifluoromethyl)halogenogermane $(CF_3)_3GeX$ (X = F, Cl, Br, I)

At 110°C (18 h) an almost equimolar mixture of $GeBr_4$ and $(CF_3)_2Hg$ reacts in a sealed tube to give 55% CF_3GeBr_3, 22% $(CF_3)_2GeBr_2$ and 18% $(CF_3)_3GeBr$ [12]. With a 2:1 molar ratio of $(CF_3)_2Hg$ to $GeBr_4$ at 150°C (24 h) 65% $(CF_3)_3GeBr$ and 10% $(CF_3)_2GeBr_2$ are obtained. The reaction of $(CF_3)_2Hg$ and $GeBr_4$ in ether at 50°C (7 d) gives only CF_3GeBr_3. Much higher temperatures (195°C) are required for the formation of $C_2F_5GeBr_3$ (45% yield) from $(C_2F_5)_2Hg$ and $GeBr_4$. The reaction of GeI_4 with $(CF_3)_2Hg$ (molar ratio based on GeI_4) at 120°C (120 h) in a sealed tube gave the following product distribution (yields in %) [2]:

Molar ratio	CF_3GeI_3	$(CF_3)_2GeI_2$	$(CF_3)_3GeI$	$(CF_3)_3GeF$	$(CF_3)_4Ge$ [b]
0.55	90	5	–	–	–
0.98	13	53	16	–	–
1.72	–	–	72	–	22
2.0	–	–	72	11 [a]	15

[a] The mechanism for the formation of $(CF_3)_3GeF$ has not been elucidated. – [b] For $(CF_3)_4Ge$, see p. 53.

$(C_2H_5)_2Hg$ and GeI_4 gave at 135°C (21 d) as the only product $C_2F_5GeI_3$ in 53% yield. At 155°C $(CF_3)_3GeI$ undergoes a redistribution reaction into $(CF_3)_2GeI_2$ and $(CF_3)_4Ge$ [2]. During direct fluorination of $Ge(CH_3)_4$ (see p. 53) some $(CF_3)_3GeF$ is formed [19]. When a large excess of AgBr was reacted with $(CF_3)_3GeI$ at 20°C (24 h) 95% of $(CF_3)_3GeBr$ was obtained. Similar reactions of $(CF_3)_3GeI$ with excess AgCl and AgF gave $(CF_3)_3GeCl$ and $(CF_3)_3GeF$ in 92 and 73% yield [2].

Pentafluorophenyltrihalogenogermane $C_6F_5GeX_3$ (X = Cl, Br)

Pentafluorophenyldichlorobromogermane $C_6F_5GeCl_2Br$

Pentafluorophenylchlorodibromogermane $C_6F_5GeClBr_2$

Bis(pentafluorophenyl)dihalogenogermane $(C_6F_5)_2GeX_2$ (X = Cl, Br)

Tris(pentafluorophenyl)halogenogermane $(C_6F_5)_3GeX$ (X = F, Cl, Br)

1,1,1-Tris(pentafluorophenyl)-2,2,2-trichlorodigermane $(C_6F_5)_3GeGeCl_3$

Poly[tris(pentafluorophenyl)germylgermanium(II) fluoride $[(C_6F_5)_3GeGeF]_n$

1,1,1,3,3,3-Hexakis(pentafluorophenyl)-2,2-difluorotrigermane $(C_6F_5)_3GeGeF_2Ge(C_6F_5)_3$

(Trifluoromethyl)fluorogermanates $M'_2[(CF_3)_nGeF_{6-n}]$ (n = 1, M' = Na, NH_4; n = 2, M' = Na, K, NH_4) and $M[(CF_3)_3GeF_2]$ (M = NH_4, Na)

A solution of $GeCl_4$ in C_6H_6 was added to an etheric solution of C_6F_5MgBr. The ether was driven off and replaced by more C_6F_6. The mixture was refluxed for 10 h giving 14% $C_6F_5GeCl_3$, 18% $C_6F_5GeCl_2Br$, 17% $C_6F_5GeClBr_2$ and 51% $C_6F_5GeBr_3$. Additionally, $(C_6F_5)_2GeBr_2$ and $(C_6F_5)_3GeBr$ were identified as well [13]. When Br_2 was added to a solution of $(C_6F_5)_3GeBi(C_2H_5)_2$ in benzene 94% $(C_6F_5)_3GeBr$ are formed [17]. The reaction of $[(C_6F_5)_3Ge]_2Hg \cdot (C_6F_5)_3GeTl$ and $HgCl_2$ in tetrahydrofuran gives at 20°C (10 min) 90% $(C_6F_5)_3GeCl$ [6]. Similarly $[(C_6F_5)_3Ge]_2Pr \cdot Hg[Ge(C_6F_5)_3]_2$, dissolved in tetrahydrofuran, reacted with HCl at 20°C (12 h) with subsequent heating at 70°C (2 h) to yield 95.8% $(C_6F_5)_3GeCl$ [7]. The Ge-Ge bond in $(C_6F_5)_3GeGe(C_2H_5)_3$ is cleaved by $BiCl_3$ in tetrahydrofuran at 100°C (1 h) to produce 83% $(C_6F_5)_3GeCl$ [5]. Similarly, $HgCl_2$ decomposes $(C_6F_5)_3GeGe(C_6F_5)_3$ in tetrahydrofuran at 70°C (1 h) to form 99% $(C_6F_5)_3GeCl$ [5, 8]. Analogous reactions are observed between $(C_6F_5)_3GeGe(C_6F_5)_3$ and $CuCl_2$ (100°C, 0.75 h), C_2H_5HgCl (70°C, 0.5 h), $ZnCl_2 + I_2$ (100°C, 6 h), $GeCl_4$ (100°C, 1 h) to give $(C_6F_5)_3GeCl$ in yields of 97, 63, 84 and 126%, respectively. The reaction with $GeCl_4$ also leads to the formation of $(C_6F_5)_3GeGeCl_3$ in 33% yield [8]. In benzene solution, $(C_6F_5)_3GeHgPt[P(C_6H_5)_3]_2Ge(C_6F_5)_3$ forms with HCl at 80°C (2 h) 68% $(C_6F_5)_3GeCl$ and with Br_2 at 20°C (5 min) 98% $(C_6F_5)_3GeBr$ [4]. In C_6H_6 at 20°C $(C_6F_5)_3GePt[P(C_6H_5)_2]_2H$ reacts with Br_2 to yield 74% $(C_6F_5)_3GeBr$ [9]. Heating a benzene solution of $[(C_6F_5)_3Ge]_2Hg$ with I_2 at 60°C (1.5 h) results in the formation of 31% $(C_6F_5)_3GeI$ [13].

In the reaction of GeF_2 and $(C_6F_5)_3GeGe(C_2H_5)_3$ at 100°C (2 h) in tetrahydrofuran an amorphous solid (decomposing on fusion) was isolated and shown to be $[(C_6F_5)_3GeGeF]_n$ (no physical data). Similarly equimolar amounts of GeF_2 and $(C_6F_5)_3GeGe(C_6F_5)_3$ in tetrahydrofuran reacted at 100°C (5 h), then left at 20°C (10 h), to yield 37% $(C_6F_5)_3GeGeF_2Ge(C_6F_5)_3$. The insoluble amorphous solid consisted of a mixture of $(C_6F_5)_3GeF$ and $[(C_6F_5)_3GeGeF]_n$ in 43% yield [15].

In aqueous solution $(CF_3)_nGeX_{4-n}$ reacts [14] with M′F according to:

$$(CF_3)_nGeX_{4-n} + M'F \rightarrow M'_2[(CF_3)_nGeF_{6-n}]$$
$$(M' = Na, NH_4 \text{ for } n = 1;\ M' = Na, K, NH_4 \text{ for } n = 2)$$

and with MF according to:

$$(CF_3)_3GeX + MF \rightarrow M[(CF_3)_3GeF_2]\ (M = NH_4, Na;\ X = F, Cl, Br, I)$$

For n = 2 and M′ = K the *trans*-isomer was shown by ^{19}F NMR spectroscopy to have a yield of 90%. The *cis*-compound $K_2[(CF_3)_2GeF_4]$ is less soluble in water and was isolated. Its nature was characterized by an X-ray structure determination. When $(CF_3)_4Ge$ is dissolved in a saturated NH_4F solution mainly $[(CF_3)_3GeF_2]NH_4$ is formed [14], for the ^{19}F NMR data of the anions see Table 11, p. 61.

Bis[tris(pentafluorophenyl)germyl] sulfide $[(C_6F_5)_3Ge]_2S$

Bis[tris(pentafluorophenyl)germyl] selenide $[(C_6F_5)_3Ge]_2Se$

Shaking a mixture of $(C_6F_5)_3GeGe(C_6F_5)_3$ and sulfur or selenium in tetrahydrofuran at 60°C (3 h) or 100°C (5 h) gives 52% $[(C_6F_5)_3Ge]_2S$ or 41% $[(C_6F_5)_3Ge]_2Se$, respectively [5, 8].

Tetrakis(trifluoromethyl)germane $(CF_3)_4Ge$

A most convenient preparation of $(CF_3)_4Ge$ (43% yield) at ambient temperature is the reaction of $(CF_3)_2Cd \cdot CH_3OCH_2CH_2OCH_3$ with GeI_4 in 1,2-dibromoethane [42].

A small excess of $GeBr_4$ reacted with $Hg(CF_3)_2$ at 110°C (18 h) forms 4% $(CF_3)_4Ge$. In a 1:2 molar ratio, $GeBr_4$ and $Hg(CF_3)_2$ reacted at 150°C (24 h) to yield 20% $(CF_3)_4Ge$. On recycling the less substituted products with more $Hg(CF_3)_2$ the yield of $(CF_3)_4Ge$ increases to 40%. For the reaction GeI_4 and $Hg(CF_3)_2$ at 120°C (120 h) see p. 51 [2]. For the preparation of $(CF_3)_4Ge$ in the plasma-initiated reaction of CF_3 radicals (from C_2F_6) with $GeBr_4$, as already described in Part 4, p. 168, see also [21]. The direct fluorination of $Ge(CH_3)_4$ by He-diluted F_2 at −100 to −60°C gave only 1 to 6% $Ge(CF_3)_4$. When the temperature was raised from −100 to −20°C 66% $Ge(CF_3)_4$ are obtained [19].

Hexakis(trifluoromethyl)digermane $(CF_3)_3GeGe(CF_3)_3$

Hexakis(pentafluorophenyl)digermane $(C_6F_5)_3GeGe(C_6F_5)_3$

Bis[tris(pentafluorophenyl)germyl]mercury $[(C_6F_5)_3Ge]_2Hg$

Tris[tris(pentafluorophenyl)germyl]praseodymium-bis[tris(pentafluorophenyl)germyl]mercury $[(C_6F_5)_3Ge]_3Pr \cdot Hg[Ge(C_6F_5)_3]_2$

Bis[tris(pentafluorophenyl)germyl]praseodymium halides $[(C_6F_5)_3Ge]_2PrX$ (X = Cl, Br)

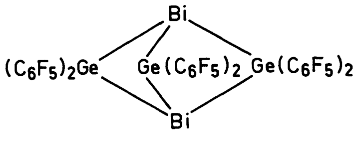
Tris(pentafluorophenyl)germylthallium-bis[tris(pentafluorophenyl)germyl]mercury $(C_6F_5)_3GeTl \cdot Hg[Ge(C_6F_5)_3]_2$

Tris[bis(pentafluorophenyl)germyl]dibismutane $[(C_6F_5)_2Ge]_3Bi_2$

The reaction between $(CF_3)_3GeI$ and sodium amalgam (0.5% Na) at 20°C (72 h) gave 60% $(CF_3)_3GeGe(CF_3)_3$ [2]. Photolysis of $(C_6F_5)_3GeHgPt[P(C_6H_5)_3]_2Ge(C_6F_5)_3$, dissolved in toluene, at 40 to 50°C (4 h) gave only a yield of 3% [4]. The condensation of $(C_6F_5)_3GeBr$ in ether with lithium amalgam at 20°C (50 min) provided 89% $(C_6F_5)_3GeGe(C_6F_5)_3$ [8]. In tetrahydrofuran $(C_6F_5)_3GeGe(C_2H_5)_3$ reacted at 20°C (2 to 3 min) with $(C_6F_5)_3GeBr$ to form 66% digermane. While $(C_6F_5)_3GeGe(C_2H_5)_3$ in tetrahydrofuran reacts with $CuCl_2$ at 20°C (0.5 h) to give 20% $(C_6F_5)_3GeGe(C_6F_5)_3$, the reaction with $HgCl_2$ at 20°C (3 h) leads to the formation of 72% $[(C_6F_5)_3Ge]_2Hg$ [3]. At 130°C (3.5 h) $(C_6F_5)_3GeBr$ reacts with $Bi(C_2H_5)_3$ to form 54% $(C_6F_5)_3GeGe(C_6F_5)_3$ [7].

A mixture of $[(C_6F_5)_3Ge]_2Hg$ and finely divided praseodymium was shaken at 20°C (50 h). From the resulting green solution 85.8% $[(C_6F_5)_3Ge]_2Hg \cdot Pr[Ge(C_6F_5)_3]_3$ was isolated. Treating this complex in tetrahydrofuran at 20°C (12 or 1 h) with HCl or with $(C_6F_5)_3GeBr$ gives 70% $[(C_6F_5)_3Ge]_2PrCl$ or 70% $[(C_6F_5)_3Ge]_2PrBr$ together with 83.5% $(C_6F_5)_3GeGe(C_6F_5)_3$ [7].

A solution of $[(C_6F_5)_3Ge]_2Hg$ in dimethoxyethane was added to finely divided thallium. After shaking the mixture at 90°C for 5 h 84.5% $(C_6F_5)_3GeTl \cdot Hg[Ge(C_6F_5)_3]_2$ is obtained. The thallium complex reacts in tetrahydrofuran with HCl at 20°C (immediately) and with $HgCl_2$ at 20°C (10 min) to give $(C_6F_5)_3GeHgGe(C_6F_5)_3$ (about 95% yield). The reaction of the complex with $(C_6F_5)_3GeBr$ at 20°C (12 h) yields 81% $(C_6F_5)_3GeGe(C_6F_5)_3$ [6]. When $(C_6F_5)_3GeBr$ was heated with $Bi(C_2H_5)_3$ at 130°C (3.5 h) 54% $(C_6F_5)_3GeGe(C_6F_5)_3$ was obtained [17]. A mixture of Hg and $(C_6F_5)_3GeBi(C_2H_5)_3$ in tetrahydrofuran was shaken at 20°C (6 d) to form 61% $[(C_6F_5)_3Ge]_2Hg$ [17]. The reaction of $(C_6F_5)_2GeH_2$ with $Bi(C_2H_5)_3$ in toluene at 110°C (4 h) leads not to the formation of $[(C_6F_5)_2GeBi(C_2H_5)_2]_2$ [17] but forms 59% $[(C_6F_5)_2Ge]_3Bi_2$ with the following structure as was shown by X-ray analysis [18]:



4.3.2 Physical Properties

Physical data for the germanium compounds are collected in **Table 16**, p. 60. Additional investigations are reported below.

4.3.2.1 Crystal Structure

Single crystal X-ray investigations gave the following results:

$K_2[cis\text{-}(CF_3)_2GeF_4]$ forms orthorhombic crystals with space group Ibca-D_{2h}^{27} (No. 73). The unit cell with the dimensions a = 17.815(2) Å, b = 11.474(1) Å, c = 8.4782(6) Å contains eight molecules, density D = 2.80 g · cm^{-3}. Bond distances and angles are presented in [14].

Table 11

Fundamental Vibrations ν_i of $(CF_3)_3GeX$ (X = F, Cl, Br, I) [27].

Symmetry group A_1, A_2 and E, with activity of the vibration in the IR and Raman spectrum in parentheses, ν, δ, ϱ and τ are stretching, deformation, rocking and torsion vibrations, s and as mean symmetric and antisymmetric, respectively.

		$(CF_3)_3GeF$	$(CF_3)_3GeCl$	$(CF_3)_3GeBr$	$(CF_3)_3GeI$	Approximate description
A_1	ν_1	1 160[1]	1 153[1]	1 150[1]	1 143[1]	$\nu_{as}(CF_3)$
(Ra/IR)	ν_2	1 198	1 196	1 192	1 189	$\nu_s(CF_3)$
	ν_3	528	527	528	528	$\delta_{as}(CF_3)$
	ν_4	725	736	736	735	$\delta_s(CF_3)$
	ν_5	302	289	255[1]	245[1]	$\varrho(CF_3)$
	ν_6	237[1]	238[1]	232[1]	344	$\nu(GeC_3)$
	ν_7	741	465	367	206[1]	$\nu(GeX)$
	ν_8	80[2]	82[1]	82[2]	80[1]	$\delta(GeC_3)$
A_2	ν_9	1 145[2]	1 138	1 137[2]	1 135[2]	$\nu_{as}(CF_3)$
(−)	ν_{10}	525[2]	522[2]	522[2]	522[2]	$\delta_{as}(CF_3)$
	ν_{11}	223[2]	223[2]	223[2]	223[2]	$\varrho(CF_3)$
	ν_{12}	—	—	—	—	τ
E	ν_{13}	1 132	1 131	1 129	1 128	$\nu_{as}(CF_3)$
(Ra/IR)	ν_{14}	1 176	1 178[1]	1 167	1 164	$\nu_{as}(CF_3)$
	ν_{15}	1 180[1]	1 178	1 175[1]	1 170[1]	$\nu_s(CF_3)$
	ν_{16}	528	527	528	528	$\delta_{as}(CF_3)$
	ν_{17}	528	527	528	528	$\delta_{as}(CF_3)$
	ν_{18}	736[2]	736	736	735	$\delta_s(CF_3)$
	ν_{19}	232	224[1]	222[1]	218[1]	$\varrho(CF_3)$
	ν_{20}	250	251[1]	255[1]	254[1]	$\varrho(CF_3)$
	ν_{21}	360	353	351	347[1]	$\nu(GeC_3)$
	ν_{22}	70[1]	70[1]	68[1]	65[1]	$\delta(GeC_3)$
	ν_{23}	143[1]	110[1]	89[1]	80[1]	$\delta(XGeC)$
	ν_{24}	—	—	—	—	τ

[1] Liquid phase. — [2] Calculated values.

$(C_6F_5)_3GeHgGe(C_6F_5)_3$ forms orthorhombic crystals with space group Pbcn-D_{2h}^{14} (No. 60). The unit cell with the dimensions a = 17.77(2) Å, b = 12.653(7) Å, c = 16.897(8) Å contains four molecules, density D = 2.36 g · cm^{-3}. Bond distances and angles are given in [24].

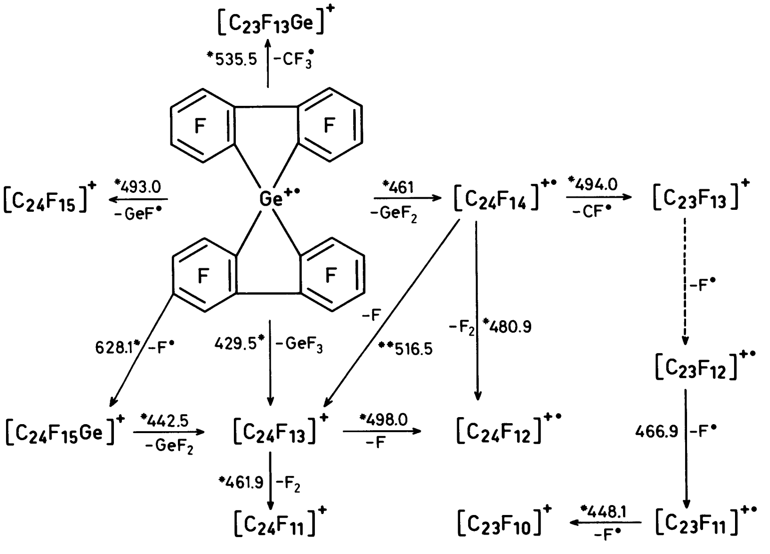
$[(C_6F_5)_2Ge]_3Bi_2$ forms (at −120 °C) monoclinic crystals with space group C2/c-C_{2h}^{6} (No. 15). The unit cell with the dimensions a = 41.561(7) Å, b = 8.492(2) Å, c = 23.320(8) Å contains eight molecules, density D_0 = 2.63 g · cm^{-3}, pycnometric density D = 2.55 g · cm^{-3}. Bond distances and angles of the heteroelement framework are given in the original paper [18].

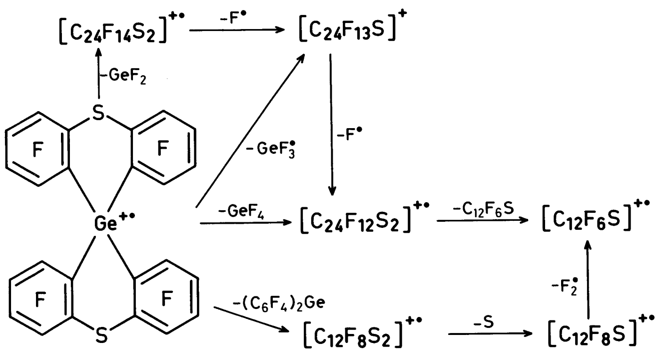
4.3.2.2 Mass Spectrum of $(C_{12}F_8)_2Ge$ and $(C_{12}F_8S)_2Ge$

Fragmentation and rearrangement processes found in the mass spectra of $(C_{12}F_8)_2Ge$ and $(C_{12}F_8S)_2Ge$ are presented in [25]. The partial mass spectra of these compounds are shown in tables in the original reference [25]. Extensive metastable peaks for $(C_{12}F_8)_2Ge$

References p. 65

permit this assignment of partial fragmentation schemes, see below. Although no metastable ions were observed for $(C_{12}F_8S)_2Ge$, a tentative fragmentation scheme, see below, was suggested [25].





4.3.2.3 Molecular Structures, Rotational and Vibrational Spectra

Hydrides

In the IR spectrum of $CF_3C{\equiv}CGeH_3$ (D_3 symmetry), the fine structure, due to overall or unrestricted internal rotation in perpendicular bonds associated with motions of the GeH_3 group, has been investigated. The IR bands were assigned as follows: ν = 2131.6 (Ge-H stretching), 2ν = 4195.3, δ = 882.0 (GeH_3 deformation), δ = 622.7 (GeD_3 deformation), ϱ = 626.6 (GeH_3 rocking). The rotational constants (in cm^{-1}) for the symmetric top molecules in the vibrational ground state are A'' = 2.750, B'' = 0.018 for $CF_3C{\equiv}CGeH_3$ and A'' = 1.375, B'' = 0.016 for $CF_3C{\equiv}CGeD_3$. For details see the original paper [31].

Microwave spectra of five isotopic species of CF_3GeH_3 have been investigated in the region 15000 to 31000 MHz. The height of the potential barrier hindering the internal rotation equals 1250 ± 150 cal · mol^{-1} [20].

From the integral intensity (A) of the Si-H stretching band in IR spectra of 30 R_3GeH and 20 R_2GeH_2 compounds a correlation between $A^{1/2}$ and the sum of inductive Taft ($\Sigma\sigma^*$) constants of the substituents R was established. As stretching frequency is taken for $(C_6F_5)_3GeH$ ν(Ge-H) = 2150 cm^{-1} [33], and for $(C_6F_5)_2GeH_2$ ν(Ge-H) = 2140 cm^{-1} [34]. In an earlier work the equation $\nu = 23\,\Sigma\sigma^* + 2015$ was found for R_3GeH compounds [35].

Halides

The vibrational spectra of CF_3GeX_3 and $(CF_3)_2GeX_2$ (X = F, Cl, Br, I) were published in Part 4, pp. 171/3 as private communications. The full papers have appeared by now [27, 28].

The gase phase IR and liquid phase Raman spectra of $(CF_3)_3GeX$ (X = F, Cl, Br, I) are reported in [27]. The solid phase Raman spectrum of $(CF_3)_3GeF$ is interpreted assuming a dimeric structure with Ge-F-Ge bonds. The assignment of the bands to the molecular vibrations bases on the assumption of C_{3v} molecular symmetry. A normal coordinate analysis has been performed, for details see the original reference [27]. In **Table 11**, p. 55, are reported the observed and calculated frequencies, in **Table 13**, p. 58, the force constants for these molecules.

Table 12
Observed Fundamental Vibrations of $(CF_3)_4Ge$ (in cm^{-1}) [30].
For abbreviations see Table 11, p. 55.

IR (gas)	Raman (liquid)	Assignment and approximate description	
	66 m	ν_8 (e)	ν(Ge-C_4)
78 w-m		ν_{19} (f_2)	δ(Ge-C_4)
		ν_{11} (f_1) ~225[a)]	$\varrho(CF_3)$
	232 vs, p	ν_3 (a_1)	ν(Ge-C)
244 w	247 m-s	ν_{17} (f_2)	$\varrho(CF_3)$
	225 m	ν_7 (e)	$\varrho(CF_3)$
359 vs	359	ν_{18} (f_2)	ν(Ge-C)
528 m	528 w	ν_6 (e), ν_{15} (f_2)	$\delta_{as}(CF_3)$
	733 s, p	ν_2 (a_1)	$\delta_s(CF_3)$
737 s		ν_{16} (f_2)	$\delta_s(CF_3)$
1125 m-s		ν_9 (f_1)	$\nu_{as}(CF_3)$
	1144 w	ν_5 (e)	$\nu_{as}(CF_3)$
1174 vs	1158 w	ν_{15} (f_2)	$\delta_{as}(CF_3)$
	1190 w	ν_{14} (f_2)	$\nu_s(CF_3)$
	1208 vw p	ν_1 (a_1)	$\nu_s(CF_3)$

[a)] Derived from combination band.

Table 13
Force Constants (in N · cm^{-1}) of $(CF_3)_4Ge$, $(CF_3)_6Ge_2$ and $(CF_3)_3GeX$ (X = F, Cl, Br, I). Internuclear distances r = r(C-F), s = r(Ge-C), t = Ge-X.

Compound	f_r	f_{rr}	f_s	f_{ss}	f_t	f_{tt}	f_{st}	Ref.
$(CF_3)_4Ge$	5.86	0.96	2.30	0.11	–	–	–	[30]
$(CF_3)_6Ge_2$	5.83	0.93	2.29	0.16	1.62	–	0.00	[30]
$(CF_3)_3GeF$	5.84	0.88	2.40	0.10	4.73	–	0.12	[29]
$(CF_3)_3GeCl$	5.80	0.88	2.31	0.13	2.90	–	0.09	[29]
$(CF_3)_3GeBr$	5.78	0.87	2.29	0.14	2.21	–	0.08	[29]
$(CF_3)_3GeI$	5.75	0.86	2.23	0.15	1.83	–	0.07	[29]

$(CF_3)_4Ge$ and $(CF_3)_3GeGe(CF_3)_2$

Electron diffraction investigations of $(CF_3)_4Ge$ yield the following internuclear distances r (in Å) and angles α: r(C-F) = 1.330 ± 0.002, r(Ge-C) = 1.989 ± 0.005, α(FCF) = 108.9° ± 0.3°. CNDO/2 calculations agree very well with these results [26]. The gas phase IR and liquid phase Raman spectra of $(CF_3)_4Ge$ and $(CF_3)_6Ge_2$ (additionally the solid phase Raman spectrum) are reported and assigned to T_d and D_{3d} symmetry, respectively. A normal coordinate analysis has been performed and force constants as well as frequencies of inactive vibrations have been obtained [30]. The observed fundamental bands and their assignment to the molecular vibrations are given in **Table 12**, p. 57, and **Table 14**. For observed overtones and combination bands as well as for a full set of the fundamentals and the potential energy distribution, see the original paper [30]. The calculated force constants are covered in Table 13.

Table 14
Observed Fundamental Vibrations of $(CF_3)_6Ge_2$ (in cm^{-1}) [30].
For abbreviations see Table 11, p. 55.

IR (gas)	Raman (liquid)	Raman (solid)	Assignment and approximate description	
	67 p?	66 m-s	ν_7 (a_{1g}), ν_{22} (e_g)	$\delta(\text{Ge-C}_3)$
80 s			ν_{47} (e_u)	$\varrho(\text{Ge-C}_3)$
	80	81 m-s	ν_{23} (e_g)	$\varrho(\text{Ge-C}_3)$
	178 p	178 vs	ν_8 (a_{1g})	$\nu(\text{Ge-Ge})$
	228	228 m	ν_{19} (e_g)	$\varrho(\text{CF}_3)$
	244 p	245 s	ν_5 (a_{1g})	$\varrho(\text{CF}_3)$
	255	255 m	ν_{20} (e_g)	$\varrho(\text{CF}_3)$
302 s			ν_{34} (a_{2u})	$\varrho(\text{CF}_3)$
342 s			ν_{45} (e_u)	$\nu(\text{Ge-C})$
	348	348 w	ν_{21} (e_g)	$\nu(\text{Ge-C})$
	373 p	373 w	ν_6 (a_{1g})	$\nu(\text{Ge-C})$

Table 14 (continued)

IR (gas)	Raman (liquid)	Raman (solid)	Assignment and approximate description	
527 w			ν_{32} (a_{2u}), ν_{40} (e_u), ν_{41} (e_u)	$\delta_{as}(CF_3)$
	529	526 w	ν_3 (a_{1g}), ν_{16} (e_g), ν_{17} (e_g)	$\delta_{as}(CF_3)$
		530 w		
	732 p	732 s	ν_4 (a_{1g})	$\delta_s(CF_3)$
734.5 s			ν_{33} (a_{2u}), ν_{42} (e_u)	$\delta_s(CF_3)$
			[ν_9 (a_{2g}), ν_{30} (a_{2u}), ~1 122][a]	$\nu_{as}(CF_3)$
1 135 s			ν_{37} (e_u)	$\nu_{as}(CF_3)$
	1 136	1 137 w	ν_{13} (e_g)	$\nu_{as}(CF_3)$
1 169 vvs			ν_{30} (a_{2u}), ν_{38} (e_u)	$\nu_{as}(CF_3)$
1 178 vs			ν_{25} (a_{1u}), ν_{39} (e_u)	$\nu_{as}(CF_3)$, $\nu_s(CF_3)$
	1 168	1 165 vw	ν_1 (a_{1g}), ν_{15} (e_g)	$\nu_{as}(CF_3)$, $\nu_s(CF_3)$
	1 203	1 204 vw	ν_2 (a_{1g})	$\nu_s(CF_3)$

[a] Derived from combination band.

Table 15
UV Absorption Spectra of Germanium Compounds in Pentane [32].
Wavelength λ in nm.

Compound	λ	Compound	λ
$(C_6F_5)_3GeH$	267	$(C_6F_5)_2GeHGeH(C_6F_5)_2$	267
$(C_6F_5)_4Ge$	267	$(C_6F_5)_3GeOGe(C_6F_5)_3$	268
$C_6F_5GeH_3$	268	$(C_6F_5)_3GeSGe(C_6F_5)_3$	268
$(C_6F_5)_3GeCl$	269	$(C_6F_5)_3GeSeGe(C_6F_5)_3$	270
$(C_6F_5)_3GeBr$	270	$(C_6F_5)_3GeCdGe(C_6F_5)_3$	260
$(C_6F_5)_3GeOC(O)CF_3$	268	$(C_6F_5)_3GeHgGe(C_6F_5)_3$	250, 257(sh)
$(C_6F_5)_3GeGe(C_6F_5)_3$	239(sh), 268	$[(C_6F_5)_3GeHg(C_6F_5)_2Ge]_2$	256, 287, 317

4.3.2.4 Electronic Spectra

The electronic spectra are covered in **Table 15**.

The longwave absorption bands are assigned to the C_6F_5Ge group and indicate in $(C_6F_5)_3GeXGe(C_6F_5)_3$ (X = Hg, Cd) the presence of intramolecular coordination of ortho-fluorine atoms and the X atom [32].

By means of electronic emission spectroscopy it was shown that at 77 K the quenching of the luminescence of $(C_6F_5)_nGeH_{4-n}$ (n = 1, 2, 3, 4) and $(C_6F_5)_2GeHGeH(C_6F_5)_2$ conforms to the Stern-Volmer relation. For details see [36].

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Table 16

Physical Data of Perfluorohalogenoorgano Germanium Compounds.

Boiling point (b.p.) in °C/pressure in Torr, melting point (m.p.) in °C, NMR spectra (chemical shifts δ in ppm are positive lowfield from the standard, spin-spin coupling constant J); IR spectrum in cm^{-1}, mass spectra (m/e, ion, relative intensity).

Compound	b.p./Torr (m.p.) in °C	^1H, ^{19}F and ^{13}C NMR, IR and mass spectra
$CF_3C{\equiv}CGeH_3$ [41]	$18^{20)}$	^1H NMR$^{21)}$: $\delta = 3.91$ (qu), J(F-H) = 1.8 Hz IR(gas): 2 218(m), 2 126(s), 1 255(vs), 1 218(m), 1 167(vs), 888(m), 822(s), 627(m), 320(w), 268(m), 235(w)
CF_3GeH_3 [20]	–	^{19}F NMR: J(H-F) = 8.6 Hz ^1H NMR$^{2)}$: $\delta = 4.13$(qu), J(F-H) = 8.7 Hz
$(CF_3)_2GeH_2$ [2]	–	^{19}F NMR$^{1)}$: $\delta(CF_3) = 26.2$ ^1H NMR$^{2)}$: $\delta = 4.55$; J(H-F) = 7.8 Hz IR: 2 155(s), 1 168(vs), 1 137(vvs), 722(s) MS: $CF_3(CF_2)GeH_2^+$; $CF_3GeFH_2^+$
$(CF_3)_3GeH$ [2]	31.6 (−102)	^{19}F NMR$^{1)}$: $\delta(CF_3) = 26.4$ ^1H NMR$^{2)}$: $\delta = 5.23$; J(H-F) = 6.7 Hz IR: 2 155(s), 1 167(vvs), 734(s) MS: $(CF_3)_2(CF_2)GeH^+$; $(CF_3)_2GeH^+$
$(C_6F_5)_2GeHCl$ [17]	93 to 94/1 (41 to 42)	IR: ν(Ge-H) = 2 165
$(C_6F_5)_2GeHBr$ [10]	109 to 110/ $1.5^{3)}$	–
$(C_6F_5)_2GeHGeH(C_6F_5)_2$ [10]	(149 to 150)	–
$(CF_3)_3GeOGe(CF_3)_3$ [2]	98	^{19}F NMR$^{1)}$: $\delta(CF_3) = 21.8$ IR: 1 175(vs), 1 155(vs), 735(vs) MS: $(CF_3)_5Ge_2O^+$, $(CF_3)_4Ge_2OF^+$
$(C_6F_5)_3GeOH$ [8]	(112 to 113)	–
$(C_6F_5)_3GeOGe(C_6F_5)_3$ [8]	(269 to 270)	–
CF_3GeBr_3 [12]	–	^{19}F NMR$^{1)}$: $\delta(CF_3) = 13.3$ IR: ν(C-F) = 1 165(vs), $\delta(CF_3)$ = 735(vs) MS: $CF_3GeBr_3^+$; $GeFBr_3^+$, $CF_3GeBr_2^+$
$C_2F_5GeBr_3$ [2]	–	^{19}F NMR$^{1)}$: $\delta(CF_3) = 1.0$, $\delta(CF_2) = -38.8$, $J(CF_3\text{-}CF_2) = 2.9$ Hz
$C_2F_5GeI_3$ [2]	–	^{19}F NMR$^{4),12)}$: $\delta(CF_3) = 0.9$(tr), $\delta(CF_2) = -41.3$(qu), $J(CF_3\text{-}CF_2) = 2.2$ Hz MS: $C_2F_5GeI_3^+$, $FGeI_3^+$, GeI_3^+
$(CF_3)_2GeBr_2$ [12]	–	^{19}F NMR$^{1)}$: $\delta(CF_3) = 19.1$ IR: ν(C-F) = 1 165(vs), $\delta(CF_3)$ = 735(vs) MS: $(CF_3)_2GeBr_2^+$, $CF_3GeCF_2Br_2^+$, CF_3GeBr_2

Table 16 (continued)

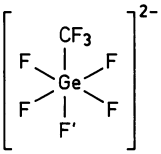
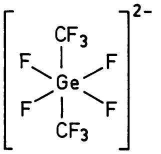
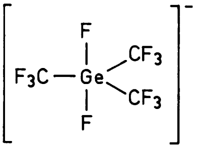
Compound	b.p./Torr (m.p.) in °C	^{1}H, ^{19}F and ^{13}C NMR, IR and mass spectra
$(CF_3)_3GeF$ [2]	19.1 5) (27 to 30) 6)	^{19}F NMR 1): $\delta(CF_3) = 22.1$, $\delta(GeF) = -142.6$; $J(CF_3\text{-}GeF) = 3.7$ Hz IR: 1263(s), 1176(vs), 725(s), for a complete assignment see p. 55 MS: $(CF_3)_3Ge^+$, $(CF_3)_2GeF^+$
$(CF_3)_3GeCl$ [2]	37 (−98)	^{19}F NMR 1): $\delta(CF_3) = 22.6$ IR: 1193(s), 1168(vs), 736(s), for a complete assignment see p. 55 MS: $(CF_3)_2Ge(CF_2)Cl^+$, $(CF_3)_3Ge^+$
$(CF_3)_3GeBr$ [2]	49 (−63)	^{19}F NMR 1): $\delta(CF_3) = 23.1$ IR: 1256(s), 1164(vs), 737(s), for a complete assignment see p. 55 MS 7): $(CF_3)_3GeBr^+$, $(CF_3)_2GeBrCF_2^+$
$(CF_3)_3GeI$ [2]	72 (−39.8)	^{19}F NMR 1): $\delta(CF_3) = 23.9$ IR: 1258(s), 1165(vs), 735(s), for a complete assignment see p. 55 MS: $(CF_3)_3GeI^+$, $(CF_3)_2GeICF_2^+$
$(C_6F_5)_3GeCl$ [8]	(104 to 107)	–
$(C_6F_5)_3GeI$ [13]	(118 to 120)	–
$(C_6F_5)_3GeGeCl_3$ [8]	(81 to 83) 8)	–
$(C_6F_5)_3GeGeF_2Ge(C_6F_5)_3$ [15]	(174 to 176)	–
 [14]	–	^{19}F NMR 9): $\delta(CF_3) = 14.05$, $\delta(GeF) = -45.4$, $\delta(GeF') = -42.1$; $J(CF_3\text{-}GeF) = 14.6$ Hz, $J(CF_3\text{-}GeF') < 0.3$ Hz, $J(GeF\text{-}GeF') = 23.7$ Hz
 10) [14]	–	^{19}F NMR 9): $\delta(CF_3) = 14.13$, $\delta(GeF) = -47.1$, $J(CF_3\text{-}GeF) = 14.5$ Hz
 [14]	–	^{19}F NMR 9) 11): $\delta(CF_3) = 15.10$, $\delta(GeF) = -60.5$; $J(CF_3\text{-}GeF) = 9.5$ Hz
$(C_6F_5)_3GeSGe(C_6F_5)_3$	(165 to 168) [5] (167 to 169) [8]	–
$(C_6F_5)_3GeSeGe(C_6F_5)_3$ [5]	(158 to 161)	–

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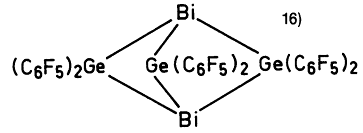
Table 16 (continued)

Compound	b.p./Torr (m.p.) in °C	^{1}H, ^{19}F and ^{13}C NMR, IR and mass spectra
$(CF_3)_4Ge$	31.7 (−19.7) [2]	^{19}F NMR: $\delta(CF_3) = 27.0^{12)}$ [19], $27.6^{12)}$ [12], $27.4^{12)}$ [42], $-46^{17)}$ [22], $-49.2^{19)}$ [26] ^{13}C NMR$^{18)}$: $\delta(C) = 126.1$, $J(^{13}C\text{-}F) = 330.7$ Hz [23] IR: For the analysis of the vibrational spectrum see p. 57 MS: m/e = 331, $(CF_3)_3GeCF_2^+$ (8); 281, $(CF_3)_3Ge^+$ (44) [42], see also [2, 12]
$(CF_3)_3GeGe(CF_3)_3$ [2]	20/20 (72 to 74)	^{19}F NMR$^{1)}$: $\delta(CF_3) = 22.1^{13)}$ IR: 1170(vs), 1135(s), 737(s), for a complete assignment see p. 58 MS: $(CF_3)_5Ge_2CF_2^+$; $(CF_3)_5Ge_2^+$
$(C_6F_5)_3GeGe(C_6F_5)_3$	220/0.1$^{14)}$ (308 to 315) [4] 210 to 230/0.02$^{14)}$ (312 to 318) [8] 210 to 230/0.01$^{14)}$ (312 to 318) [3]	–
$(C_6F_5)_3GeHgGe(C_6F_5)_3$ [3]	(229 to 231)	–
$[(C_6F_5)_3Ge]_3Pr \cdot Hg[Ge(C_6F_5)_3]_2^{15)}$ [7]	(270 to 280)$^{8)}$	–
$[(C_6F_5)_3Ge]_2PrX$ [7] X = Cl	(255 to 260)$^{8)}$	–
X = Br	(240 to 245)$^{8)}$	–
$(C_6F_5)_3GeTl \cdot Hg[Ge(C_6F_5)_3]_2$ [6]	(129 to 131)$^{8)}$	–
 16)	(>160)$^{8)}$ [17, 18]	IR: ν(C-Bi) = 630(w) [18]
$[(C_6F_5)_3Ge]_2Cd$ [39]	–	IR: $\nu(C_6F_5\text{-}Ge) = 812$

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1) Neat compounds, CF_3COOH as external standard. — 2) External standard $(CH_3)_4Si$. — 3) The sample contained 22% $(C_6F_5)_2GeH_2$ and 4% $(C_6F_5)_2GeBr_2$. — 4) Dissolved in diethylether. — 5) Extrapolated.

6) Sealed capillary. — 7) Additional ions: $(CF_3)_2GeBr^+$, $(CF_3)_3Ge^+$. — 8) Decomposition. — 9) Internal standard CF_3COONH_4. — 10) The dianion exists in solution in more than 90% as the trans isomer.

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[11] Measured in a saturated NH_4F solution. — [12] External standard CF_3COOH. — [13] Solution in $C_2H_5OC_2H_5$. — [14] Sublimation. — [15] Pale green solid.

[16] Light orange crystalline product. — [17] External standard $CFCl_3$. — [18] External standard $Si(CH_3)_4$. — [19] Standard $CFCl_3$. — [20] Extrapolated from the equation log p(Torr) = 7.705 − 1710/T (between 213 and 253 K), fitting measured vapor pressures, evaporation enthalpy $\Delta H_v = 32.7 \pm 0.6$ kJ · mol^{-1}, $\Delta H_v/T_s = 111.2$ J·mol^{-1}·K^{-1}.

[21] Internal standard $Si(CH_3)_4$.

4.3.3 Chemical Reactions

Thermal Stability, Solvolysis Reactions

No decomposition occurred when each of the compounds $(CF_3)_4Ge$, $(CF_3)_3GeI$, $(CF_3)_3GeCl$, and $(CF_3)_2GeI_2$ was heated at 145°C (7 d). At 190°C (7 d) slow decomposition to perfluorocyclopropane and the expected germanium fluoride, e.g., $(CF_3)_3GeF$ from $(CF_3)_4Ge$, occurs. The trifluoromethylgermaniumhalides are stable towards C_3F_6 formation but redistribution reactions occur slowly. When $(CF_3)_3GeI$ is heated at 155°C in a sealed tube, $(CF_3)_4Ge$ and $(CF_3)_2GeI_2$ are formed. The following relative amounts are obtained starting from 1.00 $(CF_3)_3GeI$: After 15 h 0.06 and 0.08; after 30 h 0.11 and 0.12; after 90 h 0.19 $(CF_3)_4Ge$ and 0.19 $(CF_3)_2GeI_2$ [2].

$(C_6F_5)_3GeGeCl_3$ is thermally unstable. It decomposes slowly even at 0°C forming $(C_6F_5)_3GeCl$ and the polymer $[GeCl_2]_n$ [8]. Solvolysis of $(C_6F_5)_3GeGe(C_6F_5)_3$ with CH_3OH at 60°C (0.25 h) or CH_3COOH at 100°C (1 h) yields 85% $(C_6F_5)_3GeOCH_3$ or 69% of $(C_6F_5)_3GeOC(O)CH_3$ [5, 8].

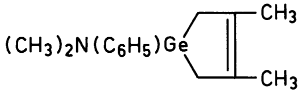
Reactions with Organometallic Compounds

At 20°C a mixture of $(C_6F_5)_3GeH$ and $Bi(C_2H_5)_3$ was prepared and heated to 70°C. Finally the temperature was raised gradually to 110°C (1 h), and 75% $(C_6F_5)_3GeBi(C_2H_5)_2$ was formed (melting point 92 to 94°C). When the mixture with a molar ratio of 2:1 was heated from 70 to 120°C (0.5 h) and then to 170°C (1 h), 72% $[(C_6F_5)_3Ge]_2BiC_2H_5$ is obtained (melting point 148 to 150°C) [17]. Reactions of $(C_6F_5)_3GeH$ or $(C_6F_5)_2GeH_2$ with $(C_2H_5)_3GeN(C_2H_5)_2$ in hexane at 100°C (1 h) lead respectively to 73% $(C_6F_5)_3GeGe(C_2H_5)_3$ (boiling point 144 to 151°C/1.5 Torr; melting point 98 to 102°C) and 66% $(C_2H_5)_3GeGe(C_6F_5)_2Ge(C_2H_5)_3$ (boiling point 164 to 166°C/1.5 Torr; melting point 41 to 44°C) [3].

A twofold excess of $Cd(CH_3)_2$ reacts with $(CF_3)_3GeI$ at 20°C (24 h) to give 90% $(CF_3)_3GeCH_3$ (boiling point 57.5°C; melting point −48.5°C). Analogously, $(CF_3)_2GeI_2$ gives 92% $(CF_3)_2Ge(CH_3)_2$ (boiling point 78°C) and $C_2F_5GeI_3$ yields 100% $C_2F_5Ge(CH_3)_3$. For NMR and IR spectra see [2]. $(C_6F_5)GeCl_3$ reacts in boiling C_6H_6 (10 h) with C_2H_5MgBr to form $C_6F_5Ge(C_2H_5)_3$ (boiling point 108 to 114°C, $n_D^{20} = 1.4683$, $D_4^{20} = 1.3954$ g · cm^{-3}). Analogously, $(C_6F_5)_2GeBr_2$ gave 67% $(C_6F_5)_2Ge(C_2H_5)_2$ (boiling point 134°C/5 Torr, $n_D^{20} = 1.4805$). The reaction of $(C_6F_5)_3GeBr$ and C_2H_5MgBr yields 60% $(C_6F_5)_3GeC_2H_5$ (boiling point 156°C/1 Torr, melting point 89 to 92°C) [13]. In 19% yield $(C_6F_5)_3GeGe(C_2H_5)_3$ is formed from $(C_2H_5)_3GeBr$ and $[(C_6F_5)_3Ge]_2Hg \cdot TlGe(C_6F_5)_3$ in tetrahydrofuran [6].

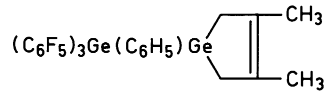
The reaction of a mixture of $(C_6F_5)_3GeGe(C_6F_5)_3$ and GeF_2 with 100% excess of C_6H_5MgBr in ether gave $(C_6F_5)_3GeGe(C_6H_5)_2Ge(C_6F_5)_3$. A mixture of $(C_6F_5)_3GeGe(C_6F_5)_3$ reacted with C_6H_5GeCl at 100°C (2 h) to yield 24% of $(C_6F_3)_3GeGe(C_6H_5)ClGe(C_6F_5)_3$ [8].

Reactions with $(C_6H_5P)_5$, $C_6H_5PLi_2$, Dimethylbutadiene and



A

A suspension of $(C_6F_5)_3GeGe(C_6F_5)_3$ and $(C_6H_5P)_5$ in benzene was heated at 180°C (15 h) in a carius tube forming 39% of $(C_6F_5)_3GeP(C_6H_5)Ge(C_6F_5)_3$ (melting point 90 to 92°C). The same product can also be made from $C_6H_5PLi_2$ and $(C_6F_5)_3GeCl$ in 45% yield. When $(C_6F_5)_3GeH$ was mixed with the heterocycle A in tetrahydrofuran, crude



was formed, which exploded during an attempted distillation. The germaheterocycle was also made from $(C_6F_5)_3GeGe(C_6F_5)_3$, GeF_2, C_6H_5MgBr and dimethylbutadiene at 130 °C (2 h) in 27% yield [15].

Complexing Reactions

A solution of $Pt[P(C_6H_5)_3]_3$ in benzene and $[(C_6F_5)_2Ge]_3Bi_2$ gave 98% $[(C_6F_5)_2Ge]_3Bi_2Pt[P(C_6H_5)_3]_3$. A X-ray structure of the complex is provided [18]. Insertion reactions are shown between Ge-H bonds and $Pt[P(C_6H_5)_3]_3$. This is demonstrated by the following examples: A mixture of $(C_6F_5)_3GeH$ and $Pt[P(C_6H_5)_3]_3$ reacted at 20 °C (1 h) to yield $(C_6F_5)_3GePt[P(C_6H_5)_3]_2H$ (62%). Similarly $(C_6F_5)_2GeH_2$ and $Pt[P(C_6H_5)_3]_3$ gave on standing at 20 °C after 1 h $(C_6F_5)_2GeHPt[P(C_6H_5)_3]_2H$. Depending on the molar ratio of $(C_6F_5)_2GeHGeH(C_6F_5)_2$ to $Pt[P(C_6H_5)_3]_3$, the reaction in benzene takes place according to:

$$(C_6F_5)_2GeHGeH(C_6F_5)_2 + Pt[P(C_6H_5)_3]_3 \rightarrow (C_6F_5)_2GeHGe(C_6F_5)_2Pt[P(C_6H_5)_3]_2H \xrightarrow{Pt[P(C_6H_5)_3]_3}$$

$$(C_6F_5)_2GePt[P(C_6H_5)_3]_2HGe(C_6F_5)_2Pt[P(C_6H_5)_3]_2H$$

The complex $(C_6F_5)_3GeSPt[P(C_6H_5)_3]_2H$ is obtained from $(C_6F_5)_3GeSH$ and $Pt[P(C_6H_5)_3]_3$ in benzene at 20 °C (1 h) [9]. Similar insertions are given in the following examples [4]:

$$[(C_6F_5)_3Ge]_2M + Pt[P(C_6H_5)_3]_3 \xrightarrow[20\,^{\circ}C]{benzene} (C_6F_5)_3GeMPt[P(C_6H_5)_3]_2Ge(C_6F_5)_3$$

(M = Hg, Cd, Zn)

The platinum complex can be replaced by $Pd[P(C_6H_5)_3]_2$ to form $(C_6F_5)_3GeHgPd[P(C_6H_5)_3]_2Ge(C_6F_5)_3$ [4], see also [37, 40]. At 20 °C (1 h) $[(C_6F_5)_3Ge]_2Hg$ and $Cr(C_6H_6)_2$ react to $[(C_6H_5)_2Cr^+]_2\{[(C_6F_5)_3Ge]_4Hg\}^{2-}$ [38]. Several complexes of $[(C_6F_5)_3Ge]_2Cd$ were synthesized with donor ligands L. All together eighteen substances of the formula $[(C_6F_5)_3Ge]Cd\text{-}xL$ were made [39].

Polymerization Reactions

When a mixture of $(C_6F_5)_2GeHGeH(C_6F_5)_2$ was heated with $(C_6F_5)_3GeHgC_2H_5$ in toluene at 80°C (1 h) and then heated to 110°C, an oligomer (77% yield) forms with the empirical formula $C_{60}F_{50}Ge_4Hg_2$ (melting point 221 to 223°C). When $Pt[P(C_6H_5)_3]_3$ in benzene or $Hg\{N[Si(CH_3)_3]_2\}_2$ in toluene is added to this digermane at 20°C (1 or 20 h) the polymers $C_{150}H_{78}F_{50}Ge_4Hg_2P_4Pt_2$ and $(C_{24}F_{10}Ge_2Hg)_4$ (86% yield) are produced, respectively [10].

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4.4 Perfluorohalogenoorgano Compounds of Tin

4.4.1 Preparation and Physical Properties

Tris(pentafluorophenyl)stannane $(C_6F_5)_3SnH$

Bis(pentafluorophenyl)dichlorostannane $(C_6F_5)_2SnCl_2$

Tetrakis(pentafluorophenyl)stannane $(C_6F_5)_4Sn$

Hexakis(pentafluorophenyl)distannane $(C_6F_5)_3SnSn(C_6F_5)_3$

[Hexakis(pentafluorophenyl)distannyl]mercury $(C_6F_5)_3SnHgSn(C_6F_5)_3$

[Tris(pentafluorophenyl)stannyl-tris(pentafluorophenyl)germyl]mercury $(C_6F_5)_3SnHgGe(C_6F_5)_3$

In benzene $SnCl_2$ reacts with $(C_6F_5)_2TlBr$ to give $(C_6F_5)_2SnCl_2$ [4]; see also Part 4, p. 182.

No new syntheses have been published for the other compounds, since Part 4, pp. 181/92, has appeared. New details on physical properties are given below, for chemical reactions see Chapter 4.4.2, p. 69.

UV absorption spectra (λ in nm) [11]:

$(C_6F_5)_3SnH$: λ_{max} (in pentane) = 267, λ_{max} (in CH_2Cl_2) = 267

$(C_6F_5)_3SnSn(C_6F_5)_3$: λ_{max} (in pentane) = 243 (sh), 268 (sh); λ_{max} (in CH_2Cl_2) = 268 (sh)

$[(C_6F_5)_3Sn]_2Hg$: λ_{max} (in pentane) = 260, 276 (sh); λ_{max} (in CH_2Cl_2) = 260 (sh), 278

^{199}Hg NMR of saturated solutions of $[(C_6F_5)_3Sn]_2Hg$ in toluene (a) and in CH_2Cl_2 (b): Chemical shift [standard $(CH_3)_2Hg$] $\delta = -644.5$ (a) and -682 ppm (b), J(Hg-$^{117/119}$Sn) = 18380/17550 (±10) Hz (a), J(Hg-$^{117/119}$Sn) = 18690/17862 (±5) Hz (b) [19].

Table 17
Fundamental Vibrations of $(CF_3)_4Sn$ according T_d symmetry [12].
For abbreviations see Table 11, p. 55.

	A_1 (Raman, p)	A_2 (−)	E (Raman, dp)	F_1 (−)	F_2 (Raman, dp; IR)
$\nu_{as}(CF_3)$			ν_5	ν_9	ν_{13}
$\nu_s(CF_3)$	ν_1				ν_{14}
$\delta_{as}(CF_3)$			ν_6	ν_{10}	ν_{15}
$\delta_s(CF_3)$	ν_2				ν_{16}
$\varrho(CF_3)$			ν_7	ν_{11}	ν_{17}
$\nu(SnC_4)$	ν_3				ν_{18}
$\delta(SnC_4)$			ν_8		ν_{19}
τ		ν_4		ν_{12}	

Table 18
IR and Raman Spectra of $(CF_3)_4Sn$ [12].

IR (gas)	Raman (liquid)	Assignment	IR (gas)	Raman (liquid)	Assignment
	52 m	ν_8	1115 vs	1108 w	ν_5, ν_{13}
	58 m	ν_{19}	1147 vvs	~1135 vw, sh	ν_{14}
	211.5 vs, p	ν_3		1178 w, p	ν_1
	223 m	ν_7, ν_{17}	1190 w, sh		$\nu_{14} + \nu_8$
284 s	284 w	ν_{18}	1238 vw		$\nu_{15} + \nu_{16}$
	520 w	ν_6, ν_{15}	1286 vw		impurity
723.7 s	722.0 s, p	ν_2, ν_{16}	1393 vw		$\nu_{13} + \nu_{18}$
895 vw		$\nu_{13} - \nu_{17}$	1832 vw		$\nu_{13} + \nu_{16}$
905 vw		$\nu_{13} - \nu_3$	1865 vw		$\nu_{14} + \nu_{16}$
936 vw		$\nu_3 + \nu_{16}$	2214 vw		$2\nu_9$
968 vw		?	2240 vw		$\nu_9 + \nu_{14}$
1005 vw		$\nu_{16} + \nu_{18}$	2258 vw		$\nu_{13} + \nu_{14}$
1033 w		$2\nu_{16}$	2283 vw		$2\nu_{14}$
1058 w		$\nu_{13} - \nu_{19}$	2319 vw		$\nu_1 + \nu_{14}$
1068 w		$\nu_{13} - \nu_8$			
1091 w		$\nu_{14} - \nu_{19}$			

Trifluoromethylstannane CF_3SnH_3

Trifluoromethyltribromostannane CF_3SnBr_3

Bis(trifluoromethyl)dibromostannane $(CF_3)_2SnBr_2$

Tris(trifluoromethyl)bromostannane $(CF_3)_3SnBr$

Tetrakis(trifluoromethyl)stannane $(CF_3)_4Sn$

The reduction of CF_3SnBr_3 with $LiAlH_4$ in dry diethyl ether at −78 °C (1.5 h) gave a mixture of compounds, which contains about 10% CF_3SnH_3. The rather unstable compound was characterized by ^1H NMR at −40 °C [external standard $Si(CH_3)_4$, positive sign downfield: $\delta = 7.00$ ppm (quartet), J(F-H) = 2 to 3 Hz (not unambiguously resolved)] and by the mass spectrum. The most intense ions are $CF_3{}^{120}SnH_2^+$ (m/e = 191) and a series of ions $CF_3SnH_n^+$, $FSnH_n^+$ and SnH_n^+ [1].

On heating a mixture of $SnBr_4$ and $Hg(CF_3)_2$ in a sealed tube at 125 °C (67 h), 54% CF_3SnBr_3 and 19% $(CF_3)_2SnBr_2$ were obtained [2, 3]. When $SnBr_4$ and $Hg(CF_3)_2$ were reacted at 112 °C (42 h) 46% CF_3SnBr_3 and 3% $(CF_3)_2SnBr_2$ were isolated. The yields of CF_3SnBr_3 and $(CF_3)_2SnBr_2$ as a function of time and temperature are presented in [1]. The reaction of $(CF_3)_2Cd \cdot CH_3OCH_2CH_2OCH_3$ with $SnBr_4$ in 1,6-dibromohexane yields, along with the main product $(CF_3)_4Sn$, the compounds CF_3SnBr_3 and $(CF_3)_3SnBr$ in yields of 10 and 5%, respectively [18].

CF_3SnBr_3: ^{19}F NMR (neat samples, positive shifts are lowfield from external standard CF_3COOH): $\delta(CF_3) = 31.2$ ppm, $^2J(Sn\text{-}F) = 875/831$ Hz [1], $\delta(CF_3) = 29.8$ ppm, $J(Sn\text{-}F) = 868$, 822 Hz, $\delta(CF_3) = 30.8$ ppm, $J(Sn\text{-}F) = 871/835$ Hz; IR: 1212 (w), 1142 (s), 1130 (vs), 1091 (w), 1070 (sh), 1040 (w), 730 (w) cm^{-1} [2, 3]. Mass spectrum at 70 eV [m/e, ion (relative intensity)]: 413, $CF_2SnBr_3^+$ (11); 363, $SnBr_3^+$ (100); 282, $SnBr_2^+$ (11); 201, $SnBr^+$ (77); 139, SnF^+ (33); 120, Sn^+ (88) [1]. Also observed were $SnBr_3^+$, $CF_3SnBr_2^+$, CF_3SnBr^+ and CF_3Sn^+; the first two ions were the most intense [3].

$(CF_3)_2SnBr_2$: ^{19}F NMR: $\delta(CF_3) = 33.3$ ppm, $J(Sn\text{-}F) = 721/689$ Hz [1]; $\delta(CF_3) = 34.7$ ppm, $J(Sn\text{-}F) = 717/689$ Hz. IR: 1180 (sh), 1140 (vs), 1114 (m), 1095 (sh), 1040 (vw), 730 (w) cm^{-1} [2, 3]. Mass spectrum [m/e, ion (relative intensity)]: 399, $CF_3(CF_2)SnBr_2^+$ (2); 351, $CF_3SnBr_2^+$ (81); 337, $(CF_3)_2SnBr^+$ (32); 299, $FSnBr_2^+$ (23); 280, $SnBr_2^+$ (27); 201, $SnBr^+$ (100); 139, SnF^+ (68); 120, Sn^+ (64) [1], see also [18]. Also observed were $CF_3SnBr_2^+$ (base peak), $(CF_3)_2SnBr^+$, $SnBr_2^+$, SnBr [3].

$(CF_3)_3SnBr$: ^{19}F NMR (external standard CF_3COOH): $\delta = 36.3$ ppm, $J(Sn\text{-}F) = 678$, 656 Hz. Mass spectrum: m/e = 337, $(CF_3)_2CF_2SnBrF^+$ (20); 287, $CF_3SnF_2Br^+$ (20) [18].

A most convenient method of preparing $(CF_3)_4Sn$ is the reaction of $(CF_3)_2Cd \cdot CH_3OCH_2CH_2OCH_3$ with $SnBr_4$ [18]. $(CF_3)_4Sn$ is also formed by reacting SnI_4 with CF_3 radicals (e.g., from C_2F_6), formed in a low-energy plasma [5], ^{19}F NMR (external standard $CFCl_3$): $\delta(CF_3) = -43$ ppm, ^{13}C NMR [external standard $Si(CH_3)_4$]: $\delta(C) = 132.7$ ppm, $J(^{13}C\text{-}F) = 349.2$ Hz [7], ^{19}F NMR (external standard CF_3COOH): $\delta = 38.8$ ppm, $J(Sn\text{-}F) = 537$, 514 Hz. Mass spectrum: m/e = 377, $(CF_3)_3SnCF_3^+$ (5); 327, $(CF_3)_3Sn^+$ (51) [18].

The molecular structure of $(CF_3)_4Sn$ has been determined by electron diffraction yielding the geometric parameters $r_a(C\text{-}F) = 1.338 \pm 0.002$ Å, $r_a(Sn\text{-}C) = 2.201 \pm 0.005$ Å and $\alpha(F\text{-}C\text{-}F) = 108.2°$. The molecule has T_d symmetry [12]. The IR spectrum in the gas phase and the Raman spectrum in the liquid phase have been recorded (see **Table 18**, p. 67). The assignment is supported by means of a normal coordinate analysis. Distribution and notation of the fundamental vibrations are given in **Table 17**, p. 67).

Tetrakis(3,3,3-trifluoropropynyl)stannane $(CF_3C{\equiv}C)_4Sn$

Tetrakis(pentafluorophenylethynyl)stannane $(C_6F_5C{\equiv}C)_4Sn$

$(CF_3C{\equiv}C)_4Sn$ was prepared by reaction of $CF_3C{\equiv}CMgI$ with $SnBr_4$ in ether solution [8]. A gas-phase electron diffraction study of $(CF_3C{\equiv}C)_4Sn$ yields the following internuclear distances r (in Å) and angles α, based on T_d symmetry for the C-Sn skeleton and on C_{3v} symmetry for the CF_3 groups: $r(Sn\text{-}C) = 2.070 \pm 0.007$ Å, $r(C{\equiv}C) = 1.215 \pm 0.006$ Å, $r(C\text{-}C) = 1.460 \pm 0.007$ Å, $v(C\text{-}F) = 1.343 \pm 0.002$ Å, $\alpha(CCF) = 111.3° \pm 0.2°$ [8]. These values are confirmed by a further diffraction study [9].

In 60 to 80% yield $(C_6F_5C{\equiv}C)_4Sn$ forms in the reaction of $[(C_2H_5)_2N]_4Sn$ with $C_6F_5C{\equiv}CH$. The melting point is 186 to 188 °C; ^{19}F NMR (internal standard C_6F_6, values recalculated to the standard $CFCl_3$): $\delta(F^2, F^6) = -135.05$, $\delta(F^3, F^5) = -162.01$, $\delta(F^4) = -150.40$ ppm, $J(F^2\text{-}F^4) = 3.0$ Hz, $J(F^3\text{-}F^4) = -20.0$ Hz [10].

4.4.2 Chemical Reactions

For an improved quantitative determination of fluorine in C_6F_5 and CF_3 compounds, among them $(C_6F_5)_4Sn$, by combustion of the sample in a closed tube filled with O_2, followed by titration of F^- with $Th(NO_3)_4$ solution in the presence of Alizarine Red S, see [6].

Thermal Stability. Reactions with $Cd(CH_3)_2$, CH_3Li, $(CH_3)_3CC{\equiv}CSn(CH_3)_3$

CF_3SnH_3 which is thermally less stable than SnH_4 decomposes rapidly at −40°C to yield a brown unidentified solid [1]. A neat sample of $(CF_3)_2SnBr_2$ decomposed totally in 72 h at 125°C in an evacuated sealed tube [1]. Complete decomposition is also observed when $(CF_3)_4Sn$ was heated to 100°C (24 h) in a sealed tube. The decomposition products consist of one equivalent cyclo-C_3F_6, a small amount of SiF_4 and a nonvolatile residue. At 66°C (24 h) only 58% of $(CF_3)_4Sn$ was decomposed to yield the same products. CF_3SnBr_3 was only slightly decomposed at 125°C (24 h), since traces of $(CF_3)_2SnBr_2$ were observed [3].

CF_3SnBr_3 reacts with a small excess $Cd(CH_3)_2$ at 20°C (15 min) to give 92% $CF_3Sn(CH_3)_3$. With a tenfold excess $Cd(CH_3)_2$ under the same conditions $CF_3Sn(CH_3)_3$ is formed immediately and quantitatively. The reaction of CF_3SnBr_3 with substoichiometric amounts of $Cd(CH_3)_2$ yielded 58% $CF_3Sn(CH_3)_3$, 8% $CF_3(CH_3)_2SnBr$ and 11% $CF_3(CH_3)SnBr_2$, along with unreacted CF_3SnBr_3. At 20°C (15 min) $(CF_3)_2SnBr_2$ reacted with $Cd(CH_3)_2$ to give 91% $(CF_3)_2Sn(CH_3)_2$. In an ether solution CH_3Li and CF_3SnBr_3 reacted at 20°C (3 min) to give 71% $CF_3Sn(CH_3)_3$. With a large excess of CH_3Li, 31% $CF_3Sn(CH_3)_3$ and 70% $(CH_3)_4Sn$ were isolated. ^1H, ^{19}F NMR and mass spectra of the methylated tin compounds are given in [1].

When $(CF_3C{\equiv}C)_4Sn$ is heated with $(CH_3)_3CC{\equiv}CSn(CH_3)_3$ to 140°C, $CF_3C{\equiv}CSn(CH_3)_3$ is formed [13].

Complex Formation

Insertion reactions between $[(C_6F_5)_3Sn]_2Hg$ or $(C_6F_5)_3SnHgGe(C_6F_5)_3$ with $Pt[P(C_6H_5)_3]_3$ take place in benzene at 20°C (2 h) according to $(C_6F_5)_3SnHgM(C_6F_5)_3 + Pt[P(C_6H_5)_3]_3 \rightarrow (C_6F_5)_3SnHgPt[P(C_6H_5)_3]_2M(C_6F_5)_3 + P(C_6H_5)_3$ (M = Sn, Ge) [14, 15]. The reaction between $(C_6F_5)_3SnHgGe(C_6F_5)_3$ and $Pt[P(C_6H_5)_3]_3$ gives the two isomers $(C_6F_5)_3SnPt[P(C_6H_5)_3]HgGe(C_6F_5)_3$ and $(C_6F_5)_3GePt[P(C_6H_5)_3]_2HgSn(C_6F_5)_3$ in 90 and 10% yield. An X-ray structure of $(C_6F_5)_3SnPt[P(C_6H_5)_3]_2HgGe(C_6F_5)_3$ is provided [16]. The complex $(C_6F_5)_3SnHgPt[P(C_6H_5)_3]_2Sn(C_6F_5)_3$ was separated by chromatography [17].

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4.5 Perfluorohalogenoorgano Compounds of Lead

Since the appearance of Part 4 in 1975, no new papers on lead compounds have been published.

5 Perfluorohalogenoorgano Compounds of Main Group 5 Elements

5.1 Preliminary Remarks

The compounds of the Main Group 5 elements phosphorus, arsenic, antimony, and bismuth, are covered to the end of 1973 in "Perfluorhalogenorgano-Verbindungen der Hauptgruppenelemente", Part 3, 1975 (cited here as Part 3), for further details see the preface of this Supplement Volume. The compounds with nitrogen will be reported separately.

5.2 Perfluorohalogenoorgano Compounds of Phosphorus

5.2.1 Cyclic Perfluorohalogenoorgano Compounds of Phosphorus

5.2.1.1 Homocyclic Phosphorus Compounds

5.2.1.1.1 Preparation and Physical Properties

Tetrakis(trifluoromethyl)cyclotetraphosphine $(CF_3P)_4$

Pentakis(trifluoromethyl)cyclopentaphosphine $(CF_3P)_5$

On dropping R_4Pb ($R = CH_3, C_2H_5$) into stirred CF_3PI_2 under inert-gas atmosphere $(CF_3P)_4$ is formed according:

$$CF_3PI_2 + R_4Pb \rightarrow (CF_3P)_4 + RI + R_3PbI$$

R_3PbI forms a deposit. After the end of the reaction the mixture is heated to 100 to 120 °C for 3 to 8 h and distilled in vacuo [1]. Mixtures of $(CF_3P)_4$ and $(CF_3P)_5$ are obtained by reaction of CF_3PHI and AgCN (20 °C, 2 h) [2] and by reduction of CF_3PI_2 with Hg in presence of less than stoichiometric amounts of HI [3].

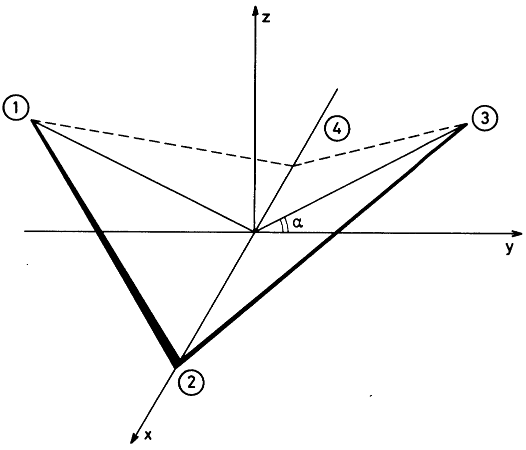


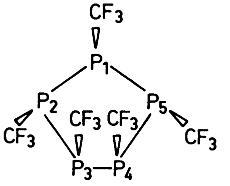
Fig. 1. Ring shape characterization of $(CF_3P)_4$. The phosphorus atoms are designated by numbers.

References p. 74

^{31}P NMR Spectra. Molecular Structure

$(CF_3P)_4$ shows in benzene the chemical shift $\delta(^{31}P) = -76.4$ ppm [4] or -76.71 ppm at 30 °C [5], referred to 85% H_3PO_4 (negative sign means highfield from the standard). The ^{19}F-decoupled ^{31}P NMR spectra were investigated in nematic solvents [4, 5]. Measurements in "Merck Phase 4" give δ values between -67.08 (at 9.5 °C) and -70.21 ppm (at 40 °C) at different ordering parameters S_{zz} of the molecule in the liquid-crystal phase (obtained by varying the temperature). These values are corrected for the temperature dependence of the phosphorus chemical shift, $\Delta\delta/\Delta t = 0.052$ ppm/°C. From a relation between the shifts in the isotropic phase (benzene solution, see above) and in the nematic phase (for $S_{zz} \rightarrow 0$) the chemical shift anisotropy $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp} = 129 \pm 15$ ppm results ($\sigma_{\parallel} = \sigma_{zz}$, $\sigma_{\perp} = (\sigma_{xx} + \sigma_{yy})/2$, for the coordinate system see **Fig. 1**, p. 71). The spin-spin coupling constant $J_{1,2} = \mp 100.6$ Hz is obtained from the ^{31}P NMR in a 60:40 mixture of N-(4-methoxybenzylidene-4-n-butylaniline) and butyl-4-(4-ethoxyphenoxycarbonyl)phenylcarbonate. Assuming that the $J_{1,2}$ coupling is isotropic, the dependence of the dipole-dipole coupling constants $D_{1,2}$ and $D_{1,3}$ from S_{zz} gives a ring folding angle $\alpha = 24.8° \pm 0.7°$ [4, 5]. The P-P-P angle is 84.5° [5]. The ^{19}F-decoupled 40 MHz-^{31}P spectrum of $(CF_3P)_5$ at 40 °C shows a well-resolved AA′BB′C system spread over 1000 Hz. The shifts δ (in ppm, external standard 85% H_3PO_4) and coupling constants J (in Hz) are given in the following [6]:

$\delta(P_1)$	$\delta(P_2) = \delta(P_5)$	$\delta(P_3) = \delta(P_4)$
7.5	10.0	−1.1



$J_{1,2} = J_{1,5}$	$J_{1,3} = J_{1,4}$	$J_{2,5}$	$J_{2,4} = J_{3,5}$	$J_{2,3} = J_{4,8}$	$J_{3,4}$
∓214.5	±36.9	±0.8	∓5.3	∓223.3	∓343.2

The analysis of the spectrum shows that the phosphine has a rigid C_s symmetry or that a conformational change, fast on the NMR time scale, occurs to produce an average C_s symmetry. According to X-ray structural data (see Part 3, p. 4) the latter hypothesis seems more likely [6].

Photoelectron Spectra

The analysis of the He(I) photoelectron spectra of $(CF_3P)_4$ gives the vertical ionization energies $E_i = 10.18$ and 10.58 eV, which are assigned to ionization from the phosphorus lone-pair MO's of symmetry a_1 and e, respectively, further $E_i = 12.38$ eV (ionization from σ_{pp} MO, symmetry e), and $E_i = 12.89$ eV (overlap of ionizations from the b_2 phosphorus lone pair MO and the a_1 and b_1 σ_{pp} MO's). The assignment used in an earlier analysis, see Part 3, p. 3, is changed in this investigation in the light of MO calculations [7]. For $(CF_3P)_5$, the five peaks at 9.79, 10.13, 10.71, 11.21, and 12.1 eV are assigned to the ionization of the phosphorus lone pair MO's of the symmetries a″, a′, a′, a″, and a′ (in order of increasing energy) [7].

Tris(pentafluorophenyl)cyclotriphosphine $(C_2F_5P)_3$

Tetrakis(pentafluorophenyl)cyclotetrakisphosphine $(C_2F_5P)_4$

Pentakis(pentafluorophenyl)cyclopentaphosphine $(C_2F_5P)_5$

For preparation and properties, see Part 3, p. 1. — The question of the existence of the trimer and pentamer is investigated by ^{19}F-decoupled ^{31}P NMR spectroscopy [8]. The reaction of $C_2F_5PI_2$ and Hg (see Part 3, p. 1) forms mixtures which are said to contain $(CF_3P)_3$ and $(CF_5P)_4$ according to [9] or $(CF_3P)_5$ and $(CF_3P_4)_4$ according to [10]. In freshly prepared mixtures the ^{31}P NMR shows a singlet at $\delta = -72.9$ and a multiplet at $\delta = -145.1$ ($J_{P\text{-}P} = 168$ Hz, external standard 85% H_3PO_4). The singlet is assigned to the tetramer, the multiplet corresponds to the AB_2 spin system of a trimer [8]. This fact confirms the assignment of the -71.9 ppm [10] signal, but contradicts the interpretation [10] of a shift of -144.2 ppm as the signal of the pentamer [8]. On standing for several weeks at room temperature there is observed a 100% conversion of the trimer to the tetramer [8, 10], see also the investigation of this conversion in [11], which is corrected and discussed in [8].

The analysis of the He(I) photoelectron spectrum of $(C_2F_5P)_4$ gives the vertical ionization energies $E_i = 9.9$ and 10.48 eV (ionization from the phosphorus lone-pair MO's of symmetry a_1 and e, respectively), further $E_i = 11.95$ (ionization from σ_{pp} MO, symmetry e) and $E_i =$ 12.65 eV (overlap of ionization from the b_2 phosphorus lone-pair MO and the a_1 and b_1 σ_{pp} MO's). For $(C_2F_5P)_3$ the peaks at 10.39, 10.83 and 11.69 eV are assigned to the ionization from the lone-pair MO's of symmetry a′, a″ and a′, respectively. The ionization from σ_{pp} MO's leads to $E_i = 12.76$ (a″) and 14.42 eV (a′) [7].

Tris(heptafluoropropyl)cyclotriphosphine $(C_3F_7P)_3$

Tetrakis(heptafluoropropyl)cyclotetrakisphosphine $(C_3F_7P)_4$

Pentakis(heptafluoropropyl)cyclopentakisphosphine $(C_3F_7P)_5$

$(i\text{-}C_3F_7P)_3$ forms in quantitative yield by reaction of $i\text{-}C_3F_7PI_2$ with Hg. The stable and transparent liquid solidifies at 20 °C. The vapor pressure at 25 °C is 0.75 Torr. The ^{31}P NMR spectrum shows a chemical shift $\delta = -130$ ppm (standard H_3PO_4); UV: broad absorption band at 200 to 260 nm, IR: 1270 (s), 1240 (s), 1160 (m), 950 (w), 900 (w) cm^{-1} [12]. The reaction of $n\text{-}C_3F_7PI_2$ with an excess of mercury in a closed ampule overnight gives $(n\text{-}C_3F_7P)_4$ which was identified by its $^{31}P\{^{19}F\}$ NMR spectrum, a sharp singlet at $\delta = -62.6$ ppm (85% H_3PO_4 as external standard, C_6D_6 as solvent) [8]. The second resonance at $\delta = -141.4$ ppm, which was earlier observed in such a reaction mixture and assigned to the pentamer [10, 13] could not be found [8]. Similar to the interpretation of the perfluoromethyl system (see above), this signal should have been assigned to the three-membered ring [8].

Tetrakis(pentafluorophenyl)cyclotetraphosphine $(C_6F_5P)_4$

For preparation and physical properties, see Part 3, p. 2; additional reactions are given on p. 74.

References p. 74

5.2.1.1.2 Chemical Reactions

Cyclic phosphines react with fluoroiodoalkanes at temperatures between 160 to 220°C in 4 to 10 h forming secondary unsymmetrically substituted iodophosphines (see pp. 106/7) [14, 15, 16] according to:

$^1/_4\ (RP)_4 + R'I \rightarrow R(R')PI \qquad R = CF_3, C_2F_5, R' = n\text{-}C_3F_7, i\text{-}C_3F_7, CHFCF_2Cl$

The kinetics of the reaction were studied in the temperature range from 145 to 185°C. The kinetic curves for conversion of the phosphine from 0 to 0.6 to 0.8 are represented by first-order equations. The reaction constants k and activation energies E_a (in kcal/mol) in the case of $R = CF_3$ are given in the following [14]:

$R' = n\text{-}C_3F_7$, $k = 26 \times 10^2\ h^{-1}$, $E_a = 31$, $R' = i\text{-}C_3F_7$, $k = 10 \times 10^2\ h^{-1}$, $E_a = 36$, $R' = CHFCF_2Cl$, $k = 17 \times 10^2\ h^{-1}$, $E_a = 33$

The determination of the reaction order with respect to the phosphine for the reaction with excess C_3F_7I gave n = 1. This fact, together with the overall first-order behavior of the reaction, leads to suppose that the reaction passes through the intermediate formation of a molecular complex, the rate of breakdown of which determines the rate of the whole process [17]. $(CF_3P)_5$ also forms secondary unsymmetrically substituted iodophosphines. The reaction proceeds not directly but with intermediate conversion of the pentamer to the tetramer which reacts with the fluoroiodophosphines [18].

On condensing $(CH_3)_3P$ into a solution of $(CF_3P)_4$, of $(CF_3P)_5$ or of a mixture of both phosphines in $C_6H_5CF_3$, a phosphine-phosphinidene $(CH_3)_3PPCF_3$, an analogue of a Wittig reagent, is formed. The NMR spectra are measured in presence of $(CH_3)_3P$ under slow-exchange conditions. ^{19}F NMR (external standard $CFCl_3$): $\delta(CF_3) = -26.7 \pm 1.4$ (doublet of doublets, position solvent-dependent), $J(CF_3\text{-}P) = 37.2$ Hz, $J(CF_3P\text{-}P) = 23.6$ Hz, ^{31}P NMR (external standard 85% H_3PO_4): $\delta(CF_3P) = -81.0$ ppm (doublet of quartets) and $\delta[P(CH_3)_3] = 12.7$ ppm (doublet of quartets), $J(P\text{-}P) = 436.5$ and 436.3 Hz, respectively, $J(P\text{-}CF_3) = 37.4$ Hz, $J(P\text{-}PCF_3) = 23.3$ Hz. Positive signs mean downfield values. ^1H and ^{13}C NMR data are also presented [19].

$(CF_3P)_4$ reacts with $(CH_3)_3SiH$ and with $(CH_3)_3GeH$ to a negligible extent at 20°C in nine weeks. The reaction with $(CH_3)_3SnH$ is complete within 15 min [20] according to:

$(CF_3P)_4 + (CH_3)_3SnH \rightarrow (CH_3)_3SnPHCF_3 + (CH_3Sn)_2PCF_3 + CF_3PH_2$

$(C_6F_5P)_4$ cleaves on reaction with $Pt[P(C_6H_5)_3]_3$ in boiling benzene in N_2 atmosphere. The fragments act as ligands forming $Pt[P(C_6H_5)_3]_2[PC_6F_5]_2$ [21].

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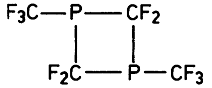
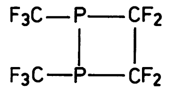
5.2.1.2 Heterocyclic Phosphorus Compounds

2,2,4,4-Tetrafluoro-1,3-bis(trifluoromethyl)-1,3-diphosphetane

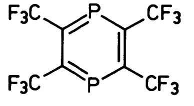


3,3,4,4-Tetrafluoro-1,2-bis(trifluoromethyl)-1,2-diphosphetane



A mixture of 80% 1,3-diphosphetane and 20% 1,2-diphosphetane forms in 40 to 50% yield in the BF_3-catalyzed decomposition of $(CF_3)_2PSiH_3$ at 60 °C in 20 to 40 h. The reaction time decreases with increasing BF_3 concentration. The diphosphetanes are obtained in 40% yield on decomposing $(CF_3)_2PSi(CH_3)_3$ at 20 °C (5 h) in the presence of BF_3 (molar ratio phosphine/BF_3 1 : 2). The ^{19}F NMR spectrum of the 1,2-diphosphetane (the ^{19}F NMR spectrum of the 1,3-diphosphetane is covered in Part 3, p. 11) shows the signals of the CF_3 groups as doublet of triplets, $\delta = -47$ ppm (standard $CFCl_3$), spin-spin coupling constants $^2J = 92$ Hz, $^3J = 12.2$ and 3.4 Hz. The CF_2 groups give a spectrum of second order, $\delta = -81$ ppm. This pattern was bounded by two major multiplets whose centers were 278 Hz apart [1].

2,3,5,6-Tetrakis(trifluoromethyl)-1,4-diphosphabenzene

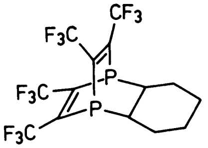


The compound forms on refluxing 2,3,5,6,7,8-hexakis(trifluoromethyl)-7-methoxy-1,4-diphosphabicyclo[2.2.2]octa-2,5-diene (see compound C, p. 77) in an oxygen-free stream of argon for 40 h [2, 3] or pyrolyzing 4,5,9,10,11,12-hexakis(trifluoromethyl)-1,8-diphosphatetracyclo-$[6.2.2.0^{2,7}.0^{3,6}]$-dodeca-4,9,12-triene (see compound F, p. 78) at 180 °C for 3 h [4].

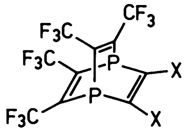
The phosphabenzene is very sensitive to oxygen and base, but it is thermally stable (no change on heating at 180 °C for 3 h). The UV spectrum in hexane shows a strong absorption band at 282 nm (molar absorptivity >4000 to 5000). ^{19}F NMR (benzotrifluoride as internal standard): δ = 11.6 ppm [doublet, J(P-F) = 66 Hz]. ^{31}P NMR (external standard 50% solution of H_3PO_4 in D_2O): δ = 287.1 ppm. ^{13}C NMR [external standard $(CH_3)_4Si$, in $CDCl_3$, decoupled by ^{19}F]: δ(-C=P-) = 163.9 ppm [quartet, J(PC^2) = 80.5 Hz, J(PC^3) = 5.0 Hz], $\delta(CF_3)$ = 123.5 ppm (multiplet) [3]. (Downfield shifts are shown as positive.) In the mass spectrum a relatively weak molecular ion peak appears at m/e = 386 and a strong peak at m/e = 317 ($M^+ - CF_3$) [2, 3].

The reaction of the diphosphabenzene with hexafluoro-2-butyne [2, 3], the photolysis [5, 6] and the thermolysis in presence of sulfur [7] yield new title compounds, see pp. 77, 79.

The phosphabenzene reacts with cyclohexene thioxide forming the following cycloadduct in addition to the 7-thia-1,4-diphosphanorbornadiene (see p. 80) [7]:



The diphosphabenzene reacts with acetylenic compounds to give 1 : 1 Diels-Alder adducts. The reactions with dimethylacetylene [3] and methylacetylenedicarboxylate [2, 3] in n-pentane as solvent in a sealed stainless-steel tube at 90 to 95 °C (14 h) yield the compounds A and B, respectively:

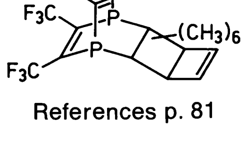


A: X = CH_3
B: X = CO_2CH_3

A: 78.7% yield, colorless needles, melting point 152 to 153 °C, IR: ν(C=C) = 1600 cm^{-1}, UV (in CH_3OH): λ_{max} = 272 nm (log ε = 2.96), 326 nm (log ε = 2.79), ^{19}F NMR [standard benzotrifluoride, in $(CD_3)_2CO$]; δ = 6.30 ppm [doublet, $^1/_2(J_{PF} + J_{PF'})$ = 37 Hz], MS: m/e = 440 (M^+), ^{1}H NMR see [3].

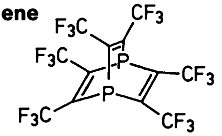
B: 51.2% yield, pale yellow plates, melting point 108 to 110°C, λ_{max} = 317 nm (shoulder), ^{19}F NMR (in $CDCl_3$): δ = 6.60 ppm [doublet, $^1/_2(J_{JP} + J_{PF'})$ = 40 Hz], MS: m/e = 528 (M^+), ^{1}H NMR see [2, 3].

The reaction with hexamethyl-Dewar-benzene at 80 °C (1 h) in a sealed tube gives the following 1 : 1 Diels-Alder adduct [3]:



Yield 56%, yellow plates, melting point 182 to 184 °C, IR: ν(C-H) = 2960, 2920, 2860 cm^{-1}, ν(C=C) = 1610, 1585 cm^{-1}, ^{19}F NMR: δ = 5.76 ppm [6F, doublet, $^1/_2(J_{PF} + J_{PF'}) = 49.6$ Hz, CF_3], 6.36 ppm [6F, doublet, $^1/_2(J_{PF} + J_{PF'}) = 54.1$ Hz, CF_3]; MS: m/e = 548 (M^+), ^1H NMR see [3].

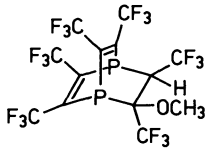
2,3,5,6,7,8-Hexakis(trifluoromethyl)-1,4-diphospha-bicyclo[2.2.2]-octa-2,5,7-triene



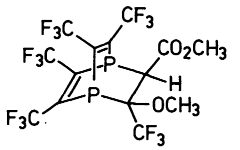
The compound (see also Part 3, p. 10) forms on reacting 2,3,5,6-tetrakis(trifluoromethyl)-1,4-diphosphabenzene with hexafluoro-2-butyne in a sealed stainless-steel tube in pentane at 90 to 95 °C for 14 h [3], see also [2]. It is also obtained in quantitative yield by the thermolysis of 2,3,5,6,7,8-hexakis(trifluoromethyl)-7-methoxy-1,4-diphosphabicyclo[2.2.2]octa-2,5-diene (compound C, see below) with 0.5 molar equivalent of sulfur [7].

Physical Properties are given in Part 3, p. 12.

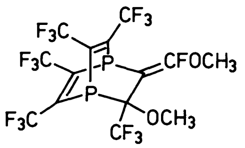
Stirring the octatriene in CH_3OH in presence of $RhCl_3$ gave the three products C, D and E [2, 3].



C



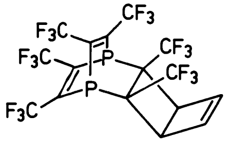
D



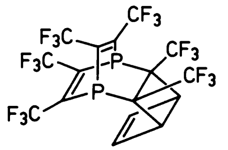
E

Compound **C** is the main product of the reaction (55% yield), melting point 68 to 70 °C, ^{19}F NMR (internal standard benzotrifluoride, solvent $CDCl_3$): δ = −3.36 ppm (3F, multiplet, CF_3), 6.80 ppm (15F, multiplet, CF_3), UV (in CH_3OH): λ_{max} = 243 nm (log ε = 3.29), 332 nm (log ε = 3.00), IR (in KBr): ν(C=C) = 1600 cm^{-1}, ^1H NMR see [3]. Compound **D** is obtained in 3.8% yield, melting point 85 to 86 °C, ^{19}F NMR: δ = −3.88 ppm (3F, multiplet, CF_3), 6.40 ppm (12F, multiplet, $4 \times CF_3$), ν(C=O) = 1740, ν(C=C) = 1710 cm^{-1}, ^1H NMR see [3]. Compound **E** (5.3% yield) melts at 81 to 82 °C, ^{19}F NMR: δ = −2.20 ppm (3F, multiplet, CF_3), 5.80 ppm [13F, multiplet, $4 \times CF_3$ + C=CF(OCH_3)], ν(C=C) = 1645, 1620 cm^{-1}, ^1H NMR see [3].

The reaction with diazomethane yields quantitatively at 20 °C 3,4-bis(trifluoromethyl)-pyrazole [4, 8] (after sublimation at 90 °C/6 Torr colorless needles, melting point 122 °C [8]). The reaction with phenylazide (sealed Pyrex tube, heating at 80 °C for 50 h in a solution of C_6H_6 and CH_3CN) gives quantitatively 1-phenyl-4,5-bis(trifluoromethyl)-1,2,3-triazole [4, 8], a pale yellow oil, ^{19}F NMR: δ = 8.0 and 3.8 ppm [both doublets, J(F-F) = 6.8 Hz] [4]. With furan, 2,5-dimethylfuran and tetraphenylcyclopentadienenone no reaction of the octatriene occurs. The reaction with cyclobutadiene (generated from cyclobutadiene ironthiocarbonyl) gives the following compounds, which are separated by SiO_2-column chromatography [4, 9].



exo adduct F



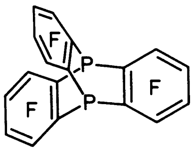
endo adduct G

Exo adduct: Yield 23.7%; melting point 97 to 98 °C; ^{19}F NMR (standard benzotrifluoride): δ = 5.40 ppm [6 F, doublet, $^1/_2(J_{PF} + J_{PF'})$ = 40.6 Hz, CF_3], 6.06 ppm [6 F, doublet, $^1/_2(J_{PF} + J_{PF'})$ = 38.4 Hz, CF_3], 6.16 ppm [6 F, doublet, $^1/_2(J_{PF} + J_{PF'})$ = 38.8 Hz, CF_3].

Endo adduct: Yield 33.2%, melting point 111 to 112 °C, ^{19}F NMR: δ = 2.84 ppm [6 F, doublet, $^1/_2(J_{PF} + J_{PF'})$ = 41.7 Hz, CF_3], 6.04 ppm [6 F, doublet, $^1/_2(J_{PF} + J_{PF'})$ = 39.5 Hz, CF_3], 6.08 ppm [6 F, doublet, $^1/_2(J_{PF} + J_{PF'})$ = 39.5 Hz, CF_3] [4, 9].

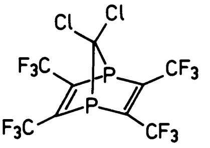
The reaction with 2,3-dimethylbutadiene (stainless-steel tube, 100°C, 5 h) does not give the expected primary adduct but 1,2-dimethyl-4,5-bis(trifluoromethyl)-1,4-cyclohexadiene as a decomposition product and additionally an unidentified compound (for the physical properties of both compounds, see the original reference) [4]. The reaction with butadiene is mentioned, but no details are given [4].

Dodecafluoro-13,14-diphosphatriptycene



The compound is obtained in 15% yield on heating red phosphorus with 1,2-diiodotetrafluorobenzene for 3 d at 250 °C. In the mass spectrum the molecular ion peak appears at m/e = 506. A strong metastabile peak is found for the reaction $C_{18}F_{12}P_2^+ \rightarrow C_{18}F_{10}P^+ + PF_2$ [10].

2,3,5,6-Tetrakis(trifluoromethyl)-7,7-dichloro-1,4-diphosphabicyclo[2.2.1]hepta-2,5-diene



The compound is obtained in 54% yield by heating 2,3,5,6,7,8-hexakis(trifluoromethyl)-7-methoxy-1,4-diphosphabicyclo[2.2.2]octa-2,5-diene in CCl_4 in an evacuated Pyrex tube [3]. The compound forms yellow needles (sublimation at 30 °C/760 Torr) [3], melting point 39 to 39.5 °C, IR (KBr) ν(C=C) = 1600 cm^{-1}, ^{19}F NMR (standard benzotrifluoride): δ = 8.00 ppm [doublet, $^1/_2(J_{PF} + J_{PF'})$ = 22.6 Hz], mass spectrum m/e = 468 (M^+) [3, 11].

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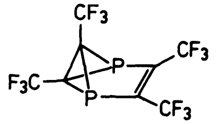
1,3,4,6-Tetrakis(trifluoromethyl)-2,5-diphosphatricyclo[3.1.0.$0^{2,6}$]hex-3-ene

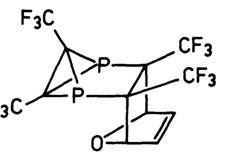


Irradiation (high-pressure lamp) of a solution 2,3,5,6,7,8-hexakis(trifluoromethyl)-7-methoxy-1,4-diphosphabicyclo [2.2.2]octa-2,5-diene in perfluoropentane sealed in vacuo in a Pyrex tube for 72 h at room temperature yields the compound after trap-to-trap distillation. It is a colorless volatile oil which solidified at −78 °C. The yield is 41%, based on octa-2,5-diene. The compound is also obtained by irradiation of 2,3,5,6-tetrakis(trifluoromethyl)-1,4-diphosphabenzene (formed in situ by thermolysis of the diphosphabicyclooctadiene in n-hexane) in perfluoropentane at 20°C (72 h, Ar atmosphere) [6]. IR (in n-pentane): ν(C=C) = 1620 [10, 11], 1300 to 1100 cm^{-1} [6]. ^{19}F NMR (in n-pentane, internal standard benzotrifluoride): δ = 10.2 ppm [6F, doublet, $^1/_2(J_{PF} + J_{PF'})$ = 22.6 Hz], 6.0 ppm (6F, triplet, J_{PF} = 5.2 Hz). ^{13}C NMR ($CDCl_3$): δ = 71.71 ppm (triplet, J_{PC} = 47.5 Hz), 191.1 to 123.0 ppm (multiplet, CF_3) [6] (^{19}F-decoupled spectrum pictured in [10]). ^{31}P NMR ($CDCl_3$, external standard 85% H_3PO_4): δ = 17.96 ppm [5, 6]. Mass spectrum m/e = 386 (M^+) [5, 6].

The compound is stable at room temperature and is not attacked by oxygen. On heating it isomerizes to 2,3,5,6-tetrakis(trifluoromethyl)-1,4-diphosphabenzene. The half-life of the diphosphacyclohexene in perfluorobenzene at 198 °C is found to be 75 min. Irradiation of the compound with a low pressure mercury lamp also yields the 1,4-diphosphabenzene (see p. 75) [6].

The Diels-Alder reaction with 2,3-dimethyl-1,3-butadiene gave the stable 8,9-dimethyl-1,3,4,6-tetrakis(trifluoromethyl)-2,5-diphosphatetracyclo[4.4.0.$0^{2,4}$.$0^{3,5}$]dec-8-ene, melting point 55 to 56 °C. ^{19}F NMR ($CDCl_3$, internal standard benzotrifluoride) δ = 9.2 ppm (6F, multiplet), 3.2 ppm (6F, doublet, J_{PF} = 22.6 Hz), ^1H NMR see [6].

The reaction with furan in n-pentane at 20 °C (5d) under stirring yields the adduct (colorless crystals)



Melting point 66 to 70 °C. ^{19}F NMR ($CDCl_3$, internal standard benzotrifluoride): δ = 10.8 ppm (6F, doublet, J_{PF} = 31.6 Hz), 8.8 ppm (6F, multiplet), for ^1H NMR, see the original [6].

The treatment with phenylazide in n-pentane in a sealed Pyrex tube (50 °C, 2 d) gave 9-phenyl-1,3,4,6-tetrakis(trifluoromethyl)-2,5-diphosphatriazatetracyclo [4.3.0.$0^{2,4}$.$0^{3,5}$]non-7-ene as a pale yellow oil, boiling point 70 °C/7 Torr. ^{19}F NMR (internal standard benzotrifluoride, $CDCl_3$): δ = 10.8 ppm (3F, multiplet), 10.0 ppm (3F, multiplet), 5.2 to −2.8 ppm (CF, multiplet), ^1H NMR see [6].

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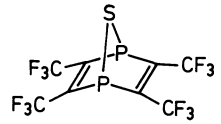
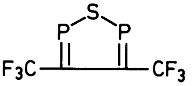
2,3,5,6-Tetrakis(trifluoromethyl)-7-thia-1,4-diphosphanorbornadiene

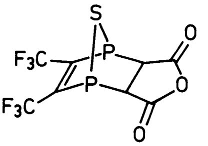


The thermolysis of 2,3,5,6,7,8-hexakis(trifluoromethyl)-7-methoxy-1,4-diphosphabicyclo-[2.2.2]octa-2,5-diene with excess sulfur in pentane in a sealed tube at 100 °C (48 h) gave the title compound as an air-stable yellow oil. It is also obtained in almost quantitative yield in the reaction of 2,3,5,6-tetrakis(trifluoromethyl)-1,4-diphosphabenzene with cyclohexene thioxide. The compound shows the C=C stretching band at 1610 cm^{-1}, ^{19}F NMR (in pentane, external standard benzotrifluoride): $\delta = 6.8$ ppm ($J_{PF} = 24.8$ Hz). The desulfurization of the norbornadiene with $(C_6H_5)_3P$ leads to the 1,4-diphosphabenzene [7].

3,4-Bis(trifluoromethyl)thiadiphosphole

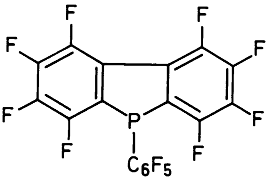


The compound forms on the thermolysis of 2,3,5,6,7,8-hexakis(trifluoromethyl)-7-methoxy-1,4-diphosphabicyclo[2.2.2]octa-2,5-diene with 0.5 molar equivalent of sulfur in almost quantitative yield as a very air-sensitive oil. IR: ν (C-F) = 1238, 1175 cm^{-1}, ^{19}F NMR (in pentane, external standard benzotrifluoride): $\delta = 12.8$ ppm ($J_{PF} = 51$ Hz), UV (in hexane): $\lambda_{max} = 248$ ($\varepsilon > 1100$), 322 nm ($\varepsilon > 850$). The compound is a good diene for Diels-Alder reactions. With hexafluoro-2-butyne it reacts forming 2,3,5,6-tetrakis(trifluoromethyl)-7-thia-1,4-diphosphanorbornadiene quantitatively. Treatment with maleic anhydride in pentane gave the adduct



in 57% yield, melting point 135 to 136°C, ^{19}F NMR (in $CDCl_3$): $\delta = 9.6$ ppm ($J_{PF} = 27.1$ Hz) [7].

5-Pentafluorophenyloctafluorodibenzophosphole



The phosphole (melting point 151 to 153 °C) is prepared [12] using the method given in [13] for the preparation of 5-phenyloctafluorodibenzophosphole from octafluoro-2,2′-dilithiobiphenyl and phenyldichlorophosphine. The mass spectrum of the compound is discussed in [12]. It gives rise to a large variety of fluoroaromatic fragments, many of which result from PF_n losses (n = 1, 2, 3) [12].

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5.2.2 Perfluoroorganophosphines

5.2.2.1 Preparation and Formation

2,2-Difluorophosphaethylene $F_2C{=}PH$

$F_2C{=}PH$ was postulated as an intermediate in the reaction of phosphines containing the group $>$CFPH— with aqueous bases [1] and its ion was found in the mass spectra of some trifluoromethylphosphines [2]. The short-lived compound has been detected by MW spectroscopy in the flow-system pyrolysis of CF_3PH_2 at 1000 °C at pressures in the range from 10 to 30 μm, as half-live 1.3 min were determined [3]. It forms also on passing of a CF_3PH_2 stream at 30 Torr at room temperature through a tube filled with broken KOH pellets [4, 5].

Trifluoromethylphosphine CF_3PH_2

The phosphine is formed in quantitative yield by the reaction of CF_3PI_2 with Hg and excess HI (>2 mol) [6]; for this reaction see also Part 3, p. 14. CF_3PH_2 is obtained on decomposition of CF_3PHCl or CF_3PHBr and on decomposition of CF_3PHI in presence of AgCl, AgBr, AgCN, $HgCl_2$ and SbF_3 (all reactions at room temperature) [7]. Cleavage of $CF_3PHPHCF_3$ by HCl [7] or HI [6] at room temperature as well as the reaction of $(CF_3P)_4$ with $(CH_3)_3SnH$ (15 min at room temperature) [8] gives CF_3PH_2. It also forms in a low-pressure silent discharge of $CF_3PHPHCF_3$ and of $(CF_3)_2PH$ [30]. Very high yields of the phosphine are found in the reaction of CF_3PI_2 with $(CH_3)_3SnH$ in sealed tube at room temperature within a few minutes [9]. CF_3PH_2 forms quantitatively on reacting $[(CH_3)_3M]_2PCF_3$ or $(CH_3)_3MPHCF_3$ (M = Si, Ge, Sn) with HBr and by decomposition of $(CH_3)_3MPHCF_3$.

Bis(trifluoromethyl)phosphine $(CF_3)_2PH$

The phospine forms in the reaction of $(CH_3)_3SnH$ with $(CF_3)_3PI$ at 20°C in a few minutes in >95% yield [9] and with $(CF_3)_4P_2$ at 20°C in one hour [8]. CF_3AsH_2 or $(CH_3)_3MAsHCF_3$ cleaves off $(CF_3)_2PH$ from compounds of the type $(CH_3)_3MP(CF_3)_3$ (M = Si, Ge, Sn) [13]. The phosphine is obtained quantitatively by decomposition of $(CF_3)_2PAsH_2$ above −40°C or by the reaction of $(CF_3)_2PAsH_2$ with Br_2, HBr, $(CH_3)_2AsH$, $(CH_3)_3SiH$ and $(CH_3)_4As_2$ [11]. The cleavage of $R(CF_3)PP(CF_3)_2$ by HCl at 20°C gives the phosphine in yields increasing in the order R = CH_3, CH_2F, CHF_2; it is also obtained by the reaction of $(CF_3)_2PCH_2P(CF_3)P(CF_3)_2$ with HCl [12].

Cleavage reactions of $(CF_3)_2PP(CF_3)_2$ with $(CH_3)_3GeH$ at 150°C or with $(CH)_3SnH$ at 20°C form $(CF_3)_2PH$, which is also obtained from $(CF_3)_2PAs(CH_3)_2$ and $(CH_3)_3SnH$ at 20°C. $(CF_3)_2PXCF_3$ (X = S, Se) reacts with $(CH_3)GeH$ at 100°C and with $(CH_3)_3SnH$ at −10°C for X = S, and at 0°C for X = Se, quantitatively to yield the phosphine. The formation of $(CF_3)_2PH$ is also observed in the reaction of $(CF_3)_2PYCH_3$ (Y = Se, Te) with HI, of $(CF_3)_2PTeCH_3$ with HBr at 20°C, of $(CF_3)_2PXCH_3$ (X = S, Se) with $(CH_3)_3SnH$ (at 0°C and 0.4 h for X = S and −40°C and 0.4 h for X = Se) and with $(C_6H_5)_3SnH$ (at 20°C and 1 d for X = S, Se), furthermore in the reaction of $(CF_3)_2PSn(CH_3)_3$ with CH_3XH (X = S, Se) at −40°C (0.2 h) and with $(CH_3)_2AsH$ at 20°C (1 d) [13]. The phosphine forms in the reaction of $(CF_3)_2PSn(CH_3)_3$ with $Cr(CO)_5(CH_3)_2AsH$ at 20°C [14] and in the hydrolysis of $(CF_3)_2PSeP(CF_3)_2$ with hydrochloric acid [15].

$(CF_3)_2PH$ forms in a low-pressure silent discharge of CF_3PH_2 [30].

Trifluoromethylcyanophosphine CF_3PHCN

The compound has been detected by NMR spectroscopy in solutions of $CF_3P(CN)_2$ and CF_3PH_2 after standing for several weeks [7].

1,1-Bis(trifluoromethyl)diphosphine $(CF_3)_2PPH_2$

1,2-Bis(trifluoromethyl)diphosphine $CF_3PHPHCF_3$

$(CF_3)_2PPH_2$ is obtained by the reaction of F_3SiPH_2 with $(CF)_2PI$ in a sealed tube at 20°C (5 d) [16].

On reacting CF_3PI_2 with a less than stoichiometric amount of anhydrous HI in the presence of mercury, $CF_3PHPHCF_3$ is formed and can be separated easily from the by-products [CF_3PH_2, $(CF_3P)_n$, n = 4,5] by fractional distillation [6]. Shaking CF_3PHI with dry mercury for 20 min yields the diphosphine in 96% yield. $CF_3PHPHCF_3$ is also formed in the reaction of CF_3PHI with $HgCl_2$, AgCl, SbF_3 CdF_2, and with NaF in acetonitrile, also in the reaction of CF_3PH_2 with Cl_2 and with $CF_3P(CN)_2$ as well as in the thermal decomposition of CF_3PHBr [7]. The diphosphine is obtained by a low-pressure silent discharge of CF_3PH_2 [30].

5.2.2.2 Physical Properties

F_2C=PH

The analysis of the microwave spectrum gives the experimental rotational constants A_0 = 11107.33, B_0 = 4766.33 and C_0 = 3330.79 MHz. Rotational constants have been calculated from preliminary structural data; r(C-F) = 1.315 Å and α(F-C-F) = 107° have been transferred from F_2CS, r(P-H) = 1.420 Å from $(CH_3)_2PH$. The distance r(C=P) = 1.671 Å and the angle α(C-P-H) = 100° have been obtained by variation to give the best agreement between the experimental and calculated rotational constants [3]. Ab initio MO-SCF calculations with the bases STO-3G and STO 4-31G resulted in the following values for the molecular energy E_T, the geometry parameters and the dipole moment μ [17]:

Basis	E_T	r(C=P)	r(P-H)	α(C-P-H)	μ
STO-3G	−570.91108 a.u.	1.67 Å	1.39 Å	92.6°	2.60 D
STO 4-31G	−570.25194 a.u.	1.74 Å	1.67 Å	94.4°	1.024 D

The calculation of the charge distribution shows that there is a substantial positive charge on the phosphorus atom. The barrier to in-plane inversion is calculated (STO-3G basis) to be 315 kJ/mol and the barrier for the out-of-plane rotation of the C-P-H fragment to be 570 kJ/mol [17].

The ^1H, ^{19}F and ^{31}P NMR spectra show the following chemical shifts δ (in ppm) and spin-spin coupling constants J (in Hz), lowfield shifts are positive from the standards $(CH_3)_4Si$, $CFCl_3$ and $P(OCH_3)_3$ [5, 18]:

$\delta(F^1) = 4.2$, $\delta(F^2) = 24.6$, $\delta(P) = -201.4$, $\delta(H) = 3.55$, $J(P\text{-}H) = 166.6$, $J(F^1\text{-}H) = 19.2$, $J(F^2\text{-}H) = 40.0$, $J(P\text{-}F^1) = 213.6$, $J(P\text{-}F^2) = 82.3$, $J(F^1\text{-}F^2) = 25.4$

CF_3PH_2 and $(CF_3)_2PH$

The investigation of the He(I) photoelectron spectra of both phosphines gives the following vertical ionization potentials (in eV) which are tentatively assigned to localized molecular orbitals assuming C_s skeletal symmetry [19].

Assignment	Lone electron pair on phosphorus	P-C σ bond	P-H σ bond	F nonbonding orbitals on CF_3 groups		
symmetry	A′	A″	A′	A_2	E	E
CF_3PH_2	11.50	13.21	13.86	15.34	16.16	16.93
symmetry	A′(n)	A′	A″	A_2	E	E
$(CF_3)_2PH$	11.18	13.24	14.08	15.06	15.83	16.69

The analysis of the IR and Raman spectra of $(CF_3)_2PH$ in [20] agrees well with the results of investigations covered in Part 3, p. 17. NMR spectra of $(CF_3)_2PH$: The chemical shifts (in ppm, negative sign mean upfield to the standard) and the spin-spin coupling constants J (in Hz) are given in the following [21].

^{13}C NMR (standard C_6D_6): $\delta = -0.09$, $J(C\text{-}F) = 314$, $J(C\text{-}P) = 13.55$, $J(CP\text{-}CF) = 6.3$, $J(C\text{-}PH) = 4.7$

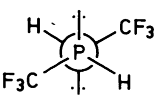
^{31}P NMR (standard 15% H_3PO_4 in D_2O, calibration against 85% H_3PO_4): $\delta = -49.6$, J(P-CF) = 69.4, J(P-H) = 216

^{19}F NMR (standard $CFCl_3$, measured in D_2O solution of CF_3COOH): $\delta = -48.9$, J(FC-P) = 70, J(FC-PH) = 10

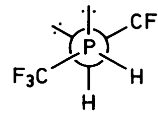
^{1}H NMR [standard $(CH_3)_4Si$, solvent $CHCl_3$]: $\delta = 4.06$, J(H-P) = 214, J(HC-PF) = 9.86

$CF_3PHPHCF_3$

The diphosphine can exist in two diastereomeric forms [22]:



meso form (a)



d, l diastereomer (b)

The ^{19}F NMR spectrum shows for each diastereomer a doublet (with large spacing) of doublets (with small spacing) plus weaker peaks as expected for the M part of a MM'AA'XX' system. The values observed (internal standard $CFCl_3$) are as follows: for the low field diastereomer $\delta = -40.7$ ppm [J(P-CF) + J(P-P-CF) = 69 Hz, J(HP-CF) + J(HP-P-CF) = 12.5 Hz], for the highfield diastereomer $\delta = -41.5$ ppm (61 Hz, 11.5 Hz) [30]. Both isomers could be distinguished by further NMR experiments. The temperature-dependent $^1H\{^{19}F\}$ and $^{31}P\{^{19}F\}$ spectra show the expected AA'XX' spin systems. The spin-spin coupling constants J were obtained by triple resonance experiments (^{19}F decoupling, ^{31}P tickling, ^{1}H resonance). The following chemical shifts (δ in ppm, positive sign lowfield to the standards $(CH_3)_4Si$ and 85% H_3PO_4) and coupling constants J (in Hz) have been evaluated [22]:

Temperature	Isomer	$\delta(^1H)$	$\delta(^{31}P)$	J(P-P)	J(P-H)	J(P-PH)	J(HP-PH)
35 °C	a	3.68	−90.3	−135.2	+205.6	+3.2	+9.2
	b	3.82	−92.0	−183.7	+213.9	+15.2	+3.0
100 °C	a	—	−91.5	−114.8	+213.7	+1.8	+7.4
	b	—	−95.1	−203.4	+223.2	+15.5	±0.5

5.2.2.3 Chemical Reactions

5.2.2.3.1 Pyrolysis

On the pyrolysis of CF_3PH_2 at 1000 °C, $F_2C{=}PH$ is detected by MW spectroscopy [3]. On passing gaseous CF_3PH_2 slowly at 20 °C over solid KOH two HF units are eliminated to give $FC{\equiv}P$. Increasing the rate of the CF_3PH_2 stream or lowering the quantity of reacting KOH gives $F_2C{=}PH$ [4, 5, 23]. The pyrolysis of $(CF_3)_2PH$ on flowing over KOH pellets gives the compound $CF_3P{=}CF_2$ [18].

5.2.2.3.2 Reactions of CF_3PH_2 and $(CF_3)_2PH$

CF_3PH_2 reacts at 20°C with a deficiency of iodine forming CF_3PHI which reacts further with iodine to give CF_3PI_2 [7]. Equimolar mixtures of CF_3PH_2 and CF_3PI_2 react with sizeable rates above 40°C or on irradiation by an Hg lamp forming CF_3PHI. The same reaction is observed for CF_3PD_2. Reactions with CF_3PBr_2 and with CF_3PCl_2 forming CF_3PHX, X = Br, Cl, occur only on irradiation, no reaction is found for CF_3PF_2. A mixture of CF_3PH_2 and Cl_2 on standing for 7 d at 20°C yields CF_3PHCl, CF_3PCl_2 and HCl. Subsequent reaction of CF_3PHCl with CF_3PH_2 yields $CF_3PHPHCF_3$. Smaller amounts of the diphosphine are formed in the reaction of CF_3PH_2 with CF_3PHBr, no reaction occurs between CF_3PH_2 and CF_3PHI to form the diphosphine. At room temperature, CF_3PH_2 forms with $CF_3P(CN)_2$, after some weeks, CF_3PHCN, which reacts with excess CF_3PH_2 to give $CF_3PHPHCF_3$, $(CF_3P)_4$ and HCN. These products are also found on heating the reaction mixture for 14 d at 50°C [7].

The reaction of the phosphine with $Fe_2(CO)_9$ (6 d, 21°C, sealed tube) gives $Fe(CO)_4[CF_3PH_2]$, which is an orange-brown liquid with a vapor pressure of about 1 Torr at 20°C [24].

$(CF_3)_2PH$. On warming a mixture of $(CF_3)_2PH$ and NH_3 in a glass tube (sealed by a stopcock) from −196 or −130°C to −50 or 0 or 25°C, a reaction mixture forms in which $(CF_3)_2PNH_2$, $CH_2F(CF_3)PNH_2$, $CHF_2(CF_3)PNH_2$ and $HN[P(CF_3)_2]_2$ are detected by NMR spectroscopy. The yield of the products depends on the manner of raising the temperature [25].

On elevation of the temperature from −78 to 0°C $(CH_3)_3N$ dehydrofluorinates $(CF_3)_2PH$ forming $(CH_3)_3NH_2F_2$ and presumably $CF_3P{=}CF_2$ as primary compounds and initiating a series of further reactions yielding $(CF_3)_2P_4$, $R(CF_3)PP(CF_3)_2$ (R = CHF_2, CH_2F or CH_3), $(CF_3)_2PCH_2P(CF_3)P(CF_3)_2$ and less volatile products. With $(CH_3)_3SiCl$ as a further added reactant leading to the formation of $(CH_3)_3NHCl$ and $(CH_3)_3SiF$, the same volatile phosphines as above are formed, but the yields are higher. $(CH_3)_3SiP(CF_3)_2$ is also found. For $(CF_3)_2PCH_2P(CF_3)P(CF_3)_2$, the vapor pressure p (in Torr) is given by $\log p = 6.627 + 1.75\,T - 0.005\,T - 2546/T$, boiling point 164°C, Trouton constant 27.7 $cal \cdot mol^{-1} \cdot K^{-1}$ [12]. In the presence of $(CH_3)_3N$ the phosphine $(CF_3)_2PH$ reacts with $CH_3(CF_3)PCl$ (sealed tube, warming to −78°C, then to 25°C) yielding the chiral diphosphine $CH_3(CF_3)PP(CF_3)_2$, which is characterized by NMR data [29]. $(CF_3)_2PH$ reacts with $IM(CO)_5$ in C_6H_6 at 25°C to give $(CF_3)_2PM(CO)_5$, for M = Mn (30 h) and for M = Re (8 h) [26].

Under UV irradiation (240 h, in vacuo), $(CF_3)_2PH$ reacts with $F_2C{=}CCl_2$ to form CF_3H, $(CF_3)_3P$, $(CF_3)_4P_2$ and, along with other compounds, $HCCl_2CF_2P(CF_3)_2$, melting point 115 to 118°C/731 Torr, ^{19}F NMR (external standard CF_3COOH): $\delta(CF_3) = 27.8$ ppm (doublet of triplets), $\delta(CF_2) = -21.2$ ppm (doublet of octets). The irradiation of the phosphine and $HClC{=}CFH$ gives a complex product mixture, from which two compounds could be isolated and tentatively characterized by their ^{19}F NMR spectra to be $H_2CClCFHP(CF_3)_2$ and $HCFClCH_2P(CF_3)_2$. The phosphine underwent no reaction with $F_2C{=}CCl_2$ at 50°C (120°C), with $FHC{=}CHCl$ at 100°C (120 h), with hexafluoropropene on UV irradiation (20°C, 22 h) or on heating for 120 h at 100°C [27].

Condensation Reactions of CF_3PH_2 and of $(CF_3)_2PH$

Both phosphines react with $[(CH_3)_3M]_3P$ and $(CH_3)_3MPH_2$ (M = Si, Ge, Sn) at room temperature to form mixtures of products, whose composition depends on the ratio of the starting compounds, see **Table 19**. The rate of formation is greater for $[(CH_3)_3M]_3P$ than for $(CH_3)_3MPH_2$ and decreases in the order Sn > Ge > Si [10].

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Table 19
Condensation Reactions of CF_3PH_2 and $(CF_3)_2PH_2$ [10].

Reaction components (quantities in mmol), conditions		Products (yields)	
$(CF_3)_2PH$			
(15)	$[(CH_3)_3Si]_3P$ (1.0) 20 °C, 16 d	$(CH_3)_3SiP(CF_3)_2$ (77%)	$(CH_3)_3SiF$ (23%)
(15)	$[(CH_3)_3Sn]_3P$ (1.0) 20 °C, 0.4 d	$(CH_3)_3SnP(CF_3)_2$ (12%)	$(CH_3)_3SnF$ (88%)
CF_3PH_2			
(8.5)	$[(CH_3)_3Si]_3P$ (2.0) 20 °C, 21 d	–	–
(16.8)	$[(CH_3)_3Ge]_3P$ (2.5) 20 °C, 63 d	$(CH_3)_3GeP(H)CF_3$ (80%)	$[(CH_3)_3Ge]_2PCF_3$ (15%)
(8.0)	$[(CH_3)_3Sn]_3P$ (2.0) 20 °C, 7 d	$(CH_3)_3SnP(H)CF_3$ (30%)	$[(CH_3)_3Sn]_2PCF_3$ (10%)
(6.0)	$(CH_3)_3SiPH_2$ (3.0) 50 °C, 35 d	no reaction	
(2.0)	$(CH_3)_3SiPH_2$ (2.0) 50 °C, 21 d	no reaction	
(3.5)	$(CH_3)_3GePH_2$ (2.0) 20 °C, 150 d	$(CH_3)_3GeP(H)CF_3$ (2 to 3% as mixture)	$[(CH_3)_3Ge]_2PCF_3$
(7.0)	$(CH_3)_3SnPH_2$ (7.0) 20 °C, 7 d	$(CH_3)_3SnP(H)CF_3$ (20% as mixture)	$[(CH_3)_3Sn]_2PCF_3$

5.2.2.3.3 Reactions of $CF_3PHPHCF_3$

Excess HI cleaves the P-P bond in the diphosphine [6, 7] according to the reactions $CF_3PHPHCF_3 + HI \rightarrow CF_3PH_2 + CF_3PHI$, $2\,CF_3PHI \rightarrow CF_3PH_2 + CF_3PI_2$.

5.2.2.3.4 Reactions of $(C_6F_5)_2PH$

The phosphine reacts in organic solvents with the stable radicals diphenylpicrylhydrazyl, triphenylverdazyl, indophenoxyl and their leuco compounds. The phosphorus-containing nitroxide $(C_6F_5)_2PN(O^{\cdot})C(CH_3)_3$ which is relatively stable (the ESR spectrum is observable for several days) is obtained in the reaction of the diphenylpycrylhydrazyl radical with the phosphine in benzene in air in presence of 2-methyl-2-nitrosopropane [28].

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5.2.3 Perfluorohalogenoorganophosphorus Oxygen Compounds

5.2.3.1 Preparation and Formation

Tris(perfluoroalkyl)phosphine oxides $(R_f)_3PO$

R_f = CF_3, C_2F_5, n-C_3F_7, n-C_4F_9, n-C_5F_{11}, i-C_5F_{11}, n-C_6F_{13}, n-C_7F_{15}, n-C_8F_{17}, C_9F_{19}

Tris(pentafluorophenyl)phosphine oxide $(C_6F_5)_3PO$

Pentafluorophenylbis(pentafluorophenylethynyl)phosphine oxide $C_6F_5(C_6F_5C{\equiv}C)_2PO$

$(CF_3)_3PO$ (see Part 3, p. 31) forms on the decomposition of $(CF_3)_3P(F)OSi(CH_3)_3$ at room temperature in 4 h in quantitative yield [1].

The phosphine oxides $(R_f)_3PO$, R_f = C_2F_5 to C_8F_{17}, have been prepared from the corresponding alkylphosphine oxides R_3PO by the electrochemical fluorination of a 10 to 25% alkylphosphine oxide solution in anhydrous HF. The preferable conditions for the electrolysis are current densities from 0.02 to 0.05 A/cm^2 and voltages across the electrodes of 5.0 to 6.0 V. In order to obtain oxides of higher tris(perfluoroalkyl)phosphines ($\geqq C_5$) their hydrocarbon analogues are first brominated to avoid the cleavage of the C-P bond on electrolysis. The bromination is carried out on introducing bromine into a mixture consisting of 15 to 20% hydrogen fluoride and 85 to 75% trialkylphosphine oxide and stirring the mixture for 3 to 4 h at room temperature [2]. For $(C_9F_{19})_3PO$ no details for preparation are given.

$(C_6F_5)_3PO$ is prepared in 93% yield by the reaction of $(C_6F_5)_3P$ with $(CF_3)_2NO$ in Cl_2CFCF_2Cl as solvent (sealed tube, −70 °C for one day, shaking at room temperature for 20 min, left standing for another day). The recrystallization from petroleum ether gives white needles [3]. The oxide forms on dissolving $(C_6F_5)_3P$ in a SbF_5-HSO_3F mixture (1 : 1) or in pure HSO_3F followed by addition of H_2O [20].

$C_6F_5(C_6F_5C{\equiv}C)_2PO$ (yield 67%) is obtained by dissolving $C_6F_5(C_6F_5C{\equiv}C)_2P$ in HSO_3F followed by addition of H_2O [20].

Bis(trifluoromethyl)phosphinous trifluoroacetic anhydride $(CF_3)_2POC(O)CF_3$

Bis(trifluoromethyl)phosphinous pentafluoropropionic anhydride $(CF_3)_2POC(O)C_2F_5$

Bis(trifluoromethyl)phosphinous heptafluorobutyric anhydride $(CF_3)_2POC(O)C_3F_7$

The compounds have been obtained by the reaction of the silver salts $AgOC(O)R_f$ (R_f = CF_3, C_2F_5, C_3F_7) with $(CF_3)_2PCl$ or $(CF_3)_2PI$. The reaction components are mixed at low temperature and then brought to room temperature within 10 min. After fractional condensation the yields are as follows [4].

	$(CF_3)_2PCl$	$(CF_3)_2PI$
$(CF_3)_2POC(O)CF_3$	43.6%	82.1%
$(CF_3)_2POC(O)C_2F_5$	60.5%	80.0%
$(CF_3)_2POC(O)C_3F_7$	18.6%	92.9%

2-Cyano-2(η-oxo-bis(trifluoromethyl)phosphine)hexafluoropropane $(CF_3)_2POC(CF_3)_2CN$

Tetrakis(trifluoromethyl)phosphinous acid anhydride $(CF_3)_2POP(CF_3)_2$

Tetrakis(trifluoromethyl)phosphinic acid anhydride $(CF_3)_2P(O)OP(O)(CF_3)_2$

Bis(trifluoromethyl)phosphoryl-μ-oxo-bis(trifluoromethyl)phosphine $(CF_3)_2POP(O)(CF_3)_2$

$(CF_3)_2POC(CF_3)_2CN$ forms in 97% yield when $(CF_3)_2PI$ is frozen into a reactor containing $NaOC(CF_3)_2CN$ at −196 °C and allowed to warm to room temperature over a period of 30 min. After trap-to-trap rectification the compound is held in the −95 °C trap. The results were unchanged when $(CF_3)_2PCl$ was substituted for the iodo derivative [4].

$(CF_3)_2POP(CF_3)_2$ (see Part 3, p. 32) is obtained by the decomposition of the compounds $(CF_3)_2POC(O)R_f$ with R_f = CF_3, C_2F_5, C_3F_7 [4].

A new route for preparing $(CF_3)_2P(O)OP(O)(CF_3)_2$ (see Part 3, p. 32) is the reaction of $(CF_3)_2POP(CF_3)_2$ with $(CF_3)_2P(O)Cl$ at 25 °C (18 h). One other way is the oxidation of $(CF_3)_2POP(CF_3)_2$ with NO to give the compound in high yield (83%, 113 °C, 65 h, sealed tube). The oxidation of $(CF_3)_4P_2$ with NO by raising the temperature from −78 to +25 °C within 5 min yields the compound in 90% yield [5].

$(CF_3)_2POP(O)(CF_3)_2$ has been obtained by the reaction of $(CF_3)_2POP(CF_3)_2$ with $(CF_3)_2P(O)Cl$ (sealed glass tube, 25 °C, 11 d), or with $(CF_3)_2P(O)OP(O)(CF_3)_2$ (yield 94%, 25 °C, 26 h) and by oxidation of $(CF_3)_2PP(CF_3)_2$ with NO (sealed bulb, 50 °C, 84% yield) [5].

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Bis(trifluoromethyl)aminooxy-bis(trifluoromethyl)phosphine $(CF_3)_2PON(CF_3)_2$

Bis[bis(trifluoromethyl)aminooxy]-tris(trifluoromethyl)phosphorane $(CF_3)_3P[ON(CF_3)_2]_2$

Bis[bis(trifluoromethyl)aminooxy]-bis(trifluoromethyl)fluorophosphorane $F(CF_3)_2P[ON(CF_3)_2]_2$

Bis[bis(trifluoromethyl)aminooxy]-bis(trifluoromethyl)chlorophosphorane $Cl(CF_3)_2P[ON(CF_3)_2]_2$

Bis[bis(trifluoromethyl)aminooxy]-bis(trifluoromethyl)bromophosphorane $Br(CF_3)_2P[ON(CF_3)_2]_2$

Bis[bis(trifluoromethyl)aminooxy]-bis(trifluoromethyl)cyanophosphorane $CN(CF_3)_2P[ON(CF_3)_2]_2$

Tetrakis[bis(trifluoromethyl)aminooxy]-trifluoromethylphosphorane $CF_3P[ON(CF_3)_2]_4$

The preparation of $(CF_3)_2PON(CF_3)_2$, $Cl(CF_3)_2P[ON(CF_3)_2]_2$ and $(CF_3)_3P[ON(CF_3)_2]_2$ is mentioned in Part 7, p. 100.

$(CF_3)_2PON(CF_3)_2$ is obtained in 74% yield on reacting $(CF_3)_2PI$ and CF_3NO for 3 d at −74 °C in a sealed glass ampule. Traces of iodine formed in the reaction are removed by shaking the mixture with mercury. The compound is purified by fractional condensation [6]. The reaction of $(CF_3)_2NON(CF_3)_2$ with $(CF_3)_3P$ (molar ratio 1 : 1) in a sealed tube (15 h at −78 °C, then 3 to 4 h at room temperature) followed by fractionational trapping at −88 °C gives the compound in about 100% yield [7]. With a molar ratio of 2:1 $CF_3P[ON(CF_3)_2]_2$ was obtained in a yield of about 61% (70 °C, 46 h, trapping at −60 °C) [7].

On reacting $(CF_3)_2PON(CF_3)_2$ with $(CF_3)_2PF$, $(CF_3)_2PCl$, $(CF_3)_2PBr$ or $(CF_3)_2PCN$ one obtains $F(CF_3)_2P[ON(CF_3)_2]_2$ (24 h, 20 °C, 93.5% yield), $Cl(CF_3)_2P[ON(CF_3)_2]_2$ (24 h, 20 °C, 93.5% yield), $Br(CF_3)_2P[ON(CF_3)_2]_2$ (3 d, 20 °C, 76.8% yield) and $CN(CF_3)_2P[ON(CF_3)_2]_2$ (16 h, −74 °C, 98% yield) [6].

The reaction of $(CF_3)_3P$ with $(CF_3)_2NO$ in a Pyrex tube on standing overnight at room temperature followed by fractional condensation gives at −20 °C $(CF_3)_3P(ON(CF_3)_2)_2$ in 96.1% yield. The pyrolysis of the phosphorane at 80 °C for 30 h in a closed vessel yields after vacuum distillation $CF_3P[ON(CF_3)_2]_4$ in 67% yield [8].

5.2.3.2 Physical Properties

Phosphine Oxides

$(C_6F_5)_3PO$ melts at 168 to 169 °C. The P-O stretching vibration is observed at 1230 cm^{-1} [3]. The ^{31}P and ^{19}F NMR spectra of $(C_6F_5)_3PO$ in acetonitrile (standards 85% H_3PO_4 and C_6F_6) show the chemical shifts $\delta(P) = -7.2$ ppm, $\delta(F^2,F^6) = 33.8$, $\delta(F^3,F^5) = 2.4$, $\delta(F^4) = 15.6$ ppm [20].

$C_6F_5(C_6F_5C{\equiv}C)_2PO$ melts at 125 to 127 °C. The ^{31}P and ^{19}F NMR spectra (standards 85% H_3PO_4 and C_6F_6) show the chemical shifts $\delta(P) = -11.7$ ppm, $\delta(F^2,F^6) = 32.2$ and 29.8 ppm, $\delta(F^3,F^5) = 3.7$ and 0.5 ppm, $\delta(F^4) = 17.2$ and 19.4 ppm. The UV maxima (molar absorptivity ε) are observed at 219 ($\log \varepsilon = 4.25$) and 260 nm ($\log \varepsilon = 4.49$) [20].

$(CF_3)_3PO$. Density $D_4^{-5} = 1.66_1$ g/cm³, $D = 1.649 - 2.7 \times 10^{-3}$ (−10 °C < t > 20 °C) [9]. ^{13}C NMR (internal standard $CDCl_3$, converted to $(CH_3)_4Si$): $\delta = 119.50 \pm 0.003$ ppm [quartet of doublets of septets, $J(C\text{-}P) = 163.3 \pm 0.7$ Hz, $J(C\text{-}F) = 316.9 \pm 0.7$ Hz, $J(C\text{-}P\text{-}C\text{-}F) = 3 \pm 0.7$ Hz] [10]. ^{31}P NMR (external standard P_4O_6, $CDCl_3$ solution): $\delta = -110$ ppm. Faraday effect $P_M = 316$ (−5 and 0 °C), 317 (10 °C), 314 μr (14 and 20 °C) [11].

Boiling points, densities, refractive indices as well as dielectric constants and dipole moments of the tris(perfluoroalkyl)phosphine oxides $(C_nF_{2n+1})_3PO$, $n > 1$ are given in **Table 20**. The dipole moments are directed toward the perfluoroalkyl groups. In the solid phase at −190°C the limiting values for the dielectric constant (ε_∞), polarization (P_∞) and the density D (in g/cm^3) for $(C_4F_9)_3PO$ and for $(i\text{-}C_5F_{11})_3PO$ has been found to be $\varepsilon_\infty = 2.12$ and 2.09, $P_\infty = 102$ and 119, D = 2.11 and 2.16, respectively [12].

Table 20
Physical Properties of Tris(perfluoroalkyl)phosphine Oxides $(C_nF_{2n+1})_3PO$, $n > 1$.
Boiling point (b.p.) in °C/pressure in Torr, density D, refractive index, dielectric constant ε, dipole moment μ.

Compound	b.p./Torr in °C [2]	D_4^{20} (g/cm^3) [2]	n_D^{20} [2]	ε [12]	μ in D [12]
$(C_2F_5)_3PO$	96 to 98/760	1.774	1.2859	2.34 (at 40 °C) 2.20 (at 80 °C)	0.86
$(n\text{-}C_3F_7)_3PO$	150 to 151/760	1.8598	1.2948	–	
$(n\text{-}C_4F_9)_3PO$	185 to 187/760 82 to 84/18	1.8930	1.3038	2.21 (at 20 °C)	0.86
$(i\text{-}C_5F_{11})_3PO$	120 to 122/18 107 to 109/14	1.9052	1.3102	2.12 (at 20 °C)	0.86
$(n\text{-}C_5F_{11})_3PO$	102 to 104/14	1.9050	1.3080	–	–
$(n\text{-}C_6F_{13})_3PO$	142 to 144/14	1.9240	1.3126	–	–
$(n\text{-}C_7F_{15})_3PO$	121 to 123/0.4	1.9450	1.3146	–	–
$(n\text{-}C_8F_{17})_3PO$	138 to 140/0.3	1.948	1.3184	–	–

$(CF_3)_2POC(O)R_f$ ($R_f = CF_3$, C_2F_5, C_3F_7) and **$(CF_3)_2POC(CF_3)_2CN$**

Melting points and NMR data are covered in **Table 21**, a presentation of IR data is given in **Table 22**. The mass spectra of the compounds are characterized by the molecule-ion peak (M^+), by the fragments $M^+ - F$ and $M^+ - CF_3$ as well as by fluorocarbon and fluorophosphorus fragments [4].

Table 21
Melting Point (m.p.) in °C and ^{19}F NMR$^{1)}$ Spectra of $(CF_3)_2POC(O)R_f$ ($R_f = CF_3$, C_2F_5, C_3F_7) and $(CF_3)_2POC(CF_3)_2CN$ [4].
Chemical shift δ in ppm (negative values means highfield from the standard), spin-spin coupling constant in Hz.

Compound	m.p.	^{19}F NMR$^{1)}$
$(CF_3^a)_2POC(O)CF_3^{b)}$	−56.1	$\delta(CF_3^a) = -60.8$, $\delta(CF_3^b) = -74.7$, J(P-F) = 87.5
$(CF_3^a)_2POC(O)CF_2CF_3^b$	−89.1	$\delta(CF_3^a) = -58.2$, $\delta(CF_3^b) = -79.4$, $\delta(CF_2) = -115.0$, J(P-F) = 90.0

Table 21 (continued)

Compound	m.p.	^{19}F NMR[1]
$(CF_3^a)_2POC(O)CF_2^{\alpha}CF_2^{\beta}CF_3^b$	−117.3	$\delta(CF_3^a) = -61.5$, $\delta(CF_3^b) = -81.3$, $\delta(CF_2) = -118.3$ (α), 126.2 (β), J(P-F) = 92.0, $J(CF_3\text{-}CF_2^{\alpha,\beta}) = 8.8$ (α), 8.8 (β)
$(CF_3^a)_2POC(CN)(CF_3^b)_2$[2]	−84.0	$\delta(CF_3^a) = -66.5$, $\delta(CF_3^b) = -79.0$, J(P-F) = 96.8

[1] Internal standard $CFCl_3$. — [2] ^{31}P NMR spectrum: δ = 78.60 ppm (internal standard 40% H_3PO_4), J(P-F) = 91.7 Hz.

Table 22
IR Spectra (in cm^{-1}) and Tentative Assignments for $(CF_3)_2POC(O)R_f$ ($R_f = CF_3$, C_2F_5, C_3F_7) and $(CF_3)_2POC(CF_3)_2CN$ [4].
(ν, δ are stretching or deformation vibrations, s or as means symmetric or antisymmetric.)

$(CF_3)_2POC(O)CF_3$	$(CF_3)_2POC(O)C_2F_5$	$(CF_3)_2POC(O)C_3F_7$	$(CF_3)_2POC(CF_3)_2CN$	
3 573 (w)	3 568 (w)	3 567 (w)		2ν(C=O)
—	—	—	2 260 (w)	ν(C≡N)
1 815 (s)	1 800 (s)	1 808 (s)	—	ν(C=O)
1 774 (m)	—	1 776 (w)	—	
1 341 (m)	1 346 (m)	1 350 (m)	1 307 (s)	ν_{as} and ν_s of the CF_3 group
	1 287 (vs)	1 293 (m)		
1 246 (vs)		1 247 (vs)	1 255 (vs)	
1 225 (vs)	1 223 (vs)	1 223 (vs)	1 225 (vs)	
1 196 (sh)		1 206 (vs)	1 203 (sh)	
1 176 (vs)	1 172 (vs)	1 176 (vs)	1 179 (vs)	
1 133 (vs)	1 129 (vs)	1 135 (vs)	1 132 (s)	
1 103 (vs)	1 015 (vs)	1 069 (m)	1 073 (s)	
		962 (m)	980 (ms)	
850 (vs)	825 (m)	—	836 (m)	ν(P-O-C)
779 (m),	778 (m)	776 (m)		
764 (sh)				
749 (sh)	748 (sh)	748 (m)	748 (w)	$\delta(CF_3)$
726 (w)	732 (w)	716 (w)	733 (w)	ν_{as}(P-C)

Phosphorus Acid Anhydrides

$(CF_3)_2POP(CF_3)_2$. Density D = 1.608_2 g/cm^3 [11]. ^{19}F NMR (standard $CFCl_3$): δ = −66.5 ppm, J(F-P) = 98.8 Hz (second-order spectra), ^{31}P NMR (standard H_3PO_4): δ = 99.3 (complex F-P coupling) [5], (standard P_4O_6): δ = −13 ppm [9]. The Raman spectrum of the liquid and the IR spectrum of the gaseous compound have been recorded and analyzed under the

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assumption of the highest possible symmetry for a nonlinear bridged structure resulting in point group C_{2v}, see **Table 23** [13]. Though strong p-d interactions could lead to a linear or nearly linear P-O-P bridge, the occurrence of two IR active ν(P-O-P) vibrations shows that the skeleton is bent. No evidence is given for the existence of more than one rotamer [13]. The unassigned IR spectrum is also given in [5]. The magnetooptical rotation of $(CF_3)_2POP(CF_3)_2$ has been determined: $|P|_M$(exp.) = 626 and compared with the value calculated from additivity band rotations $|P_M|$(cal.) = 688 [11, 14].

Table 23
Vibrational Frequencies ν (in cm^{-1}) and Assignments for $(CF_3)_2POP(CF_3)_2$ from the Analysis of the IR and Raman Spectrum[1] [13].
w = weak; m = medium; s = strong; sh = shoulder; p = polarized; dp = depolarized; v = very.

Raman (liquid)	IR (gas)	Assignment	Raman (liquid)	IR (gas)	Assignment
94 m dp 120 w sh		PC_2 twisting + scissoring	566 w dp 716 m s p	563 m s 712 m s	POP symmetric stretching
158 w sh 164 w		PC_2 deformation	748 vs p	748 m	CF_3 symmetric deformation
200 s p 238 m dp		POP bending CF_3 wagging; PC_2 wagging	930 vw	923 vs	POP asymmetric stretching
263 m sh dp 279 vs p 301 w sh	 276 w	CF_3 rocking	1 142 vw 1 171 w 1 229 vw	1 140 v vs 1 177 v vs 1 221 v vs sh 1 230 vs	CF_3 stretching
452 s p? 458 s sh 468 m p	 458 vs 466 s sh	PC_2 stretching + POP stretching			
529 w sh 538 m dp	 540 m	CF_3 antisymmetric deformation			

[1] Overtone and combination bands 372 m, 380 m (s), 639 (w), 854 (w, s), 884 (s), 944 (s), 961 (ms, s), 987 (m, s), 1 278 (w), 1 292 (w, s) cm^{-1}.

$(CF_3)_2P(O)OP(O)(CF_3)_2$. White crystals, melting point −42 °C. ^{19}F NMR (standard $CFCl_3$): $\delta = -72.03$ ppm [doublet, J(F-P) = 137.5 Hz]. ^{31}P NMR (standard H_3PO_4): $\delta = -5.4$ ppm [septet, J(F-P) = 137.5 Hz]. IR (in cm^{-1}; relative intensities in parentheses): 1 360 (14), 1 342 (24), 1 204 (164), 1 161 (11), 993 sh (9), 965 (39), 769 (1.4), 752 (1.6), 584 (30), 555 (5), 508 (7), 454 (7), 385 (4) [5].

$(CF_3)_2POP(O)(CF_3)_2$. Crystalline at −60°C, melting point at −41.7 to −41.4°C, vapor pressure p (in Torr) fits the equation $\log p = 7.7805 + 1.75 \log T - 0.007\,T - 2518/T$, boiling point 97 °C, Trouton constant 22.7 cal · mol^{-1} · K^{-1}. ^{19}F NMR (standard $CFCl_3$): $\delta = -65.6$ ppm [J(F-P) = 93.1 Hz], 72.5 ppm [J(F-P) = 131.9 Hz]. ^{31}P NMR (standard H_3PO_4): $\delta = 91.4$ ppm [J(P-F) = 92.9 Hz], −0.3 ppm [J(P-F) = 131.8 Hz]. IR (in cm^{-1}, relative intensities in parentheses): 1340 (13), 1221 (63), 1202 (73), 1182 (95), 1154 (25), 1138 (46), 959 (44), 921 (7), 764 (0.3), 750 (1.7), 697 (0.9), 582 (13), 503 (6), 443 (5), 380 (6) [5].

Aminooxy Derivatives of Phosphorus

The physical properties of $(CF_3)_2PON(CF_3)_2$, $(CF_3)_3P[ON(CF_3)_2]_2$ and of $X(CF_3)_2P[ON(CF_3)_2]_2$, X = F, Cl, Br, CN are covered in **Table 24** and **25**.

Table 24
Vapor Pressure p (in Torr), Extrapolated Boiling Points (b.p.), Enthalpy of Vaporization ΔH_v (in kcal/mol) and ^{19}F NMR Data (δ in ppm, standard $CFCl_3$, upfield shifts have negative sign) of the Compounds $X(CF_3)_2P[ON(CF_3)_2]_2$ (X = F, Cl, Br, CN), $(CF_3)_2PON(CF_3)_2$ [6] and $(CF_3)_3P[ON(CF_3)_2]_2$ [8].

Compound	log p = A − B/T A	 B	Temperature range (in °C)	b.p. in °C	ΔH_v	^{19}F NMR $\delta(CF_3N)$	 $\delta(CF_3P)$
$(CF_3)_2PON(CF_3)_2$	7.940	1800	−7 to 40	83	8.250	—	—
$(CF_3)_3P[ON(CF_3)_2]_2$	7.44	1930	34 to 65	149	8.83	—	—
$F(CF_3)_2P[ON(CF_3)_2]_2$	6.270	1390	24 to 55	138	6.380	−68.1	−55.4 (J_{PF} = 114 Hz)
$Cl(CF_3)_2P[ON(CF_3)_2]_2$	8.120	2125	24 to 77	132	9.750	−68.2	−59.0
$Br(CF_3)_2P[ON(CF_3)_2]_2$	6.340	1600	26 to 53	190	7.350	—	—
$CN(CF_3)_2P[ON(CF_3)_2]_2$	7.600	1950	26 to 68	140	8.940	—	—

Table 25
Vibrational Spectra (in cm^{-1}) and Tentative Assignment for $X(CF_3)_2P[ON(CF_3)_2]_2$ (X = F, Cl, Br, CN) and $(CF_3)_3P[ON(CF_3)_2]_2$ [6].
In the headings Y stands for $ON(CF_3)_2$.

$(Y)_2(CF_3)_2PF$	$(Y)_2(CF_3)_2PCl$	$(Y)_2(CF_3)_2PBr$	$(Y)_2(CF_3)_2PCN$	$(Y)_2P(CF_3)_3$	Tentative assignment
			2200 w		CN stretch
1314 vs	1310 vs	1319 vs	1320 vs	1324 vs	
1205 vs	1268 vs	1275 vs	1270 vs	1265 vs	C-F stretch
1235 vs	1234 vs	1235 s	1240 vs	1235 vs	(of CF_3N)
1215 vs	1215 vs	1220 s	1220 vs	1220 vs	
1182 s	1173 s	1175 s	1190 s	1209 vs	C-F stretch
1150 sh	1154 s	1151 sh	1160 m	1150 m	(of CF_3P)
		1134		1120 sh	

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Table 25 (continued)

$(Y)_2(CF_3)_2PF$	$(Y)_2(CF_3)_2PCl$	$(Y)_2(CF_3)_2PBr$	$(Y)_2(CF_3)_2PCN$	$(Y)_2P(CF_3)_3$	Tentative assignment
1030 s	1032 s	1025 m	1035 s	1026 m	N-O stretch
974 s	972 s	972 m	975 s	972 m	C-N stretch
893 s					P-F stretch
850 s	858 s	853 m	865 s	860 m	P-ON stretch
832 sh	823 m	825 w	820 w	834 w	C-N-C stretch
	815 sh		790 w	820 w	
	786 w		760 w	800 w	
730 w			735 w		
716 s	717 s	718 m	716 s	715 m	
625 m	638 s	652 w	665 s	—	
	614 m	610 w	600 m	615 w	CF_3 deformation
590 m	590 m				
		575 w	555 w	580 m	
497 w	512 m	500 w	510 w	505 w	
473 m	408 m		470 w	490 w	

5.2.3.3 Chemical Reactions

Phosphine Oxides

The decomposition of $(CF_3)_3PO$ in a sealed glass tube has been studied [15]:

On standing at 25°C for two years in an NMR tube the compound forms $(CF_3)_3PF_2$, CF_3PF_4, $(CF_3)_3P$, $(CF_3)_2PF_3$, PF_5, CO, COF_2. At 100°C after two hours 10% $(CF_3)_3PO$ had decomposed giving $(CF_3)_3P$, OCF_2, $(CF_3)_2P(O)F$, after six hours 50% to $(CF_3)_3P$, $(CF_3)_2P(O)F$, $(CF_3)_2PF$, $CF_3P(O)F_2$, CF_3PF_2, OPF_3, PF_3, OCF_2, after 29 h the decomposition is complete giving OCF_2, $(CF_3)_3P$, $(CF_3)_2PF$, CF_3PF_2, OPF_3, PF_3, CO, C_2F_4. At 130°C after 20 h in presence of C_2F_4, the compounds $(CF_3)_3P$ and OPF_3 are obtained [15].

Tris(perfluoroalkyl)phosphine oxides are proton acceptors. This property is investigated in a system of solvents consisting of perfluoroheptane (as solvent) and of n-decanol (proton donor). The formation of 1 : 1 associates of phosphine oxides and decanol is investigated by IR and NMR spectroscopy in order to obtain information on the thermodynamics of association. For details see the original paper [16].

Tris(perfluoroalkyl)phosphine oxides react with aliphatic alcohols ROH at room temperature to form adducts of the type $R_FPO \cdot 3\,ROH$ which are colorless oils and can be vacuum-distilled. One alcohol molecule is coordinated to each fluorocarbon group of the phosphine oxide, in which the OH group is the proton donor and the α dimethylene group is the proton acceptor. Boiling points, refractive indices and densities of the adducts with $R_f = C_3F_7$ and $R = CF_3$, C_2H_5, C_3H_7, C_4H_9, C_5H_{11} as well as with $R_f = C_4H_9$ and $R = CH_3$, C_2H_5, C_3H_7, C_5H_{11} are given in the original paper [17]. The phosphine oxides also react with water (10 to 15°C, 30 to 40 min) to give the adducts $R_fPO \cdot n\,H_2O$, $n>3$. After vacuum distillation colorless oils are obtained with the following physical properties: for $(C_3F_7)_3PO$ an adduct with a boiling point of 33 to 34°C (0.05 Torr), $n_D^{20} = 1.3200$, and for $(C_4F_9)_3PO$ an adduct with a boiling point of 44°C (0.05 Torr), $n_D^{20} = 1.3062$, $D = 1.8750\ g/cm^3$ [17].

$(C_6F_5)_3PO$ reacts with C_6F_5Li (6 h at 25°C) in an ether/hexane 1:1 solution to produce $C_{12}F_8$, $C_{6n}F_{4n+1}H$ (n = 1 to 4), $(C_6F_5)_3P$ and $C_{12}F_9(C_6F_5)_2P$; and in the presence of BrC_6F_5, $C_{6n}F_{4n+1}Br$ (n = 1 to 4) and $C_{12}F_8HBr$ were also formed [19]. The NMR spectra of $(C_6F_5)_3PO$ in an SbF_5-HSO_3F mixture (1:1) and in pure HSO_3F are investigated in [20].

$(CF_3)_2P(O)C(O)R_f$

The compounds $(CF_3)_2POC(O)R_f$, $R_f = CF_3$, C_2F_5 and C_3F_7, undergo a partial decomposition within 24 h according to:

$$2\ (CF_3)_2POC(O)R_f \rightarrow (CF_3)_2POP(CF_3)_2 + R_fC(O)OC(O)R_f$$

Under these conditions the compound $(CF_3)_2POC(CF_3)_2CN$ is thermally stable [4].

Phosphorus Acid Anhydrides

Reactions of $(CF_3)_2POP(CF_3)_2$ yielding title compounds are given on p. 88.

$(CF_3)_2POP(CF_3)_2$ can be used as a monofunctional non-chelating ligand in the reaction with iron carbonyl compounds. ^{19}F NMR investigations show that only one P atom goes into a donor bond to the iron. The reaction with $Fe(CO)_2(NO)_2$ (16 d, 20°C, 64% yield) gives $Fe(CO)(NO)_2[(CF_3)_2POP(CF_3)_2]$, with $Fe_2(CO)_9$ (19 d, 84% yield) $Fe(CO)_4[(CF_3)_2POP(CF_3)_2]$ and with $[(\pi\text{-}C_5H_5)_2Fe(CO)_2]_2$ (1 d, 40°C, 63% yield) $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3[(CF_3)_2PO(CF_3)_2]$, for ^{19}F NMR and IR data see the original paper [18].

$(CF_3)_2POP(O)(CF_3)_2$ disproportionates at 60 to 70°C partially to $(CF_3)_2POP(CF_3)_2$ and $(CF_3)_2P(O)OP(O)(CF_3)_2$. The reaction with HCl at 25°C gives $(CF_3)_2PCl$ and $(CF_3)_2P(O)OH$, with KCl at 25°C $(CF_3)_2PCl$ and $(CF_3)_2P(O)OK$, with NO at 113°C (65 h) $(CF_3)_2P(O)OP(O)(CF_3)_2$, and with $Ni(CO)_4$ at 25°C after 16 h a colorless liquid, which is assumed to be $(CF_3)_2POP(O)(CF_3)_2Ni(CO)_3$ [18].

Aminooxy Derivatives of Phosphorus

Hydrolysis of $(CF_3)_2PON(CF_3)_2$ with 20% NaOH at 100°C for 15 h gives fluoroform. On reacting $CF_3P[ON(CF_3)_2]_2$ with $(CF_3)_2NON(CF_3)_2$ no reaction occurs at 70°C (70 h), but at 100°C for another 70 h $[(CF_3)_2NO]_3P$ (colorless liquid in the −45°C trap) was obtained [7].

On prolonged standing (three months) only the compounds $X(CF_3)_2P[ON(CF_3)_2]_2$ with X = F and CN are stable. The least stable compound is that with X = Br which became yellow. The order of stability follows the sequence $F \sim CN > Cl > Br$. All four compounds as well as $(CF_3)_2PON(CF_3)_2$ hydrolyze in contact with moist air. The reaction with 20% NaOH for 30 to 96 h hydrolyzes the compounds almost completely forming CF_3SH [6]. The reaction of $(CF_3)_2P[ON(CF_3)_2]_2$ with 20% NaOH at 120°C yields fluoroform as a product [8].

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5.2.4 Perfluoroorganophosphorus Acids, Their Ions and Salts

Trifluoromethylphosphonic acid $CF_3P(O)(OH)_2$

Bis(trifluoromethyl)phosphinic acid $(CF_3)_2P(O)OH$

Trifluoromethylphosphonous acid $CF_3P(OH)_2$

Bis(trifluoromethyl)phosphinous acid $(CF_3)_2POH$

The hydrolysis of phosphoranes in 10% aqueous NaOH produces quantitatively $CF_3PO_3^{2-}$ ions according the following equations [1]:

$(CF_3)_3PXY + 3\,H_2O \rightarrow CF_3PO_3^{2-} + 2\,CF_3H + 2\,H^+ + HX + HY$,
$X = F$, $Y = OCH_3$, SCH_3, $N(CH_3)_2$ [$H_2N(CH_3)_2^+$ formation]; $X = Y = OCH_3$

Similarly these ions form in the alkaline hydrolysis (2 d, 20 °C) of the compounds $(CF_3)_2P(O)OCH_2CH_3$, $(CF_3)_2P(O)OCH(CH_3)_2$, $(CF_3)_2P(O)SCH_3$, $(CF_3)_2P(O)SCH_2CH_3$ [2], $CF_3PF_3(SCH_3)$ and $(CF_3)_2PF_2(SCH_3)$ [17]. Equations describing relationships between phosphonic acids and the corresponding carboxylic acids, among them $CF_3P(O)(OH)_2$ and CF_3COOH, are given in [3].

The hydrolysis of phosphoranes in water yields quantitatively $(CF_3)_2PO_2^-$ ions [1] according to:

$(CF_3)_3PXY + 2\,H_2O \rightarrow (CF_3)_2PO_2^- + CF_3H + H^+ + HX + HY$
$X = F$, $Y = OCH_3$, SCH_3, $N(CH_3)_2$ [$H_2N(CH_3)_2^+$ formation]; $X = Y = OCH_3$

The anion also forms by neutral and by alkaline (NaOH) hydrolysis of $(CF_3)_2PFBr_2$ (5 d at room temperature) [4] and on reacting the esters $(CF_3)_2P(O)OCH_2CH_3$ or $(CF_3)_2P(O)OCH(CH_3)_2$ with $(CH_3)_3N$ at 20 °C (24 h) [2]. The cleavage of $(CF_3)_2POP(O)(CF_3)_2$ with HCl at 25 °C gives $(CF_3)_2P(O)OH$. The following signals (negative shifts δ to higher fields) are observed in the NMR spectra: ^{19}F NMR (standard $CFCl_3$): $\delta = -73.7$ ppm (doublet, J = 130.1 Hz), ^{31}P NMR (standard H_3PO_4): $\delta = 0.3$ ppm (septet, J = 129.8 Hz), ^{1}H NMR (standard $(CH_3)_4Si$): $\delta = 13.63$ ppm [5].

$CF_3P(OH)_2$ forms in the hydrolysis of $(CF_3)_2POH$ with water. ^{19}F NMR (standard CF_3COOH): $\delta = 10.4$ ppm [doublet, J(F-P) = 83 Hz]. ^{1}H NMR [standard $(CH_3)_4Si$]: $\delta = 4.30$ ppm [6].

$(CF_3)_2POH$ is produced in the reaction of $(CF_3)_2POC(CH_3)_3$ with HCl at 70 °C (20 h), on reacting $(CF_3)_2PCl$ with $(CH_3)_3COH$ (70 °C, 18 h), or with $C_6H_5CH_2OH$ (70 °C, 4 h), on reacting $(CF_3)_2POCH_3$ with $(CH_3)_3N$ [2] and by hydrolysis of $(CF_3)_2POP(CF_3)_2$ with water [6]. Physical properties: Density $D^4_{20} = 1.568_2$ g/cm^3. ^{19}F NMR (standard CF_3COOH): $\delta = 10.4$ ppm (doublet, J(F-P) = 83 Hz), ^1H NMR [standard $(CH_3)_4Si$]: $\delta = 4.30$ ppm [6]. ^{31}P NMR (external standard P_4O_6): $\delta = -35$ ppm. Faraday effect $|P|_M = 351$ μr (at 20 °C) [7]. Heating of $(CF_3)_2POH$ with $(CH_3)_3CCl$ at 70 °C (64 d) yields $(CF_3)_2POC(CH_3)_3$ [2].

Bis(heptafluoropropyl)phosphinic acid $(C_3F_7)_2P(O)OH$

Perfluoroalkylphosphonic acids $R_fP(O)(OH)_2$ and Salts ($R_f = C_nF_{2n+1}$, n = 4 to 24)

Bis(perfluoroalkyl)phosphinic acids $(R_f)_2P(O)OH$ and Salts ($R_f = C_nF_{2n+1}$, n = 4 to 24)

$(C_3F_7)_2P(O)OH$ (melting point 34°C) forms in 83% yield on heating a solution of $(C_3F_7)_3PO$ and C_2H_5OH (for preparation see [7]) for 5 h to 125°C, followed by treatment of the reaction mixture with $SOCl_2$ at 80°C (30 min) and subsequent distillation at 102 to 104°C (0.04 Torr) [8].

Explicit methods of preparation of the acids $R_fP(O)(OH)_2$ and $(R_f)_2P(O)OH$, $R_f = C_nF_{2n+1}$, are only given for the compounds with n = 4, 6, 8 and 10 in Part 3, p. 43.

The formation of micelles is observed in aqueous solutions of ammonium salts of $C_3F_7P(O)(OH)_2$ [9] and $(C_3F_7)_2P(O)OH$ [10, 11], of sodium salts of $(C_3F_7)_2P(O)OH$ [10, 11, 12], of $(C_4F_9)_2P(O)OH$ and $(C_5F_{11})_2P(O)OH$ [9, 12], of $(C_6F_{13})_2P(O)OH$ [11] and of the calcium salt of $(C_3F_7)_2P(O)OH$ [10]. The ^{19}F NMR spectra of the solutions at different concentrations of the acids and at different temperatures give information on the number of aggregated particles, the critical concentration of the micelle formation and the thermodynamics of this self-association which depend on the acid and on the chain length of the perfluorinated alkyl group, for details see the original papers [9 to 12]. For the investigation of the self-association of $(C_6F_{13})_2P(O)ONa$ in acetonitrile and for the association reaction of the salt with substituted benzotrifluorides see [13].

The compounds $R_fP(O)(OH)_2$ and $(R_f)_2P(O)OH$ with $R_f = C_nF_{2n+1}$ (n = 4 to 24) were used as antifoaming agents for detergent solutions and for solutions containing surfactants [14].

Pentafluorophenylphosphonic acid $C_6F_5P(O)(OH)_2$

Bis(pentafluorophenyl)phosphinic acid $(C_6F_5)_2P(O)OH$

The phosphonic acid forms in 88% yield by the hydrolysis of $C_6F_5PF_4$ in water at 20 °C [6], by the reaction of $C_6F_5PF_2$ with HSO_3F followed by addition of H_2O [9] and by the hydrolysis of $C_6F_5PF_4$ at 20 °C (10 h) (melting point of the acid: 141 to 142 °C) [16].

The separation of mixtures of organic phosphorus acids by paper chromatography, among them $C_6F_5P(O)(OH)_2$ and $(C_6F_5)_2P(O)OH$, is described in [15]. The best solvent systems for the separation of the phosphonic acids from each other and from other components are mixtures of acetone-pyridine-25% ammonia-H_2O and isoamyl alcohol-pyridine-25% ammonia-H_2O. The phosphinic acids are separated most effectively using an acetone-25% ammonia-H_2O mixture [15].

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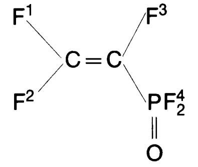
5.2.5 Perfluoroorganophosphonic and -phosphinic Halides

Trifluorovinylphosphonic difluoride $F_2C{=}CFP(O)F_2$

Routine handling of $F_2C{=}CFPF_4$ invariably generated small amounts of the difluoride. It is also formed on deliberate exposure of $F_2C{=}CFPF_4$ to small amounts of air or on attempts to chromatograph the compound. **Table 26** gives the physical data of the difluoride [1].

Table 26
IR and ^{19}F NMR Data of $F_2C{=}CFP(O)F_2$ [1].
Chemical shift δ (in ppm, negative values highfield from the internal standard $CFCl_3$), spin-spin coupling constant J (in Hz).



IR (gas) in cm^{-1}		^{19}F NMR		
1745 s	1025 (?) w	$\delta(F^1) = -71.6$	$J(F^1\text{-}F^2) = 16.1$	$J(F^2\text{-}F^4) = 4.2$
1388 s	945 s	$\delta(F^2) = -92.9$	$J(F^1\text{-}F^3) = 29.5$	$J(F^2\text{-}P) = 20.1$
1348 m	888 s		$J(F^1\text{-}F^4) = 11.9$	$J(F^3\text{-}F^4) = 8.1$
1217 s	685 w	$\delta(F^3) = -199.8$	$J(F^1\text{-}P)$ not determined	$J(F^3\text{-}P) = <1$
1170 w	545 s	$\delta(F^4) = -65.2$	$J(F^2\text{-}F^3) = 121.3$	$J(F^4\text{-}P) = 1090$

Pentafluorophenylphosphonic difluoride $C_6F_5P(O)F_2$

The difluoride (see Part 3, p. 52) forms on heating $C_6F_5PF_4$ with $(CH_3)_3SiOC_2H_5$ at 70 °C for one hour. The boiling point is 60 °C/8 Torr [10]. It is also obtained by the reaction of $C_6F_5PF_2$

with HSO_3F and converts on addition of water to $C_6F_5P(O)(OH)_2$ [12]. The fragmentation processes in the mass spectrum are investigated in [9].

The ^{31}P and ^{19}F NMR spectra of the liquid difluoride (see Part 3, p. 52) show the chemical shifts (external standards 85% H_3PO_4 and $CFCl_3$) $\delta(P) = -5.5$ ppm [J(P-F) = 1140 Hz], $\delta(PF_2) = 110$, $\delta(F^2,F^6) = 37.3$, $\delta(F^3,F^5) = 6.4$, $\delta(F^4) = 26.5$ ppm [J(F-P) = 1150 Hz]. The NMR spectra of a solution of the difluoride in SbF_5 indicate the formation of a donor-acceptor complex between the difluoride and SbF_5 [2]. The NMR data for a solution of the difluoride in HSO_3F and in SbF_5-HSO_3F are given in [12].

Bis(pentafluorophenyl)phosphinic fluoride $(C_6F_5)_2P(O)F$

The monofluoride (see Part 3, p. 52) is obtained by heating $(C_6F_5)_2PF_3$ with $(CH_3)_3SiOC_2H_5$ at 100 °C for 10 h (yield 75%), boiling point 100 to 105 °C/0.01 Torr, melting point 82 °C [10]. The fragmentation processes in the mass spectrum are investigated in [9].

Pentafluorophenylphosphonic dichloride $C_6F_5P(O)Cl_2$

The dichloride forms as by-product (10% yield) in the reaction of $C_6F_5PCl_2$ with SbF_3 at 150 °C (2 h) in an atmosphere of air; boiling point 195 °C, refractive index $n_D = 1.6752$, UV spectrum: $\lambda_{max} = 214$ ($\log \varepsilon = 3.52$), 264 nm ($\log \varepsilon = 2.83$) [11].

Trifluoromethylphosphonic difluoride $CF_3P(O)F_2$

A new preparation of the difluoride (see Part 3, p. 51) is the reaction of CF_3PF_2 with N_2O_4 [3]. $CF_3P(O)F_2$ is also formed by thermal decomposition of $(CF_3)_3PO$ (6 h, 100°C) and of $(CF_3)_2P(O)F$ (for 1 h at 125°C or more than 4 d at 25°C) [3].

The thermal decomposition of $CF_3P(O)F_2$ at 100 °C is completed after 16 h (50% decomposition in 3.5 h) and gives as products OPF_2, OCF_2, CO, PF_3, CF_3PF_2, CF_3PF_4, PF_5, $(CF_3)_3PF_2$, and $(CF_3)_2PF_3$ [3].

Trifluoromethylphosphonic dichloride $CF_3P(O)Cl_2$

For preparation and properties see Part 3, p. 51. ^{31}P NMR (external standard P_4O_6, $CDCl_3$ solution): $\delta = -101$ ppm [7]. ^{13}C NMR [internal standard $CDCl_3$, value converted to TMS by $\delta(TMS) = \delta(CDCl_3) + 77.06$]: $\delta = 118.84 \pm 0.03$ ppm [quartet of doublets, J(C-P) = 272.1 ± 0.7 Hz, J(C-F) = 314.7 ± 0.7 Hz]. The ^{35}Cl nuclear quadrupole resonance at 77 K was observed at 28.054 MHz. The temperature dependence of the spectrum is pictured in the original publication [8].

Bis(trifluoromethyl)phosphinic fluoride $(CF_3)_2P(O)F$

The best preparation (see also Part 3, p. 51) is very slow mixing (to avoid ignition) of 3 mmol $(CF_3)_2PF$ with $^1/_2$ atm of air in a 1-L flask. After 16 h at 25°C the reaction is complete [3]. The compound (boiling point 5°C/760 Torr, melting point −110°C) is also formed during the oxidation of $(CF_3)_3P$ with oxygen at 25 °C and during the thermal decomposition of $(CF_3)_3PO$ (100°C, 2 to 6 h) [3]. Thermal decomposition of $(CF_3)_2P(O)F$ in a glass tube at 125°C for 1 h gave OCF_2, $(CF_3)_2PF$ (main products), CF_3PF_2, OPF_3, $CF_3P(O)F_2$, $(CF_3)_3PF_2$, and CO; on standing at 25 °C for 4 d $CF_3P(O)F_2$ and $(CF_3)_2PF_3$ were formed, and after 10 d at 25 °C the decomposition of $(CF_3)_2POF$ was complete yielding CO, CF_3POF_2 (main products) and $(CF_3)_2PF_3$, CF_3PF_4, CF_3PF_2, $(CF_3)_3PF_2$, OPF_3, and $(CF_3)_2PF$ [3].

Bis(trifluoromethyl)phosphinic chloride $(CF_3)_2P(O)Cl$

The compound is prepared in a yield of 70% by the oxidation of $(CF_3)_2PCl$ with NO_2 [6].

^{19}F NMR (internal standard $CFCl_3$): $\delta = -72.3$ ppm [J(F-C-P) = 129.8 Hz]; ^{31}P NMR (standard H_3PO_4): $\delta = 10.8$ ppm [J(P-C-F) = 129.4 Hz] [4]; ^{31}P NMR (external standard P_4O_6, $CDCl_3$ solution): $\delta = -102$ ppm [7]. ^{13}C NMR (internal standard $CDCl_3$, value converted to TMS by $\delta(TMS) = \delta(CDCl_3) + 77.06$): $\delta = 119.29 \pm 0.03$ ppm [quartet of doublets of quartets, J(C-P) = 205.2 ± 0.7 Hz, J(C-F) = 316.2 ± 0.7 Hz, J(C-P-C-F) = 4 ± 0.7 Hz]. The ^{35}Cl nuclear quadrupole resonance was observed at 27.16 MHz at 77 K [8].

About the reaction of $(CF_3)_2P(O)Cl$ with $(CF_3)POP(CF_3)_2$ [4], see p. 88.

The reaction of $(CF_3)_2P(O)Cl$ with $(CH_3)_3COH$ (sealed Pyrex tube, room temperature, 3 d) yields $(CH_3)_3CCl$ (39%) and unidentified products. Reacting $(CH_3)_3CH$ under the same conditions only involatile products are formed, which have not been characterized. The reaction of $(CH_3)_3CH$ with $(CF_3)_2P(O)Cl$ in the presence of $N(CH_3)_3$ results in the consumption of 2 mol $(CH_3)_3N$ but with the evolution of isobutene along with the formation of $[(CH_3)_3NH][(CF_3)_2PSO]$ (slowly warming from −78°C to room temperature within 2 d).

In the presence of $(CH_3)_2NH$, $(CH_3)_3CSH$ gave with $(CF_3)_2P(O)Cl$ only $(CF_3)_2P(O)N(CH_3)_2$ [5].

$(CF_3)_2P(O)Cl$ reacts in the presence of an equal molar quantity of trimethylamine with ethanol, 2-propanol, ethylmercaptan, and 2-propylmercaptan to give $(CF_3)_2P(O)OC_2H_5$ (65%), $(CF_3)_2P(O)OCH(CH_3)_2$ (94%) (open vessel, warming from −78°C to room temperature), $(CF_3)_2P(O)SCH_3$ (55%), $(CF_3)_2P(O)SC_2H_5$ (86%), and $(CF_3)_2P(O)SCH(CH_3)_2$ (75%) (same conditions as before, but sealed Pyrex tube), respectively [5]. Physical properties of the phosphorus acid esters are given in **Table 27**, for ^1H NMR and IR data see the original publication [5].

Table 27
^{19}F NMR and Thermal Data of Phosphorus Acid Esters [5].
Chemical shift δ relative to $CFCl_3$ as internal standard, negative values to high field, spin-spin coupling constants J, vapor pressure p in Torr, boiling point (b.p.), enthalpy of evaporization ΔH_v in kcal/mol, Trouton constant $\Delta H_v/T_b$ in cal · mol^{-1} · K^{-1}.

Compound	^{19}F NMR		log p = A−B/T		(range in °C)	b.p. in °C	ΔH_v	$\Delta H_v/T_b$
	δ in ppm	J in Hz	A	B				
$(CF_3)_2P(O)OCH_2CH_3$	−73.5	121.8	–	–	–	–	–	–
$(CF_3)_2P(O)OCH(CH_3)_2$	−72.4	118.3	–	–	–	–	–	–
$(CF_3)_2P(O)SCH_3$	−70.6	109.0	–	–	–	–	–	–
$(CF_3)_2P(O)SCH_2CH_3$	−71.1	108.5	6.99	1767	(20 to 70°C)	157	8.080	18.8
$(CF_3)_2P(O)SCH(CH_3)_2$	−71.3	107.8	7.65	2042	(15 to 70°C)	155	9.340	21.8

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5.2.6 Perfluorohalogenoorganophosphorus Nitrogen Compounds

Bis(pentafluorophenyl)azidophosphine $(C_6F_5)_2PN_3$

The azide forms in the reaction of $(C_6F_5)_2PBr$ with NaN_3 at −2 to −10 °C within 12 to 36 h. It is a yellow oil which decomposes above −2 °C. The ^{31}P NMR chemical shift (standard 85% H_3PO_4) is δ = 38.2 ppm [J(P-F_{ortho}) = 44.6 Hz]. The symmetric and the antisymmetric stretching vibrations of the N-N-N group are found in the IR spectrum (liquid film) at 1254 and 2138 cm^{-1}, respectively. Mass spectrum (relative intensities in parentheses): M^+ (30.4), $(C_6F_5)_2PN^+$ (12.1), $(C_6F_5)_2P^+$ (9.1), $C_6F_5PN^+$ (100), $C_6F_5P^+$ (8.1), $C_6F_5^+$ (2.1), CF_3^+ (74.2). The azide reacts with $(C_6H_5)_3P$ forming the Kirsanov product $(C_6F_5)_2PN{=}P(C_6H_5)_3$, ^{31}P NMR (external standard 85% H_3PO_4): δ = 31.8 ppm [doublet of triplets (quintets)], J(P-P) = 120 Hz, J(P-F_{ortho}) = 36.0 Hz. Mass spectrum: M^+(3), $C_6F_5PNP(C_6H_5)_3^+$ (1), C_6F_5P(40), $(C_6H_5)_2PNP^+$ (6), $(C_6H_5)_2P^+$ (9), $(C_6H_5)_2PN^+$ (84), $C_6H_5PNP^+$ (36), $C_6H_5P^+$ (98), $(C_6H_5)_3PN^+$ (91), $(C_6H_5)_3P^+$ (98) [1].

Bis(trifluoromethyl)aminophosphine $(CF_3)_2PNH_2$

Bis[bis(trifluoromethyl)phosphino]amine $[(CF_3)_2P]_2NH$

Both compounds are formed in the reaction of $(CF_3)_2PH$ with NH_3, as shown by ^{19}F NMR spectroscopy. $(CF_3)_2PNH_2$ is prepared on slow warming of the reaction mixture from −130 to −110 °C during 60 min, then quickly to −70 °C, and to −50 °C in 5 min. The other compound is obtained on warming the mixture rapidly from −196 to −78 °C (5 s), then to 0 °C (15 s) and to 25 °C (10 s) [2]. $(CF_3)_2PNH_2$ (95% yield) also forms on reacting $(CF_3)_2PCl$ and NH_3 (standing overnight) [6]. The ^{19}F NMR spectra (standard $CFCl_3$) show for $(CF_3)_2PNH_2$ the chemical shift δ = −66.87 ppm [J(FC-P) = 81.1 Hz] and for $[(CF_3)_2P]_2NH$ the shift δ = −65.5 ppm (second-order spectrum) with mutually symmetrical peaks separated by 90.4, 53.0, 37.4 and 14.0 Hz [2].

For a discussion of sign changes of $^1J(^{15}N\text{-}^{31}P)$ coupling constants for three compounds, among them $(CF_3)_2PNH_2$, see [3], compare also Part 3, p. 63.

Bis(trifluoromethyl)aminobis(trifluoromethyl)phosphine $(CF_3)_2PN(CF_3)_2$

Bis[bis(trifluoromethyl)amino]trifluoromethylphosphine $CF_3P[N(CF_3)_2]_2$

The reaction of $(CF_3)_2NON(CF_3)_2$ with $(CF_3)_3P$ in 1:1 molar ratio at room temperature gives the first compound; with 2:1 molar ratio the reaction yields at 60°C the second compound [7].

Perfluoroalkylbis(trifluoromethyl)amino-halogenophosphoranes

$R_fPF_2XN(CF_3)_2$, X = Cl, Br; R_f = CF_3, CF_3CF_2, $(CF_3)_2CF$, $ClCF_2CF_2$, $CF_3CF_2CF_2$

The first compounds were prepared by the reaction of the difluorophosphine R_fPF_2 with a bis(trifluoromethyl)halogenoamine $XN(CF_3)_2$ [4]. For NMR data see **Tables 28** and **29**.

Table 28

^{19}F and ^{31}P NMR Chemical Shifts δ (in ppm) of Perfluoroalkylbis(trifluoromethyl)amino-halogenophosphoranes $R_fPF_2^aXN(CF_3^b)_2$.

The chemical shift of ^{31}P is with respect to 85% H_3PO_4 solution, that of ^{19}F with respect to $CFCl_3$ [4] or F_2 [5].

X	R_f	δ(P)	δ(F^a)		δ(F^b)	δ(CF_3)	δ(F^{α})	δ(F^{β})
		[4]	[4]	[5]	[4]	[4]	[4]	[4]
Cl	$CF_3CF_2^{\alpha}CF_2^{\beta}$	−34.9	11.8	−418.3	−52.4	−82.5	−111.9	−124.6
Br	$CF_3CF_2^{\alpha}CF_2^{\beta}$	−56.4	25.4	−404.7	−52.5	−82.2	−111.5	−124.0
Cl	$ClCF_2^{\alpha}CF_2^{\beta}$	−34.5	13.4	–	−52.2	–	−109.6	− 67.9
Br	$ClCF_2^{\alpha}CF_2^{\beta}$	−56.6	27.6	–	−51.6	–	−109.1	− 67.0
Cl	CF_3CF_2	[a]	11.1	−419.0	−52.8	−82.4	−116.4	–
Br	CF_3CF_2	−57.2	25.4	−404.7	−52.2	−81.6	−115.7	–
Cl	$(CF_3)_2CF^{\alpha}$	−32.6	17.6	−412.5	−52.2	−71.5	−170.6	–
Cl	CF_3	−38.0	7.3	−422.8	−53.5	−70.0	–	–
Br	CF_3	−58.9	21.3	−408.8	−53.1	−70.2	–	–

[a] Sample so small that a ^{31}P spectrum could not be obtained.

Table 29

Spin-Spin Coupling Constants J (in Hz) from the ^{19}F and ^{31}P NMR Spectra of Perfluoroalkylbis(trifluoromethyl)aminohalogenophosphoranes $R_fPF_2^aXN(CF_3^b)_2$ [4].

Abbreviations: d, tr, qu, qui, sept mean doublet, triplet, quartet, quintet, septet, respectively.

X	R_f	P-F^a	P-F^{α}	F^a-P	F^a-F_N	F^a-CF_3	F^a-F^{α}	F^a-F^{β}
Cl	$CF_3CF_2^{\alpha}CF_2^{\beta}$	1 007 tr	130 tr	1 017 d	15.1 sept	1.0 qu	[b]	[b]
Br	$CF_3CF_2^{\alpha}CF_2^{\beta}$	1 026 tr	132 tr	1 041 d	14.9 sept	0.9 qu	14.6 tr	13.4 tr
Cl	$ClCF_2^{\alpha}CF_2^{\beta}$	1 005 tr	132 tr	1 016 d	15.3 sept	–	15.3 tr	12.4 tr
Br	$ClCF_2^{\alpha}CF_2^{\beta}$	1 029 tr	132 tr	1 041 d	14.3 sept	–	[b]	[b]
Cl	CF_3CF_2	[a]	[a]	1 004 d	15.5 sept	9.75 qu	13.5 tr	–
Br	CF_3CF_2	1 014 tr	128 tr	1 028 d	15.3 sept	9.4 qu	12.6 tr	–
Cl	$(CF_3)_2CF^{\alpha}$	991 tr	96 d	996 d	15.0 sept	7.4 sept	0	–
Cl	CF_3	992 tr	190 qu	990 d	14.8 sept	18.2 qu	–	–
Br	CF_3	1 005 tr	186 qu	1 013 d	14.5 sept	17.5 qu	–	–

Table 29 (continued)

X	R_f	F^b-P	F^b-F^a	F^b-CF_3	F^b-F^{α}	F^b-F^{β}	CF_3-P	CF_3-F_P
Cl	$CF_3CF_2^{\alpha}CF_2^{\beta}$	1.4 d	15.3 tr	0	3.4 tr	2.1 tr	6.2 d	1.0 tr
Br	$CF_3CF_2^{\alpha}CF_2^{\beta}$	1.3 d	15.2 tr	0	3.6 tr	2.4 tr	6.0 d	0.9 tr
Cl	$ClCF_2^{\alpha}CF_2^{\beta}$	1.6 d	15.4 tr	—	3.5 tr	1.7 tr	—	—
Br	$ClCF_2^{\alpha}CF_2^{\beta}$	b)	15.1 tr	—	b)	b)	—	—
Cl	CF_3CF_2	0	15.6 tr	1.6 qu	1.6 tr	—	2.4 d	9.7 tr
Br	CF_3CF_2	0	15.2 tr	1.6 qu	1.6 tr	—	2.4 d	9.5 tr
Cl	$(CF_3)_2CF^{\alpha}$	1.1 d	15.4 tr	b)	7.6 d	—	—	7.2 tr
Cl	CF_3	0	15.0 tr	1.8 qu	—	—	188 d	18.5 tr
Br	CF_3	0	14.5 tr	1.8 qu	—	—	183 d	b)

X	R^f	CF_3-F^b	CF_3-F^{α}	CF_3-F^{β}	F^{α}-P	F^{α}-F^a	F^{α}-F^b	F^{α}-CF_3
Cl	$CF_3CF_2^{\alpha}CF_2^{\beta}$	0	11.2 tr	0	132 d	b)	b)	b)
Br	$CF_3CF_2^{\alpha}CF_2^{\beta}$	0	11.0 tr	0	134 d	14.6 tr	3.6 sept	11.0 qu
Cl	$ClCF_2^{\alpha}CF_2^{\beta}$	—	—	—	132.4 d	14.8 tr	3.6 sept	—
Br	$ClCF_2^{\alpha}CF_2^{\beta}$	—	—	—	134 d	b)	a)	—
Cl	CF_3CF_2	1.5 sept	1.6 tr	—	131 d	13.4 tr	1.6 sept	1.6 qu
Br	CF_3CF_2	1.6 sept	0	—	135 d	12.6 tr	1.8 sept	0
Cl	$(CF_3)_2CF^{\alpha}$	b)	b)	—	102 d	b)	b)	b)
Cl	CF_3	1.9 sept	—	—	—	—	—	—
Br	CF_3	b)	—	—	—	—	—	—

X	R_f	F^{α}-F^{β}	F^{β}-P	F^{β}-F^b	F^{β}-F^b	F^{β}-CF_3	F^{β}-F^{α}
Cl	$CF_3CF_2^{\alpha}CF_2^{\beta}$	b)	b)	b)	b)	b)	b)
Br	$CF_3CF_2^{\alpha}CF_2^{\beta}$	3.6 tr	4.8 d	13.4 tr	2.4	0	3.6 tr
Cl	$ClCF_2^{\alpha}CF_2^{\beta}$	3.6 tr	0	12.3 tr	1.7	—	3.4 tr
Br	$ClCF_2^{\alpha}CF_2^{\beta}$	b)	b)	11.4 tr	b)	—	b)
Cl	CF_3CF_2	—	—	—	—	—	—
Br	CF_3CF_2	—	—	—	—	—	—
Cl	$(CF_3)_2CF^{\alpha}$	—	—	—	—	—	—
Cl	CF_3	—	—	—	—	—	—
Br	CF_3	—					

a) Sample so small that a ^{31}P spectrum could not be obtained. — b) Signal could not be resolved.

Silylaminobis(trifluoromethyl)phosphine $(CF_3)_2PN(H)SiH_3$

The compound forms in 89% yield on warming a mixture of H_3SiBr and $(CF_3)_2PNH_2$ from −196°C to room temperature (standing overnight). It is a colorless liquid, ^1H NMR [external standard $(CH_3)_4Si$, solvent $CHFCl_2$]: δ = 4.30 ppm [doublet of doublets, J(P-N-Si-H) = 12.0 Hz, J(HN-SiH) = 3.0 Hz], δ(NH) = 2.1 ppm (broad peak), ^{19}F NMR (external standard $CFCl_3$): δ = −66.5 ppm [doublet, J(P-F) = 80.5 Hz] [6].

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5.2.7 Perfluorohalogenoorganophosphorus Halides and Their Anions

5.2.7.1 Perfluorohalogenoalkyl- and Perfluorovinylhalogenophosphines and -phosphoranes

5.2.7.1.1 Preparation

5.2.7.1.1.1 Perfluoroalkyl- and Perfluorovinylfluorophosphines and -phosphoranes

Trifluoromethyldifluorophosphine CF_3PF_2

Bis(trifluoromethyl)fluorophosphine $(CF_3)_2PF$

Pentafluoroethyldifluorophosphine $C_2F_5PF_2$

Trifluoromethylfluorophosphoranes $(CF_3)_nPF_{5-n}$ (n = 1 to 3)

CF_3PF_2 is produced from CF_3PI_2 and AgF [1].

For preparation of $(CF_3)_2PF$, see Part 3, p. 70.

$C_2F_5PF_2$ is obtained by fluorination of $C_2F_5PI_2$ with excess SbF_3 at 58 °C overnight and subsequent fractional condensation of the product mixture. The estimated yield is 11% based on consumed C_2F_5I which along with red phosphorus and iodine was used to synthesize $C_2F_5PI_2$ [3].

For the formation of CF_3PF_2, $(CF_3)_2PF$, $(CF_3)_3PF_2$, $(CF_3)_2PF_3$ and CF_3PF_4 during thermolysis of $(CF_3)_3PO$, $(CF_3)_2P(O)F$ and $CF_3P(O)F_2$, see pp. 94, 99/100 [34]. The formation of $(CF_3)_2PF$ during the reaction of $(CF_3)_2PI$ with F atoms in a fast-flow reactor is described in [63]; see also p. 120.

CF_3PF_4 (among other products) forms in the reaction of CF_3PF_2 with Br_2 [45].

1,2-Bis(difluorophosphino)tetrafluoroethane $F_2PCF_2CF_2PF_2$

1,2-Bis(difluorophosphino)hexafluoropropane $F_2PCF_2CF(CF_3)PF_2$

The compounds are produced by irradiation (λ = 300 nm) of a mixture of P_2F_4 and the appropriate olefin: C_2F_4 (4 to 6 h, ~10% yield) and C_3F_6 (7 h, ~6% yield). The products are purified by fractional condensation. With $2\text{-}C_4F_8$ (cis, trans) or C_6F_{10} comparable products were not obtained [4].

Trifluorovinyltetrafluorophosphorane $F_2C{=}CFPF_4$

Pyrolysis of a mixture of $C_2F_5SiF_3$ and PF_3 at 200 °C and ca. 0.5 atm for 1 h and subsequent fractional condensation produce $F_2C{=}CFPF_4$ in 54% yield [3].

5.2.7.1.1.2 Perfluoroalkylchlorophosphines

Trifluoromethyldichlorophosphine CF_3PCl_2

Bis(trifluoromethyl)chlorophosphine $(CF_3)_2PCl$

Pentafluoroethyldichlorophosphine $C_2F_5PCl_2$

Heptafluoropropyldichlorophosphine $C_3F_7PCl_2$

Heptafluoroisopropyldichlorophosphine i-$C_3F_7PCl_2$

Bis(heptafluoroisopropyl)chlorophosphine (i-$C_3F_7)_2PCl$

CF_3PCl_2 has been prepared in high yield (80 to 90%) by reaction of CF_3PI_2 with $SbCl_3$ and by condensing the product in a -65 °C trap [39]. CF_3PH_2 and Cl_2 react in 7 d at room temperature in a sealed tube giving CF_3PCl_2 along with CF_3PHCl and HCl. When HCl is removed, the amount of CF_3PCl_2 increases over a period of several months. After 10 months 0.56 mmol CF_3PH_2 yields 0.21 mmol CF_3PCl_2 [5].

$(CF_3)_2PCl$ is formed in the reaction of $(CF_3)_2PH$ with NH_3 (warming from -130 °C to $+50$ °C, treating the volatile product, among others $(CF_3)_2PNH_2$, with excess HCl, see also p. 101) [35].

$C_2F_5PCl_2$ and $C_3F_7PCl_2$ are produced in high yield (80 to 90%) by the reaction of the corresponding diiodophosphines with $SbCl_3$ and isolated by condensation in a -65 °C trap [39].

i-$C_3F_7PCl_2$ and (i-$C_3F_7)_2PCl$ are prepared in almost quantitative yield (99%) by reaction of the corresponding iodophosphines with AgCl in a sealed ampule kept in the dark for 7 d [38].

5.2.7.1.1.3 Perfluoroalkylbromophosphines and -phosphoranes

Trifluoromethyldibromophosphine CF_3PBr_2

Bis(trifluoromethyl)bromophosphine $(CF_3)_2PBr$

Trifluoromethyltetrabromophosphorane CF_3PBr_4

Bis(trifluoromethyl)tribromophosphorane $(CF_3)_2PBr_3$

Tris(trifluoromethyl)dibromophosphorane $(CF_3)_3PBr_2$

When $BrCF_2CHFI$ and $(CF_3P)_4$ are heated at 106 to 110 °C for 25.5 h, CF_3PBr_2 is formed according to the scheme

$$4\,BrCF_2CHFI + (CF_3P)_4 \rightarrow 4\,CF_2CHF + 2\,CF_3PBr_2 + 2\,CF_3PI_2$$

CF_3PBr_2 can be collected in a trap at -78 °C [40]. CF_3PBr_2 forms along with other products when CF_3PIH is shaken with AgBr [5]. CF_3PBr_2 and $(CF_3)_2PBr_3$ (along with CF_3PF_4) are postulated to be the main products of the bromination of CF_3PF_2 [45].

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$(CF_3)_2PBr$ along with $(CF_3)_2PH$ forms as volatile product in the reaction of $(CF_3)_2PAsH_2$ with the equimolar amount of Br_2. Excess Br_2 leads to the formation of $(CF_3)_2PBr_3$ [8].

For preparation of CF_3PBr_4 and $(CF_3)_2PBr_3$, see Part 3, p. 74.

$(CF_3)_3PBr_2$ is formed via the equilibrium $(CF_3)_3P + Br_2 \rightleftharpoons (CF_3)_3PBr_2$ with $K \sim 2\ L^{-1}$ at 260 K, but was not isolated [45].

5.2.7.1.1.4 Perfluorohalogenoalkyliodophosphines

Perfluorohalogenoalkyliodophosphoranes have not been described so far.

Trifluoromethyldiiodophosphine CF_3PI_2

Bis(trifluoromethyl)iodophosphine $(CF_3)_2PI$

Pentafluoroethyldiiodophosphine $C_2F_5PI_2$

Heptafluoroisopropyldiiodophosphine i-$C_3F_7PI_2$

Bis(heptafluoroisopropyl)iodophosphine (i-$C_3F_7)_2PI$

When $BrCF_2CHFI$ and $(CF_3P)_4$ are heated at 106 to 110 °C for 25.5 h, CF_3PI_2 (along with CF_3PBr_2 and CF_2CHF) is formed. For the reaction scheme, see the preparation of CF_3PBr_2. CF_3PI_2 remains in the still after separation of the other products by distillation [40].

Treatment of PI_3 with $(CF_3)_2Cd \cdot CH_3OCH_2CH_2OCH_3$ in 1,6-dibromohexane at room temperature yields $(CF_3)_2PI$ (up to 30% after 30 min) [43].

The preparation of $C_2F_5PI_2$ can be carried out by heating C_2F_5I, red phosphorus and I_2 in a sealed ampule at 220 °C for 70 h and subsequent fractional condensation where $C_2F_5PI_2$ is retained in the trap at −24 °C [3].

i-$C_3F_7PI_2$ and (i-$C_3F_7)_2PI$ form in moderate yield in the reaction between $(CF_3)_2CFI$ and red phosphorous at 220°C for 8 h. The iodophosphines can be separated by slow trap-to-trap condensation. A mixture produced in a stainless steel autoclave gave 70% iodophosphine and 30% diiodophosphine [38].

Trifluoromethyl(pentafluoroethyl)iodophosphine $CF_3(C_2F_5)PI$

Trifluoromethyl(heptafluoro-n-propyl)iodophosphine CF_3(n-C_3F_7)PI

Trifluoromethyl(heptafluoro-i-propyl)iodophosphine CF_3(i-C_3F_7)PI

Pentafluoroethyl(heptafluoro-i-propyl)iodophosphine C_2F_5(i-C_3F_7)PI

Trifluoromethyl(1-chlorotetrafluoroethyl)iodophosphine $CF_3(ClCF_2CF_2)PI$

Trifluoromethyl(1-bromotetrafluoroethyl)iodophosphine $CF_3(BrCF_2CF_2)PI$

The compounds are prepared in reactions of perfluoroalkyliodides with appropriately substituted cyclotetraphosphines in sealed tubes according:

$$\tfrac{1}{4}(RP)_4 + R'I \rightarrow R(R')PI$$

with R = CF_3, R′ = n-C_3F_7, i-C_3F_7 [14], R = C_2F_5, R′ = i-C_3F_7 [12] and R = CF_3, R′ = C_2F_5, $ClCF_2CF_2$, $BrCF_2CF_2$ [40].

$CF_3(n\text{-}C_3F_7)PI$ was obtained in 4 h at 200 °C with a yield of 69% [13, 14]. $CF_3(i\text{-}C_3F_7)PI$ was obtained in 6 h at 190 °C with a yield of 65% [14]. $C_2F_5(i\text{-}C_3F_7)PI$ was obtained after 10 h at 160 °C with a yield of 59% [12]. The conversion curves of these cleavage reactions are represented by a first-order equation in the investigated temperature region 145 to 185 °C [14], and the reaction order with respect to $(CF_3P)_4$ has been proven to be 1 [42]. $(CF_3P)_5$ instead of $(CF_3P)_4$ does not react directly with C_3F_7I but at first rearranges to $(CF_3P)_4$. This rearrangement occurs in the presence of fluoroiodoalkanes below 200 °C [$(CF_3P)_5$ alone rearranges to $(CF_3P)_4$ at 255 °C; see Part 3, p. 6]. The reactivity of $(C_2F_5P)_5$ toward fluoroiodoalkanes is lower than that of $(CF_3P)_5$ [41].

The reactivity of fluoroiodoalkanes in the reaction with $(CF_3P)_4$ has been determined by measuring the rate constants for the reaction

$$XCF_2CF_2I + \tfrac{1}{4}(CF_3P)_4 \rightarrow XCF_2CF_2(CF_3P)I$$

with X = Br, Cl, F and CF_3. The rate constants (in $10^{-2}\,h^{-1}$) at 166 °C are: 49 ± 2, 26 ± 2, 21 ± 1, and 20.1 ± 0.3 for X = Br, Cl, F and CF_3, respectively. These data show that the rate of reaction decreases with increasing electronegativity of the substituents X [40].

5.2.7.1.1.5 Trifluoromethylhalogenophosphines (mixed halogens)

Trifluoromethylfluorochlorophosphine CF_3PFCl

Trifluoromethylfluorobromophosphine CF_3PFBr

Trifluoromethylchlorophosphine CF_3PClH

Trifluoromethylchlorobromophosphine CF_3PClBr

Trifluoromethylchloroiodophosphine CF_3PClI

Trifluoromethylchlorocyanophosphine CF_3PClCN

Trifluoromethylbromophosphine CF_3PBrH

Trifluoromethylbromodeuterophosphine CF_3PBrD

Trifluoromethylbromoiodophosphine CF_3PBrI

Trifluoromethylbromocyanophosphine CF_3PBrCN

Trifluoromethyliodophosphine CF_3PIH

Trifluoromethyliododeuterophosphine CF_3PID

Trifluoromethyliodocyanophosphine CF_3PICN

The mixed phosphines form when mixtures of CF_3PX_2 and CF_3PY_2 (X, Y = H, D, F, Cl, Br, I, CN) are heated to 70 °C for 10 d or are irradiated with a medium-pressure Hg lamp in a sealed tube. In the case of thermal reaction the equilibrium is reached after 10 d and does not shift during six months (one exception: half of CF_3PFBr has decomposed after 40 d). No exchange reaction could be detected in mixtures of CF_3PF_2 with CF_3PH_2, CF_3PI_2 and $CF_3P(CN)_2$ under thermal or photochemical initiation [5].

CF_3PIH and CF_3PID can be prepared
(1) by shaking a mixture of CF_3PH_2 and I_2 for 1 h at 0 °C (yield 41%),
(2) by warming an equimolar mixture of CF_3PI_2 and CF_3PH_2 (CF_3PD_2) in CCl_3F solution for 2 h at 40 °C (yield 23%),

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(3) by photolysis (8 h) of excess of CF_3PH_2 (CF_3PD_2) with CF_3PI_2 in the liquid phase (yield 32%) [5].

CF_3PIH also forms upon cleavage of $(CF_3PH)_2$ by HI [57].

CF_3PClH forms along with HCl and CF_3PCl_2 in the reaction of CF_3PH_2 and Cl_2 (7 d at room temperature in an ampule). It also forms in small quantities by shaking CF_3PIH with AgCl or $HgCl_2$. $(CF_3PH)_2$ is cleaved by HCl to a small extent also giving CF_3PClH [5].

CF_3PBrH and CF_3PBrD are obtained in 96% yield by shaking (45 min) CF_3PIH or CF_3PID with $HgBr_2$ at 20 °C. CF_3PBrH and CF_3PBrI (and other products) were identified when CF_3PIH was shaken with AgBr [5].

For the exchange reactions $CF_3PX_2 + CF_3PY_2 \rightleftharpoons 2\ CF_3PXY$ the equilibrium constants $K = [CF_3PXY]^2/[CF_3PX_2][CF_3PY_2]$ have been approximately determined by means of ^{19}F NMR spectroscopy [5]:

XY	FCl	ClBr	ClI	ClCN	BrI	BrCN	IH	ICN
K	0.1	2.5	0.5	0.01	2.2	0.9	0.7	3.2

5.2.7.1.1.6 Perfluoroalkylhalogenophosphoranes (Halogen: F, Cl, Br)

Trifluoromethyldifluorodichlorophosphorane $CF_3PF_2Cl_2$

Pentafluoroethyldifluorodichlorophosphorane $C_2F_5PF_2Cl_2$

Heptafluoro-n-propyldifluorodichlorophosphorane $C_3F_7PF_2Cl_2$

Bis(trifluoromethyl)fluorodichlorophosphorane $(CF_3)_2PFCl_2$

Bis(trifluoromethyl)fluorodibromophosphorane $(CF_3)_2PFBr_2$

Since Part 3 (see p. 72) has been edited, no new methods of preparation for RPF_2Cl_2 (R = CF_3, C_2F_5, n-C_3F_7) and $(CF_3)_2PFCl_2$ have been published.

$(CF_3)_2PF$, Br_2 and CH_3Cl in a sealed tube were allowed to warm slowly from −196 °C to −78 °C. At −78 °C the tube was shaken whereupon a dark transparent solution was produced which became colorless in 20 s. The crude product, $(CF_3)_2PFBr_2$, was trapped at −45 °C and −78 °C and purified by trap-to-trap condensation (93% yield) [45].

5.2.7.1.2 Physical Properties

Physical data especially NMR, IR and mass spectral data, are summarized in **Table 35**, p. 115. Additional data from structure determinations and spectra are given in the following sections.

5.2.7.1.2.1 Ground State Structures of Trifluoromethylhalogenophosphoranes by Means of NMR Spectroscopy and Theoretical Results

From ^{13}C NMR spectra of a series of phosphoranes containing one or more CF_3 groups it was concluded that large values (>170 Hz) of the coupling constant J(P-C) are related to equatorial CF_3 groups and smaller values (<90 Hz) are associated with axial CF_3 groups.

The J(P-CF) coupling constants show the same trend as well [45]. All trifluoromethylhalogenophosphoranes involving two or more halogen atoms that are listed in **Table 30** (from [45]) have large J(P-C) values suggesting exclusive equatorial CF_3 substitution. However, these predictions may be at variance with structures proposed by other spectroscopic methods; see also, for instance, Part 3, p. 79.

Table 30
NMR Parameters of Trifluoromethylhalogenophosphoranes. Measured in CD_2Cl_2 solution at 22.6 MHz unless otherwise specified.

Molecule	t in °C	$\delta(^{13}C)$ [a] in ppm	J(P-C) in Hz	J(P-C-F) [b] in Hz
CF_3PF_4	−40	121.3	448	170
CF_3PCl_4	0	123.6	288	151
CF_3PBr_4	+10	116.7	138	142
$CF_3PF_2Cl_2$	0	123.5	327	155
$(CF_3)_2PF_3$ [c]	0	121.3	418	176
$(CF_3)_2PFCl_2$	0	123.0	389	183
$(CF_3)_2PCl_3$	0	122.3	379	190
$(CF_3)_2PBr_3$	0	115.5	379	182
$(CF_3)_2PFBr_2$	0	120.2	336	179
$(CF_3)_3PF_2$	+31	120.8	315	167
$(CF_3)_3PCl_2$	−20	122.6	232	139
$(CF_3)_3PBr_2$ [d]	−13	120.6	201	127

[a] Positive values indicating shifts to low field of standard $(CH_3)_4Si$. — [b] Obtained from ^{19}F and ^{31}P spectra. — [c] 40% $CFCl_3$, 60% CD_2Cl_2. — [d] 30% $CDCl_3$, 70% CD_2Cl_2; compound was immiscible in pure CD_2Cl_2.

To study the influence of fast intramolecular exchange processes involving F atoms on the value of the coupling constants the ^{19}F NMR spectrum of CF_3PF_4 has been examined to temperatures as low as −150 °C ($CFCl_3/CF_2Cl_2$ solution) but no changes consistent with stopping of intramolecular F exchange have been observed. So Berry pseudorotation with an equatorial CF_3 pivot is compatible with the proposed ground state structure of this molecule. Also in $(CF_3)_2PF_3$ no distinct axial-equatorial environments have been found even when examined at very low temperatures (^{31}P NMR to −160 °C, ^{19}F NMR to −125 °C, ^{13}C to −125 °C). This lack of axial-equatorial F atom distinction is thought to arise from "a fast permutational process with an undefined mechanism" [45].

In the series $(CH_3)_2PF_3$, $CF_3(CH_3)PF_3$, $(CF_3)_2PF_3$, extrapolation of the known barriers for permutational F atom exchange in the first two molecules (17.8 and 8.8 kcal/mol, respectively) predicts a barrier of approximately zero for the permutational exchange in $(CF_3)_2PF_3$. Extrapolation within the series H_2PF_3, $CF_3(H)PF_3$, $(CF_3)_2PF_3$ yields a predicted barrier of ~2.4 kcal for $(CF_3)_2PF_3$. Thus, a barrier, ranging from 1 to 3 kcal has been proposed, which is unobservable by available NMR techniques [46].

An electron diffraction study of $(CF_3)_2PCl_3$ and $(CF_3)_3PCl_2$ in the gas phase suggests axial substitution of CF_3 groups [16]; also see pp. 110/1. To detect the different CF_3 environments in the case of $(CF_3)_3PCl_2$ (one equatorial, two axial CF_3 groups) ^{13}C (to −130 °C), ^{19}F (to −160 °C)

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and ^{31}P NMR (to −160°C) experiments have been carried out, but without success. The resonance lines did not broaden significantly. If the structure in gas phase and solution is the same, the barrier to CF_3 permutational exchange must be unusually small or the solution structure may involve axial Cl atoms and equivalent equatorial CF_3 groups [45]. Previous vibrational spectra of $(CF_3)_2PCl_3$ were also interpreted in terms of axial CF_3 groups, see Part 3, pp. 79/80.

$(CF_3)_3PBr_2$ shows a similar behavior as $(CF_3)_3PCl_2$; the ^{19}F NMR spectrum was unchanged to −140 °C suggesting that the CF_3 groups are in equivalent equatorial positions [45]. For CF_3PBr_4 the J(P-C) value is unexpectedly small and does not correlate with J(P-CF), cf. Table 30, p. 109. This anomaly has been interpreted by assuming CF_3PBr_4 to be better described as a phosphonium salt $CF_3PBr_3^+Br^-$. This interpretation is supported by the low value of the phosphorus chemical shift which is consistent with a phosphonium salt formulation [45].

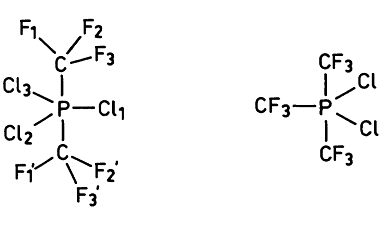
In a theoretical work the interconversion of the equatorial and the axial configurations of CF_3PF_4 due to various permutational (from axial to axial and from equatorial to equatorial) and polytopal (from axial to equatorial and vice versa) pathways have been studied. Theoretical modifications of the rotation-vibration spectra have been obtained which are characteristic of the pathways and could be used to discriminate between them [47].

5.2.7.1.2.2 Electron Diffraction

$(CF_3)_2PCl_3$, $(CF_3)_3PCl_2$

The structures of the molecules $(CF_3)_2PCl_3$ and $(CF_3)_3PCl_2$ have been determined by electron diffraction of the gases [16]. $(CF_3)_2PCl_3$ has the structure of a regular trigonal bipyramid with both CF_3 groups in axial positions (D_{3h} symmetry). The F atoms are staggered to the equatorial positions of the Cl atoms; see **Fig. 2**. The structure of $(CF_3)_3PCl_2$ is a distorted trigonal bipyramid with two CF_3 groups in axial and one CF_3 group in equatorial positions. The F atoms of the axial groups are staggered to the equatorial atoms. There is a high potential barrier in both molecules to internal rotation of CF_3 groups around the P-C bond direction. **Table 31** reproduces the interatomic distances and angles of both molecules; for the mean square amplitudes, see the original [16].

Fig. 2



Structure of $(CF_3)_2PCl_3$ and of $(CF_3)_3PCl_2$.

Table 31
Interatomic Distances r_a (in Å) and Angles of $(CF_3)_2PCl_3$ and $(CF_3)_3PCl_2$ from Electron Diffraction Data.

$(CF_3)_2PCl_3$				$(CF_3)_3PCl_2$	
C-F	1.331(2)	$Cl_1 \ldots F_1$	4.063(7)	C-F	1.329(2)
P-C	1.950(11)	$C \ldots F$	4.510(21)	$(P\text{-}C)_{eq}$	1.938(31)
P-Cl	2.036(2)	$F_1 \cdots F'_1$	4.812(101)	$(P\text{-}C)_{ax}$	1.946(14)
$F_1 \cdots F_2$	2.158(6)	$F_1 \cdots F'_2$	5.272(20)	$(P\text{-}C)_{av}$[a]	1.943(5)
$P \cdots F$	2.721(3)			P-Cl	2.053(6)
$C \cdots Cl$	2.836(8)	∢FCF	108.3(4)°	∢FCF	108.5(3)°
$Cl_1 \cdots F_2$	3.001(6)	∢PCF	110.7(6)°	∢ClPCl	133.0(17)°
$Cl \cdots Cl$	3.508(10)			∢$C_{ax}PC_{eq}$	95.5(19)°
				τ[b]	7.9(35)°

[a] Average (P-C) bond distance. — [b] Angle for rotation of the equatorial CF_3 group around the P-C axis.

5.2.7.1.2.3 ^{35}Cl Nuclear Quadrupole Resonance

CF_3PCl_2 and $(CF_3)_2PCl$ show a single ^{35}Cl line at 27.650 and 30.090 MHz, respectively, in the quadrupole resonance spectrum at 77 K. It is concluded that the ionic character of the P-Cl bond decreases in the series PCl_3, CF_3PCl_2, and $(CF_3)_2PCl$ when the number of electronwithdrawing CF_3 groups increases [50].

5.2.7.1.2.4 Photoelectron Spectra

CF_3PCl_2, $(CF_3)_2PCl$

Assuming C_s skeletal symmetry of the molecules the He(I) photoelectron spectra are interpreted by assigning the observed bands to localized molecular orbitals [17], see **Table 32**.

Table 32
Ionization Potentials E_i (in eV) from Photoelectron Spectra and Assignments for CF_3PCl_2 and $(CF_3)_2PCl$.

	P lone pair	P-C σ bond	P-Cl σ bond	F nonbonding orbitals[a]			Cl nonbonding orbitals	
	CF_3PCl_2							
Symmetry of orbitals	A′(n)	A′	A″	A_2	E	E	(2A′ + 2A″)	
E_i	10.70	13.88	12.21	15.13	15.91	16.96	12.21, 12.62, 14.18	
	$(CF_3)_2PCl$							
Symmetry of orbitals	A′(n)	A″	A′	A_2	E	E	(A′ + A″)	
E_i	11.13	13.61	12.42	15.43	16.38	17.05	12.42	14.38

[a] CF_3 groups are considered as isolated species of C_{3v} symmetry.

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CF_3PBr_2

The vertical ionization energies (in eV) due to an He(I) photoelectron spectrum are [51]:

10.23, 11.01, 11.52, 11.64, 12.81, 13.55, 14.07, 15.20, 15.90, 16.94

The first ionization energy is assigned to the phosphorus "lone pair" orbital. The energy region 15 to 17 eV is associated with fluorine nonbonding orbitals [51].

CF_3PI_2, $(CF_3)_2PI$

The first vertical (P "lone pair") ionization energies of CF_3PI_2 and $(CF_3)_2PI$ are 9.50 and 10.10 eV, respectively [52].

5.2.7.1.2.5 Vibrational Spectra

CF_3PX_2, X = F, Cl, Br, I

The IR and Raman spectra and the normal coordinate analyses as well have been reported in Part 3, p. 80. In the meantime, these data (originally from a private communication) have been published, see [1]. In addition, internal force constants (in 10^2 N/m) for the molecules CF_3PX_2 are listed in the following table [1]:

	f(CF)	f(CF/CF′)	f(CP)	f(PX)	f(PX/PX′)	f(XPX)	f(CPX)
CF_3PF_2	5.96	0.86	2.68	4.99	0.33	0.55	0.36
CF_3PCl_2	5.87	0.85	2.35	2.53	0.19	0.29	0.30
CF_3PBr_2	5.77	0.85	2.17	1.87	0.07	0.22	0.29
CF_3PI_2	5.64	0.82	2.06	1.49	0.10	0.17	0.27

$(CF_3)_2PX$, X = F, Cl, Br, I

IR spectra (400 to 4000 cm^{-1}) and Raman spectra reported in [9] have been described in Part 3, pp. 82/3. These data are completed by IR measurements in the region 200 to 400 cm^{-1} [15]. The interpretation of the vibrational spectra is performed on the basis of a normal coordinate analysis using a transferred force field [15]. Point group C_s is assumed for the $(CF_3)_2PX$ molecules; for the assignment of the 24 fundamentals on the classes A′ and A″, see Part 3, p. 17. **Table 33** (from [15]) gives the potential energy distribution and lists the calculated and observed frequencies (the torsional vibrations ν_{13} and ν_{24} are not included).

Table 33

Observed (obs.) and Calculated (cal.) Frequencies of the $(CF_3)_2PX$ Molecules and Their Potential Energy Distribution.

$(CF_3)_2PF$ obs.[a]	cal.	$(CF_3)_2PCl$ obs.[a]	cal.	$(CF_3)_2PBr$ obs.[a]	cal.	$(CF_3)_2PI$ obs.[a]	cal.	Potential energy distribution
1227	1226	1215	1215	1209	1212	1200	1201	94(1), 22(5)
1149	1152	1160	1149	1156	1147	1150	1142	62(3), 50(4), 27(9)

References p. 130

Table 32 (continued)

$(CF_3)_2PF$ obs.[a]	cal.	$(CF_3)_2PCl$ obs.[a]	cal.	$(CF_3)_2PBr$ obs.[a]	cal.	$(CF_3)_2PI$ obs.[a]	cal.	Potential energy distribution
749	744	746	743	743	742	745	740	38(4), 40(3), 14(9)
568	565			560	564	561	562	68(5), 12(1)
		570	571					46(5), 10(1), 20(11)
269	265							66(7), 35(10), 12(12)
		275	273					65(7), 20(10)
				282	283			55(7), 12(9), 16(10)
						242	244	69(7), 27(11)
465	458	443	441					50(9), 14(4), 12(12)
				441	439			22(9), 23(7), 21(11), 24(12)
						442	440	39(9), 21(7), 10(11), 23(12)
189	186							43(10), 12(7), 17(12)
		136	133					49(10), 45(12), 12(7)
				112	116			46(12), 41(10), 19(7)
						104	104	61(12), 59(10)
850	850							94(11)
		533	539					55(11), 25(5)
				467	457			37(11), 30(9), 15(10)
						419	419	31(11), 24(9), 16(10), 18(12)
350	350							53(12), 15(7), 14(10)
		136	134					45(12), 49(10), 11(7)
				112	116			46(12), 41(10), 19(7)
						104	104	61(12), 59(10)
1 217	1 220	1 215	1 210	1 206	1 204	1 200	1 204	96(14), 22(18)
1 125	1 116	1 120	1 120	1 115	1 106	1 115	1 110	70(16), 50(17), 19(22)
733	733	719	722	727	728	725	725	50(17), 33(16), 12(22)
553	556	559	558	558	557	558	557	75(18), 12(14)
237	237							40(20), 19(22), 38(23)
		268	266	262	262	262	262	94(20)
455	465							53(22), 24(23)
		443	444	441	438	440	435	66(22)
275	275							36(23), 58(20)
		167	167	148	149	143	142	90(23)

[a] Due to measurements reported in [9, 15]; see also text.

Internal force constants (in 10^2 N/m) for the molecules $(CF_3)_2PX$ are summarized in the following table [15]:

Compound	f(CF)	f(CF/CF′)	f(CP)	f(CP/CP′)	f(PX)	f(CPX)	$f(\delta_sCF_3)$	$f(\delta_{as}CF_3)$	$f(\varrho CF_3)$
$(CF_3)_2PF$	6.07	0.72	2.55	0.45	4.79	0.37	1.73	1.75	0.84
$(CF_3)_2PCl$	6.03	0.73	2.53	0.43	2.45	0.25	1.73	1.75	0.85
$(CF_3)_2PBr$	6.02	0.74	2.48	0.43	1.95	0.23	1.73	1.75	0.83
$(CF_3)_2PI$	6.00	0.73	2.45	0.40	1.70	0.22	1.73	1.75	0.81

CF_3PXH, CF_3PXD, X = Br, I

Gas-phase IR spectra and Raman spectra of the liquids have been measured [5]. The molecules have point group C_1 (no symmetry element) so all 15 fundamental modes will be IR and Raman active. **Table 34** lists the observed frequencies and an approximate description of the vibrations for the CF_3PXH molecules.

Table 34
Observed Frequencies (in cm^{-1}) and Proposed Assignment for CF_3PXH Molecules (X = Br, I). Relative Raman intensities in parentheses. IR bands: v = very, s = strong, w = weak, br = broad, and sh = shoulder.

CF_3PBrH		CF_3PIH		Approximate description
Raman	IR	Raman	IR	
117(4)		107(4)		CF_3 rock
		242(10)		CPI deformation
260(10)				CPBr deformation
275(0.5)		276(0.5)		PCF_3 deformation
		383(10)	394m	PI stretch
416(10)	425m, br	414(3)	415m	PC stretch
429(10)				PBr stretch
	458vw (sh)	467(0.5)		2×242?
539(0.5)	522vw	536(0.5)	532w	CF_3 deformation
740(6)	741mw	739(3)	739mw	CF_3 deformation
803(0.5)	804m	748(2)	754 (sh)	Br(I)PH deformation
853(0.5)	851m	844(1)	844m	CPH deformation
	1010vw		1022vw	
	1103 (sh)		1102w (sh)	
	1132vs		1124vs	CF_3 stretch
	1174vs		1167vs	CF_3 stretch
	1240vw		1228vw	
	1278vw		1278vw	
	2232vw		2242w	2×CF_3 stretch
	2300vw (sh)		2300vw (sh)	2×CF_3 stretch
2320(4)	2318m	2317(1)	2327m	PH stretch

Table 35

Physical Properties of Perfluoroalkylphosphines and -phosphoranes.

NMR spectra: coupling constants J in Hz; chemical shifts δ in ppm (positive values of δ indicate resonance to low field of the standard); ^{19}F external standard $CFCl_3$ and ^{31}P external standard 85% H_3PO_4, unless other specified; d = doublet, tr = triplet, qu = quartet, dec = decet.

IR spectra: ν in cm^{-1}; v = very, w = weak, s = strong, m = medium, br = broad, sh = shoulder.

Mass spectra: m/e (relative intensity) ion.

m. p. = melting point, b. p. = boiling point, D = density.

Compound	Physical properties
CF_3PF_2	^{19}F NMR: $\delta^{a)}(CF_3) = -84.3$, $\delta(PF) = -106.7$, $J(P\text{-}F) = 1240$, $J(P\text{-}CF_3) = 88.4$, $J(F_3C\text{-}PF) = 5.92$ [44]; $J(P\text{-}CF_3) = 87$ [45]. ^{31}P NMR: $\delta^{b)} = 160$, $J(P\text{-}CF_3) = 88.6$, $J(P\text{-}F) = 1242$ [44]. ^{13}C NMR: $\delta^{c)} = -5.23$, $J(C\text{-}F) = 318.4$, $J(C\text{-}P) = 42.8$, $J(C\text{-}PF) = 21.8$ [44]; $\delta^{d)} = 123.2$, $J(C\text{-}P) = 48$ [45].
$(CF_3)_2PF$	^{19}F NMR: $\delta^{a)}(CF_3) = -68.3$, $\delta(PF) = -221.6$, $J(P\text{-}F) = 1002$, $J(P\text{-}CF_3) = 89.9$, $J(CF_3\text{-}PF) = 3.4$ [44]; $J(P\text{-}F) = 89.5$ [45]. ^{31}P NMR: $\delta^{b)} = 124.6$, $J(P\text{-}CF_3) = 89.8$, $J(P\text{-}F) = 1007$ [44]. ^{13}C NMR: $\delta^{c)} = -2.92$, $J(C\text{-}F) = 318.9$, $J(C\text{-}P) = 29.0$, $J(C\text{-}PF) = 18.4$, $J(CPCF_3) = 6.23$ [44]; $\delta^{d)} = 125.5$, $J(C\text{-}P) = 30$ [45].
$CF_3CF_2PF_2$	^{19}F NMR: $\delta(CF_3) = -83.4$, $\delta(CF_2) = -139.4$, $\delta(PF) = -106.4$, $J(CF_2\text{-}PF_2) = 9.0$, $J(CF_3\text{-}PF_2) = 6.4$, $J(CF_3\text{-}CF_2) = 2.0$ [3]. ^{31}P NMR: $\delta^{e)} = 28.7$, $J(P\text{-}F) = 1259.3$, $J(P\text{-}CF_2) = 101.0$, $J(P\text{-}CF_3) = 7.4$ [3]. IR (gas phase): 1745 (vw, br), 1725 (vw, br), 1322 (s), 1225 (vs), 1167 (s), 1130 (s), 1087 (m, sh), 1009 (m), 978 (m), 864 (vs), 754 (m, sh), 749 (m), 746 (m), 630 (m), 627 (m), 623 (m, sh), 590 (vw, br), 540 (vw, br), 487 (m), 433 (w), 410 (w), 404 (w), 376 (w), 370 (w) [3]. Mass spectrum: m/e = 188 (<12) M^+; 119 (12 to 50) $C_2F_5^+$, CF_4P^+, 100 (>50) $C_2F_4^+$, CF_3P^+; 88 (<12) CF_4^+, F_3P^+; 81 (>50) $C_2F_3^+$, CF_2P^+; 69 (100) CF_3^+, F_2P^+; 62 (12 to 50) $C_2F_2^+$, CFP^+; 50 (>50) CF_2, FP^+; 43 (12 to 50) C_2F^+, CP^+; 31 (>50) CF^+, P^+ [3].
$F_2PCF_2CF_2PF_2$ α β	^{19}F NMR (−60 °C): doublet with a complex pattern, $\delta(PF_2) = -106$, $\delta(CF_2) = -132$, $J(P\text{-}F) = 1252$, $J(P\text{-}F_\alpha) = 86$ [4]. ^{31}P NMR (−50 °C): $\delta = 227$ [tr of tr of tr], $J(P\text{-}F) = 1258$, $J(P\text{-}F_\alpha) = 91$, $J(P\text{-}F_\beta) = 20$ [4]. IR (gas phase): 1710 (vw), 1225 (w, br), 1129 (s), 1106 (s), 844 (vvs, ν(PF)), 778 (w), 660 (vvw), 570 (m), 527 (vvw), 462 (m), 450 (m); solid phase (−196 °C), 1300 (w), 1260 (vw), 985 (vw), 947 (vw), 904 (vw), 825 (w, sh), 798 (m), 785 (sh), 762 (w), 495 (w) [4]. Mass spectrum: m/e = 238 (16.4) M^+; 169 (5.9) $C_2F_4PF_2^+$; 150 (59) $C_2F_5P^+$; 138 (4.1) $P_2F_4^+$; 131 (26) $C_2F_4P^+$; 119 (4.7) $P_2F_3^+$, $C_2F_3^+$, $C_2F_4P^+$; 100 (10) $C_2F_4^+$, $P_2F_2^+$; 88 (0.6) PF_3^+, CF_4; 81 (4.7) CF_2P^+, $C_2F_3^+$; 69 (100) PF_2^+, CF_3^+ [4].

Table 35 (continued)

Compound	Physical properties
$F_2PCF_2CF(CF_3)PF_2$	IR (gas phase): 1635 (vw), 1350 (w), 1270 (w), 1240 (m), 1195 (m), 1100 (w), 1090 (w), 1015 (m), 915 (s), 830 (s, sh, ν(PF)), 820 (vvs), 720 (vw), 650 (vw), 475 (m) [4]. Mass spectrum: m/e = 288 (0.2) M^+; 231 (0.1) $C_3F_7P_2^+$; 219 (0.7) $C_2F_7P_2^+$; 200 (0.3) $C_3F_7P^+$, $C_2F_6P_2^+$; 193 (0.1) $C_3F_5P_2^+$; 181 (1.7) $C_3F_6P^+$; 169 (1.7) $C_2F_6P^+$; 150 (0.2) $C_3F_6^+$, $C_2F_5P^+$; 138 (2.3) $P_2F_4^+$, CF_5P^+; 119 (0.8) $C_2F_5^+$, CF_4P^+; 100 (0.8) $C_2F_4^+$, CF_3P^+; 93 (0.4) $C_3F_3^+$, $C_2F_2P^+$; 88 (42.2) PF_3^+, CF_4^+; 81 (3.0) $C_2F_3^+$, CF_2P^+; 69 (100) PF_2^+, CF_3^+ [4].
$(CF_3)_nPF_{5-n}$, (n = 1, 2, 3)	For NMR data see Table 30, p. 109.
CF_3PCl_2	$D_4^{20} = 1.5351$ g/cm³ [55]. ^{19}F NMR: $\delta^{a)} = -72.8$, J(F-P) = 79.5 [44]. ^{31}P NMR: $\delta^{b)} = 131$ [44], $\delta^{f)} = 133$ [54], J(P-F) = 79.5 [44], 75 [45]. ^{13}C NMR: $\delta^{c)} = -1.65$ [44], $\delta^{d)} = 126.1$ [45], $\delta^{g)} = 126.49$ [50], J(C-F) = 323.0 [44], 322.8 [50], J(C-P) = 60.5 [44], 75 [45], 60.3 [50]. Faraday effect: magnetic rotation $\lvert\varrho\rvert_M = 568$ μr at 20 °C [54].
$(CF_3)_2PCl$	$D_4^{-5} = 1.610$ g/cm³; $1.599 - 2.1 \times 10^{-3}$ t for $-15°C < t < 5°C$ [55]. ^{19}F NMR: $\delta^{a)} = -62$ [44], $\delta = -62$ [35], -63.3 [37], J(F-P) = 86 [44], 85 [35, 45], 85.1 [37]. ^{31}P NMR: $\delta^{b)} = 51.2$ [44], $\delta^{f)} = 51$ [54], $\delta = 50.2$ [37], J(P-F) = 87 [44], 85.0 [37]. ^{13}C NMR: $\delta^{c)} = -1.93$ [44], $\delta^{d)} = 126.3$ [45], $\delta^{g)} = 126.25$ [50], J(C-F) = 320.1 [44], 320.6 [50], J(C-P) = 35.5 [44], 38 [45], 36.8 [50], J(C-P-CF) = 5.8 [44], 6 [50]. Faraday effect: magnetic rotation $\lvert\varrho\rvert_M = 421$ μr between −15 and +5 °C [54].
i-$C_3F_7PCl_2$	b.p. 88 °C IR (gas phase): 1410 (w), 1285 (m), 1280 (vs), 1235 (vs), 1170 (m), 1145 (w), 1090 (w), 980 (w), 955 (w), 930 (m), 810 (m), 750 (m), 720 (m) [38].
(i-$C_3F_7)_2PCl$	b.p. 116 °C IR (gas phase): 2360 (w), 1765 (w), 1390 (w), 1285 (vs), 1240 (vs), 1185 (w), 1160 (m), 1125 (m), 990 (m), 932 (w), 852 (w), 815 (w), 745 (m), 710 (m) [38].
$(CF_3)_nPCl_{5-n}$, (n = 1, 2, 3)	For NMR data see Table 30, p. 109.
CF_3PBr_2	^{19}F NMR: $\delta^{a)} = -67.0$ [44], J(F-P) = 67.9 [44], 68 [45]. ^{31}P NMR: $\delta^{b)} = 118$, J(P-F) = 68.3 [44]. ^{13}C NMR: $\delta^{c)} = -4.39$ [44], $\delta^{d)} = 122.9$ [45], J(C-F) = 323.6 [44], J(C-P) = 73.6 [44], 77 [45].

Table 35 (continued)

Compound	Physical properties
$(CF_3)_2PBr$	^{19}F NMR: δa) = −59.8, J(F-P) = 80.7 [44]. ^{31}P NMR: δb) = 34.1 [44], J(P-F) = 80.7 [44], 78 [45]. ^{13}C NMR: δc) = −3.40 [44], δd) = 124.6 [45], J(C-F) = 320.5 [44], J(C-P) = 40.0 [44], 43 [45], J(C-P-CF) = 5.74 [44].
CF_3PBr_4h)	m.p. 27 °C [45] ^{19}F NMR: δ = −66.8 [45]. ^{31}P NMR: δi) = −86, J(P-F) = 142 [45]. ^{13}C NMR: see Table 30, p. 109.
$(CF_3)_2PBr_3$	m.p. 7 °C ^{19}F NMR: δ = −81.4 [45]. ^{31}P NMR: δi) = −163, J(P-F) = 182 [45]. ^{13}C NMR: see Table 30, p. 109.
$(CF_3)_3PBr_2$	^{19}F NMR: δ = −65.6, J(F-P) = 127 (d) [45]. ^{31}P NMR: δi) = −177, J(P-F) = 127 (dec) [45]. ^{13}C NMR: see Table 30, p. 109.
CF_3PI_2	D_4^{20} = 2.8075 g/cm^3 [55]. ^{19}F NMR: δa) = −57.9 [44], J(F-P) = 48.4 [44], 52 [45]. ^{31}P NMR: δb) = 61.7 [44], δf) = 61 [54], J(P-F) = 48.6 [44]. ^{13}C NMR: δc) = −8.03 [44], δd) = 118.7 [45], J(C-F) = 324.5 [44], J(C-P) = 85.3 [44], 87 [45]. Faraday effect: magnetic rotation $\lvert\varrho\rvert_M$ = 2138 μr at 20 °C [54].
$(CF_3)_2PI$	D_4^{20} = 2.0433 g/cm^3 [55]. ^{19}F NMR: δa) = −55.0 [44], δj) = 22.9 [43], J(F-P) = 72 [44], 73 [45], 76 [43]. ^{31}P NMR: δb) = 0.4 [44], δf) = 0 [54], J(P-F) = 73.5 [44]. ^{13}C NMR: δc) = −4.63 [44], δd) = 122.6 [45], J(C-P) = 42.8 [44], 45 [45], J(C-F) = 320.5, J(C-P-CF) = 5.5 [44]. Mass spectrum: m/e = 296 (9%) $(CF_3)_2PI^+$, 277 (5%) $(CF_3)CF_2PI^+$ [43]. Faraday effect: magnetic rotation $\lvert\varrho\rvert_M$ = 855 μr at 20 °C [54].
$i\text{-}C_3F_7PI_2$	b.p. 195 °C [38], vapor pressure at 25 °C ~3 Torr [58], m.p. ~0 °C [58]. ^{31}P NMR: δ = 76.5, J(P-CF) = 58, J(P-C-CF) = 17 [58]. IR (gas phase): 1400 (w), 1290 (w), 1280 (vs), 1240 (vs), 1165 (w), 1148 (w), 1090 (w), 990 (w), 960 (m), 925 (m), 815 (w), 750 (m), 715 (w) [38].
$(i\text{-}C_3F_7)_2PI$	b.p. 138 °C [38] IR (gas phase): 2370 (w), 1760 (w), 1390 (w), 1292 (vs), 1240 (vs), 1190 (w), 985 (m), 932 (w), 852 (w), 820 (w), 755 (m), 702 (m) [38].
$CF_3(n\text{-}C_3F_7)PI$	b.p. 104 to 106 °C [13, 14]

Table 35 (continued)

Compound	Physical properties
$C_2F_5(i\text{-}C_3F_7)PI$	b.p. 30 to 32 °C (12 Torr) [12].
$CF_3PF_2Cl_2$ $(CF_3)_2PFCl_2$	For NMR data see Table 30, p. 109.
$CF_3CF_2PF_2Cl_2$ $\beta \quad \alpha$	^{19}F NMR: $\delta(PF) = +39.4$, $\delta(F_\alpha) = -111.5$, $\delta(F_\beta) = -80.4$, $J(P\text{-}F) = 1065$ (d), $J(PF\text{-}F_\beta) = 8.6$ (qu), $J(PF\text{-}F_\alpha) = 11.3$ (tr), $J(F_\beta\text{-}P) = 1.2$ (d), $J(F_\beta\text{-}PF) = 8.6$ (tr), $J(F_\beta\text{-}F_\alpha) = 1.4$ (tr), $J(F_\alpha\text{-}P) = 129$ (d), $J(F_\alpha\text{-}PF) = 11.3$ (tr) [48]; $\delta^{k)}(PF) = -390.7$ [49].
$CF_3CF_2CF_2PF_2Cl_2$ $\gamma \quad \beta \quad \alpha$	^{19}F NMR: $\delta(PF) = +37.8$, $\delta(F_\alpha) = -111.5$, $\delta(F_\beta) = -123.3$, $\delta(F_\gamma) = -82.4$, $J(P\text{-}F) = 1082$ (d), $J(PF\text{-}F_\gamma) = 1.0$ (qu), $J(PF\text{-}F_\alpha) = 12.4$ (tr), $J(PF\text{-}F_\beta) = 11.7$ (tr), $J(F_\gamma\text{-}P) = 5.5$ (d), $J(F_\gamma\text{-}PF) = 1.0$ (tr), $J(F_\gamma\text{-}F_\alpha) = 10.6$ (tr), $J(F_\gamma\text{-}F_\beta) = 0$, $J(F_\alpha\text{-}P) = 131$ (d), $J(F_\alpha\text{-}PF) = 12.5$ (tr), $J(F_\alpha\text{-}F_\gamma) = 10.4$ (qu), $J(F_\alpha\text{-}F_\beta) = 3.0$ (tr), $J(F_\beta\text{-}P) = 5.8$ (d), $J(F_\beta\text{-}PF) = 11.6$ (tr), $J(F_\beta\text{-}F_\gamma) = 0$, $J(F_\beta\text{-}F_\alpha) = 2.9$ (tr) [48]; $\delta^{k)}(PF) = -392.3$ [49]. ^{31}P NMR: $\delta = 13.5$, $J(P\text{-}PF) = 1069$ (tr), $J(P\text{-}F_\alpha) = 129$ (tr) [48].
$ClCF_2CF_2PF_2Cl_2$ $\beta \quad \alpha$	^{19}F NMR: $\delta(PF) = +51.5$, $\delta(F_\alpha) = -108.9$, $\delta(F_\beta) = -66.8$, $J(P\text{-}F) = 1073$ (d), $J(PF\text{-}F_\alpha) = 14.2$ (tr), $J(PF\text{-}F_\beta) = 10.7$ (tr), $J(F_\alpha\text{-}P) = 134$ (d), $J(F_\alpha\text{-}PF) = 14.2$ (tr), $J(F_\alpha\text{-}F_\beta) = 3.7$ (tr), $J(F_\beta\text{-}P) = 3.4$ (d), $J(F_\beta\text{-}PF) = 10.6$ (tr), $J(F_\beta\text{-}F_\alpha) = 3.7$ (tr) [48]. ^{31}P NMR: $\delta = 11.5$, $J(P\text{-}PF) = 1060$ (tr), $J(P\text{-}F_\alpha) = 132$ (tr) [48].
CF_3PFCl	^{19}F NMR: $\delta^{l)}(CF_3) = -76.1$, $J(CF\text{-}P) = 84$, $J(F\text{-}F) = 0.6$ [5].
CF_3PFBr	^{19}F NMR: $\delta^{l)}(CF_3) = -73.9$, $J(CF\text{-}P) = 80$, $J(F\text{-}F) = 1.8$ [5].
CF_3PClH	^{19}F NMR: $\delta^{l)} = -58.6$, $J(F\text{-}P) = 68$, $J(F\text{-}H) = 10.4$ [5]. ^1H NMR: $\delta^{m)} = 5.71$, $J(H\text{-}P) = 190$ [5].
CF_3PClBr	^{19}F NMR: $\delta^{l)} = -70.0$, $J(F\text{-}P) = 75$ [5].
CF_3PClI	^{19}F NMR: $\delta^{l)} = -66.3$, $J(F\text{-}P) = 66$ [5].
$CF_3PCl(CN)$	^{19}F NMR: $\delta^{l)} = -62.4$, $J(F\text{-}P) = 85$ [5].
CF_3PBrH	^{19}F NMR: $\delta^{l)} = -56.0$, $J(F\text{-}P) = 65$, $J(F\text{-}H) = 10.6$ [5]. ^1H NMR: $\delta^{m)} = 4.94$, $J(H\text{-}P) = 189$ [5].
CF_3PBrI	^{19}F NMR: $\delta^{l)} = -64.5$, $J(F\text{-}P) = 62$ [5].
$CF_3PBr(CN)$	^{19}F NMR: $\delta^{l)} = -60.1$, $J(F\text{-}P) = 81$ [5].
CF_3PIH	^{19}F NMR: $\delta^{l)} = -51.6$, $J(F\text{-}P) = 56$, $J(F\text{-}H) = 10.2$ [5]. ^1H NMR: $\delta^{m)} = 4.17$, $J(H\text{-}P) = 186$ [5].

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Table 35 (continued)

Compound	Physical properties
$CF_3PI(CN)$	^{19}F NMR: δ[l] = −55.9, J(F-P) = 71 [5].
$(CF_3)_2PFBr_2$	m.p. −8 ± 1°C ^{19}F NMR: δ(PF) = −101.5, δ(CF_3) = −78.6, J(P-F) = 1255, J(P-CF_3) = 179, J(PF-CF_3) = 13.0 [45]. ^{31}P NMR: δ[i] = −153 [45]. ^{13}C NMR: for data see Table 30, p. 109. IR (gas phase): 1292 (vw), 1191 (vs), 1177 (vs), 1156 (vs), 1117 (vw), 828 (m), 581 (m), 565 (m), 547 (m), 515 (m), 396 (vw) [45]. Mass spectrum (intensity as % of base peak (m/e 69) = 100): m/e = 277, 279, 281 (44.6) $CF_4PBr_2^+$; 267, 269 (31.6) $C_2F_7PBr^+$; 227, 229, 231 (3.1) $PF_2Br_2^+$; 217, 219 (11.0) CF_5PBr^+; 198, 200 (3.1) CF_4PBr^+; 188 (2.3) $C_2F_7P^+$; 179, 181, (2.5) CF_3PBr^+; 129, 131 (36.2) CF_2Br^+, $PFBr^+$; 119 (7.0) CF_3PF^+; 100 (3.1) CF_3P^+; 79, 81 (22.0) Br^+ [45].

[a] External standard CF_3COOH, calibrated against $CFCl_3$. — [b] External standard 15% H_3PO_4, calibrated against 85% H_3PO_4. — [c] External standard C_6D_6. — [d] Internal standard $(CH_3)_4Si$ in CD_2Cl_2 solution. — [e] External standard $(CH_3O)_3P$. — [f] External standard P_4O_6, calibrated against 85% H_3PO_4. — [g] Internal standard $CDCl_3$, calibrated against $(CH_3)_4Si$. — [h] Seems to be a phosphonium salt; also see p. 110. — [i] Standard P_4O_6. — [j] External standard CF_3COOH. — [k] External standard F_2. — [l] Internal standard $CFCl_3$. — [m] Internal standard $(CH_3)_4Si$.

5.2.7.1.3 Chemical Reactions

5.2.7.1.3.1 Thermolysis and Photolysis

$C_2F_5PF_2$ can be heated to 200 °C for 1 h without decomposition as indicated by IR analysis [3].

On heating to 200 °C at 0.6 atm and for 2 h, $F_2C{=}CFPF_4$ partially decomposes into PF_5, POF_3 and $F_2C{=}CFP(O)F_2$; 91 mol% of the product mixture is unreacted $F_2C{=}CFPF_4$ [3].

Less than 30% of $(CF_3)_2PFBr_2$ had decomposed mainly into $(CF_3)_2PF_2Br$ and $(CF_3)_2PBr_3$ after 40 h at 45 °C [45].

Various perfluoroalkyliodophosphines such as $(CF_3)_2PI$, $CF_3(C_2F_5)PI$, $CF_3(C_3F_7)PI$, $(C_2F_5)_2PI$, $(C_3F_7)_2PI$ have been investigated with respect to their ability to produce excited iodine atoms in photolysis processes. This property is of interest in connection with photodissociation iodide lasers, see, for instance [19, 53].

5.2.7.1.3.2 Hydrolysis

Partial hydrolysis of CF_3PF_4 leads to $CF_3P(O)F_2$ [34].

$(i\text{-}C_3F_7)_2PI$ and $i\text{-}C_3F_7PI_2$ both give $(CF_3)_2CFH$ as the volatile product by hydrolysis with 15% aqueous NaOH (overnight at room temperature) [38].

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Neutral (water) and alkaline hydrolysis (10% NaOH) of $(CF_3)_2PFBr_2$ for 5 d yields $(CF_3)_2PO_2^-$ (according to ^{19}F NMR) and a little CF_3H [45].

5.2.7.1.3.3 Reactions with Halogens, HI, Hg, Air, N_2O_4, $(CF_3)_2NO$, NH_3, and B_4H_8CO

The reaction of $(CF_3)_2PI$ with atomic fluorine has been studied by fast flow ESR methods. The initial stage of the reaction is the abstraction of I by F, to form IF and $(CF_3)_2P$ with a bimolecular rate constant of $(1.0 \pm 0.3) \times 10^{14}$ $cm^3 \cdot mol^{-1} \cdot s^{-1}$ at 297 K. In the presence of excess F, stepwise addition to the phosphoranes occurs. In the presence of excess $(CF_3)_2PI$ the reaction $(CF_3)_2P + IF \rightarrow (CF_3)_2PF + I$ appears to take place. This reaction rate is slow relative to $(CF_3)_2P + F \rightarrow (CF_3)_2PF$ [63].

$(CF_3)_2PF$, $(CF_3)_2PBr$ and CF_3PBr_2 are oxidized by Br_2 to give the corresponding phosphoranes $(CF_3)_2PFBr_2$, $(CF_3)_2PBr_3$ and CF_3PBr_4, respectively. The bromination of CF_3PF_2 yields CF_3PF_4, CF_3PBr_2, and $(CF_3)_2PBr_3$ as principal products [45].

CF_3PI_2 reacts with an excess of anhydrous HI and Hg to give CF_3PH_2 in almost quantitative yield. However, with a deficiency of HI, CF_3PH_2 is formed along with $(CF_3P)_n$ (n = 4, 5) and $CF_3PHPHCF_3$ (20 to 40%) [7].

On shaking with Hg for 2 to 3 h, CF_3PI_2 reacts almost completely to $(CF_3P)_4$ [32]. Reaction of Hg with $i\text{-}C_3F_7PI_2$ gives $(i\text{-}C_3F_7P)_3$ in quantitative yield [58].

$(CF_3)_2PF$ is oxidized by air to form $(CF_3)_2P(O)F$. During 30 min at 25 °C and 0.5 atm, there was a 5% conversion to $(CF_3)_2P(O)F$, after 16 h the reaction was essentially complete [34].

N_2O_4 oxidizes CF_3PF_2 to give $CF_3P(O)F_2$ [34].

The phosphines $(CF_3)_2PX$ (X = F, Cl, and Br) react with bis(trifluoromethyl)nitroxyl, $(CF_3)_2NO$, at room temperature to give the oxidative addition products of the type $[(CF_3)_2NO]_2P(CF_3)_2X$. However, with $(CF_3)_2PI$ the substituted phosphine $(CF_3)_2NOP(CF_3)_2$ is formed [26]. For the properties of these products, see p. 93.

The reaction of $(CF_3)_2PCl$ with NH_3 at room temperature yields $(CF_3)_2PNH_2$ (95% yield) [67]; see also p. 101.

In B_4H_8CO the CO group can be exchanged by CF_3PF_2 to give the complex $CF_3PF_2 \cdot B_4H_8$ [59], see also p. 148.

5.2.7.1.3.4 Reactions with SbX_3, AgX (X = F, Cl), $AgOC(O)R_f$, $NaOC(CF_3)_2CN$, $LiOCH(CF_3)_2$, $R(CF_3)PH$, and Alkyl Iodides

With SbF_3 and $SbCl_3$ perfluoroalkyldiiodophosphines are transformed into the corresponding difluoro- and dichlorophosphines. For the reactions between $C_2F_5PI_2$ and SbF_3, see [3] and p. 104, for the reactions between RPI_2 (R = CF_3, C_2F_5, C_3F_7) and $SbCl_3$, see [39] and p. 105.

Perfluoroalkyliodophosphines and AgX salts (X = F, Cl) may react to give the corresponding perfluoroalkylhalogenophosphines; see for CF_3PI_2 and AgF [1] and for $i\text{-}C_3F_7PI_2$ and AgCl [38] and p. 105.

$(CF_3)_2PCl$ and $(CF_3)_2PI$ readily react with silver perfluorocarboxylato salts at room temperature to form the carboxylatobis(perfluoroalkyl)phosphine-mixed anhydrides, $(CF_3)_2PX + AgOC(O)R_f \rightarrow R_fC(O)OP(CF_3)_2 + AgX$, where X = Cl, I and R_f = CF_3, C_2F_5, C_3F_7 [25]; see also p. 88. With sodium salts no reaction occurs [25].

$(CF_3)_2PCl$ and $(CF_3)_2PI$ react with the sodium cyanohydrin salt of hexafluoroacetone in high yield according to the following scheme,

$(CF_3)_2PX + NaOC(CF_3)_2CN \rightarrow (CF_3)_2C(CN)OP(CF_3)_2 + NaX$, X = Cl and I [25]; see also p. 88.

By reaction of $(CF_3)_2PI$ with $LiOCH(CF_3)_2$ the $(CF_3)_2CHO$ group can be linked to phosphorous yielding $(CF_3)_2POCH(CF_3)_2$ (warming the mixture from −196 °C to room temperature over 1 h, yield 85%). Boiling point 71 °C; ^{19}F NMR (internal standard $CFCl_3$): $\delta[OCH(CF_3)_2] = -78.8$, $\delta(CF_3P) = 65.2$ ppm, J(F-C-P) = 100 Hz; ^{31}P NMR (external standard 85% H_3PO_4): $\delta = 107$ ppm; ^1H NMR [internal standard $(CH_3)_4Si$]: $\delta = 4.4$ ppm, J(P-H) = 10.5, J(FC-CH) = 4.5 Hz [61].

Chiral diphosphines $R(CF_3)PP(CF_3)_2$ have been made by reaction of $(CF_3)_2PCl$ with $R(CF_3)PH$ (R = CH_2F, CHF_2) in presence of $(CH_3)_3N$ to remove HCl (−110 to −78 °C, yield below 50% for R = CH_2F and 83% for R = CHF_2) [56].

$CH_2F(CF_3)PP(CF_3)_2$: vapor pressure equation log (p/Torr) = 6.9037 + 1.75 log T −0.005 T −2734/T, boiling point (extrapolated) 111 °C, Trouton constant 21.2 $cal \cdot mol^{-1} \cdot K^{-1}$. ^{19}F NMR (standard $CFCl_3$): AB pattern, $\delta(CF_3\text{-}A) = -46.5$ ppm, J(F-C-P) = 67, J(F-C-P-P) = 9(?), J(F-C-P-C-F) = 8.0, J(F-C-P-P-C-F) = 2.0 Hz; $\delta(CF_3\text{-}B) = -49$ ppm, J(F-C-P) = 67 Hz; $C(CF_3)P$ group, $\delta = -50$ ppm, J(F-C-P) = 64, J(F-C-P-P) = 18 Hz; CH_2F group, $\delta = -226$ ppm, J(F-C-P) = 81 Hz, J(F-C-P-C-F) = 2.1, J(F-C-P-P-C-F) = 6(?), J(F-C-H) = 47.7 Hz. ^1H NMR [standard $(CH_3)_4Si$]: AB pattern, $\delta_A = 4.945$ ppm, J(H-C-F) = 47.5, J(H-C-P) = 11.3 Hz; $\delta_B = 5.015$ ppm, J(H-C-F) = 47.7, J(H-C-P) = 10.8 Hz.

$CHF_2(CF_3)PP(CF_3)_2$: p = 10 Torr at 0°C and 43 Torr at 26.2°C, boiling point (extrapolated) 100°C. ^{19}F NMR (standard $CFCl_3$): AB pattern, $\delta(CF_3\text{-}A) = -46.2$, $\delta(CF_3\text{-}B) = -48.1$ ppm, J(F-C-P) = 71 Hz for both; $C(CF_3)P$ group, $\delta = -51$ ppm, J(F-C-P) = 60 Hz; CHF_2 group, $\delta = -112$ ppm, J(F-C-P) = 117, J(F-C-H) = 52 Hz (by proton decoupling). ^1H NMR [standard $(CH_3)_4Si$]: $\delta = 3.58$ ppm, J(H-C-F) = 50.2, J(H-C-P) = 17.5, J(H-C-P-P) = 3.2 Hz [56].

$(CF_3)_2PCl$ reacts with $i\text{-}C_3F_7I$ in dry ether in the presence of Li metal (−78 °C for 0.5 h, then 2 h at −50 °C, finally stirring 2 h at room temperature) giving $i\text{-}C_3F_7(CF_3)_2P$ in 60% yield [38].

The reaction of $(CF_3)_2PI$ with $(CF_3)_2CFI$ and Li metal dispersed in diglyme leads (−45 °C for 4 h, then keeping at room temperature overnight) to $(CF_3)_2PCF(CF_3)_2$ in 56.3% yield along with $[(CF_3)_2CF]_2$ and $[(CF_3)_2P]_2$ [3]. For properties of $(CF_3)_2PCF(CF_3)_2$, see p. 154.

5.2.7.1.3.5 Reactions with Alcohols and Mercaptans

The reaction of $(CF_3)_2PCl$ with alcohols and mercaptans in the presence of $(CH_3)_3N$ yields phosphinous esters, $(CF_3)_2POR$, and thioesters, $(CF_3)_2PSR$, with R = CH_3, C_2H_5, $CH(CH_3)_2$ [36]. The general procedure is to slowly warm a mixture of equal molar quantities of the reactant and $(CH_3)_3N$ in a sealed ampule from −78 °C to room temperature. The yields are about 90%. In the absence of $(CH_3)_3N$, t-butyl alcohol gives $(CF_3)_2POH$, $(CF_3)_2P(O)C(CH_3)_3$ (1 : 1 molar ratio), $(CH_3)_3CCl$ and HCl. Separate reactions showed that the ester reacted with HCl to yield $(CF_3)_2POH$ and $(CH_3)_3CCl$. With benzylalcohol, $(CF_3)_2PCl$ gives after 4 h at 70 °C $(CF_3)_2POH$ and unidentified products [36]. Vapor pressure measurements (p in Torr) yield for $(CF_3)_2POCH(CH_3)_2$ log p = 7.98 − 1840/T in the range 0 to 50 °C with a boiling point of 8 °C; for $(CF_3)_2PSCH(CH_3)_2$ log p = 8.10 − 2079/T in the range 15 to 60 °C with a boiling point of 125°C. NMR data of the synthesized esters and thioesters are summarized in **Table 36**, p. 122. For IR spectral data, see the original [36].

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Table 36
NMR Data of Phosphinous Esters and Thioesters [36].
The chemical shifts δ (in ppm) are relative to internal $CFCl_3$ or relative to $(CH_3)_4Si$; positive values denote resonance to low field of standard. Coupling constants J in Hz.

Compound	δ(F)	J(F-P)	δ(CH_3)	δ (other protons)	J(P-CH_x)	J(HC-CH)	J(F-H)
$(CF_3)_2POCH_3$	−64.4	86.1	3.92		12.4		0.5
$(CF_3)_2POC_2H_5$	−65.0	87.2	1.44	4.15 (CH_2)	9.8[a]	7.0	0.3
$(CF_3)_2POCH(CH_3)_2$	−65.6	88.0	1.43	4.36 (CH)	7.8[b]	6.2	0.2
$(CF_3)_2POC(CH_3)_3$	−65.9	88.3	1.36				0.2
$(CF_3)_2PSCH_2CH_3$	−57.1	79.4	1.50	2.97 (CH_2)	14.6[a], 0.5	7.3	
$(CF_3)_2PSCH(CH_3)_2$	−57.0	80.3	1.49	3.39 (CH)	6.7[b]	6.7	
$(CF_3)_2PSC(CH_3)_3$	−56.7	81.2	1.59		1.1		

[a] J(P-CH_2). — [b] J(P-CH).

With $ClCH_2CH_2OH$, $(CF_3)_2PCl$ reacts (21 °C, 25 h) giving $(CF_3)_2POCH_2CH_2Cl$ in 91% yield. Colorless liquid, vapor pressure ca. 11 Torr at 21 °C. ^{19}F NMR (internal standard $CFCl_3$): $\delta = -64.6$ ppm, J(F-P) = 86 Hz; ^1H NMR [standard $(CH_3)_4Si$]: $\delta = 4.25$ and 3.70 ppm, J(P-O-C-H) = 9 Hz, J(H-H) = 6 Hz; IR spectrum (gas phase): P-O stretch at 1042 cm^{-1} [64].

The treatment of diiodophosphines with alcohols gives the phosphinous esters only with 35 to 40% yield. More convenient is the use of dichlorophosphines (adding alcohol at −10 °C to CF_3PCl_2, slowly warming to room temperature with shaking and then leaving the mixture for 20 h):

$$R_fPCl_2 + 2\,ROH \rightarrow R_fP(OR)_2 + 2\,HCl$$

Under these conditions, with isopropylalcohol, mainly perfluoroalkylphosphonites $R_fPH(O)OC_3H_7$-iso ($R_f = CF_3, C_2F_5, C_3F_7$) were obtained [39]. Some data of compounds with various substituents are given in **Table 37**.

Table 37
Some Data of $R_fP(OR)_2$ and $R_fPH(O)OR$ Compounds [39].

R_f	R	Yield in %	Boiling point in °C (pressure in Torr)	δ(P)[a] in ppm	J(P-CF) in Hz	J(P-H) in Hz
$R_fP(OR)_2$						
CF_3	C_2H_5	63	23 to 25 (10)	133.0	84	
CF_3	C_3H_7	82	42 to 44 (10)	133.4	80	
CF_3	iso-C_4H_9	84	60 to 63 (10)	132.7	79	
C_2F_5	CH_3	79	40 to 42 (75)	145.3	86	
C_2F_5	C_2H_5	59	24 (8)	—	—	
C_2F_5	C_4H_9	68	74 to 76 (8)	—	—	
C_2F_5	iso-C_4H_9	90	64 (8)	143.9	96	
C_3F_7	iso-C_4H_9	91	85 (12)	143.9	89	

Table 37 (continued)

R_f	R	Yield in %	Boiling point in °C (pressure in Torr)	δ(P)[a] in ppm	J(P-CF) in Hz	J(P-H) in Hz
$R_fPH(O)OR$						
CF_3	iso-C_3H_7	62	43 to 45 (12)	5.4	116	642
C_2F_5	iso-C_3H_7	83	43 to 44 (10)	8.9	89	638
C_3F_7	iso-C_3H_7	61	57 to 59 (11)	9.2	88	636

[a] ^{31}P NMR, external standard 85% H_3PO_4; positive δ values indicate resonance downfield of standard.

The reaction of CF_3PCl_2 with deficient CH_3OH and frequent removal of the HCl during the reaction time of 2 d at 25°C yields $CH_3O(CF_3)PCl$ along with $(CH_3O)_2PCF_3$ [66]. $CH_3O(CF_3)PCl$ is also obtained from the reaction of CF_3PCl_2 with $(CH_3O)_2PCF_3$ in the presence of $(CH_3)_3N$ (50% yield after 21 h at 25°C, 91% yield after brief heating to 100°C in a sealed tube) [66]. $CH_3O(CF_3)PCl$: vapor pressure 52 Torr at 0°C; ^{19}F NMR (external standard $CFCl_3$): $\delta = -72.3$ ppm, J(F-P) = 73.3, J(F-H) = 1 Hz; ^{31}P NMR (external standard H_3PO_4): $\delta = 133$ ppm, J(P-F) = 75, J(P-H) = 10.3 Hz; ^{13}C NMR (external standard C_6D_6): $\delta(CF_3) = -1.15$, $\delta(CH_3) = -72.2$ ppm, J(C-F) = 325.6, J(C-P) = 66.0, J(CH) = 148.7 Hz; ^1H NMR [external standard $(CH_3)_4Si$]: $\delta = 3.53$ ppm, J(H-P) = 11.0, J(H-F) = 0.9 Hz; for the infrared spectrum, see the original [66].

5.2.7.1.3.6 Reactions with Metal Alkyls

Perfluoromethylfluorophosphoranes and -chlorophosphoranes are methylated with $(CH_3)_4Sn$ or $(CH_3)_4Pb$ [46] according to the reaction scheme

$$(CF_3)_nPX_{5-n} + (CH_3)_4Y \rightarrow CH_3(CF_3)_nPX_{4-n} + (CH_3)_3YX$$

n = 1, 2, 3, X = F, Cl and Y = Sn or Pb.

With $(CH_3)_4Pb$ in toluene, CF_3PCl_4 gives $CH_3(CF_3)PCl_3$ as a white solid in ~30% yield (sealed vessel, agitation at room temperature for several days). In the same manner $(CH_3)_4Sn$ and CF_3PF_4 gave $CH_3(CF_3)PF_3$ (in 17 h 18% yield) as a white solid. Both compounds were characterized by ^1H, ^{19}F, ^{31}P NMR (see **Table 38**, p. 124) and IR spectra (see the original) [46].

Methylation of $(CF_3)_2PF_3$ is achieved with $(CH_3)_4Sn$ (sealed tube, room temperature, 18 h) giving $CH_3(CF_3)_2PF_2$ with a yield of 85%. As a by-product $[(CH_3)_3Sn][(CF_3)_2PF_4]$ was formed. For NMR data of $CH_3(CF_3)_2PF_2$, see Table 38; for infrared and mass spectral data, see the original [68].

$(CF_3)_2PCl_3$ and $(CH_3)_4Pb$ in toluene react (shaking for two days at room temperature) to give $(CH_3)_2(CF_3)_2PCl$ (yield 47%) along with $CH_3(CF_3)_2PCl_2$. For NMR data, see Table 38; for infrared and mass spectral data, see the original [11].

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Table 38
^1H, ^{19}F and ^{31}P NMR Data of Methyl(trifluoromethyl)halogenophosphoranes.

	$CH_3(CF_3)PF_3$		$CH_3(CF_3)PCl_3$		$CH_3(CF_3)_2PF_2$		$CH_3(CF_3)_3PF$		$CH_3(CF_3)_3PCl$	$(CH_3)_2(CF_3)_2PCl$	
	0 °C	−100 °C	+30 °C	−80 °C	+30 °C	−100 °C	+33 °C	−90 °C	+30 °C	+33 °C	−90 °C
					Chemical shifts in ppm[m]						
δ(H)[a]	1.70	1.9[d]	3.04		1.94		2.11		2.52	2.54	
δ(PF)[b]	− 46.2	− 25.9[e] − 86.5[f]			− 44.6		− 13.3 (1)[g]				
δ(CF_3)[b]	− 69.6	− 69.0	− 74.1	− 76.7	− 66.9	− 66.4	− 62.3 (6)[g]	− 59.7[i] (2)[g] − 68.2[j] (1)[g]	− 63.3	− 63.0	−65.0
δ(^{31}P)[c]	−124.2	−120	−148.4	−151.7	−148.3	−148.9	−164.1	−166.4	−165.8	−162.1	
					Coupling constants in Hz						
J(P-F)	955	909[e] 1026[f]			849	840	843	827			
J(P-C_F)	332.0	333.9	184.2	140.6							
J(P-C_H)	152.0	151.4	85.0	76.2							
J(P-C-F)	156	157.5	114.6	90.5	154	154	102.6	135.5[i] 35.5[j]	101.0	79.0	78.5
J(P-C-H)	17.5	18.0	12.4		19.3		15.4		12.8	16.2	
J(FP-CH)	8.4	9.0[d]	0.7		12.3		8.7				
J(FP-CF)	12.0	17.0, 2.2			17.5	16.5	17.3	16.0[k]			
J(FC-P-CH)					0.4		0.6		0.8		
J(FC-P-CF)								12.5			
J(F-P-F)		50.8[l]									
Ref.	[46]		[46]		[68]		[22, 62]		[22, 62]	[11]	

[a] Relative to $(CH_3)_4Si$ as external standard. — [b] Relative to $CFCl_3$ as internal standard. — [c] Relative to P_4O_6. — [d] At −80 °C. — [e] Axial fluorine. — [f] Equatorial fluorine. — [g] Relative intensity. — [i] Equatorial CF_3 group. — [j] Axial CF_3 group. — [k] J(FP-CF_{eq}); J(FP-CF_{ax}) was not observed. — [l] Coupling of axial and equatorial fluorine. — [m] Positive values indicate resonance downfield to standard.

$(CF_3)_3PF_2$ reacts with $(CH_3)_4Sn$ or $(CH_3)_4Pb$ (sealed tube, gradually warming to room temperature and shaking at room temperature for 2 days) giving $CH_3(CF_3)_3PF$ [in 82% yield for $(CH_3)_4Sn$]. $(CF_3)_3PCl_2$ reacts only with $(CH_3)_4Pb$ (sealed tube, immediately on warming to room temperature a white solid is formed, further agitation for 1.5 h) to form $CH_3(CF_3)_3PCl$ in 72% yield. With $(CH_3)_nSn$ no reaction had occurred after one week at room temperature. $CH_3(CF_3)_3PF$ (melting point 20 to 21°C) and $CH_3(CF_3)_3PCl$ (melting point 56 to 57°C) were characterized by their NMR spectra (see Table 38); for infrared and mass spectral data, see the original [22, 62].

With $(CH_3)_4Pb$ at room temperature in a sealed tube $(CF_3)_3PCl_2$ and $(CF_3)_2PCl_3$ yield $(CH_3)_2P(CF_3)_3$ (yield 75%, melting point 64 to 65°C) and $(CH_3)_3P(CF_3)_2$ (yield 44%, melting point 44 to 46°C), respectively. According to NMR data (given in **Table 39**) these pentaalkylphosphoranes have a trigonal bipyramidal structure in which CF_3 groups are preferentially located in the axial positions [23].

Table 39
^{19}F, ^{1}H and ^{13}C NMR Data of $(CF_3)_3P(CH_3)_2$ and $(CF_3)_2P(CH_3)_3$ at 33°C [23].
Chemical shifts δ in ppm and coupling constants J in Hz. Positive δ values indicate resonance downfield of standard.

Compound	Group	Chemical shifts $\delta(F)^{a)}$	$\delta(H)^{b)}$	$\delta(C)^{c)}$	Coupling constants J J(P-C)	J(P-H)	J(P-F)	$J(F-F)^{d)}$	J(F-H)
$(CF_3)_3P(CH_3)_2$	CF_3(eq)	−59.6	–	127	206	–	114.0	14.0	–
	CF_3(ax)	−70.7	–	132	≤8	–	23.5	14.0	–
	CH_3	–	1.93	7	88	13.4	–	–	–
$(CF_3)_2P(CH_3)_3$	CF_3(ax)	−74.4	–	131	29	–	6.3	–	0.7
	CH_3	–	1.66	8	102	14.0	–	–	–

[a] Relative to $CFCl_3$. — [b] Relative to $(CH_3)_4Si$. — [c] Measured relative to CD_2Cl_2, converted to $(CH_3)_4Si$ reference scale. — [d] Coupling between axial and equatorial CF_3 groups.

CF_3PI_2 and $(CF_3)_2PI$ readily react with an excess of $(CH_3)_3SnH$ at room temperature to form CF_3PH_2 and $(CF_3)_2PH$ in almost quantitative yield [6]. For the properties of these phosphines, see Part 3, p. 14 ff.

The reaction of CF_3PI_2 with R_4Pb ($R = CH_3, C_2H_5$) at 100 to 120°C yields $(CF_3P)_4$ along with RI and R_3PbI within 3 to 8 h [33].

5.2.7.1.3.7 Reactions with Trimethylsilyl Compounds, F_3SiPH_2 and $(CH_3)_3EAsH_2$ (E = Si, Sn)

$(CF_3)_2PI$ reacts with $ISiH_3$ and $ISi(CH_3)_3$ in the presence of Hg at room temperature to form $(CF_3)_2PSiH_3$ and $(CF_3)_2PSi(CH_3)_3$, respectively [31].

Properties of both compounds are described on p. 126 and in Part 3, p. 24, respectively.

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$(CF_3)_3PF_2$ reacts with trimethylmethoxysilane and -methylthiosilane, $(CH_3)_3SiOCH_3$ and $(CH_3)_3SiSCH_3$, under mild reaction conditions (e.g., room temperature or below) to give the corresponding methoxy or methylthio derivatives of tris(perfluoromethyl)phosphorane [2]. With excess $(CH_3)_3SiOCH_3$, $(CF_3)_3P(OCH_3)_2$ and $(CH_3)_3SiF$ form; deficient $(CH_3)_3SiOCH_3$ gives $(CF_3)_3P(F)OCH_3$ and $(CH_3)_3SiF$. In a similar reaction, deficient $(CH_3)_3SiOCH_3$ plus a trace of iodine produce $(CF_3)_3P(OCH_3)_2$ and $(CF_3)_3P(F)OCH_3$ along with $(CH_3)_3SiF$. The reaction of $(CF_3)_3PF_2$ with $[(CH_3)_3Si]_2O$ yields $(CF_3)_3P(F)OSi(CH_3)_3$ as was followed by NMR spectroscopy. The product decomposes after 4 h.

The reaction of $(CF_3)_3PCl_2$ with $(CH_3)_3SiOCH_3$ (excess or deficient) leads to $(CF_3)_3P(OCH_3)_2$. The methoxy- and siloxyphosphoranes were characterized by their NMR, IR and mass spectra. For NMR data, see **Table 40**; for the other spectra, see the original [2].

Table 40
^1H, ^{19}F and ^{31}P NMR Data of Tris(trifluoromethyl)phosphoranes with OCH_3 or $OSi(CH_3)_3$ Substituents [2].

Compound	t in °C	Chemical shifts in ppm[a]			
		δ(H)[b]	δ(F)[c]	δ(CF_3)[c] (rel. intens.)	δ(P)[d]
$(CF_3)_3P(OCH_3)_2$	+30	3.81		−63.4	−187.0
	−80			−61.7 (1)[e]	
				−63.6 (2)[f]	
$(CF_3)_3P(F)OCH_3$	+30	3.97	−50.2	−64.4	−169.0
	−80		−51.4	−63.0 (2)[e]	−170.9
				−67.0 (1)[f]	
$(CF_3)_3P(F)OSi(CH_3)_3$	+30	0.44	−45.5	−66.7	

Compound	t in °C	Coupling constants in Hz					
		J(P-F)	J(P-CF)	J(P-H)	J(FP-CH)	J(FP-CF)	J(FC-CF)
$(CF_3)_3P(OCH_3)_2$	+30		96.0	13.6	0.8		
	−80		108.0[e]				13.5
			88[f]				
$(CF_3)_3P(F)OCH_3$	+30	912	112.5	13.9	1.2	14.0	
	−80	909	133.0[e]			15.5	12.0
			72.0[f]				
$(CF_3)_3P(F)OSi(CH_3)_3$	+30	979	120.5			13.5	

[a] Positive values indicate resonance downfield of standard.

[b] Relative to internal $(CH_3)_4Si$.

[c] Relative to internal (solvent) $CFCl_3$.

[d] Versus P_4O_6 as external standard.

[e] CF_3 equatorial.

[f] CF_3 axial.

Table 41

^1H, ^{19}F and ^{31}P NMR Data for (Trifluoromethyl)fluoro(methylthio)phosphoranes [57].

Compound	t in °C	Chemical shifts in ppm[r] δ(H)[a]	δ(F)[b]	δ(CF_3)[b]	δ(P)[c]
$CF_3PF_3(SCH_3)$	0	2.35		−69.2	−140.0
	−90		−16.1[e] −24.8[f] −76.2[g]		
$(CF_3)_2PF_2(SCH_3)$	+33	2.28	−41.0	−67.4	−142.4
	−100		−38.7 −45.1		
$(CF_3)_3PF(SCH_3)$	+30	2.08	−1.0	−61.7	−161.5
	−70			−60.3[p] −59.9[q]	−161.5

Compound	t in °C	Coupling constants in Hz J(P-F_{eq})	J(P-F_{ax})	J(P-CF)	J(P-H)	J(FP-CH)	J(F_{ax}-F_{eq})	J(FP-CF)
$CF_3PF_3(SCH_3)$	0	1028.8[d]		168.0	23.2	1.8	82.0[j]	12.0[d]
	−90	1081.5	927[h] 1057[i]	168.8			71.0[k] 41.0[l]	16.0[m] 4.0[n] 16.0[o]
$(CF_3)_2PF_2(SCH_3)$	+33		924[d]	130.5	22.2	1.7		16.5
	−100		867[h] 986[i]					
$(CF_3)_3PF(SCH_3)$	+30		980	103.7	19.2	2.5		16.5
	−6		975	107.5[d]				
	−70			33.8[p] 134[q]				13

[a] Relative to internal $(CH_3)_4Si$.

[b] Relative to internal $CFCl_3$.

[c] Relative to external P_4O_6.

[d] Average value.

[e] Unique axial environment of one F (type A), designated F_{ax}.

[f] Unique axial environment of one F (type B), designated F'_{ax}.

[g] Equatorial fluorine atom environments.

[h] Phosphorus coupling with type A axial fluorine.

[i] Phosphorus coupling with type B axial fluorine.

[j] F'_{ax}-F_{eq} coupling constant.

[k] F_{ax}-F_{eq} coupling constant.

[l] Trans F_{ax}-F'_{ax} coupling constant.

[m] Coupling between CF_3 group and the type A axial fluorines.

[n] Coupling between the CF_3 group and the equatorial fluorine.

[o] Coupling between the CF_3 group and the type B axial fluorine.

[p] Axial CF_3 group.

[q] Equatorial CF_3 group.

[r] Positive values indicate resonance downfield of standard.

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CF_3PF_4 and $(CH_3)_3SiSCH_3$ (1:1 molar ratio, sealed tube, −23°C for 1 h) reacts to yield $CF_3PF_3(SCH_3)$. With $(CF_3)_2PF_3$, $(CH_3)_3SiSCH_3$ gives $(CF_3)_2PF_2(SCH_3)$ (sealed tube, 1 h at room temperature) in 80% yield, and with $(CF_3)_3PF_2$ (sealed tube, warming from −78°C to −15°C over a one day period) $(CF_3)_3PF(SCH_3)$ in 82% yield is obtained. The products were characterized by their NMR spectra [57]; see **Table 41**, p. 127.

The cleavage of the Si-P bond in F_3SiPH_2 by $(CF_3)_2PI$ requires 5 d at room temperature yielding F_3SiI and $(CF_3)_2PPH_2$ [30].

The cleavage of the Si-As and Sn-As bonds in $(CH_3)_3SiAsH_2$ and $(CH_3)_3SnAsH_2$ by $(CF_3)_2PI$ occurs near −78°C giving $(CH_3)_3SiI$ and $(CH_3)_3SnI$, respectively, and $(CF_3)_2PAsH_2$. The latter one (for properties, see p. 161) decomposes when the temperature is higher than −40°C [8].

5.2.7.1.3.8 Reactions with Amines

The reaction of dimethylamine with $(CF_3)_3PF_2$ in the gas phase at room temperature readily proceeds giving $(CF_3)_3P(F)N(CH_3)_2$ [2]. For NMR data, see **Table 42**; for infrared and mass spectral data, see the original [2].

$(CF_3)_2PF$ cleaves the Si-N bond in silylamines such as $(CH_3)_3SiNR_2$ (R = CH_3, C_2H_5, n-C_3H_7), forming aminophosphines,

$$(CH_3)_3SiNR_2 + (CF_3)_2PF \rightarrow (CH_3)_3SiF + (CF_3)_2PNR_2$$

The reaction occurs in benzene solution at 80°C for 30 h [20].

$(CF_3)_3PCl_2$ and $(CH_3)_3SiN(CH_3)_2$ react to give only the monosubstituted chlorophosphorane $(CF_3)_3P(Cl)N(CH_3)_2$ regardless of ratio of reactants (warming slowly from −196°C to −10°C). The product is not stable at room temperature [2]. For NMR data, see Table 42.

Table 42
^1H, ^{19}F and ^{31}P NMR Data of Tris(trifluoromethyl)aminophosphoranes [2].

Compound	t in °C	Chemical shifts in ppm [a] δ(H) [b]	δ(F) [c]	δ(CF_3) [c] (rel. intens.)	δ(^{31}P) [d]
$(CF_3)_3P(F)N(CH_3)_2$	+30	3.00	−30.5	−61.1	−174.7
	−40		−32.3	−62.3 (2) [f]	−175.9
				−59.6 (1) [g]	
$(CF_3)_3P(Cl)N(CH_3)_2$	+30	2.80		−59.0	−156.5

Compound	t in °C	J(P-F)	Coupling constants in Hz J(P-CF)	J(P-H)	J(FP-CH)	J(FP-CF)	J(FC-CF)
$(CF_3)_3P(F)N(CH_3)_2$	+30	857	109.0	10.6	2.8 (0.4) [e]	16.0	
	−40	849	130.0 [f]			16.0	16.0
			54.0 [g]				
$(CF_3)_3P(Cl)N(CH_3)_2$	+30		107.0	14.0	0.7		

[a] Positive values indicate resonance downfield of standard. — [b] Relative to internal $(CH_3)_4Si$. — [c] Relative to internal $CFCl_3$ as solvent. — [d] Versus P_4O_6 as external standard. — [e] J(FC-CH). — [f] CF_3 equatorial. — [g] CF_3 axial.

References p. 130

$(CH_3)_2NH$ reacts with $(CF_3)_2PCl_3$ to form in a stepwise process $(CF_3)_2PCl_2[N(CH_3)_2]$ and the salt $CF_3P[N(CH_3)_2]_3^+Cl^-$. The reaction proceeds in the fast initial displacement of one Cl substituted by $(CH_3)_2NH$ followed by slower replacement of Cl and one CF_3 group by $(CH_3)_2NH$. Different ratios of reactants (0.8 to 12.4) and reaction times (30 min, 4 d) at room temperature yield similar results. With CF_3PCl_4 and gaseous $(CH_3)_2NH$ in large excess, $CF_3P[N(CH_3)_2]_3^+Cl^-$ is easily obtained at room temperature within 24 h. By-products are mainly CF_3H and $(CH_3)_2NH_2^+Cl^-$ and isolation of the phosphonium ion occurs as PF_6^- salt by precipitation with aqueous KPF_6 solution.

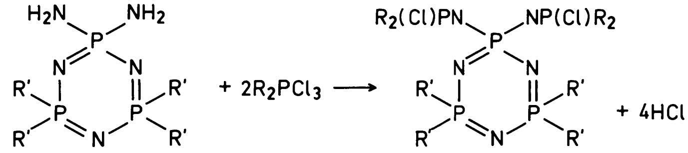
$CF_3P[N(CH_3)_2]_3^+$ in CD_3CN solution. ^{19}F NMR (external standard $CFCl_3$): $\delta = -59.8$ ppm, J(P-F) = 108 Hz. ^{31}P NMR (external standard P_4O_6): $\delta = -69$ ppm, J(P-F) = 107.5, J(P-H) = 10.3 Hz. ^1H NMR [external standard $(CH_3)_4Si$]: $\delta = 2.76$ ppm, J(P-H) = 10.5, J(F-H) = 0.75 Hz. For an infrared spectrum, see the original [18].

$(C_3F_7)_2PCl_3$ reacts with p-phenylenediamine and 1,1-diamino-3,3,5,5-tetrakis(heptafluorobutoxy)cyclotriphosphazine in the presence of $(C_2H_5)_3N$ at −30 to 20 °C in tetrahydrofuran [21] according to:

$$p\text{-}H_2NC_6H_4NH_2 + 2\,R_2PCl_3 \rightarrow R_2(Cl)PNC_6H_4NP(Cl)R_2 + 4\,HCl$$

$R = C_3F_7$; yield 45%, boiling point 93 to 95 °C (0.01 Torr)

and



$R = C_3F_7$, $R' = OCH_2C_3F_7$

Yield 57%, boiling point 141 to 143 °C (0.05 Torr).

$(CF_3)_2PCl$ reacts readily with lithium trimethylsilylamides, $(CH_3)_3SiN(R)Li$, to give the N-trimethylsilyl substituted aminophosphines $(CH_3)_3Si(R)NP(CF_3)_2$ with $R = (CH_3)_3Si$ (yield 91%), $R = (CH_3)_3C$ (yield 37%) and $R = CH_3$ (yield 73%). The lithium trimethylsilylamides were prepared from $n\text{-}C_4H_9Li$ and $[(CH_3)_3Si]_2NH$ in hexane by warming the mixture to room temperature. After cooling to −196 °C, $(CF_3)_2PCl$ was condensed into the bulb and the mixture was allowed to warm slowly to room temperature with occasional shaking [67].

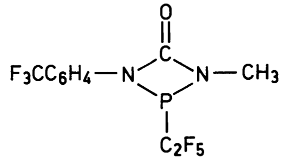
$[(CH_3)_3Si]_2NP(CF_3)_2$: colorless liquid, boiling point 56 to 57 °C (4 Torr). ^1H NMR [external standard $(CH_3)_4Si$]: $\delta = 0.18$ ppm; ^{19}F NMR (external standard $CFCl_3$): $\delta = -59.2$ ppm, J(P-F) = 93.1 Hz.

$[(CH_3)_3Si][(CH_3)_3C]NP(CF_3)_2$: colorless liquid; ^1H NMR [external standard $(CH_3)_4Si$]: $\delta = 1.51$ ppm, J(P-N-C-C-H) = 1.2 Hz; $\delta = 1.44$ ppm ($t\text{-}C_4H_9$), $\delta = 0.46$ ppm [$(CH_3)_3Si$], J(P-N-Si-C-H) = 3.2 Hz, $\delta = 0.39$ ppm [$(CH_3)_3Si$], J(FC-P-N-Si-C-H) = 0.7 Hz. ^{19}F NMR (external standard $CFCl_3$): $\delta = -54.9$ ppm, J(P-F) = 100.0 Hz, $\delta = -55.4$ ppm, J(P-F) = 101.0 Hz; ^{31}P NMR (external standard 85% H_3PO_4): $\delta = 49.7$, 34.7 ppm.

$CH_3[(CH_3)_3Si]NP(CF_3)_2$: colorless liquid; ^1H NMR [external standard $(CH_3)_4Si$]: $\delta =$ 0.05 ppm [$(CH_3)_3Si$], J(P-N-Si-C-H] = 1.5 Hz, $\delta = 2.6$ ppm (CH_3N), J(P-N-C-H) = 5.6, J(F-C-P-N-C-H) = 1.0 Hz. ^{19}F NMR (external standard $CFCl_3$): $\delta = -65.2$ ppm, J(P-F) = 83.8, J(F-C-P-N-C-H) = 1.0 Hz [24, 67].

No reaction was observed between $(H_3Si)_3N$ and $(CF_3)_2PCl$ even at 100 °C for 1 h [67].

The reaction between the urea derivative $[(CH_3)_3Si](3\text{-}CF_3\text{-}C_6H_4)NC(O)N(CH_3)[Si(CH_3)_3]$ and $C_2F_5PCl_2$ (CCl_4 solution, stirring for 2 d at room temperature) leads to the four-membered heterocycle



in 72% yield. Boiling point 106 to 107 °C at 12 Torr. ^{19}F NMR (internal standard $CFCl_3$): $\delta(CF_3) = -81.1$, $\delta(CF_2) = -126.3, -126.9$, $\delta(CF_3C_6H_4) = -63.4$ ppm, J(F-P) = 9, 69, 74 Hz. ^{31}P NMR (external standard 85% H_3PO_4): $\delta = 84.6$ ppm, J(P-F) = 69 and 74 Hz. ^1H NMR [internal standard $(CH_3)_4Si$]: $\delta(CH_3) = 3.18$, $\delta(C_6H_4) = 7.4$ to 7.8 ppm, J(H-P) = 8 Hz. The CO stretching vibration is assigned to 1790 cm^{-1}. Additional infrared and mass spectral data are given in the original [65].

5.2.7.1.3.9 Reactions of Perfluoroalkylhalogenophosphines with Transition Metal Complexes

Reaction of $(CF_3)_2PI$ with $MnCo(CO)_9$ in pentane solution (20 °C, 24 h, sealed NMR tube) gives $Mn(CO)_5I$ and $[Co(CO)_3P(CF_3)_2]_2$. On heating to 110 °C for 72 h, $MnCo(CO)_7[P(CF_3)_2]_2$ was obtained in 75% yield. IR and NMR data are given in the original [60].

$(CF_3)_nPX_{3-n}$ molecules as ligands L (n = 1 or 2, X = F, Cl, Br or I) can partly or completely substitute the CO molecules in the tricarbonylnitrosylcobalt complex $[Co(CO)_3(NO)]$. The main product in the reaction at room temperature is $[Co(CO)_2(NO)L]$ for all ligands $(CF_3)_2PX$ and CF_3PX_2 with the exception of CF_3PI_2. $(CF_3)_2PX$ and CF_3PX_2 (X = F or Cl) additionally form $[Co(CO)(NO)L_2]$, and $(CF_3)_2PF$ and CF_3PF_2 give additionally $[Co(NO)L_3]$ at 60 and 120 °C, respectively. An approximately equimolar mixture of CF_3PCl_2 and CF_3PBr_2 reacts with $[Co(CO)_3(NO)]$ to give $[Co(CO)_2(NO)(CF_3P(Cl)Br)]$ as well. IR and NMR data are given in the original [27].

Dichloro(2,7-dimethylocta-2,6-diene-1,8-diyl)ruthenium(IV), $[RuCl_2C_{10}H_{16}]_2$, reacts with CF_3PCl_2 at room temperature to give the orange-brown solid complex $RuCl_2(C_{10}H_{16})CF_3PCl_2$ (yield 76%). Melting point 92 to 98 °C, NMR data see [28].

$Re_2(CO)_{10}$ and $(CF_3)_2PI$ form at 120 °C after 139 h or at 130 °C after 48 h the complex $Re_2(CO)_8(CF_3)_2PI$ (yield 66%), NMR data see [29].

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5.2.7.2 Perfluorohalogenophenylhalogenophosphines and -phosphoranes

5.2.7.2.1 Formation and Preparation

Pentafluorophenyldifluorophosphine $C_6F_5PF_2$

Perfluoro(4-methylphenyl)difluorophosphine $4\text{-}CF_3\text{-}C_6F_4PF_2$

Bis(pentafluorophenyl)fluorophosphine $(C_6F_5)_2PF$

Pentafluorophenyldichlorophosphine $C_6F_5PCl_2$

Perfluoro(4-methylphenyl)dichlorophosphine $4\text{-}CF_3\text{-}C_6F_4PCl_2$

4-Chlorotetrafluorophenyldichlorophosphine $4\text{-}Cl\text{-}C_6F_4PCl_2$

Pentafluorophenyldibromophosphine $C_6F_5PBr_2$

Bis(pentafluorophenyl)bromophosphine $(C_6F_5)_2PBr$

No new method of preparation is reported for the compounds $C_6F_5PF_2$, $(C_6F_5)_2PF$, and $(C_6F_5)_2PBr$ (see Part 3, pp. 123/4); new physical data and chemical reactions are given in the following sections.

$C_6F_5PCl_2$ (53% yield) is obtained on heating a mixture of C_6F_5H, PCl_3 and $AlCl_3$ at 80 °C for 3 h, then at 50 °C for 1 h, followed by addition of $POCl_3$, extraction with petroleum ether and distillation. Replacing C_6F_5H by $4\text{-}CF_3\text{-}C_6F_4H$, the analogous reaction gives $4\text{-}CF_3\text{-}C_6F_4PCl_2$ (37% yield). A higher yield of 59% results on heating $4\text{-}CF_3\text{-}C_6F_4MgBr$ and SbF_3 at 150 °C (2 h) in an atmosphere of dry nitrogen. The phosphine $4\text{-}Cl\text{-}C_6F_4PCl_2$ (63% yield) is prepared by adding $4\text{-}Cl\text{-}C_6F_4MgBr$ in ether to PCl_3 in ether at −25 °C and keeping the mixture for 1 h at this temperature. $4\text{-}CF_3\text{-}C_6F_4PF_2$ is obtained by heating a mixture of $4\text{-}CF_3\text{-}C_6F_4PCl_2$ and SbF_3 at 150 °C (2 h, N_2 atmosphere) [1].

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Pentafluorophenyltetrafluorophosphorane $C_6F_5PF_4$

Perfluoro(4-methylphenyl)tetrafluorophosphorane $4\text{-}CF_3\text{-}C_6F_4PF_4$

Pentafluorophenyl(pentafluorophenoxy)trifluorophosphorane $C_6F_5(C_6F_5O)PF_3$

Pentafluorophenyltrifluorochlorophosphorane $C_6F_5PF_3Cl$

Pentafluorophenyldifluorodichlorophosphorane $C_6F_5PF_2Cl_2$

Pentafluorophenylfluorotrichlorophosphorane $C_6F_5PFCl_3$

Pentafluorophenyltetrachlorophosphorane $C_6F_5PCl_4$

Bis(pentafluorophenyl)trifluorophosphorane $(C_6F_5)_2PF_3$

Bis(pentafluorophenyl)difluorochlorophosphorane $(C_6F_5)_2PF_2Cl$

Bis(pentafluorophenyl)fluorodichlorophosphorane $(C_6F_5)_2PFCl_2$

Bis(pentafluorophenyl)trichlorophosphorane $(C_6F_5)_2PCl_3$

Tris(pentafluorophenyl)difluorophosphorane $(C_6F_5)_3PF_2$

No new method of preparation is reported for $(C_6F_5)_2PF_3$, $(C_6F_5)_2PCl_3$, and $(C_6F_5)_3PF_2$ (see Part 3, pp. 123/4), for new physical data and chemical reactions see the following sections.

$C_6F_5PF_4$ has been obtained by fluorination of $C_6F_5PF_2$ with SbF_5 (1 h, 130 °C; 57% yield). Higher yields (75%) are obtained by fluorination of $C_6F_5PF_2$ with SbF_3 in presence of Cl_2 (shaking the mixture 4 h at room temperature, then heating it at 80 °C for 2 h) [2]. The latter method is also reported in [1]. In the same way, on replacing $C_6F_5PF_2$ by $4\text{-}CF_3\text{-}C_6F_4PF_2$, the tetrafluorophosphorane $4\text{-}CF_3\text{-}C_6F_4PF_4$ is formed (82% yield) [1]. $C_6F_5PF_4$ is obtained in 10% yield in the reaction of C_6F_5MgBr with PF_5 in ether at −130 °C (2 h), followed by warming to 20 °C and adding PCl_3 [1]. Heating a solution of $C_6F_5PF_4$ and $C_6F_5OSi(CH_3)_3$ in CCl_4 at 50 °C for 1 h results in the formation of $C_6F_5(C_6F_5O)PF_3$ (73% yield) [3].

$C_6F_5PF_3Cl$ and $(C_6F_5)_2PF_2Cl$ have been synthesized by the reaction of hydrogen chloride with an ether solution of $C_6F_5PF_3N(C_2H_5)_2$ and $(C_6F_5)_2PF_2N(C_2H_5)_2$, respectively. $C_6F_5PF_2Cl_2$ is formed in the reaction of liquid Cl_2 and $C_6F_5PF_2$ in a sealed tube at room temperature (with short cooling periods during the reaction). Also, $C_6F_5PCl_4$ has been obtained by the reaction of Cl_2 with $C_6F_5PCl_2$ (solvent $CDCl_3$, sealed tube, −40 °C), further $(C_6F_5)_2PFCl_2$ by the reaction of $(C_6F_5)_2PF$ in toluene/C_6F_6 (50/50) with Cl_2, warming immediately to 50 °C, followed by cooling to −30 °C. $C_6F_5PFCl_3$ forms along with $C_6F_5PF_3Cl$ on heating $C_6F_5PF_2Cl_2$ above room temperature. The instable phosphoranes are characterized by ^{19}F NMR spectroscopy (see p. 134) [2].

5.2.7.2.2 Physical Properties

Phosphines

Boiling points (b.p.) in °C/pressure in Torr, refractive indices n, UV spectrum.

$4\text{-}CF_3\text{-}C_6F_4PF_2$: b.p. 144 to 146 °C, n_D^{20} = 1.4052 [1]
$4\text{-}CF_3\text{-}C_6F_4PF_2$: b.p. 132 to 134 °C [3]
$C_6F_5PCl_2$: b.p. 118 to 122 °C/18 Torr [1]
$4\text{-}CF_3\text{-}C_6F_4PCl_2$: b.p. 125 to 127 °C/18 Torr, n_D^{20} = 1.4915 [1]
$4\text{-}Cl\text{-}C_6F_4PCl_2$: b.p. 99 to 101 °C, n_D^{20} = 1.4975 [1]

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NMR data (positive sign of the shifts δ in ppm mean lowfield from the external standards 85% H_3PO_4 and C_6F_6) [3]:

Compound	^{31}P NMR		^{19}F NMR				
	δ(P)	J(P-F)	δ(PF_2)	δ(F^2)	δ(F^3)	δ(F^4)	J(F-P)
$C_6F_5PF_2$	193.0	1210 Hz	70.8	26.0	2.7	17.3	1220 Hz
4-CF_3-$C_6F_4PF_2$	189.5	1220 Hz	70.8	25.0	27.7	107.3	1220 Hz

The mass spectrum of $C_6F_5PF_2$ shows a very intense peak at m/e = 69 which is analyzed to be PF_2^+ (90%) and CF_3^+ (10%). The fragmentation of the compound occurs by loss of an F atom, but mainly by loss of PF_3. Both $C_6F_5PBr_2$ and $(C_6F_5)_2PBr$ undergo rearrangement and gave peaks corresponding to $(C_6F_5)_2PBr^+$ and $(C_6F_5)_3P^+$ [4].

Phosphoranes

$C_6F_5PF_4$: boiling point 67 °C (100 Torr), 124 °C/760 Torr [2].

$C_6F_5(C_6F_5O)PF_3$: boiling point 90 to 91 °C/10 Torr, wavelengths of the UV maxima in heptane (molar absorptivity ε) λ_{max} = 218 (log ε = 2.57), 268 nm (log ε = 2.19) [3].

NMR Data

The ^{19}F NMR and ^{31}P NMR data of the phosphoranes are covered in **Table 43**.

Table 43
NMR Data of the Phosphoranes.
^{31}P and ^{19}F NMR chemical shifts δ (in ppm) and spin-spin coupling constants J in Hz (85% H_3PO_4 as external standard, $CFCl_3$ as internal standard, positive shifts lowfield), spectra recorded with neat substances or diluted with toluene, if not otherwise stated.

Compound	δ(P)	δ(F_{ax})[a]	δ(F_{eq})[a]	J(F_{ax}-P)	J(F_{eq}-P)	Ref.
$C_6F_5PF_4$	−51.0	−38.5			958	[2]
	−51.4			d),e)		[3]
4-CF_3-$C_6F_4PF_4$	−52.2			d),e)		[3]
$C_6F_5(C_6F_5O)PF_3$	−57.1			d),e)		[3]
$C_6F_5PF_3Cl$	−27.0	6.0			981	[2]
$C_6F_5PF_2Cl_2$	−14.3	80.0		960		[2]
$C_6F_5PFCl_3$	−37.5	90.2		892		[2]
$C_6F_5PCl_4$[d]	−70.9	—	—	—	—	[2]
$(C_6F_5)_2PF_3$	−30.0	7.0			912	[2]
		6.7	−77.5	844	1011[c]	[5]
$(C_6F_5)_2PF_2Cl$	−25.0	50.2		835		[2]
$(C_6F_5)_2PFCl_2$	−49.0	56.0		794		[2]
$(C_6F_5)_2PCl_3$	−80.0					

[a] ax = axial, eq = equatorial. — [b] Spectrum recorded at −80°C, J(F_{ax}-F_{eq}) = 79 Hz. — [c] Spectrum recorded at −10°C, J(F_{ax}-F_{eq}) = 46 Hz, J(F_{ax}-F_{ortho}) = 15 Hz. — [d] Solvent not provided. — [e] ^{19}F NMR (external standard C_6F_6): For $C_6F_5PF_4$ δ(PF) = 126.5, δ(F^2) = 32.6, δ(F^3) = 4.1, δ(F^4) = 20.0, J(F-P) = 1000, J(P-F) = 990. For 4-CF_3-$C_6F_4PF_4$ δ(PF) = 127.5, δ(F^2) = 38.2, δ(F^3) = 32.2, δ(F^4) = 108.4, J(F-P) = 1000, J(P-F) = 980. For $C_6F_5(C_6F_5O)PF_2$ δ(PF) = 130.0, δ(F^2) = 32.4, δ(F^3) = 8.1, δ(F^4) = 17.7, J(F-P) = 920, J(P-F) = 925.

In the temperature range −150 and +30 °C, $C_6F_5PF_4$ shows a doublet in the ^{19}F NMR spectrum and a quintet in the ^{31}P NMR spectrum. These facts are interpreted by equilibration of fluorine atoms in axial and equatorial positions. In contrast, the ^{19}F NMR doublet of $C_6F_5PF_3Cl$ disappears on cooling the solution from room temperature to 0 °C. At −80 °C the splitting pattern of a trifluorophosphorane with one equatorial and two axial F atoms is observed [2]. This pattern is also found for $(C_6F_5)_2PF_3$ at −10 °C and is assigned to a structure with a trigonal-pyramidal arrangement of the ligands [5]. $C_6F_5PF_2Cl_2$ shows a doublet in the ^{19}F NMR spectrum and a triplet in the ^{31}P NMR spectrum. While the analysis of the NMR data of the fluorophosphoranes definitely gives the evidence for the preference of F atoms for axial positions, additional investigations are necessary to find the positions of the Cl atoms for the chlorophosphoranes. By measurements of the intensity of the ^{35}Cl nuclear quadrupole resonance it is shown that in $C_6F_5PCl_4$ three Cl atoms are in equatorial positions and one is in an axial position. So the C_6F_5 group is axially bonded. This agrees with the result that, in $C_6F_5PF_2Cl_2$ and $(C_6F_5)_2PCl_3$, the Cl atoms are in equatorial positions [2].

In a saturated solution of $(C_6F_5)_3PF_2$ in hexane (toluene) the $^1J(P\text{-}F)$ coupling constants are 702 (697) Hz, the constants $J(F\text{-}F)_{ortho} = 16$ Hz (for both solvents) [6].

IR Data and Crystal Structure

$(C_6F_5)_3PF_2$: The antisymmetric PF_2 valence vibration is found at 765 cm^{-1} in nujol and at 773 cm^{-1} in cyclohexane [6]. The phosphorane crystallizes in the orthorhombic system with a = 8.903(1), b = 11.152(1), c = 11.269(2) Å. There are four molecules per unit cell, density 2.08 g/cm^3. The space group is Pbcn-D_{2h}^{14} (No. 60). Trigonal-pyramidal geometry is observed for the molecule, in which the F atoms occupy the axial positions and the C_6F_5 groups lie in a "propeller-like" arrangement about the equatorial plane. A crystallographic diad axis passes through the P atom and one of the C_6F_5 groups. The two independent benzene rings make dihedral angles of 33.5° and 36.5° with the equatorial plane. The bond lengths (librationally corrected) are r(P-F) = 1.638(2), r(P-C) = 1.823(4) and 1.815 Å [7].

Mass Spectra

In the mass spectra of $(C_6F_5)_2PCl_3$ and $(C_6F_5)_3PCl_2$ no parent ion was observed. The lost of a chlorine molecule gives the highest mass peaks $(C_6F_5)_2PCl^+$ and $(C_6F_5)_3P^+$ [4]. Contrary to this fact the spectra of the phosphoranes $(C_6F_5)_nPF_{5-n}$ (n = 1, 2, 3) show the molecular ion peak and only one (n = 2) was of very low abundance. The breakdown process appears to favor stepwise loss of fluorine atoms. For further details see the original paper [8].

5.2.7.2.3 Chemical Reactions

Phosphines

$C_6F_5PF_2$ reacts in HSO_3F on warming from −60 to −20 °C to give the protonated cation $[C_6F_5PF_2H]^+$, which reacts to $C_6F_5P(O)F_2$ and after addition of H_2O to $C_6F_5P(O)(OH)_2$ [9]. In SbF_5-SO_2 at −80 to −40 °C the difluoride forms compounds of a donor-acceptor type, as shown by NMR spectroscopy. At 20 °C or higher an oxidative fluorination is indicated forming fluorophosphonium ions, which are also observed in the reaction of 4-CF_3-$C_6F_4PF_2$ with SbF_5 at 20 °C [3].

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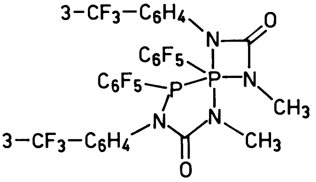
$C_6F_5PCl_2$ in CCl_4 reacts at room temperature with $[Si(CH_3)_3](3\text{-}CF_3C_6H_4)NC(O)NCH_3\text{-}[Si(CH_3)_3]$ to yield the λ^3P-λ^5P-coordinated compound (87%), which is obtained as colorless crystals, melting point 153 °C, ^{1}H NMR [external standard $(CH_3)_4Si$]: $\delta(CH_3) = 3.35$ and 3.52 ppm [J(H-P) = 6.4 Hz], $\delta(C_6H_4) = 7.73$ and 8.07 ppm, [J(H-P) = 16 Hz], ^{31}P NMR (external standard 85% H_3PO_4): $\delta = -8.6$ and -72.6 ppm [J(P-P) = 184.5 Hz, J(P-F) = 87 and 68 Hz]. For IR, mass spectrum and X ray analysis see the original paper [10]. $C_6F_5PCl_2$ reacts with $Li[OCH(CF_3)_2]$ under nitrogen to give $C_6F_5P[OCH(CF_3)_2]_2$ (60 °C, 2 h, 60% yield). The colorless liquid boils at 48 °C/10^{-3} Torr. ^{1}H NMR [internal standard $(CH_3)_4Si$]: $\delta = 4.8$ ppm [J(P-H) = 6.5 Hz, J(CF_3-H) = 6.0 Hz]. ^{19}F NMR (internal standard $CFCl_3$): $\delta(CF_3) = -78.3$ ppm, $\delta(F^2,F^6) = -139$ ppm, $\delta(F^3,F^5) = 167$ ppm, $\delta(F^4) = -153$ ppm. ^{31}P NMR (external standard 85% H_3PO_4): $\delta = 185$ ppm [11].



$(C_6F_5)_2PF$ and Cl_2 (molar ratio 1 : 1) react to yield $(C_6F_5)_2PF_2Cl$ and $(C_6F_5)_2PCl_3$. The difluorochloro compound decomposes forming $(C_6F_5)_2PF_3$ and $(C_6F_5)_2PFCl_2$ [2].

$(C_6F_5)_2PBr$ reacts with NaN_3 at -2 to -10 °C (2 to 36 h) to give $(C_6F_5)_2PN_3$ (see p. 101) [12]. On stirring an ether solution of $C_6F_5PBr_2$ and pyrocatechol for 2 h at room temperature 2-pentafluorophenyl-1,3,2-benzodioxaphosphole forms in 59% yield. The compound boils at 117 to 119 °C/0.1 Torr and melts at 86 °C. ^{1}H NMR [internal standard $(CH_3)_4Si$, solvent CS_2]: $\delta(C_6H_4) = 6.9$ ppm. ^{31}P NMR (internal standard C_6H_6 as solvent): $\delta = 162.0$ ppm [triplet of triplets, J(P-F^2) = 21.0 Hz, J(P-F^3) = 5.6 Hz] [13].

Phosphoranes

$C_6F_5PF_4$ reacts with $(CH_3)_3SiNR_2$ (R = CH_3, C_2H_5) at 60 °C (10 h) yielding $C_6F_5PF_3NR_2$, R = CH_3, 88% yield, boiling point (b.p.) 51 °C/1 Torr, R = C_2H_5, 67% yield, b.p. 65 °C/1 Torr [6]. Heating of $(C_6F_5)_2PF_3$ with $(CH_3)_3SiN(C_2H_5)_2$ at 100 °C (12 h) results in the formation of $(C_6F_5)_2PF_2N(C_2H_5)_2$, 73% yield, melting point 75 °C [2]. The diazadiphosphetidine $[C_6F_5PF_2NCH_3]_2$ is obtained by the reaction of $C_6F_5PF_4$ with $[(CH_3)_3Si]_2NCH_3$ at 90 °C (2 h), 93% yield, melting point 168 °C, for crystal structure see [14]. The analogous reaction of $(C_6F_5)_2PF_3$ (90 °C, 0.5 h, then 130 °C, 4 h) gives the diazaphosphetidine $[(C_6F_5)_2PFNCH_3]_2$, 50% yield, melting point 199 to 201 °C. Heating $C_6F_5PF_4$ and $(CH_3)_3SiSC_2H_5$ at 80 °C (2 h) yields $C_6F_5PF_3SC_2H_5$, 63% yield, b.p. 70 to 72 °C/1.5 Torr. The analogous reaction of $(C_6F_5)_2PF_3$ (140 °C, 25 h) gives $(C_6F_5)_2PF_2SC_2H_5$, yield 90%, b.p. 90 °C/0.05 Torr, melting point 85 to 86 °C [2]. In **Table 44** the NMR data of these substituted fluorophosphoranes are gathered.

$C_6F_5PF_2Cl_2$ is stable at room temperature for several hours. It decomposes on heating to 50 °C forming $C_6F_5PF_3Cl$ and $C_6F_5PFCl_3$. These two compounds are also unstable. $C_6F_5PF_3Cl$ decomposes yielding $C_6F_5PF_4$ and $C_6F_5PF_2Cl_2$, $C_6F_5PFCl_3$ gives $C_6F_5PCl_4$ and $C_6F_5PF_2Cl_2$ [2].

$C_6F_5PF_4$, 4-CF_3-$C_6F_4PF_4$ and $C_6F_5(C_6F_5O)PF_3$ form cations in SbF_5 or SbF_5-SO_2 solutions (see p. 138). The formation of cations is indicated by changes of the electrical conductivity and in the ^{19}F and ^{31}P NMR spectra observed on dissolving the compounds in the solvents. For details see the original paper [3].

Table 44
NMR Data of Substituted Fluorophosphoranes.
^{31}P and ^{19}F NMR chemical shifts δ in ppm, positive sign means downfield from the external standard 85% H_3PO_4 and from the internal standard $CFCl_3$, spin-spin coupling constant J in Hz. ax and eq mean axial and equatorial positions of the F atoms.

Compound	δ(P)	$\delta(F_{ax})$	$\delta(F_{eq})$	$J(F_{ax}\text{-}P)$	$J(F_{ax}\text{-}P)$	$J(F_{ax}\text{-}F_{eq})$	Ref.
$C_6F_5PF_3N(CH_3)_2$	−57.4	−26.1	−61.5	805	966	64	[2]
$C_6F_5PF_3N(C_2H_5)_2$	−57.3	−28.3	−59.0	808	970	63	[2]
$(C_6F_5)_2PF_2N(C_2H_5)_2$	−60.3	−16.0		720			[2]
$[C_6F_5PF_2NCH_3]_2$	−65.5	−54,5		891 [a]			[14]
$[(C_6F_5)_2PFNCH_3]_2$	−80.0	− 6.8		772 [a]			[2]
$C_6F_5PF_3SC_2H_5$	−18.0	+ 3.1	−66.0	909	1046	63	[2]
		+ 3.0, +0.2 [b]		845, 971			
$(C_6F_5)_2PF_2SC_2H_5$	−35.8	+ 1.0		760			[2]
		+ 2.5, −4.1 [c]		695, 808			

[a] In $CDCl_3$, $^1J(F\text{-}P) + {}^3J(F\text{-}P)$. — [b] At −10 °C. — [c] At 0 °C.

References:

[1] G. G. Yakobson, G. G. Furin, T. V. Terent'eva (Zh. Org. Khim. **9** [1973] 1707/13; J. Org. Chem. [USSR] **9** [1973] 1729/34). — [2] M. Fild, R. Kurpat, T. Stankiewicz (Z. Anorg. Allgem. Chem. **439** [1978] 145/52). — [3] G. G. Furin, T. V. Terent'eva, A. I. Rezvukhin, G. G. Yakobson (Zh. Obshch. Khim. **45** [1975] 1473/9; J. Gen. Chem. [USSR] **45** [1979] 1441/6). — [4] J. M. Miller (J. Chem. Soc. **1967** 828/34). — [5] M. Fild, T. Stankiewicz (Z. Anorg. Allgem. Chem. **406** [1974] 115/23).

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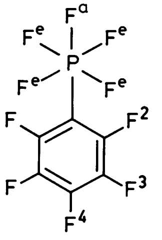
[11] D. Dakternieks, G.-V. Röschenthaler, R. Schmutzler (Z. Naturforsch. **33b** [1978] 507/10). — [12] H. G. Horn, M. Gersemann, U. Niemann (Chemiker-Ztg. **100** [1976] 197/8). — [13] M. Wieber, K. Foroughi, H. Klingl (Chem. Ber. **107** [1974] 639/43). — [14] M. Fild, W. S. Sheldrick, T. Stankiewicz (Z. Anorg. Allgem. Chem. **415** [1975] 43/50).

5.2.7.3 Partially Protonated and Unprotonated Perfluoroorganophosphorus Halide Ions

$[(CF_3)_3PF_3]^-$. On admitting gaseous $(CH_3)_2NH$ to gaseous $(CF_3)_3PF_2$ at room temperature a white solid forms along with $(CF_3)_3PFN(CH_3)_2$. The ^{19}F NMR spectrum of a solution of this solid in acetonitrile shows four multiplets, three of which are centered at −67.0, −90.8 and −99.9 ppm (negative sign means highfield from the external standard $CFCl_3$). The coupling constant J(P-F) is found to be 860 Hz. The spectrum is assigned to the anion $[(CF_3)_3PF_3]^-$ [1], see also Part 3, p. 137.

$[C_6F_5PF_5]^-$. ^{19}F NMR investigations show that the reaction of $C_6F_5PF_4$ with CsF in sulfolane (50°C, 1 h) yields the salt $[Cs]^+[C_6F_5PF_5]^-$. The spectrum taken in acetonitrile (C_6F_6 as internal standard) shows five signals: $\delta(F^e)$ = 119 ppm [doublet of triplets of quartets, $J(P\text{-}F^e)$ = 800 Hz, $J(F^e\text{-}F^2)$ = 20 Hz, $J(F^e\text{-}F^a)$ = 20 Hz], $\delta(F^a)$ = 101.1 ppm [doublet of multiplets, $J(P\text{-}F^a)$ = 710 Hz, $J(F^a\text{-}F^e)$ = 43 Hz], $\delta(F^2)$ = 30.2 ppm [doublet of multiplets, $J(F^2\text{-}F^e)$ = 20 Hz, $J(F^2\text{-}F^3)$ = 13 Hz], $\delta(F^4)$ = 4.4 ppm [triplet, $J(F^4\text{-}F^3)$ = 20 Hz], $\delta(F^3)$ = −1.8 ppm [doublet of doublets, $J(F^3\text{-}F^2)$ = 13 Hz, $J(F^3\text{-}F^4)$ = 20 Hz] [2].



The cations $[C_6F_5PF_3]^+$, $[4\text{-}CF_3\text{-}C_6F_4PF_3]^+$ and $[C_6F_5(C_6F_5O)PF_2]^+$ form in SbF_5 solutions of the parent compounds $C_6F_5PF_4$, $4\text{-}CF_3\text{-}C_6F_4PF_4$ and $C_6F_5(C_6F_5O)PF_3$, respectively. The ions are characterized by their NMR spectra (positive shifts δ in ppm lowfield from the external standards 85% H_3PO_4 and $CFCl_3$) [5]:

	^{31}P		^{19}F				
Ion	δ(P)	J(P-F)	$\delta(PF_2)$	$\delta(F^2)$	$\delta(F^3)$	$\delta(F^4)$	J(P-F)
$[C_6F_5PF_3]^+$	25.9	1240 Hz	105.0	47.8	16.8	52.5	1250 Hz
$[4\text{-}CF_3\text{-}C_6F_4PF_3]^+$	23.5	1260 Hz	101.5	48.8	37.8	107.5	1250 Hz
$[C_6F_5(C_6F_5O)PF_2]^+$	20.9	1210 Hz	102.0	45.0	13.8	49.0	1220 Hz

The cations $(C_6F_5)_2PF_2H^+$ and $(C_6F_5)_2PF_2OH^+$ (as well as $(C_6F_5)_3PH^+$) which are formed in $SbF_5\text{-}HSO_3F$ solutions of $C_6F_5PF_2$ and $C_6F_5P(O)F_2$ (as well as $(C_6F_5)_3P$), respectively, are investigated by NMR spectroscopy, for details see the original paper [4].

References:

[1] K. J. The, R. G. Cavell (Inorg. Chem. **15** [1976] 2518/25). — [2] G. G. Yakobson, G. G. Furin, T. V. Terent'eva (Zh. Org. Khim. **9** [1973] 1707/13; J. Org. Chem. [USSR] **9** [1973] 1729/34). — [3] G. G. Furin, T. V. Terent'eva, A. I. Rezvukhin, G. G. Yakobson (Zh. Obshch. Khim. **45** [1975] 1473/9; J. Gen. Chem. [USSR] **45** [1975] 1441/6). — [4] O. I. Andreevskaya, S. A. Krupoder, G. G. Furin, G. G. Yakobson (Izv. Sibirsk. Otd. Akad. Nauk SSSR Ser. Khim. Nauk **1980** 97/104; C.A. **94** [1981] No. 191447).

5.2.8 Perfluoroalkyl- and Perfluorophenylphosphorus Sulfur Compounds

5.2.8.1 Preparation and Formation

Tris(trifluoromethyl)phosphine sulfide $(CF_3)_3PS$

Bis[bis(trifluoromethyl)phosphoryl]disulfane $(CF_3)_2P(S)SSP(S)(CF_3)_2$

Bis[bis(trifluoromethyl)phosphino]sulfane $(CF_3)_2PSP(CF_3)_2$

[Bis(trifluoromethyl)thiophosphoryl]thio-bis(trifluoromethyl)phosphine $(CF_3)_2P(S)SP(CF_3)_2$

Mercury-bis[bis(trifluoromethyl)dithiophosphinate] $Hg[SP(S)(CF_3)_2]_2$

$(CF_3)_3PS$ (see Part 3, p. 137) forms in the thermal decomposition of $(CF_3)_3P(F)SCH_3$ along with other compounds [1]. The reaction of $(CF_3)_2P(S)SPF_2$ with chlorine for 24 h at room temperature gives a product mixture containing 28 mol% $(CF_3)_2P(S)SSP(S)(CF_3)_2$ (see Part 3, p. 137) [2]. On heating $(CF_3)_2PSeP(CF_3)_2$ with excess of flowers of sulfur for 2 d at 100 °C, $(CF_3)_2PSP(CF_3)_2$ (see Part 3, p. 137) is obtained as the main product. This compound is converted to $(CF_3)_2P(S)SP(CF_3)_2$ on heating for 6 d at 150 °C (see Part 3, p. 137) [5]. $Hg[SP(S)(CF_3)_2]_2$ (see Part 3, p. 138) is obtained in low yield on shaking $(CF_3)_2P(S)SPF_2$ with metallic Hg for several days at room temperature [2].

[Fluoro(trifluoromethyl)thiophosphoryl]thio-bis(trisfluoromethyl)phosphine $F(CF_3)P(S)SP(CF_3)_2$

[Fluoro(trifluoromethyl)thiophosphoryl]thio-difluorophosphine $F(CF_3)P(S)SPF_2$

[Bis(trifluoromethyl)thiophosphoryl]thio-fluoro(trifluoromethyl)phosphine $(CF_3)_2P(S)SP(CF_3)F$

(Difluorothiophosphoryl)thio-fluoro(trifluoromethyl)phosphine $F_2P(S)SP(CF_3)F$

[Fluoro(trifluoromethyl)thiophosphoryl]thio-fluoro(trifluoromethyl)phosphine $F(CF_3)P(S)SP(CF_3)F$

[Bis(trifluoromethyl)thiophosphoryl]thio-difluorophosphine $(CF_3)_2P(S)SPF_2$

(Difluorothiophosphoryl)thio-bis(trifluoromethyl)phosphine $F_2P(S)SP(CF_3)_2$

The preparation of the compounds is performed by reactions in sealed Pyrex tubes at 20 to 25°C [2, 6]. A sample of $F(CF_3)P(S)SH$, contaminated with $F_2P(S)SH$, was reacted with $(CF_3)_2PN(CH_3)_2$. The fractionation of the product mixture yielded $F(CF_3)P(S)SP(CF_3)_2$ along with other products. $F(CF_3)_2P(S)SH$, contaminated with a small amount of $F_2P(S)SH$ and a trace of SiF_4, reacts with $F_2PN(CH_3)_2$ yielding $F(CF_3)P(S)SPF_2$. The reaction of $F(CF_3)PN(CH_3)_2$ and $(CF_3)_2P(S)SH$ gives $(CF_3)_2P(S)SP(CF_3)F$, a volatile liquid, which decomposes slowly at room temperature (yield after purification 42%) [6]. On reacting $F_2P(S)SH$ and $F(CF_3)PN(CH_3)_2$, pure $F_2P(S)SP(CF_3)F$ is formed. $F(CF_3)P(S)SH$ and $F(CF_3)PN(CH_3)_2$ yield an undetermined amount of $F(CF_3)P(S)SP(CF_3)F$ as the major volatile product (identified by its NMR spectrum), a viscous oil of the composition $[(CH_3)_2NH_2][CF_3PS_2]$, and a small amount of $[(CH_3)_2NH_2][F_2PS_2]$ [6]. $F_2P(S)SH$ and $(CF_3)_2PN(CH_3)_2$ give 99% yield of $F_2P(S)SP(CF_3)_2$; $F_2PN(CH_3)_2$ and $(CF_3)_2P(S)SH$ form $(CF_3)_2P(S)SPF_2$ only in low yield [2]. All compounds can be purified by fractional condensation [2, 6].

Trifluoromethylthiophosphonic difluoride $CF_3P(S)F_2$

Fluoro(trifluoromethyl)dithiophosphonic acid $F(CF_3)P(S)SH$

Bis(trifluoromethyl)dithiophosphinic acid $(CF_3)_2P(S)SH$

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Bis(trifluoromethyl)thiophosphinic acid $(CF_3)_2P(S)OH$

Trifluoromethylthiophosphonate Ion $CF_3P(S)O_2^{2-}$

Trifluoromethyldithiophosphonate Ion $CF_3P(S)SO^{2-}$

Bis(trifluoromethyl)thiophosphinic chloride $(CF_3)_2P(S)Cl$

Bis(trifluoromethyl)thiophosphinic iodide $(CF_3)_2P(S)I$

$CF_3P(S)F_2$ is prepared by the reaction of $CF_3PFN(CH_3)_2$ with excess sulfur at 150 °C (3 d) in a sealed tube. The pure compound is obtained by fractional condensation (−196 °C fraction) of the reaction mixture [6]. $F(CF_3)P(S)SH$ (72%) along with $F_2P(S)SH$ (28%) forms on adding a great excess of concentrated H_2SO_4 to $[(CH_3)_2NH_2][F(CF_3)PS_2]$ in vacuo. The mixture was found to be unseparable by fractional distillation [6].

The anions of the thioacids and of the oxothioacids are detected on hydrolyzing the corresponding ester or reacting the esters with $(CH_3)_3N$:

$(CF_3)_2PS_2^-$ is found in the reaction of $(CF_3)_2P(S)SCH_3$, $(CF_3)_2P(S)SC_2H_5$, $(CF_3)P(S)SCH(CH_3)_2$, $(CF_3)_2P(S)C(CH_3)_3$ with excess of $(CH_3)_3N$ in a sealed tube at 24 h [7].

$(CF_3)PSO_2^{2-}$ is detected in the alkaline hydrolysis (10% NaOH, sealed tube, room temperature, 2 d) of $(CF_3)_2P(S)SCH(CH_3)_2$, $(CF_3)_2P(S)SC_2H_5$, $(CF_3)_2P(S)SCH_3$, $(CF_3)_2P(S)OCH(CH_3)_2$, $(CF_3)_2P(S)OC_2H_5$, and $(CF_3)_2P(S)OCH_3$ [7]. Similarly $CF_3PS_2O^{2-}$ forms from $(CF_3)_2P(S)SC(CH_3)_3$ [7].

$(CF_3)_2PSO^-$ is formed on hydrolyzing the esters $(CF_3)_2P(O)SCH_3$, $(CF_3)_2P(O)SC_2H_5$, $(CF_3)_2P(O)SCH(CH_3)_2$, $(CF_3)_2P(S)OCH_3$, $(CF_3)_2P(S)OC_2H_5$, and $(CF_3)_2P(S)OCH(CH_3)_2$ with $(CH_3)_3N$ under the same conditions like above. The ion also results from the alkaline hydrolysis of $(CF_3)_2P(S)OCH(CH_3)_2$ (10% NaOH, sealed tube, room temperature, 2 d) [7].

The thiophosphinic halides $(CF_3)_2P(S)X$ (X = Cl, I) are described in Part 3, p. 140. For new chemical reactions see p. 145.

Pentafluorophenylthiophosphonic halides $C_6F_5P(S)X_2$ (X = F, Cl, Br)

Bis(pentafluorophenyl)thiophosphinic halides $(C_6F_5)_2P(S)X$ (X = F, Cl, Br)

The compounds are covered in Part 3, p. 141. In addition, mass spectral fragmentation processes are investigated and discussed in [8].

5.2.8.2 Physical Properties

$(CF_3)_2PSP(CF_3)_2$

The IR spectra have been recorded for gaseous and solid samples and the Raman spectra for the liquid and solid phases. Detailed assignments have been proposed in terms of a nonlinear P-S-P skeleton. The positions and intensities of the skeletal modes discount the possibility of a linear bridge P-S-P bridge. No evidence is found for the existence of more than one conformer [3]. The results of the vibrational analysis are given in **Table 45**.

Table 45
Vibrational Frequencies[1] and Assignments for $(CF_3)_2PSP(CF_3)_2$ from the Analysis of the IR and Raman Spectrum [3].
w = weak, m = medium, s = strong, sh = shoulder, pol = polarized, dp = depolarized, v = very.

Raman (liquid)	IR (gas)	Assignment	Raman (liquid)	IR (gas)	Assignment
91 m dp 106 w sh		PC_2 twisting + scissoring	547 w 564 w sh 577 m pol	543 mw 557 m 576 mw	CF_3 antisymmetric deformation
			520 m pol?	524 m w sh	PSP symmetric stretching
160 vs pol 244 m dp		PSP bending CF_3 wagging; PC_2 wagging	726 vw 748 vs pol	721 w 750 m 753 m sh	CF_3 symmetric deformation
268 m dp 283 s pol 293 m sh		CF_3 rocking	507 m dp?	509 s	PSP antisymmetric stretching
446 m dp 461 m pol	444 s 462 m	PC_2 stretching + PSP stretching		1 111 s sh 1 131 vs 1 142 vvs 1 173 vvs 1 202 vs	CF_3 stretching

[1] Overtone and combination bands: 341 mw, 825 w, 1 028 w, 1 272 w, 1 289 w.

$F(CF_3)P(S)SH$

^{19}F NMR (internal standard $CFCl_3$): $\delta = -75.0$ ppm [doublet of doublets, J(F-P) = 132 Hz, J(F-F) = 3.1 Hz, CF_3], $\delta = -54.1$ ppm [doublet of quartets, J(F-P) = 1 169 Hz, J(F-F) = 3.1 Hz, F], ^1H NMR [standard $(CH_3)_4Si$]: $\delta = 3.33$ ppm, IR (in cm^{-1}): 2600 (w), 2580 (vw) (ν_{SH}); 1 190 (vs, br) (ν_{CF}); 910 (s), 830 (m, br) (ν_{PF}, δ_{SH}); 765 (m), 725 (s) ($\delta_{sym\ CF_3}$, $\nu_{P=S}$); 570 (s), 535 (m), 415 (m) ($\delta_{antisym\ CF_3}$, $\nu_{P=S}$, ν_{PC}), mass spectrum: $M^+ = 183.9$ [6].

Thiophosphorylthiophosphines

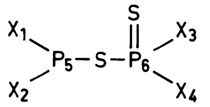
Table 46 covers the NMR spectra. The data show that P^{III} as well as P^V are found in these compounds. The variation of the NMR spectra with temperature shows the different extent of exchange processes in these compounds which have chiral phosphorus centers leading to magnetic nonequivalence in the molecules. For details see the original papers [2, 6].

References p. 145

Table 46

NMR Parameters for the Thiophosphorylthiophosphines.

Numbering scheme



A

A: $(CF_3)_2P(S)SPF_2$
B: $F_2P(S)SP(CF_3)_2$
C: $F(CF_3)P(S)SP(CF_3)_2$
D: $F(CF_3)P(S)SPF_2$
E: $(CF_3)_2P(S)SP(CF_3)F$
F: $F_2P(S)SP(CF_3)_2$
G: $F(CF_3)P(S)P(CF_3)F$

	A [2]	B [2]	C [6]	D [6]	E [6]	F [6]	G[g] [6]	
							65%	35%
Position number of the substituent								
CF_3	1, 2	3, 4	1, 2, 3	3	1, 3, 4	2	1, 3	2, 3
F	3, 4	1, 2	4	1, 2, 4	2	1, 3, 4	2, 4	1, 4
^{19}F and ^{31}P chemical shifts[a][b]								
δ_1	−55.0	−61.2	−54.2	−59.3	−62.0	−167.1	−63.6	−166.4
δ_2			−54.5	−63.7	−164.7	−64.1	−164.8	−63.6
δ_3	−17.9	−71.2	−74.0	−80.1	−68.5	−16.1	−74.1	−74.5
δ_4			−59.2	−56.3	−68.7	−18.0	−59.1	−58.9
δ_5	−107.2	+81.4	−100.5	+76.5	+34.6	+37.2	+38.0	+38
δ_6	−42.1	−80.5	−34.8	−39.0	−67.3	−31.3	−28.6	−30.6
Major coupling constants J								
1−5	78[d]	1331[e]	78.5[d]	1370.0[e]	77.8[d]	1154.0[e]	74[d]	1148[e]
2−5			78.5[d]	1291.0[e]	1161.2[e]	72.6[d]	1156[e]	75[d]
3−6	1223[e]	113[d]	134.5[d]	136.0[d]	112.5[d]	1224.0[e]	134[d]	134[d]
4−6			1173.4[e]	1174.0[e]	112.5[d]	1203.0[e]	1165[e]	1180[e]
5−6	96.5[f]	73[f]	100.0[f]	63.0[f]	92.4[f]	104.7[f]	86[f]	103[f]
Minor coupling constants J								
1−2			9.0	92.5	3.4	4.2	5.0	4.3
1−3			0.0	0.0	0.0	8.8	0	<0.5
1−4			1.2	6.0	0.0	1.3	0	[c]
1−6		18	0.0	9.0	0.0	1.2	0	<0.5
2−3			0.0	0.0	1.4	0.0	1.2	0
2−4			0.0	7.0	0.0	1.3	[c]	0
2−6			0.0	23.0	3.8	0.0	5	0
3−4			0.0	2.6	7.2	82.5	2.8	2.8
3−5	>2[c]	1.8[c]	7.0	0.0	6.0	0.5	5.2	2.8
4−5			10.5	22.0	2.5	16.3	[c]	[c]

[a] ^{19}F chemical shifts (δ_1 to δ_4) are given in ppm relative to $CFCl_3$. Except for compound A, B, and C which were measured directly against $CFCl_3$, all values were measured with respect to CF_2Cl_2 and converted to the $CFCl_3$ scale by the addition of the measured difference between the two scales (5.9 ppm). Negative values indicate resonance to high field of standard. — [b] ^{31}P chemical shifts (δ_5, δ_6) measured in ppm from P_4O_6 at 36.4 MHz. Negative values indicate resonance to high field of standard. The chemical shift of H_3PO_4 is +112 ppm on the P_4O_6 scale. — [c] Not resolved. — [d] $^2J_{PF}$ in Hz. — [e] $^1J_{PH}$ in Hz. — [f] $^2J_{PP}$ in Hz. — [g] Mixture of two racemates.

5.2.8.3 Chemical Reactions

The reactions of the phosphorus-sulfur compounds are covered in **Table 47**. Additional investigations are reported below.

$(CF_3)_2PSP(CF_3)_2$ acts as non-chelating bifunctional ligand towards iron carbonyl compounds. ^{19}F NMR investigations show that only one P atom forms a donor bond with the iron. $(CF_3)_2PSP(CF_3)_2$ reacts with $Fe(CO)_2(NO)_2$ (16 d, 20°C, 51% yield) forming $Fe(CO)(NO)_2$-$[(CF_3)_2PSP(CF_3)_2]$, with $Fe_2(CO)_9$ (19 d, 93% yield) forming $Fe(CO)_4[(CF_3)_2PSP(CF_3)_2]$ and with $[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ (6 d, 20°C, $CFCl_3$ as solvent, 96% yield) forming $Fe(CO)_2(\pi\text{-}C_5H_5)[P(S)(CF_3)_2]$ [4].

Thiophosphorylthiophosphines

The reaction of these mixed-valence compounds with protic species appears to proceed generally with the cleavage of the P-S bond on the trivalent P atom to form phosphines and dithiophosphinic acids or their salts. The reaction with $(CH_3)_2NH$ often yields the ammonium salts of the dithiophosphinic acid [2, 6], see Table 47.

On heating $F_2P(S)SP(CF_3)_2$ at 200°C for 3 d, only 1% of the compound is found to be decomposed. Much less thermally stable is $(CF_3)_2P(S)SPF_2$, which decomposes on heating at 70°C (24 h) and then at 100°C (2 h) forming PF_3, further a mixture of $(CF_3)_2P(S)SP(CF_3)_2$ (38%), $F_2P(S)SP(CF_3)_2$(51%) and $(CF_3)_2P(S)SP(CF_3)_2$ (11%) as well as a white solid residue. For the investigation of the possibility of exchange of trivalent P and pentavalent P fragments with unique substituents, the equilibrium

$$\underset{A}{F_2P(S)SP(CF_3)_2} + \underset{B}{(CF_3)_2P(S)SPF_2} \rightleftharpoons \underset{C}{F_2P(S)SPF_2} + \underset{D}{(CF_3)_2P(S)SP(CF_3)_2}$$

was investigated by ^{19}F NMR spectroscopy. On mixing A and B in $CFCl_3$ at room temperature all four compounds are observed. The equilibrium constant is found to be $K = c_C \cdot c_D/c_A \cdot c_B = 1.6 \pm 0.7$ (40°C), 2.1 ± 0.7 (−80°C). The reaction is exothermic by no more than 500 cal/mol. The reverse reaction by mixing equal proportions of C and D which equilibrated at room temperature gives K = 1.1 at 40°C. This labile equilibration shows no change in the valence of the P atom associated with a particular substituent [2].

Table 47
Reactions of Perfluoroalkylphosphorus Sulfur Compounds.
If not otherwise stated, the reactions are investigated at room temperature.

Compound	Reactant (conditions of reaction)	Main products (yield in %)
$F_2P(S)SP(CF_3)_2$ [2]	10% aqueous NaOH (3 h)	CF_3H
	anhydrous HCl (10 d)	SPF_2SH, $(CF_3)_2PCl$
	anhydrous $(CH_3)_2NH$ (2 d)	$(CF_3)_2PN(CH_3)_2$, $[(CH_3)_2NH_2][F_2PS_2]$
	CH_3SH (about 12 h)	$(CF_3)_2PSCH_3$, SPF_2SH
	Hg (7 d)	$(CF_3)_2PP(CF_3)_2$ (10%), $Hg(S_2PF_2)_2$
	anhydrous CH_3OH (−)	$(CF_3)_2PSH$, $(CF_3)_2POCH_3$, SPF_2SH
	Cl_2 (−)	$(CF_3)_2PCl$ (25%), $(CF_3)_2PCl_3$ (27.5%), $(SPF_2)_2S_2$ (45%), SPF_2Cl (1.5%)

References p. 145

Table 47 (continued)

Compound	Reactant (conditions of reaction)	Main products (yield in %)
$(CF_3)_2P(S)SPF_2$ [2]	10% aqueous NaOH (12 h)	CF_3H
	anhydrous HCl (6 d)	$(CF_3)_2P(S)SH$, PF_2Cl, PF_3
	anhydrous $(CH_3)_2NH$	$PF_2N(CH_3)_2$, PF_3, $[(CH_3)_2NH_2][(CF_3)_2PS_2]$
	CH_3SH (30 min)	$(CF_3)_2P(S)SH$, $(CF_3)_2PSH$, PF_3
	Hg (some days)	$(CF_3)_4P_2S$, $(CF_3)_4P_2$, PF_3, $Hg[S_2P(CF_3)_2]_2$
	anhydrous CH_3OH (6 d)	$(CF_3)_2P(S)SCH_3$, $(CF_3)_2P(S)SH$, PF_3
	Cl_2 (1 d)	$(CF_3)_2P(S)SSP(S)(CF_3)_2$ (28%), $(CF_3)_2P(S)Cl$ (15%), PF_2Cl (52%), SPF_2Cl (4%)
$(CF_3)_2P(S)SP(CF_3)_2$ [2]	anhydrous $(CH_3)_2NH$ (–)	$[H_2N(CH_3)_2][(CF_3)_2PS_2]$, $(CF_3)_2PN(CH_3)_2$
$F(CF_3)P(S)SP(CF_3)_2$ [6]	$(CH_3)NH$	$(CF_3)_2PN(CH_3)_2$
	20% aqueous NaOH	CF_3H
$F(CF_3)P(S)SPF_2$ [6]	$(CH_3)_2NH$	$PF_2N(CH_3)_2$, PF_3
	20% aqueous NaOH	no volatile products
$(CF_3)_2P(S)SP(CF_3)F$ [6]	$(CH_3)_2NH$	$[(CH_3)_2NH_2][(CF_3)_2PS_2]$, $F(CF_3)PN(CH_3)_2$
	20% aqueous NaOH	CF_3H
$F_2P(S)SP(CF_3)F$ [6]	$(CH_3)_2NH$	$[(CH_3)_2NH_2][F_2PS_2]$, $F(CF_3)PN(CH_3)_2$
	20% aqueous NaOH	CF_3H, F
$F(CF_3)P(S)SH$ [6]	$(CF_3)_2PN(CH_3)_2$	$F(CF_3)P(S)SP(CF_3)_2$, $[(CH_3)_2NH_2][F(CF_3)PS_2]$
$F(CF_3)P(S)S^-$ [6] (as dimethyl ammonium salt)	H_2SO_4	$F_2P(S)SH$, $F(CF_3)P(S)SH$
$(CF_3)_2P(S)SH$	CH_3ONa, $(CH_3)_3Cl$ [6] (18 h) [7]	$(CF_3)_2P(S)SC(CH_3)_3$
	$F(CF_3)PN(CH_3)_2$ [6]	$[(CH_3)_2NH_2][(CF_3)_2PS_2]$, $(CF_3)_2P(S)SP(CF_3)F$
	anhydrous CH_3OH (12 h) [2]	$(CF_3)_2P(S)SCH_3$
$(CF_3)_2P(S)SH$ [6]	CH_3ONa, $(CH_3)_3Cl$ (18 h) [7]	$(CF_3)_2P(S)C(CH_3)_3$
	$F(CF_3)PN(CH_3)_2$ [6]	$[(CH_3)_2NH_2][(CF_3)_2PS_2]$, $(CF_3)_2P(S)SP(CF_3)F$
	anhydrous CH_3OH (12 h) [2]	$(CF_3)_2P(S)SCH_3$

References p. 145

Table 47 (continued)

Compound	Reactant (conditions of reaction)	Main products (yield in %)
$(CF_3)_2P(S)Cl$ [7]	CH_3CH_2OH, $(CH_3)_3N$	$(CF_3)_2P(S)OCH_2CH_3$ (80%)
	$(CH_3)_2CHOH$, $(CH_3)_3N$	$(CF_3)_2P(S)OCH(CH_3)_2$ (88%)
	CH_3CH_2SH, $(CH_3)_3N$	$(CF_3)_2P(S)SCH_2CH_3$ (66%), $(CF_3)_2PSCH_2CH_3$
	$(CH_3)_2CHSH$, $(CH_3)_3N$	$(CF_3)P(S)SCH(CH_3)_2$ (76%)
	CH_3OH	$(CF_3)_2P(S)OCH_3$
	$(CH_3)_3COH$, $(CH_3)_3N$	$(CH_3)_3NH(CF_3)_2PSO$, $(CF_3)_2P(S)N(CH_3)_2$
$(CF_3)_2P(S)I$ [5]	$(CF_3)_2PSeP(CF_3)_2$	Se, $(CF_3)_2PI$, $(CF_3)_2PSP(CF_3)_2$
$(CF_3)_2P(S)ONa$ [7]	$(CH_3)_3Cl$ (pentane)	$(CF_3)_2P(S)OC(CH_3)_3$ (66%)
$(CF_3)_2P(S)OH$ [7]	$NaOCH_3$ (pentane) (20 h)	$(CF_3)PSONa$

References:

[1] K. J. The, R. G. Cavell (Inorg. Chem. **15** [1976] 2518/25). — [2] L. F. Doty, R. G. Cavell (Inorg. Chem. **13** [1974] 2722/9). — [3] R. C. Dobbie, M. J. Hopkinson, B. P. Straughan (J. Mol. Struct. **23** [1974] 141/3). — [4] R. C. Dobbie, M. J. Hopkinson (J. Chem. Soc. Dalton Trans. **1974** 1290/3). — [5] R. C. Dobbie, M. J. Hopkinson (J. Fluorine Chem. **3** [1973] 367/74).

[6] R. G. Cavell, L. F. Doty (Inorg. Chem. **17** [1978] 3086/93). — [7] R. G. Cavell, A. A. Pinkerton, W. Sim, A. J. Tomlinson (Inorg. Chem. **18** [1979] 2901/8). — [8] T. R. B. Jones, J. M. Miller, M. Fild (Org. Mass Spectrom. **12** [1977] 317/25).

5.2.9 Perfluoroalkylphosphorus Selenium Compounds

Trifluoromethylselenobis(trifluoromethyl)phosphine $(CF_3)_2PSeCF_3$

Bis[bis(trifluoromethyl)phosphino]selane $(CF_3)_2PSeP(CF_3)_2$

The first compound will be incorporated into the Chapter on Perfluoroorganoselenium Compounds, see Suppl. Vol. 2 and the remark in Part 3, p. 160.

For preparation and chemical reactions of $(CF_3)_2PSeP(CF_3)_2$ see Part 3, p. 160. The IR spectra have been recorded for gaseous and solid samples and Raman spectra for the liquid solid phases. Detailed assignments have been proposed in terms of a nonlinear P-Se-P skeleton. The positions and intensities of the skeletal modes discount the possibility of a linear bridge P-Se-P bridge. No evidence is found for the existence of more than one conformer [1]. The results of the vibrational analysis are given in **Table 48**, p. 146.

Table 48
Vibrational Frequencies[1] (in cm^{-1}) and Assignments for $(CF_3)_2PSeP(CF_3)_2$ from the Analysis of the IR and the Raman Spectrum [1].
w = weak, m = medium, s = strong, sh = shoulder, pol = polarized, dp = depolarized, v = very.

Raman (liquid)	IR (gas)	Assignment	Raman (liquid)	IR (gas)	Assignment
91 m dp		PC_2 twisting + scissoring	553 w dp	545 w sh	CF_3 antisymmetric deformation
118 w sh			563 w dp	556 m	
153 s pol		PSeP bending		724 w	CF_3 symmetric deformation
246 w sh dp		CF_3 wagging; PC_2 wagging	750 s pol	747 s	
260 s pol		CF_3 rocking			
269 m dp					
288 m dp?				1110 s sh	CF_3 stretching
				1127 vs	
424 w dp	422 m	PC_2 stretching + PSeP stretching	1122 vw	1140 vvs	
446 m dp	445 vs			1150 vs sh	
456 m pol	456 m sh			1170 vvs	
				1195 vs	

[1] Overtone and combination bands: 1010 vw, 1026 vw, 1095 w sh, 1278 w, 1290 w.

The compound reacts with $Fe(CO)_2(NO)_2$ (16 d at 20°C) to form $Fe(CO)(NO)_2[(CF_3)_2PSeP(CF_3)_2]$. By ^{19}F NMR spectroscopy, it is shown, that one P atom is coordinated directly to the Fe atom. The reaction with $Fe_2(CO)_9$ gave $Fe_2(CO)_6P_2(CF_3)_4Se$ (black crystals, melting point 139°C) for which spectroscopic investigations indicate a cyclic structure with Fe-Fe- and P-Se-Fe bonding. The reaction with $[\pi\text{-}(C_5H_5)Fe(CO)_2]_2$ (in $CFCl_3$, 6 d, 20°C) gave orange-colored crystals of the composition $(\pi\text{-}C_5H_5)Fe(CO)_2P(Se)(CF_3)_2$ [2], for spectroscopic data of the compounds see the original paper.

Reference:

[1] R. C. Dobbie, M. J. Hopkinson, B. P. Straughan (J. Mol. Struct. **23** [1974] 141/3). — [2] R. C. Dobbie, M. J. Hopkinson (J. Chem. Soc. Dalton Trans. **1974** 1290/3).

5.2.10 Perfluoroalkylphosphorus Boron Compounds

1- and 2-Bis(trifluoromethyl)phosphinopentaborane(9) $1\text{-}(CF_3)_2PB_5H_8$ and $2\text{-}(CF_3)_2PB_5H_8$

On repeating the synthesis of $1\text{-}(CF_3)_2PB_5H_8$ (described in Part 3, p. 161, cited there as preparation of $(CF_3)_2PB_5H_8$), now the 2-isomer has been isolated. The best yield has been obtained using fairly pure LiC_2H_5 and B_5H_9. After standing for 2 h at −50°C (formation of C_2H_6), $(CF_3)_2PCl$ is added at −125°C and is reacted during a 12 h warming period to −78°C. The ether and the excess B_5H_9 were distilled off and the phosphinoboranes were delivered during slow warming, finally to 50°C. The isomers were separated by repeated fractional condensation at −20 to −30°C. The yields are 30% and 15% for the 1- and 2-isomer, respectively (the report of 57% yield of the 1-isomer in Part 3, p. 161, is based on the consumption of LiB_5H_8; when based on consumed $(CF_3)_2PCl$, the original yield is only 36%) [1].

The equilibrium pressures p (in Torr) of the 2-isomer fit the equation $\log p = 6.312 + 1.75 \times \log T - 0.005\,T - 2486/T$ (T in K), yielding the extrapolated boiling point 147°C and the Trouton constant of 21 cal · mol^{-1} · K^{-1}. The ^1H NMR spectrum [standard $(CH_3)_4Si$] shows the chemical shifts $\delta = 1.33$ ppm (quartet, J = 178 Hz, 3-BH, 5-BH units) and $\delta = -3.18$ ppm (spectrum pictured in [1]). ^{11}B NMR (negative values upfield from methylborate): $\delta = -29.6$ ppm (doublet, J = 178 Hz; 3,4,5-BH units), $\delta = -34$ ppm (singlet, since coupling B-P is not resolved), −71.0 ppm (doublet, J = 182 Hz, 1 B) [1]. ^{31}P NMR (negative values upfield from the standard H_3PO_4): $\delta = -36$ ppm (ragged peak); ^{19}F NMR (negative values upfield from $CFCl_3$): $\delta = -48.6$ ppm (doublet, J = 68 Hz) [1].

IR spectrum (in cm^{-1}, relative intensities in parentheses) [1]:

1-$(CF_3)_2PB_5H_8$: 2626 (6.7), 1865 (2.5), 1470 (2.5), 1434 (2.8), 1395? (1.7), 1292? (0.4), 1189 (28), 1153 (40), 1141 (42), 1105 (22), 1060 (0.2), 1033? (0.2), 993? (0.1), 903? (2.3), 883 (2.9), 805 (0.3), 741 (0.6), 678 (2.7), 558 (0.6), 458 (4.5), 435 (1.1).

2-$(CF_3)_2PB_5H_8$: 2627 (14), 2618 (12), 1930? (0.1), 1882 (0.3), 1842 (1.3), 1500? (0.5), 1455 (2.3), 1403 (8), 1319 (0.4), 1288 (0.7), 1190 (48), 1158 (53), 1136 (54), 1109 (25), 1038 (1.6), 976 (0.5), 923 (3.4), 888 (4.6), 847 (1.3), 747 (1.2), 697 (1.0), 670 (3.4), 612 (1.7), 570 (1.4), 545 (0.5), 498? (0.4), 453 (7), 419 (1.4).

Pure 2-$(CF_3)_2PB_5H_8$ remains stable for at least 24 h in a sealed tube at 25°C. In presence of a catalytic trace of hexamethylenetetramine a complete isomerization is observed on standing at 25 h after 36 h [1]. With $Ni(CO)_4$ in a sealed tube at 0°C (1 h) the complex 2-$(CF_3)_2PB_5H_8Ni(CO)_3$ is formed, which is characterized by ^{11}B, ^{31}P and ^{19}F NMR data [1].

Tris[bis(trifluoromethyl)phosphinoborane] $[(CF_3)_2PBH_2]_3$

Boraniumbis(phosphinide) Anion $[(CF_3)_2PBH_2P(CF_3)_2]^-$

Boraniumtris(phosphinide) Anion $[(CF_3)_2PBH_2P(CF_3)_2BH_2P(CF_3)_2]^-$

The synthesis of the phosphinoborane is described in Part 3, p. 161. A more direct procedure is to heat a mixture of diborane and $(CF_3)_2PI$ in a sealed tube at 100°C and to remove the BI_3 by action of water or by brief treatment with $(CH_3)_3N$ at 25°C. However, this method could be hazardous, when one attempts to sublime out the last traces of the desired trimer by heating the residue in vacuo, a very shattering detonation can occur. ^{11}B NMR (in C_6D_6, standard $B(OCH_3)_3$, positive value upfield) $\delta = 60.1$ ppm [triplet (J = 105 Hz, BH_2) of triplets (J = 52 Hz, BP_2)] [2].

Chemical Reactions, Formation and Properties of the Anions

The ring trimer $[(CF_3)_2PBH_2]_3$ is easily cleaved by excess trimethylamine to give nearly equal yields of the sublimable monomer complex $(CH_3)_3N \cdot BH_2P(CF_3)_2$ (melting point 81°C) and the ionic oil $[(CH_3)_3N]_2BH_2^+(CF_3)_2PBH_2P(CF_3)_2^-$. The similar but faster trimethylphosphine reaction yields a more volatile monomer complex (melting point 48°C) and an analogous ionic oil. With deficient base, the ion $(CF_3)_2PBH_2P(CF_3)_2BH_2P(CF_3)_2^-$ persists as major product; less persistent, especially in the amine reaction, is the dimer complex base · BH_2-$P(CF_3)_2$ · $BH_2P(CF_3)_2$. Yet longer chains are obscure but seem to be favored in the phosphine reaction. In all of these ring-cleavage products, any three-bonded P atom easily forms a BH_3 complex of the nonpolar, nonhydridic type, which HCl attacks at a central BH_2 group rather than at an end BH_3 group. **Table 49** gives the boron and fluorine NMR spectra of the anions and their BH_3 complexes; for further details of reaction and for physical data of the base complexes see [2].

Table 49
^{11}B and ^{19}F NMR Spectra of the Phosphinide Anions and Their BH_3 Complexes [2].
Chemical shifts δ are negative upfield from the standards $B(OCH_3)_3$ and $CFCl_3$, respectively.

Compound	^{11}B NMR	^{19}F NMR
$[(CF_3)_2P]_2BH_2^-$	$\delta(BH_2) = -51.4$ (J = 104 Hz)	δ = −52.7 (J = 65 Hz)
$[(CF_3)_2PBH_3]_2BH_2^-$	$\delta(BH_2) = -55.0$, $\delta(BH_3) = -58.7$	δ = −62.8 (J = 58.5 Hz)
$[(CF_3)_2PBH_2]_2P(CF_3)_2^-$	$\delta(BH_2) = -55.0$	δ = −53.5 (J = 64.5 Hz), δ = −60.0[a] (J = 57.0, 11.0 Hz)
$[(CF_3)_2P(BH_3)BH_2]_2P(CF_3)_2^-$	$\delta(BH_2) = -55.4$, $\delta(BH_3) = -59.0$	δ = −59.2[b] (J = 67 Hz), δ = −62.5[c] (J = 59 Hz)

[a] Doublet of triplets, of total intensity half that of the δ = −53.3 doublet. — [b] Doublet for central $P(CF_3)_2$ unit; half-height width 18 Hz. — [c] Doublet for end $(CF_3)_2PBH_3$ units; half-height width 16 Hz.

Trifluoromethyldifluorophosphinetetraborane $CF_3PF_2 \cdot B_4H_8$ Adduct

$CF_3PF_2 \cdot B_4H_8$ has been obtained by the reaction of B_4H_8CO and CF_3PF_2 at 0°C until CO evolution ceased. (For removing CO the reaction tube was several times frozen at −196°C.) The volatile reaction products were purified on a low temperature distillation column. Physical data: Melting point −153 to −149°C; ^{11}B NMR [external standard $BF_3 \cdot O(C_2H_5)_2$]: δ = −58.0 ppm [doublet, J(P-B) = 125 Hz, B_1]; +0.2 ppm (singlet, B_3), −5.6 ppm (singlet, B_2, B_4): ^{31}P NMR (external standard 85% H_3PO_4) at −27°C: δ = 125.1 ppm [triplet of septets, J(P-F) = 1177 Hz, J(P-B) = 125 Hz, J(F-C-P) = 108 Hz, the septet results from the overlapping of two quartets]; ^{19}F NMR (external standard CF_3COOH) at −21°C: δ = −6.3 ppm [doublet, J(P-F) = 1177 Hz, PF_2], 10.2 ppm [doublet, J(F-C-P) = 108 Hz, CF_3].

At −125°C two new doublets have appeared beside the CF_3 resonance. The two new doublets are attributed to the presence of two nonequivalent fluorine atoms, each of which is spin-spin coupled to a phosphorous atom, δ = −24.6 ppm [doublet, J(P-F) = 1170 Hz], 5.1 ppm [doublet, J(P-F) = 1180 Hz]. For the CF_3 resonance at −135°C δ = 8.2 ppm [doublet, J(F-C-P) = 110 Hz] is found. Based on the low temperature spectrum it is concluded that the $CF_3PF_2 \cdot B_4H_8$ molecule exists only in one geometrical isomer (in contrast to other molecules of the type $P_2FX \cdot B_4H_8$, X = OCH_3, SCH_3, CH_3, t-C_4H_9). The low temperature spectrum arises from one rotational isomer at low temperature [3].

References:

[1] A. B. Burg (Inorg. Chem. **12** [1973] 3017/9). — [2] A. B. Burg (Inorg. Chem. **17** [1978] 593/9). — [3] J. D. Odom, A. J. Zozulin (Inorg. Chem. **20** [1981] 3740/5).

5.2.11 Tris(perfluorohalogenoorgano)phosphines. Perfluorophosphapropene. Fluorophosphaethyne

5.2.11.1 Preparation and Formation

1,1,3,3,3-Pentafluoro-2-phospha-1-propene $CF_3P{=}CF_2$

$CF_3P{=}CF_2$ was postulated as an intermediate in the basic hydrolysis of $(CF_3)_2PH$ at room temperature [1], in the reaction of $(CF_3)_2PH$ with ammonia [2], in the conversion of $(CF_3)_2PH$ with dimethylzinc to the ring dimer $(CF_3PCF_2)_2$ [3], and in the reaction of $(CF_3)_2PH$ with trimethylamine [4]. The compound was detected by its ^{31}P and ^{19}F NMR spectrum when gaseous $(CF_3)_2PH$ passes in a vacuum line several times in a U trap, containing KOH pellets [5].

Fluorophosphaethyne $FC{\equiv}P$

The compound was first detected by MW spectroscopy during the flow pyrolysis of CF_3PH_2. In this system it appears to be unstable [6]. The compound is produced in a very high yield by passing CF_3PH_2 slowly at room temperature and low pressure (about 30 μm Hg) over solid KOH pellets [7], see also [8, 9]. The compound obtained in this way seems quite stable (1 h or more) at low pressures (<50 μm Hg) and at room temperature [4].

Tris(trifluoromethyl)phosphine $(CF_3)_3P$

The phosphine (see Part 3, p. 163) forms in the photolysis of a mixture of $(CF_3)_2PH$ and $Cl_2C{=}CF_2$ (240 h, mercury medium pressure lamp) [10], in a low-pressure silent discharge of CF_3PH_2 and of $(CF_3)_2PH$ [45], by ligand exchange between PI_3 and $(CF_3)_2Cd \cdot CH_3CH_2CH_2OCH_3$ (room temperature, 30 min, 20% yield) [11] and in the pyrolysis of $(CF_3)_3PO$ (see p. 94) [12].

Bis(trifluoromethyl)heptafluoro-n-propylphosphine $(CF_3)_2PC_3F_7$

Trifluoromethylbis(heptafluoro-n-propyl)phosphine $CF_3P(C_3F_7)_2$

Tris(heptafluoro-n-propyl)phosphine $(C_3F_7)_3P$

The propyl compounds can be prepared by the reaction of C_3F_7I with the corresponding diphosphine according to:

$$RR'PPR'R + C_3F_7I \rightarrow RR'PC_3F_7 + RR'PI$$
$$(R = R' = CF_3;\ R = CF_3,\ R' = C_3F_7;\ R = R' = C_3F_7)$$

Detailed conditions for these reactions are not given. Photolysis of the mixture accelerates the reaction giving higher yields. For example, $CF_3P(C_3F_7)_2$ is obtained in 93% yield at 16°C within 1 h on irradiation, while the same mixture on heating at 167°C in the dark only gives a yield of 50% [13].

Bis(trifluoromethyl)hexafluoroisopropylphosphine $(CF_3)_2PCF(CF_3)_2$

On heating a mixture of $(CF_3)_3P$ and $C_2F_5SiF_5$ at 0.5 atm for 1 h at 200°C, the reaction of the carbene CF_3CF (formed from $C_2F_5SiF_5$) with the phosphine gives the isopropylphosphine. The compound is obtained in 44% yield after fractional condensation and gas chromatographic separation [14].

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Tris(trifluorovinyl)phosphine $(F_2C{=}CF)_3P$

Bis(trifluorovinyl)pentafluorobutadienylphosphine $(F_2C{=}CF)_2P(FC{=}CFCF{=}CF_2)$

Both compounds are prepared in a yield of 7% [15] and 2.5% [16], respectively, in the reaction of $F_2C{=}CFLi$ (obtained from $F_2C{=}CFBr$ and CH_3Li in situ) with PCl_3 in ether at −78°C followed by gas chromatographic separation [15, 16], for the first compound see also Part 3, p. 163.

Tris(1,1,1-trifluoropropynyl)phosphine $(CF_3C{\equiv}C)_3P$

The compound is formed in 50% yield (as already described according a private communication in Part 3, p. 163) in a two-step process via the preparation of $CF_3C{\equiv}CLi$ followed by the reaction of the lithium compound with PCl_3 in $(C_2H_5)_2O$ [17]. Lower yields are obtained by the reaction of $CF_3C{\equiv}CZnCl$ with PCl_3 in dimethylformamide or pyridine [17].

Trifluoromethyldicyanophosphine $CF_3P(CN)_2$

Bis(trifluoromethyl)cyanophosphine $(CF_3)_2PCN$

The cyanophosphine (see Part 3, p. 164) and the dicyanophosphine are prepared by condensing $(CF_3)_2PI$ and CF_3PI, respectively, on excess $Hg(CN)_2$ in a high vacuum [18]. $CF_3P(CN)_2$ also forms in the reaction of CF_3PHI with $Hg(CN)_2$ at 110 to 120°C in 24 h [19].

Tris(pentafluorophenyl)phosphine $(C_6F_5)_3P$

Pentafluorophenylbis(2-pentafluorophenylethynyl)phosphine $C_6F_5(C_6F_5C{\equiv}C)_2P$

Nonafluorobiphenylylbis(pentafluorophenyl)phosphine $C_{12}F_9(C_6F_5)_2P$

Bis(nonafluorobiphenylyl)pentafluorophenylphosphine $(C_{12}F_9)_2C_6F_5P$

For $(C_6F_5)_3P$ (see Part 3, p. 164) only new chemical reactions (see p. 157) are reported.

$C_6F_5(C_6F_5C{\equiv}C)_2P$ forms on reacting $C_6F_5C{\equiv}CH$ with pentafluorophenylchlorophosphine, yield 50% [44].

The other two compounds form in the reactions of C_6F_5Li (from C_6F_5H and n-C_4H_9Li in hexane/ether at −78°C in 2 h) with $(C_6F_5)_3P$ or $(C_6F_5)_3PO$ at 25°C (6 h, molar ratio 1:1) as well in the reaction of C_6F_5Li (from C_6F_5Br and n-C_4F_9Li in hexane/ether at −78°C in 1 h) with $(C_6H_5)_3P$ [20].

Tris(4-perfluorooxaalkylphenyl)phosphines $[4\text{-}(R_fOR'_fCF_2)\text{-}C_6F_4]_3P$

In the following are given the synthesized compounds, characterized by the groups $R_fOR'_f$-, the yields and the boiling points [21]:

R'_fOR_f-	Yield	b.p. in °C/Torr	R'_fOR_f-	Yield	b.p. in °C/Torr
$CF(CF_3)OC_3F_7$	78%	189/0.01	$CF(CF_3)[OCF_2CF(CF_3)]_4OC_3F_7$	30%	178/0.003
$CF(CF_3)OCF_2CF\text{-}(CF_3)OC_3F_7$	70%	201/0.005	$CF_2(OC_2F_4)_2OC_2F_5$	69%	157/0.005
			$CF_2(OCF_2)_3OCF_3$	59%	157/0.005

These compounds have been synthesized by the reaction of PCl_3 with the corresponding lithium compounds of the 4-perfluoroalkylphenylether. To $4\text{-}BrC_6F_4CF_2R_fOR'_f$ in an anhydrous tetrahydrofuran-diethylether solution at −78 °C a hexane solution of n-butyllithium was added. After 1 h the solution of PCl_3 in diethylether at −78 °C was added. After warming the solution to room temperature (15 h), it is stirred for 15 h, then hydrolyzed with 6 N HCl and the products are separated by distillation. The compounds are viscous liquids at room temperature, have a low volatility, soluble in fluorinated solvents, and are resistant to oxidation, much like $(C_6F_5)_3P$ [21]. They are used as protecting agents in the oxidative high-temperature treatment of perfluoroalkyl-terminated perfluoropolymethylenepolyethylene glycols (contained in vessels of various alloys) [22].

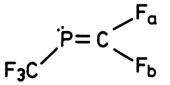
5.2.11.2 Physical Properties

$C_6F_6(C_6F_5C{\equiv}C)_2P$ melts at 127 to 128 °C. The ^{31}P and ^{19}F NMR spectra (standard 85% H_3PO_4 and C_6F_6) show the chemical shifts $\delta(P) = -93.7$ ppm, $\delta(F^2,F^6) = 34.7$ and 27.0 ppm, $\delta(F^3,F^5) = 2.6$ and 1.4 ppm, $\delta(F^4) = 15.4$ and 13.0 ppm [44].

The melting points of the compounds $[4\text{-}(R'_fOR_fCF_2)\text{-}C_6F_4]_3P$ are given in context with the preparation of the compounds.

$CF_3P{=}CF_2$

The ^{31}P spectrum (recorded at −78 °C) consists of an overlapping doublet of doublets of quartets from spin coupling to F^a, F^b, and the CF_3 group.



The chemical shifts [positive shifts are lowfield relative to the standards $P(OCH_3)_3$ and $CFCl_3$] are $\delta(P) = -121.4$, $\delta(F^a) = 3.9$, $\delta(F^b) = -38.7$ ppm, $J(P\text{-}F^a) = 213.6$, $J(P\text{-}F^b) = 82.3$, $J(F^a\text{-}F^b) = 29.3$ Hz [5].

$FC{\equiv}P$

The linear molecule has 16 valence electrons and is expected to have the ground state electron configuration $(6\sigma)^2(7\sigma)^2(8\sigma)^2(2\pi)^4(9\sigma)^2(3\pi)^4$. The photoelectron spectrum shows three bands, see **Table 50**. The first band at 10.75 eV is assigned to the ionization from the 3π orbital, the second band at 13.55 eV to the ionization from the 9σ orbital localized mainly at the phosphorus atom. The third band corresponds to the ionization of the fluorine lone pair electrons (2π). Calculations are performed to minimum energy assuming Koopmans theorem, $r(C\text{-}F) = 1.2995$, $r(C{\equiv}P) = 1.5365$ Å, total energy $E_T = 12988.748$ eV. The calculation indicates that the π orbital has a small amount of C-F antibonding character, whereas the σ orbital is slightly C-F bonding, as expected, though it consists mainly of a phosphorus σ lone pair atomic orbital. The charge distribution indicates a large positive charge on the P atom (+0.48), a small negative charge on the C atom (−0.09), and a large negative charge on the F atom (−0.39) [7].

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Table 50
Experimental and Calculated Ionization Energies E_i of $FC{\equiv}P$ and Vibrations of the $FC{\equiv}P^+$ Ion [7].

Electronic state of the ion	E_i(exp.) (in eV)	E_i(calc.) (in eV)	Vibrational structure (in cm^{-1})
$^2\Pi$	10.57 ± 0.01	10.53	1725 ± 30 [ν(C≡P)] 760 ± 40 [ν(C-F)]
$^2\Sigma^+$	13.55 ± 0.01	13.94	860
$^2\Pi$	17.63 ± 0.03	20.08	–
$^2\Sigma^+$	–	22.31	–

The ^{31}P and the ^{19}F NMR spectrum show the chemical shifts $\delta(^{31}P) = -346.4$ ppm and $\delta(^{19}F) = -96.6$ ppm [negative shifts are highfield from the standards $P(OCH_3)_3$ and $CFCl_3$]; the spin-spin coupling constant is J = 182.0 Hz. In the IR spectrum the C≡P stretching vibration is observed at 1660 cm^{-1} [8]. In the microwave spectrum, transitions belonging to the two isotopic species $^{19}F^{12}C^{31}P$ and $^{19}F^{13}C^{31}P$ have been observed and analyzed. The resulting structural parameters are r(C-F) = 1.285 ± 0.005 and r(C≡P) = 1.541 ± 0.005 Å. For $^{19}F^{12}C^{31}P$ the rotational constants $B_0 = 5257.80$ MHz and $D_J = 1.0 \pm 1.7$ kHz are evaluated. The analysis of the vibrational satellites of the $J = 3 \leftarrow 2$ ground-state transition yields the bending vibration $\nu_2 = 390 \pm 10\ cm^{-1}$ and the antisymmetric stretching vibration $\nu_3 = 790 \pm 60\ cm^{-1}$. From the Stark effect the dipole moment $\mu = 0.279 \pm 0.001$ D was obtained. The comparison with the dipole moment of HC≡P indicates that the F-C bond moment opposes that of the C≡P group [9].

$(CF_3)_3P$

The structure of the phosphine has been reinvestigated (see Part 3, p. 165) by gas-phase electron diffraction and liquid-phase Raman spectroscopy assuming C_{3v} symmetry for the PC_3 skeleton and also for the CF_3 groups. The principal structural parameters are $r_g = 1.904(7)$ Å, r_g(C-F) = 1.340(3) Å, α(C-P-C) = 97.2(0.7)°, α(F-C-F) = 107.5(0.3)°. A striking result is that the P-C bond is 0.058 Å longer than in $(CH_3)_3P$. Trifluoromethyl groups, in or close to staggered conformations, are tilted by 5.3(0.9)°. This indicates that the threefold axes of the CF_3 groups are not collinear with the P-C bonds but lie in planes defined by P, C and F_{axial}, so that a positive value the P-C-F_{axial} angles increases by the amount of the angle of tilt. The angle of twist 5.5(6.0)° for a given CF_3 group implies that the group is twisted about its threefold axis away from the all-staggered conformation. The Raman spectrum of liquid $(CF_3)_3P$ is given in **Table 51** together with the IR gas-phase spectrum (from [24], see Part 3, p. 165). In comparison to [24] a revised assignment of the skeletal PC_3 bending modes was found to be necessary (for distribution to the symmetry of the fundamental vibrations to the symmetry groups see Part 3, p. 165). Shrinkage corrections and amplitudes of vibration, which agree well with the measured vibrational amplitudes, were calculated from a plausible set of valence force constants constructed to reproduce the vibrational frequencies. From the estimated barrier to rotation (2.8 kcal/mol), the torsional frequencies $\nu_{22} = 43$ and $\nu_{11} = 40\ cm^{-1}$ have been calculated. An indirect evidence of these torsional modes τ is given as combination bands (see Table 51) [23].

Table 51
Liquid-phase Raman Spectra [23], Gas-phase IR Spectra [24].
For the numbering of the vibrations ν, see the Part 3, p. 165, I = relative intensities, s, m, w = strong, medium, weak, v = very, br = broad, sh = shoulder, p = polarized, dp = depolarized.

Raman [23] (in cm^{-1})	I	IR [24] (in cm^{-1})	Calculated frequencies (in cm^{-1})	Assignment and symmetry
1234 br	1	1235 vvs	1219	ν_{12} (e)
1215 br, sh	$\leqslant 1$		1213	ν_1 (a_1)
1180 dp	2	1189 vvs	1172	ν_{13} (e)
1158 sh	$\leqslant 1$	1157 vvs	1158	ν_2 (a_1)
1119 dp	3	1129, 1134 vvs	1131	ν_{14} (e)
786 p	6			$\nu_4 + \tau$
747 p	73	757 s	747	ν_4 (a_1)
609 p	<1			$\nu_3 + \tau$
571 p	5	573 m	587	$\nu_3 + \tau$
562 sh	<1	559 s	552	ν_{15} (e)
532 dp	1	535 w	535	ν_{16} (e)
503 dp	<1			$\nu_{20} + \tau$
489 p	2			$\nu_6 + \tau$
465 dp	20	464 vs	481	ν_{20} (e)
451 p	38	455 s	464	ν_6 (a_1)
324 dp	1			$\nu_{18} + \tau$
308 p	8			$\nu_5 + \tau$
286 dp	20	280 vvw	274	ν_{18} (e)
270 p	100	269 vw	274	ν_5 (a_1)
250 dp	9	250 w	259	ν_{19} (e)
190	$\leqslant 1$			$\nu_7 + \tau$
151 p	4		151	ν_7 (a_1)
110 dp	7		110	ν_{21} (e)
			43	ν_{22} (e)
			40	ν_{11} (a_2)

The investigation of the He(I) photoelectron spectrum of $(CF_3)_3P$ gives the following vertical ionization potentials E_i which are assigned to localized molecular orbitals assuming C_{3v} skeletal symmetry [25]:

Assignment	Lone electron pair on phosphorus	P-C bond	F nonbonding orbitals on CF_3 groups		
Symmetry	A_1	E	A_2	E	E
E_i in eV	11.70	13.52	15.63	16.54	17.18

For a correlation between the phosphorus core binding energies and the phosphorus lone-pair ionization energies of trivalent phosphorus compounds, among them $(CF_3)_3P$, see [26].

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NMR spectra (positive shifts downfield from the standards):

^{19}F NMR (external standard CF_3COOH, shifts converted to $CFCl_3$): δ = −50.7 ppm [J(P-F) = 85.7 Hz] [27]; ^{19}F NMR (external standard CF_3COOH): δ = 24.4 ppm [J(F-P) = 83 Hz] [11].

^{31}P NMR (external standard 15% H_3PO_4 in D_2O, converted to 85% H_3PO_4): δ = −2.5 ppm [J(P-F) = 85 Hz] [27]; ^{31}P NMR (external standard P_4O_6, hexane solution): δ = −117 ppm [28].

^{13}C NMR (external standard C_6D_6): δ = −2.16 ppm [J(C-F) = 318 Hz, J(C-P) = 10.7 Hz, J(C-P-C-F) = 5.35 Hz] [27]. ^{13}C {^{19}F} NMR [internal standard $(CH_3)_4Si$, solvent $CDCl_3$, at 31 °C]: δ = 126.4 ppm [J(P-C) = 14 Hz] [29]. ^{13}C NMR [converted to $\delta(CH_3)_3Si$ = $\delta(CDCl_3)$ + 77.06 ppm]: δ = 125.97 ± 0.03 ppm [quartet of doublets of septets, J(C-P) = 11.5 ± 0.7 Hz, J(C-F) = 318.0 ± 0.7 Hz, J(C-P-C-F) = 5 ± 0.7 Hz] [30].

The Faraday effect has been studied between −10 and +10°C to give a mean value of 350 μr. The density is found to be D_4^{-5} = 1.675 g/cm^3, between −20 and +5°C the density is represented by D = 1.646 − 2.4 × 10^{-3} t. The boiling point is 17°C [31].

$(n\text{-}C_3F_7)_3P$

^{31}P NMR: low-field shift δ = 20.6 ppm (standard 85% H_3PO_4) [32].

$(CF_3)_2PCF(CF_3)_2$

IR gas-phase spectrum (in cm^{-1}): 1285 (s), 1255 (sh), 1245 (s), 1172 (s), 1145 (s), 1102 (m), 1085 (sh), 963 (w), 950 (w), 930 (m), 750 (m), 712 (m), 618 (vw), 555 (vw), 535 (w), 480 (vw), 448 (m), 413 (w) [1].

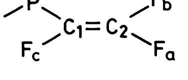
NMR spectra of $(CF_3^a)_2PCF^b(CF_3^c)_2$ (negative shifts δ mean upfield from the standard).

^{31}P NMR [external standard $P(OCH_3)_3$]: δ = −129.1 ppm, coupling constants $J(P\text{-}F_a)$ = 88.8, $J(P\text{-}F_b)$ = 56.0, $J(P\text{-}F_c)$ = 15.8 Hz. ^{19}F NMR (external standard $CFCl_3$): δ = −49.2 (F^a), −187.2 (F^b), −75.0 (F^c) ppm, $J(F^a\text{-}F^c)$ = 6.1, $J(F^a\text{-}F^b)$ = 8.7, $J(F^b\text{-}F^c)$ = 10.1 Hz [14].

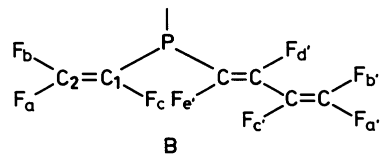
Mass spectrum (fragment, m/e, intensities in parentheses, w: intensity <12%, m: 12 to 50%, s: >50%, referred to the peak m/e = 69): M^+, 338 (w); $C_4F_{12}P^+$, 319 (w); $C_3F_{10}P^+$, 269 (w); $C_3F_9P^+$, 250 (w); $C_3F_8P^+$, 231 (w); $C_3F_6P^+$, 181 (w); $C_2F_6P^+$, $C_3F_7^+$, 169 (w); $C_3F_5P^+$, 162 (w); $C_2F_5P^+$, $C_3F_6^+$, 150 (w); $C_3F_4P^+$, 143 (m); $C_2F_4P^+$, $C_3F_5^+$, 131 (m); CF_4P^+, 119 (m); $C_2F_3P^+$, 112 (m); F_4P^+, 107 (w); CF_3P^+, $C_2F_4^+$, 100 (s); $C_2F_2P^+$, $C_3F_3^+$, 93 (m); CF_2P^+, $C_2F_3^+$, 81 (m); C_2FP^+, 74 (m); F_2P^+, CF_3^+, 69 (100%); CFP^+, $C_2F_2^+$, 62 (m); FP^+, CF_2^+, 50 (m); C_2F^+, CP^+, 43 (w); CF^+, P^+, 31 (s) [14].

$(F_2C{=}CF)_3P$

NMR (positive sign of δ means downfield) according to the designation of the nuclei given below (A):



A



B

^{31}P NMR (standard 85% H_3PO_4): $\delta = -76.9 \pm 0.9$ ppm.

^{19}F NMR (standard $CFCl_3$): $\delta(F_a) = -81.9$ ppm [$J(F_a\text{-}P) = 13.6$ Hz, $J(F_a\text{-}F_c) = 34.6$ Hz, $J(F_a\text{-}F_b) = 43.0$ Hz], $\delta(F_b) = 105.4$ ppm [$J(F_b\text{-}P) = 55$ Hz, $J(F_b\text{-}F_c) = 120.5$ Hz], $\delta(F_c) = 175.0$ ppm [$J(F_c\text{-}P) = 10$ to 13 Hz].

^{13}C NMR [standard $(CH_3)_4Si$]: $\delta(C_1) = 124.6$ ppm [$J(C_1\text{-}F_c) = 292$ Hz, $J(C_1\text{-}F_a) = 8.5$ Hz, $J(C_1\text{-}P) = 49$ Hz], $\delta(C_2) = 160.2$ ppm [$J(C_2\text{-}F_a) = 288.1$ Hz, $J(C_2\text{-}F_b) = 207.6$ Hz, $J(C_2\text{-}F_c) = 40$ Hz, $J(C_2\text{-}P) = 40$ Hz] [15].

IR: 1725 (vs) ($\nu_{C=C}$), 1330 (vs) ($\nu_{C\text{-}F}$), 1180 (vs) ($\nu_{C\text{-}F}$), 1040 (vs) ($\nu_{C\text{-}F}$).

Mass spectrum: 274, M^+ (59.4); 131, $FPC_2F_3^+$ (34.4); 124, $CPC_2F_3^+$ (30.4); 112, $PC_2F_3^+$ (79.2); 105, $PC_3F_2^+$ (52.8); 93, $PC_2F_2^+$ (83.3); 69, PF_2^+, CF_3^+ (100%) [18].

$(F_2C{=}CF)_2(F_2C{=}CF\text{-}CF{=}CF)P$

Colorless oil. ^{31}P NMR (external standard 85% H_3PO_4): $\delta = -71.3$ ppm (multiplet). ^{19}F NMR (external standard $CFCl_3$, designation of the atoms see compound B, above: $\delta(F_a) = -80.4$, $\delta(F'_a) = -92.5$, $\delta(F_b) = -104.9$, $\delta(F'_b) = -104.9$, $\delta(F_c) = -174.3$, $\delta(F'_c) = -148.8$, $\delta(F'_d) = -135.0$, $\delta(F'_e) = -183.9$ ppm. IR (film): 1778 (vs) ($\nu_{C=C}$), 1750 (vs) ($\nu_{C=C}$), 1725 (vs) ($\nu_{C=C}$), 1330 (vs) ($\nu_{C\text{-}F}$), 1180 (vs) ($\nu_{C\text{-}F}$); 1070 (vs) ($\nu_{C\text{-}F}$), 1043 ($\nu_{C\text{-}F}$).

Mass spectrum: m/e = 336, M^+ (21.5); 117, $PC_4F_2^+$ (28.1); 112, $PC_2F_3^+$ (81.1); 93, $PC_2F_2^+$ (4.6); 69, PF_2^+, CF_3^+ (100%) [16].

$(CF_3C{\equiv}C)_3P$

The mass spectrum which is already covered in Part 3, p. 167, according to a private communication, has now been published; for the fragmentation scheme see the original [17].

$CF_3P(CN)_2$ and $(CF_3)_2PCN$

From He(I) photoelectron spectra the following ionization energies (in eV) result:

$CF_3P(CN)_2$	11.81	13.43	13.53	14.05	14.25?	14.48	15.30	15.98	16.62	17.68
$(CF_3)_2PCN$	11.72	13.1	13.59	14.02	15.8	17.48				

For interpretation by an MO model see [18].

5.2.11.3 Chemical Reactions

The chemical properties of the compounds $[4\text{-}(R'_fOR_fCF_2)\text{-}C_6F_4]_3P$ are covered in the section on preparation, see p. 150.

Reaction of $CF_3P{=}CF_2$

Addition of water to the double bond of the phosphaalkene followed by alkali cleavage of the fluorocarbon substituents of the resulting phosphine, gives CF_3H and CF_2H_2 which are identified by NMR spectroscopy [5].

Reactions of $(CF_3)_3P$

On heating $(CF_3)_3P$ to 320°C for 20 h (sealed glass tube, 1 atm), 70% of the phosphine decomposed yielding PF_3, SiF_4, and C_2F_6. On heating for 16 h at 320°C, the phosphine was recovered essentially unchanged (only 2% PF_3 were found) [12].

Oxygen reacts with $(CF_3)_3P$ in a chain reaction involving the trifluoromethyl radical and its autooxidation. Under the conditions of spontaneous ignition (0.5 atm O_2, 25°C) a yellow flame front passes the gas mixture. OCF_2, OPF_3, CF_4, C_2F_6, $(CF_3O)_3PO$, CO_2 and PF_3 are the products. Higher concentrations of $(CF_3O)_3PO$ beside the other products, OCF_2, OPF_3, CF_4, C_2F_6, PF_3, CO_2, and a trace of $CF_3P(O)(OH)_2$, are obtained by warming the reaction mixture in a sealed glass tube from −196°C to room temperature. The presence of toluene inhibits this reaction. Without ignition the oxidation of $(CF_3)_3P$ yields $(CF_3O)_3PO$ as the main product besides OCF_2 and $(CF_3)_2P(O)F$; for details, especially the reaction mechanism, see the original paper [12]. Physical properties of $(CF_3O)_2PO$: boiling point 52°C (extrapolated), melting point −86°C, vapor pressure p (in Torr): $\log p = 7330 - 1445/T$, ^{19}F NMR (standard $CFCl_3$): $\delta = -55.6$ ppm [doublet, J(P-F) = 6 Hz]; IR: (strong absorption bands only are given): 1390, 1380, 1280, 1260, 1250, 1163, 1036, 815 cm^{-1} [12].

$(CF_3)_3P$ reacts with bromine in $CD_2Cl_2/CFCl_3$ solution forming an oxidation equilibrium (equilibrium constant $K = 2\ l^{-1}$ at 260 K) $(CF_3)_3P + Br_2 \rightleftharpoons (CF_3)_3PBr_2$ (see p. 105) which was investigated by ^{19}F, ^{31}P and ^{13}C NMR spectroscopy [29].

With the carbene-precursor $CHF_2CF_2SiF_3$ (giving the carbene CHF_2CF), the phosphine (1:10 molar ratio) reacts at 150°C (5 h) giving unchanged $(CF_3)_3PSiF_4$ (95%), trifluoroethylene (15%), 1,2,2-trifluoroethylidenetris(trifluoromethyl)phosphorane $(CF_3)_3\overset{+}{P}\overset{-}{C}FCHF_2$, a high-boiling unidentified yellow oil and tar. The physical properties of $(CF_3)_3\overset{+}{P}\overset{-}{C}FCHF_2$ are: IR: $\nu_{max} = 1661\ cm^{-1}$; ^1H NMR (external standard benzene): $\delta = -0.46$ ppm; mass spectrum: m/e = 263, $M^+ - CF_4$ (5); 262, $M^+ - CHF_4$ (4); 69, CF_3^+ (100) [33]. With the carbene CF_3CF at 200°C $(CF_3)_2PCF(CF_3)_2$ is formed [14].

No reaction occurs with $HM(CH_3)_3$ (M = Si, Ge, Sn) below 200°C [34]. The reaction of $(CF_3)_3P$ with CF_3NO at room temperature yields $(CF_3)_3P[ON(CF_3)_2]_2$ (see p. 89) [35]. The reaction with $(CF_3)_2NON(CF_3)_2$ gives $(CF_3)_{3-n}P[N(CF_3)_2]_n$ (see p. 101) and $(CF_3)_2NOCF_3$ [43].

In contrast to $(CH_3)_nP(CF_3)_{3-n}$ (n = 1 to 3) the reactions of $(CF_3)_3P$ with the Lewis acids BX_3 (X = H, CH_3, F, Cl, Br) form no donor-acceptor compounds [36]. But this compound acts as a good ligand yielding the transition-metal complexes $M(CO)_5P(CF_3)_3$ and *cis*-$M(CO)_4[P(CF_3)_3]_2$ (M = Cr, Mo, W) [37], see **Table 52**. From this it is concluded that $(CF_3)_3P$ is the weakest donor within the series $(CH_3)_nP(CF_3)_{3-n}$ (n = 0 to 3). On the other hand, the increase of the wave number of the CO stretching bands of the complexes from $(CH_3)_3P$ to $(CF_3)_3P$ shows that $(CF_3)_3P$ has the strongest acceptor strength [38].

Reactions of $(CF_3)_2PCF(CF_3)_2$

The pyrolysis at 420 Torr and 200°C (1 h) in presence of $C_2F_5SiF_3$ yields $(CF_3)_2CFCF(CF_3)_2$, *cis*- and *trans*-$CF_3CF{=}CFCF_3$, $(CF_3)_3P$ and SiF_4. The hydrolysis with 5% aqueous NaOH at 24°C (2 h) forms almost quantitatively CF_3H and $(CF_3)_2CFH$ (molar ratio 2:1) [14].

Reactions of $CF_3P(CN)_2$ and $(CF_3)_2PCN$

$CF_3P(CN)_2$ reacts with CF_3PH_2 at 50°C (14 d) in a sealed tube via the non-isolated compound $CF_3PH(CN)$ to form $(CF_3P)_4$, HCN and $(CF_3PH)_2$ [19].

Table 52
Reactions of $(CF_3)_3P$ with Metal Carbonyls [37].

Compound	Conditions of reaction	Product
$Cr(CO)_6$[a]	25°C (15 h)	$Cr(CO)_5P(CF_3)_3$
$Mo(CO)_6$[a]	25°C (24 h)	$Mo(CO)_5P(CF_3)_3$
$W(CO)_6$[a]	25°C (20 h)	$W(CO)_5P(CF_3)_3$
$Cr(CO)_6$	110 to 180°C (1 to 135 h)	$Cr(CO)_5P(CF_3)_3$, *trans*-$Cr(CO)_4[P(CF_3)_3]_2$
$Mo(CO)_6$	70 to 140°C (72 to 160 h)	$Mo(CO)_5P(CF_3)_3$, *trans*-$Mo(CO)_4[P(CF_3)_3]_2$
$W(CO)_6$	85 to 80°C (2 to 18 h)	$W(CO)_5P(CF_3)_3$
$C_7H_8Cr(CO)_4$[b]	50°C (11 d)	$C_7H_8Cr(CO)_3P(CF_3)_3$, *trans*-$Cr(CO)_4[P(CF_3)_3]_2$
$C_7H_8Mo(CO)_4$[b]	25°C (14 d)	*cis*-$Mo(CO)_4[P(CF_3)_3]_2$
$C_7H_8W(CO)_4$[b]	50°C (15 h)	*cis*-$W(CO)_4[P(CF_3)_3]_2$
$C_7H_8Cr(CO)_3$[c]	60 to 80°C/3 d	$Cr(CO)_5P(CF_3)_9$, *trans*-$Cr(CO)_4[P(CF_3)_2]_2$
$C_7H_8Mo(CO)_3$[c]	5 to 40°C/4 to 1 d	$Mo(CO)_5P(CF_3)_3$, *trans*-$Mo(CO)_4[P(CF_3)_3]_2$

[a] The products are formed by UV irradiation of $M(CO)_6$ in tetrahydrofuran (THF) forming the $M(CO)_5(THF)$ complexes, followed by an exchange reaction with $(CF_3)_3P$. — [b] C_7H_8: norbornadiene. — [c] C_7H_8: cycloheptatriene.

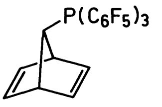
$(CF_3)_2PCN$ reacts with $(CF_3)_2NO$ at −74°C in 16 h to give $[(CF_3)_2NO]_2P(CF_3)_2CN$ (see p. 89) [39]. On standing at 25°C for 28 h, $(CF_3)_2PCN$ reacts with $(CF_3)_2PSiH_3$ forming $(CF_3)_4P_4$, SiH_3CN and $(CF_3)_2PH$ [40].

Reactions of $(C_6F_5)_3P$

In solution (Cl_2CFCF_2Cl as solvent) $(C_6F_5)_3P$ is oxidized by $(CF_3)_2NO$ (sealed ampule at −70°C for one day, shaking at room temperature for 20 min and left standing for another day) to form $(C_6F_5)_3PO$ (see p. 87) and $(CF_3)_2NON(CF_3)_2$ [41].

With C_6F_5Li (from C_6F_5H and n-C_4H_9Li in a solution of hexane and ether at −78°C, 2 h), $(C_6F_5)_3P$ reacts at 25°C (6 h, 1:1 mole equivalents) yielding $C_{6n}F_{4n}H_2$ (n = 2, 3), $C_{6n}F_{4n+1}H$ (n = 1 to 4), $(C_{12}F_9)(C_6F_5)_2P$, and $(C_{12}F_9)_2(C_6F_5)P$. If C_6F_5Li is prepared from C_6F_5Br and C_4F_9Li in hexane/ether at −78°C (1 h) additionally $C_{6n}F_{4n}$ (n = 2, 3), $C_{6n}F_{4n}Br_2$ (n = 1 to 3), $C_{6n}F_{4n+1}Br$ (n = 1 to 4), and $C_{12}F_8HBr$ are found [20].

$(C_6F_5)_3P$ reacts with the 7-norbornadienyl and $AgBF_4$ in liquid SO_2 to yield the substituted norbornadienylphosphonium compound, for ^1H NMR see the original publication [42].



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5.2.12 **Bis(trifluoromethyl)phosphinosilane** $(CF_3)_2PSiH_3$

The compound forms on shaking $(CF_3)_2PI$ and $ISiH_3$ with Hg at 25°C ($ISiH_3$ has been produced in the reaction vessel from $C_6H_5SiH_3$ and HI).

The vapor-pressure equation is represented by $\log p = 7.767 - 1532/T$ (p in Torr, T in K), evaluated from the experimental equilibrium pressures p = 3.0 at −63°C, 44 at −23°C and 144 Torr at 0°C. The ^1H NMR spectrum shows a doublet of septets, centered 3.76 ppm downfield from $(CH_3)_4Si$, coupling constants J(P-H) = 19.5 Hz, J(H-F) = 1.35 Hz, $J(^{29}Si\text{-}H)$ = 229 Hz. The ^{19}F NMR spectrum shows a doublet of quartets at $\delta = -46.7$ ppm (standard $CFCl_3$), J(F-P) = 68.5 Hz, J(F-H) = 1.35 Hz. The ^{31}P NMR spectrum shows a septet of quartets, centered at $\delta = -42.4$ ppm (upfield from H_3PO_4) and confirms the coupling constants 68.5 and 19.5 Hz. IR (in cm^{-1}, relative intensities in parentheses): 2203 (6.3), 1192 (19), 1157 (21), 1118 (21), 930 (2.6), 896 (9), 745 (1.2), 595 (0.3), 417 (2.5).

The reactions of the silane are summarized in **Table 53**. In almost all reactions a cleavage of the P-Si bond occurs.

Table 53
Reactions of $(CF_3)_2PSiH_3$.
Equimolar mixtures, quantities in mmol (in parentheses).

Reactant	Conditions	Products
BF_3 (0.85)	64 h/25°C, 26 h/60°C	$(CF_3PCF_2)_2$ (0.20), BF_3, H_2SiF_2, B_2H_6, $HSiF_3$ (1.37), H_2, $(CF_3)_2PH$, $P_2(CF_3)_4$
BCl_3 (0.75)	20 h/25°C	BF_3 (0.4), SiH_3Cl (0.02), H_2SiCl_2 (0.73), $(CF_3)_2PH$ (0.13), $P_2(CF_3)_4$ (0.125), $(H_2PBF_2)_x$ (empirical formula of the residue)
$B(OCH_3)_3$ (0.15 used of 0.50)	24 h/50°C	SiH_4 (0.2), $(CF_3)_2PH$ (0.24), $(CF_3)_2PCH_3$ (0.26), nonvolatile products
CH_3OBCl_2 (0.45)	rapid/<25°C	$(CF_3)_2PCH_3$ (0.36), SiH_3Cl (0.3), H_2SiCl_2 (0.2), $(CF_3)_2PH$ (<0.05)
$(CH_3)_2PCl$ (0.46)	rapid/<25°C	$(CH_3)_2PP(CF_3)_2$ (0.12), H_2SiCl_2 (0.45), $(CF_3)_2PH$ (0.07), $(CF_3)_4P_2$ (0.02)
$(CF_3)_2PCN$ (0.5)	28 h/25°C	$P_2(CF_3)_4$ (0.22), SiH_3CN (0.34), $(CF_3)_2PH$ (0.17)
PF_3	1 h/105°C	no reaction
PF_5	rapid/<25°C	$(CF_3)_2PH$, $(CF_3)_2PF$, H_2SiF_2
CH_3CN (0.5)	3 h/65°C	$P_2(CF_3)_4$, SiH_4
CH_3NC (0.45)	rapid/<25°C	SiH_4 (0.1), $(CF_3)_2PH$ (0.03), $P_2(CF_3)_4$ (0.06), brown solids
$BrSiF_3$ (0.07 used of 0.5)	16 h/50°C, 24 h/120°C	$BrSiH_3$, $(CF_3)_2PH$, SiF_4 (total 0.13)

Reference:

L. Maya, A. B. Burg (Inorg. Chem. **14** [1975] 698/700).

5.2.13 Perfluoroalkyldiphosphines. Bis(trifluoromethyl)phosphinoarsine

The diphosphines $(CF_3)_2PH_2$ and $CF_3PHPHCF_3$ are covered on p. 82.

Tetrakis(trifluoromethyl)diphosphine $(CF_3)_2PP(CF_3)_2$

1,1-Bis(heptafluoropropyl)-2,2-bis(trifluoromethyl)diphosphine $(C_3F_7)_2PP(CF_3)_2$

1,2-Bis(heptafluoropropyl)-1,2-bis(trifluoromethyl)diphosphine $(C_3F_7)CF_3PPCF_3(C_3F_7)$

Preparation and Formation, Physical Properties

$(CF_3)_2PP(CF_3)_2$ (see Part 3, p. 127) forms by dehydrofluorination of $(CF_3)_2PH$ with $(CH_3)_3N$. The highest yield (46%) is obtained when, in presence of $(CH_3)_3SiCl$, the reaction mixture is stored at −78°C for 18 h, then for many hours at −60 to −70°C, followed by rapid warming with subsequent standing at 0°C for 16 h or at 40°C for 5 min [1]. The diphosphine is also formed by decomposition (25°C, 6 weeks) and by acidolysis (with hydrochloric acid) of $(CF_3)_2PCH_2P(CF_3)P(CF_3)_2$ [1], by the reaction of $(CF_3)_2PSP(CF_3)_2$ with Hg (shaking for 7 d, 10% yield) [2], in a low-pressure silent discharge of CF_3PH_2 [18], and as a by-product during the preparation of $R(CF_3)PP(CF_3)_2$ ($R = CH_3$, CHF_2, CH_2F) from $R(CF_3)PH$ and $(CF_3)_2PCl$ in the presence of $(CH_3)_3N$ [3]. ^{19}F NMR: $\delta = -47$ ppm (standard $CFCl_3$), J(P-F) = 84.9 Hz [4], see also [3, 5]. The IR spectrum is given in [4], for assignment see Part 3, p. 177. The ^{31}P NMR chemical shift is $\delta = -127$ ppm (upfield from P_4O_6 as external standard) [6]. Faraday effect $|P|_M = 697$ μr at 20°C [6]. Density $D_4^{20} = 1.665_9$ g/cm³ [7].

$(C_3F_7)_2PP(CF_3)_2$ (yield 48%, boiling point 40 to 42°C) and $(C_3F_7)CF_3PPCF_3(C_3F_7)_2$ (yield 66%, 95 to 100°C/12 Torr) form on reacting the corresponding iodophosphines with antimony at 150 to 200°C [8].

Chemical Reactions

All three diphosphines are cleaved in the reaction with C_3F_7I yielding the mixed tris-substituted phosphines according:

$$R_1R_2PPR_2R_1 + C_3F_7I \rightarrow R_1R_2PC_3F_7 + R_1R_2PI \quad (R_1, R_2 = CF_3, C_3F_7)$$

The reactivity decreases in the order $(CF_3)_4P_2 > (C_3F_7)_2(CF_3)_2P_2 > (C_3F_7)_4P_2$, the activation energy (first order) is 17, 26, and 40 kcal/mol, respectively. Visible light accelerates the reaction [8].

$(CF_3)_2PP(CF_3)_2$ reacts with selenium at 100°C (4 d) almost quantitatively forming $(CF_3)_2PSeP(CF_3)_2$ [9]. About the vapor-phase oxidation of the diphosphine by NO yielding $(CF_3)_2POP(O)(CF_3)_2$ and $[(CF_3)_2PO]_2O$ [4] see Chapter 5.2.3. The diphosphine reacts with trimethylstannane and a number of metal carbonyls under cleavage of the P-P bond. These reactions are surveyed in **Table 54**, for ^{19}F NMR and IR data see the original papers. The reaction with $(CH_3)_2CHOH$ (room temperature for 4 d, then 70°C for 7 h) gives $(CF_3)_2POCH(CH_3)_2$ and, among the volatile products, $(CF_3)_2PH$ [16]. In the presence of $R(CF_3)PP(CF_3)_2$ ($R = CH_3$, CHF_2, CH_2F) the diphosphine is cleaved by HCl at 65°C giving $(CF_3)_2PH$ and $(CF_3)_2PCl$ (if the phosphine is pure, it resists toward HCl even at 300°C) [1].

Bis(trifluoromethyl)phosphinoarsine $(CF_3)_2PAsH_2$

The compounds forms in yields between 30 and 60% by reacting $(CH_3)_3SnAsH_2$ and $(CF_3)_2PI$ at −78°C for 24 h [solvent $(CH_3)_4Si$, sealed and evacuated tube]. It is purified by fractional

Table 54
Reactions of $(CF_3)_2PP(CF_3)_2$ with $HSn(CH_3)_3$ and with Metal Carbonyls.

Compound	Conditions	Products (yield in %)
$HSn(CH_3)_3$ [10]	20°C/1 h	$Sn(CH_3)_3P(CF_3)_2$ (quantitatively)
$HMn(CO)_5$ [11, 12]	20°C/1 h [11] 35°C/2.5 min [12]	$Mn(CO)_5P(CF_3)_2$ (85%) yellow oil
$Re_2(CO)_{10}$ [13]	120/150/175/190°C 115/25/20/32 h	$Re_2(CO)_8[P(CF_3)_2]_2$ (64%)
$Re(CO)_5Cl$ [14]	70°C/82 h	$Re_2(CO)_8P(CF_3)_2Cl$ (65%)
$Re(CO)_5Br$ [14]	70°C/85 h	$Re_2(CO)_8P(CF_3)_2Br$ (70%)
$Re(CO)_5I$ [14]	90°C/40 h	$Re_2(CO)_8P(CF_3)_2I$ (75%)
$Mn(CO)_5Cl$ [14]	70°C/40 h	$Mn_2(CO)_8P(CF_3)_2Cl$ (89%)
$Mn(CO)_5Br$ [14]	60°C/40 h	$Mn_2(CO)_8P(CF_3)_2Br$ (82%)
$Mn(CO)_5I$ [14]	60°C/104 h	$Mn_2(CO)_8P(CF_3)_2I$ (73%)
$HRe(CO)_5$ [12]	35°C/2.5 min	$Re(CO)_5P(CF_3)_2$ (82%)
cis-$HMn(CO)_4P(CH_3)_3$ [12]	35°C/2.5 min	$(CF_3)_2PMn(CO)_4P(CH_3)_3$ (74%)
cis-$HMn(CO)_4As(CH_3)_3$ [12]	35°C/2.5 min	$(CF_3)_2PMn(CO)_4As(CH_3)_3$ (70%)
$MnCo(CO)_9$ [17]	90°C/20 h	$MnCo(CO)_7[P(CF_3)_3]_2$ (90%)

condensation and is found in the −63°C-trap. The pure compound decomposes at room temperature within several minutes. A 10% solution of the arsinophosphine in toluene is at −40°C stable enough to allow the investigation of reactions without noticeable decomposition of the compound. At temperatures above −40°C a slow decomposition starts [15] according

$$n\ (CF_3)_2AsH_2 \rightarrow n\ (CF_3)_2PH + (AsH)_n$$

yielding dark brown solids. ^1H NMR [external standard $(CH_3)_4Si$]: $\delta = 2.42$ ppm [doublet (J_{PH} = 10 Hz) of septets (F-H coupling not resolvable)], ^{19}F NMR (external standard $CFCl_3$): $\delta = -50.4$ ppm [doublet (J_{PF} = 65.0 Hz) of triplets (J_{HF} = 0.5 Hz)], ^{31}P NMR (external standard 85% H_3PO_4): $\delta = -16.0$ ppm [septet (J_{PF} = 65 Hz) of triplets (J_{PH} = 9.9 Hz)].

The reactions with polar and nonpolar reagents which proceed by cleavage of the P-As bond are described in **Table 55** [15].

Table 55
Cleavage Reactions of $(CF_3)_2PAsH_2$ [15].
Equimolar reaction mixtures if not otherwise stated, solvent: toluene.

Compound	Conditions	Main products
HBr (small excess)	−78°C/4 h	$(CF_3)_2PH$, AsH_3, $(CF_3)_2PBr$
$(CH_3)_2AsH$	–	$(CF_3)_2PH$, $(CH_3)_2AsH$
$(CH_3)_3SiH$	−40°C	$(CF_3)_2PH$
$(CH_3)_4As_2$	–	$(CF_3)_2PAs(CH_3)_2$, $(CF_3)_2PH$, $(CH_3)_2AsH$
$(CH_3)_2PN(CH_3)_2$ (small excess)	20°C/5 min	$(CF_3)_2PN(CH_3)_2$, $(CF_3)_2PP(CH_3)_2$, $(CH_3)_2NH$
Br_2	20°C	$(CF_3)_2PBr$, $(CF_3)_2PH$, $(CF_3)_2PBr_3$

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5.3 Perfluorohalogenoorgano Compounds of Arsenic

5.3.1 Homocyclic and Heterocyclic Perfluoroorgano Compounds of Arsenic

Tetrakis(trifluoromethyl)cyclotetraarsine $(CF_3As)_4$

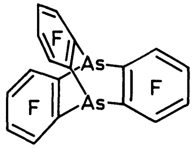
Pentakis(trifluoromethyl)cyclopentaarsine $(CF_3As)_5$

A mixture of $(CF_3As)_n$ ($n = 4$, 5) is formed along with CF_3AsH_2 by decomposition of $CF_3AsHAsHCF_3$ in the liquid phase at room temperature, and along with CF_3AsH_2 and $CF_3AsHAsHCF_3$ in the reaction of CF_3AsI_2 with Hg and anhydrous HI (in less than stoichiometric quantity) [1]. A mixture of the cycloarsines reacts with $(CF_3)_3SnH$ at room temperature (19 d) forming $(CH_3)_3SnAsHCF_3$ (95%) and $[(CH_3)_3Sn]_2AsCF_3$ [2].

Tetrakis(pentafluorophenyl)cyclotetraarsine $(C_6F_5As)_4$

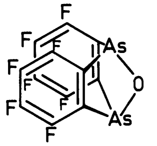
The tetraarsine (see Part 3, p. 187) reacts with $Pt(PC_6H_5)_3$ in benzene (reflux, 4 h) to yield the platinum compound $Pt[P(C_6H_5)_3]_2[As(C_6F_5)]_2$ [3]. With $Fe(CO)_5$ (in benzene, 120°C/15 h or UV irridiation at 60°C/4 h), $Fe(CO)_4(AsC_6F_5)_2$ is formed [4].

Dodecafluoro-13,14-diarsatriptycene



The compound is obtained in 13% yield from elemental arsine and 1,2-diiodotetrafluorobenzene when the reactants are heated at 300°C (3 d) in an evacuated bomb. The colorless compound is purified by vacuum sublimation [5]. The triptycene is formed in 70% yield by the reaction of 1,2-dilithiumtetrafluorobenzene and $AsCl_3$ at −78°C in tetrahydrofuran. Upon completion of the reaction the mixture was allowed to warm to room temperature. The obtained white solid was recrystallized from hexane [7]. Another way to prepare the triptycene is the reaction of arsenic powder with dodecafluorotribenzo[b,e,h][1.4.7]-trimercuronin [6]. $(C_6F_4)_3As_2$ melts at 210 to 211°C [5] or 200°C [7]. The ^{19}F NMR spectrum (AA'XX', negative shifts upfield from the internal standard $CFCl_3$) shows two signals, at −122.8 [6] (corrected value of [5]) or −122.4 [7] (F^3,F^6) and at −152.6 [6] or −153.0 ppm [7] (F^4,F^4). The parent ion in the mass spectrum occurs at m/e = 594. Strong peaks were observed for the ions $AsC_{18}F_{10}^+$, $C_{18}F_{12}^+$, $As(C_6F_4)_2^+$, $C_{12}F_8^+$, $C_{12}F_6^+$, $AsC_6F_4^+$, and AsF_2^+. Principal IR peaks (nujol mull) were 1296 (m), 1260 (m), 1101 (s), 1026 (s), 830 (m), 771 (m), 730 (m), and 389 (m) cm^{-1} [6].

Octafluoro-5,10-epoxy-5,10-dihydroarsanthrene



The compound is obtained by heating partially oxidized arsenic powder and 1,2-diiodotetrafluorobenzene at 250°C for 18 h in a sealed evacuated tube, followed by extraction with 60 to 80° petroleum ether and fractional crystallization. The colorless compound is soluble in all common organic solvents but is insoluble in water. The mass spectrum shows the parent ion at m/e = 462; further significant ions are $C_{12}F_8^+$, $C_{12}F_6^+$, $AsC_6F_4^+$, AsF_2^+, AsO^+. A peak in the IR spectrum at about 950 cm^{-1} is assigned to the ortho-linked C_6F_4 groups. An X-ray study of single crystals shows that the molecule has a butterfly conformation. The compound forms monoclinic crystals, space group $P2_1/2$ (standard setting $P2_1/c$)-C_{2h}^5 (No. 14) with a = 26.660(5), b = 19.220(5), c = 4.990(5) Å, β = 90.3(1)°, Z = 8, D = 2.04 g/cm^3. The unit cell contains two types of crystallographically nonequivalent molecules. The average of the eight measured As-C bond lengths is 1.97 ± 0.002 Å, and the average of the four As-O bonds is 1.81 ± 0.01 Å. As-As intramolecular distances are 2.973(3) and 2.979(3) Å. Bond angles involving As are close to 90° [8].

References:

[1] R. C. Dobbie, P. D. Gosling (J. Chem. Soc. Chem. Commun. **1975** 585/6). — [2] S. Ansari, J. Grobe (Z. Naturforsch. **30b** [1975] 531/4). — [3] P. S. Elmes, M. L. Scudder, B. O. West (J. Organometal. Chem. **122** [1976] 281/8). — [4] P. S. Elmes, P. Leverrett, B. O. West (Chem. Commun. **1971** 747/8). — [5] C. M. Woodard, G. Hughes, A. G. Massey (J. Organometal. Chem. **112** [1976] 9/19).

[6] T. K. Mistry, A. G. Massey (J. Organometal. Chem. **209** [1981] 45/7). — [7] W. R. Cullen, A. W. Wu (J. Fluorine Chem. **8** [1976] 183/7). — [8] D. S . Brown, A. G. Massey, T. K. Mistry (J. Fluorine Chem. **16** [1980] 483/7).

5.3.2 Perfluoroalkylarsines

Trifluoromethylarsine CF_3AsH_2

Bis(trifluoromethyl)arsine $(CF_3)_2AsH$

The synthesis of the two arsines by reaction of CF_3AsI_2 or $(CF_3)_2AsI$, respectively, with Hg and anhydrous HI is described in Part 3, p. 191. It is useful for the preparation of small quantities (1 to 2 mmol). On a larger scale (10 mmol), the arsines are prepared in almost quantitative yield at room temperature in few minutes by the reaction of CF_3AsI_2 or $(CF_3)_2AsI$

with $(CH_3)_3SnH$. The $(CH_3)_3SnI$ also formed in the reaction can be returned to the process after reduction with $LiAlH_4$. Thus the net reaction is the conversion of the iodine compounds into the hydrogen compounds by $LiAlH_4$. The direct reaction with $LiAlH_4$ gives only small yields since $LiAlH_4$ also attacks the CF_3 groups [1]. CF_3AsH_2 is formed by decomposition of $CF_3AsHAsHCF_3$ at room temperature, in the reaction of CF_3AsI_2 with Hg and anhydrous HI (in less than stoichiometric quantity) [2], and by decomposition of $(CF_3)_2AsAsH_2$ above −78°C [3].

In the following reactions $(CF_3)_2AsH$ is formed:

$(CF_3)_2AsTeCH_3$ + HBr or HI at 20°C;
$(CF_3)_2AsSn(CH_3)_3$ + CH_3SH or CH_3SeH at 0°C (24 h);
$(CF_3)_2AsAs(CF_3)_2$ + $(CH_3)_3MH$ (M = Sn, Ge) at 20°C;
$(CF_3)_2AsXCF_3$ (X = S, Se) + $(CH_3)_3GeH$ at 80°C;
$(CF_3)_2AsXCF_3$ + $(CH_3)_3SnH$, for X = S at −20°C, for X = Se at −10°C; in both cases the formation of $(CF_3)_2AsH$ is quantitative [8].

In benzene, $(CF_3)_2AsMn(CO)_5$ reacts with HI at 25°C (600 h) to form $(CF_3)_2AsH$ [9].

Chemical Reactions

CF_3AsH_2 reacts with $(CF_3As)_n$ (n = 4 and 5) to form $(CF_3AsH)_2$ [2]. The reaction with compounds of the types $[(CH_3)_3M]_3P$ and $(CH_3)_3MPH_2$ (M = Si, Ge, Sn) at room temperature forms $(CH_3)_3MAs(CF_3)_2$, $(CH_3)_3MAsHCF_3$, and $[(CH_3)_3M]_2AsCF_3$, see **Table 56**. Within these reaction systems two trends concerning the reactivity are observed [4]:

a) Si < Ge < Sn and b) $(CH_3)_3MPH_2 < [(CH_3)_3M]_2PH < [(CH_3)_3M]_3P$

CF_3AsH_2 can be used to replace the $(CF_3)_2P$ group in compounds of the type $(CH_3)_3MP(CF_3)_2$ [4]:

$(CH_3)_3MP(CF_3)_2 + CF_3AsH_2 \rightarrow (CH_3)_3MAsHCF_3 + (CF_3)_2PH$
$(CH_3)_2MP(CF_3)_2 + (CH_3)_3MAsHCF_3 \rightarrow [(CH_3)_3M]_2AsCF_3 + (CF_3)_2PH$

Table 56
Reactions of CF_3AsH_2 with $[(CH_3)_3M]_3P$ and $(CH_3)_3MPH_2$ [4].

Compound	Molar ratio of phosphine to arsine	Reaction time in weeks	Product	Yield in %
Me_3SiPH_2	2:2.5	6	$Me_3SiAsHCF_3$	40
			$(Me_3Si)_2AsCF_3$	25
$(Me_3Si)_3P$	2:8.5	3	$Me_3SiAsHCF_3$	50
			$(Me_3Si)_2AsCF_3$	35
Me_3GePH_2	4:7.2	8	$Me_3GeAsHCF_3$	80
			$(Me_3Ge)_2AsCF_3$	20
Me_3SnPH_2	2:6.0	3	$Me_3SnAsHCF_3$	70
			$(Me_3Sn)_2AsCF_3$	20
$(Me_3Sn)_3P$	2:10.0	3	$Me_3SnAsHCF_3$	60
			$(Me_3Sn)_2AsCF_3$	30

Similarly, the CF_3P group and the $(CH_3)_3Sn$ group can be replaced as follows [4]:

$(CH_3)_3GePHCF_3 + CF_3AsH_2 \rightarrow (CH_3)_3GeAsHCF_3 + CF_3PH_2$
$[(CH_3)_3Sn]_2AsCF_3 + CF_3AsH_2 \rightarrow 2(CH_3)_3SnAsHCF_3$

The mixture of $(CF_3)_2AsH$ and $(CH_3)_3SnAs(CF_3)_2$ formed from $(CF_3)_4As_2$ and $(CH_3)_3SnH$ at 20°C (1 h) reacts with excess $(CH_3)_3SnH$ on standing for four weeks at room temperature to yield CF_3AsH_2, $(CH_3)_3SnAsHCF_3$, $[(CH_3)_3Sn]_2AsCF_3$, $(CH_3)_3SnAs(CF_3)_2$, and CF_3H [5].

$(CF_3)_2AsH$ reacts with $Co_2(CO)_8$ in pentane at 100°C in two days [6] according:

$Co_2(CO)_8 + (CF_3)_2AsH \rightarrow HCo(CO)_4 + (CF_3)_2AsCo(CO)_4$
$HCo(CO)_4 + (CF_3)_2AsH \rightarrow (CF_3)_2AsCo(CO)_4 + H_2$

The reaction with $MnCo(CO)_9$ starts above 80°C producing $Mn(CO)_5As(CF_3)_2$ and $[Co(CO)_2As(CF_3)_2]_n$. On raising the temperature to 100°C, $MnCo(CO)_7[As(CF_3)_2]_2$ is formed [7].

References:

[1] S. Ansari, J. Grobe (Z. Naturforsch. **30b** [1975] 651/2). – [2] R. C. Dobbie, P. O. Gosling (J. Chem. Soc. Chem. Commun. **1975** 585/6). – [3] A. Breckner, J. Grobe (Z. Anorg. Allgem. Chem. **414** [1975] 269/76). – [4] S. Ansari, J. Grobe (Z. Naturforsch. **30b** [1975] 523/30). – [5] S. Ansari, J. Grobe (Z. Naturforsch. **30b** [1975] 531/4).

[6] G. Beysel, J. Grobe, W. Mohr (Z. Anorg. Allgem. Chem. **418** [1975] 121/31). – [7] G. Beysel, J. Grobe, W. Mohr (J. Organometal. Chem. **170** [1979] 319/36). – [8] P. Dehnert, J. Grobe, D. LeVan (Z. Naturforsch. **36b** [1981] 48/54). – [9] J. Grobe, R. Rau (J. Organometal. Chem. **157** [1978] 281/97).

5.3.3 Perfluoroorganoarsenic Oxygen Compounds

Tris[bis(trifluoromethyl)aminooxy]arsine $As[ON(CF_3)_2]_3$

Bis[bis(trifluoromethyl)aminooxy]trifluoromethylarsine $CF_3As[ON(CF_3)_2]_2$

Bis(trifluoromethyl)aminooxy-bis(trifluoromethyl)arsine $(CF_3)_2AsON(CF_3)_2$

$As[ON(CF_3)_2]_3$ was prepared in about 75% yield by the reaction of $Hg[ON(CF_3)_2]_2$ with $AsCl_3$ in $ClCF_2CFCl_2$ at room temperature in two days (sealed ampule, occasional shaking). The compound is a colorless crystalline solid, which melts at 29.5°C. The yield of the arsine resulting from the reaction of $(CF_3)_2NO$ with $(CF_3)_3As$ or As or from the interaction of $Hg[ON(CF_3)_2]_2$ with As is usually low [1]. For the other two compounds no new preparation is given (see Part 3, p. 197).

All three compounds remained unchanged on heating for two days at 120°C. They are sensitive to moisture. They react at 100°C (1 d) in a sealed tube with anhydrous HCl, whereby the As-O bond is cleaved [1]:

$$[(CF_3)_2NO]_nAs(CF_3)_{3-n} + nHCl \rightarrow (CF_3)_{3-n}AsCl_n + n(CF_3)_2NOH \qquad (n = 1, 2, 3)$$

Hydrolysis of the mono- and disubstituted compounds gives fluoroform. $[(CF_3)_2NO]_3As$ reacts with $(CH_3)_3SiH$ at 80°C (7 d) to form small amounts of $(CF_3)_2NOH$; the reaction with methanol gives $[(CF_3)_2NO]_2AsOCH_3$ and $(CF_3)_2NOH$ [1].

Tetrakis(pentafluoroethyl)arsinous anhydride $(C_2F_5)_2AsOAs(C_2F_5)_2$

The ^{19}F NMR of the compound (see Part 3, p. 197) shows two signals, $\delta(CF_3) = -4.83$ ppm and $\delta(CF_2) = -40.30$ ppm, highfield from CF_3COOH as external standard [2].

Bis[bis(trifluoromethyl)aminooxy]-tris(pentafluorophenyl)arsine $[(CF_3)_2NO]_2As(C_6F_5)_3$

The compound is formed by the reaction of $(CF_3)_2NO$ and $(C_6F_5)_3As$ in a sealed ampule containing Cl_2CFCF_2Cl as solvent at room temperature within seven days. The arsenic derivative, when freshly prepared, is a nonvolatile, colorless, highly viscous liquid, which is stable in air. Upon standing in air over a period of half an hour it slowly converts to a white paste. The IR spectrum shows strong absorptions at 1640, 1515, 1380, 1285, 1085, and 966 cm^{-1}, which are characteristic of the C_6F_5 groups, further bands at 1310, 1255, and 1205 cm^{-1} (C-F stretching vibrations of the CF_3 groups) and at 1030 and 980 cm^{-1} (N-O and C-N stretching, respectively) [2].

References:

[1] H. G. Ang, Y. C. Syn (J. Fluorine Chem. **8** [1976] 481/96). — [2] H. G. Ang, W. S. Lien (J. Fluorine Chem. **9** [1979] 73/80). — [3] Yu. L. Kopaevich, Z. A. Stumbrevichute, L. A. Fedorov, L. S. German (Zh. Obshch. Khim. **43** [1973] 1140/7; J. Gen. Chem. [USSR] **43** [1973] 1132/7).

5.3.4 Perfluoroalkylarsenic Nitrogen Compounds

Bis(trifluoromethyl)aminobis(trifluoromethyl)arsine $(CF_3)_2AsN(CF_3)_2$

Bis[bis(trifluoromethyl)amino]trifluoromethylarsine $CF_3As[N(CF_3)_2]_2$

The reaction of $(CF_3)_2NON(CF_3)_2$ with $(CF_3)_3As$ in 1:1 molar ratio in a sealed evacuated ampule gives on heating at 98°C (60 h, then trapped at −89°C) $(CF_3)_2AsN(CF_3)_2$ in a yield of 82.5%, based on $(CF_3)_2NON(CF_3)_2$ consumed. Similarly, in a molar ratio of 2:1, the reaction at 70°C (42 h, then trapped at −60°C) yields $CF_3As[N(CF_3)_2]_2$ (89.5%). On heating $CF_3As[N(CF_3)_2]$ with $(CF_3)_2NON(CF_3)_2$ at 100°C for 72 h only $(CF_3)_2NOCF_3$, and no $[(CF_3)_2N]_3As$ is formed. It is also a by-product in the other two reactions.

Reference:

H. G. Ang, W. S. Lien (J. Fluorine Chem. **11** [1978] 419/32).

5.3.5 Perfluorohalogenoorganohalogenoarsines

5.3.5.1 Preparation and Physical Properties

Trifluoromethyldihalogenoarsines CF_3AsX_2 (X = F, Cl, Br, I)

Bis(trifluoromethyl)halogenoarsines $(CF_3)_2AsX$ (X = F, Cl, Br, I)

Trifluoromethyliodoarsine CF_3AsHI

CF_3AsF_2 is obtained by the reaction of CF_3AsI_2 with AgF [1]. CF_3AsHI is formed from $CF_3AsHAsHCF_3$ and HI [2]. New methods of preparation for some of the other compounds (see Part 3, p. 203) are given in the following. The reaction of $CF_3As[ON(CF_3)_2]_2$ or $(CF_3)_2AsON(CF_3)_2$ with hydrogen chloride at 100°C (1 d, then trapped at −60°C) gives CF_3AsCl_2 and $(CF_3)_2AsCl$, respectively [3]. CF_3AsBr_2 is obtained from CF_3AsI_2 and $HgBr_2$ [1], $(CF_3)_2AsBr$ from $(CF_3)_2AsI$ and $HgBr_2$ [4].

Molecules and Vibrational Spectra

CF_3AsX_2 (X = F, Cl, Br, I)

Assuming a symmetrically staggered conformation with respect to the AsX_2 groups, the molecules belong to the C_s point group. The 15 fundamental modes comprise nine vibrations of the species A′ and six vibrations of the species A″. The fundamental modes obtained from the analysis of the IR spectra of the gases (and partially of the liquids) and of the Raman spectra of the liquids are given in **Table 57**. A normal coordinate analysis was performed to support the assignment and to limit the force constants (see **Table 58**). An extensive discussion of the assignment and of the potential energy distribution is given in the original paper [1].

Table 57

Fundamental Vibrations of the Molecules CF_3AsX_2 from the Analysis of the Vibrational Spectra and Approximate Assignment to Vibrations [1].

*) Values from liquid-phase spectra. ν, δ, ϱ, τ: valence, deformation, rocking, torsion vibration; s, as: symmetric, antisymmetric.

ν_i in cm^{-1}	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7
X = F	1207	1146	532	737	246*)	343	714
X = Cl	1197	1135	534	734	254*)	316	417*)
X = Br	1185	1126	528	733	238*)	312	295*)
X = I	1174	1117	530*)	729*)	270*)	302*)	207*)
species	A′	A′	A′	A′	A′	A′	A′
assignment	$\nu_{as}(CF_3)$	$\nu_s(CF_3)$	$\delta_{as}(CF_3)$	$\delta_s(CF_3)$	$\varrho(CF_3)$	ν(AsC)	ν(AsX)

ν_i in cm^{-1}	ν_8	ν_9	ν_{10}	ν_{11}	ν_{12}	ν_{13}	ν_{14}	ν_{15}
X = F	286*)	—	—	523	273*)	698	175*)	—
X = Cl	167*)	136*)	1145	527	—	412	117*)	—
X = Br	99*)	124*)	1141	526*)	243	305	—	—
X = I	76*)	107*)	1139	526*)	279*)	213*)	—	—
species	A′	A′	A″	A″	A″	A″	A″	A″
assignment	δ(XAsX)	δ(CAsX)	$\nu_{as}(CF_3)$	$\delta_{as}(CF_3)$	$\varrho(CF_3)$	ν(AsX)	δ(CAsX)	τ

Table 58

Internal Force Constants of CF_3AsX_2 (X = F, Cl, Br, I).

Values in 10^2 N/m. a) Normalized to r^2_{AsX}. b) Normalized to $r_{AsX} \cdot r_{AsC}$.

	f_{CF}	$f_{CF/CF'}$	f_{CAs}	f_{AsX}	$f_{AsX/AsX'}$	$f^{a)}_{XAsX}$	$f^{b)}_{CAsX}$
CF_3AsF_2	6.03	0.88	2.42	4.47	0.23	0.33	0.32
CF_3AsCl_2	5.88	0.88	2.20	2.40	0.16	0.23	0.24
CF_3AsBr_2	5.79	0.84	2.13	1.77	0.09	0.19	0.23
CF_3AsI_2	5.71	0.83	1.97	1.45	0.07	0.15	0.22

$(CF_3)_2AsX$ (X = F, Cl, Br, I)

The molecules belong to the C_s point group on the assumption of a symmetric orientation of the CF_3 groups. The fundamental modes of vibration comprise 13 vibration of the species A′ and 11 of the species A″, see **Table 59**. The vibrational spectra are given in **Table 60**. A normal coordinate analysis was performed to support the assignment and to limit the force constants, see Table 61. For details see the original paper [4].

Table 59
Fundamental Vibrations of ν_i (i = 1 to 24) $(CF_3)_2AsX$ (X = F, Cl, Br, I) [4].
ν, δ, ϱ, τ mean valence, deformation, rocking and torsion vibration, A′ and A″ are symmetry classes.

A′	A″	Assignment	A′	A″	Assignment
ν_1, ν_2	ν_{14}, ν_{15}	$\nu_{as}(CF_3)$	ν_9	ν_{22}	$\nu(AsC_2)$
ν_3	ν_{16}	$\nu_s(CF_3)$	ν_{10}		$\delta(AsC_2)$
ν_4	ν_{17}	$\delta_s(CF_3)$	ν_{11}		$\nu(AsX)$
ν_5, ν_6	ν_{18}, ν_{19}	$\delta_{as}(CF_3)$	ν_{12}	ν_{23}	$\delta(CAsX)$
ν_7, ν_8	ν_{20}, ν_{21}	$\varrho(CF_3)$	ν_{13}	ν_{24}	τ

Table 60
IR Spectra (Gas Phase) and Raman Spectra (Liquid Phase) of $(CF_3)_2AsX$ (X = F, Cl, Br, I).
For overtone and combination bands see the original paper [4].

$(CF_3)_2AsF$		$(CF_3)_2AsCl$		Assignment
IR	Raman	IR	Raman	
293	290 w(p)		103 w(dp?)	ν_{12}
216 w	219 w(dp)		120 vw	ν_{23}
	149 w	232 w	230 m	ν_{10}
253 w	250 vs(p)	248 w	249 vs(p)	ν_7, ν_{20}
325 s	321 m(dp)	337 s	334 m(dp)	ν_{22}
347 s	343 m(p)	348 s	347 m(p)	ν_9
693 s	679 m(p)	428 m	424 vw	ν_{11}
535 w	535 w(dp?)	523 w	528 vw	ν_5, ν_{18}
		530 m		
736 s	734 s(p)	737 s	736 s(p)	ν_4, ν_{17}
1137 vs	1120 vw	1110 vs	1100 vw(dp)	ν_{16}
1158 vs		1152 vs		ν_3
1186 vs	1195 vw	1179 vs	1162 vw	ν_{14}
1233 vs		1219 vs	1210 vw	ν_1

$(CF_3)_2AsBr$		$(CF_3)_2AsI$		Assignment
IR	Raman	IR	Raman	
	94 w(dp?)		86 m(p)	ν_{12}
	124 w(p)		118 vw(dp?)	ν_{23}
225 w	222 w	256 w	254 w(p)	ν_{10}
243 w	243 vs(p)	243 w	242 w	ν_7, ν_{20}

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Table 60 (continued)

$(CF_3)_2AsBr$ IR	Raman	$(CF_3)_2AsI$ IR	Raman	Assignment
260 m	260 m(dp)	305 m	301 m	
312 ms	312 m(dp)	311 s	310 w(dp?)	ν_{22}
333 s	333 m(p)	332 s	330 w(p)	ν_9
325 s	324 m(p)	216 w	215 vs(p)	ν_{11}
521 w	522 vw	523 vw	530 vw(dp?)	ν_5, ν_{18}
533 m	533 vw	534 w		
734 s	732 s(p)	734 s	730 s(p)	ν_4, ν_{17}
1104 vs	1095 vw	1104 vs	1094 vw(dp)	ν_{16}
1137 vs	1139 vw	1135 vs	1136 vw	ν_3
1160 vs		1159 vs		ν_{14}
1203 vs	1195 vw	1197 vs		ν_1

Table 61
Internal Force Constants of $(CF_3)_2AsX$ (X = F, Cl, Br, I).
Values in 10^2 N/m^2. [a] Normalized to $r_{AsX} \cdot r_{AsC}$ [4].

Molecule	f(CF)	f(CF/CF′)	f(CAs)	f(CAs/CAs′)	f(AsX)	f(CAsX)[a]
$(CF_3)_2AsF$	6.22	0.86	2.34	0.46	4.27	0.29
$(CF_3)_2AsCl$	6.11	0.80	2.32	0.43	2.45	0.16
$(CF_3)_2AsBr$	5.95	0.80	2.25	0.45	1.85	0.15
$(CF_3)_2AsI$	5.90	0.79	2.23	0.43	1.65	0.14

Molecule	$f(\delta_s(CF_3))$	$f(\delta_{as}(CF_3))$	$f(\varrho(CF_3))$
$(CF_3)_2AsF$	1.70	1.54	0.80
$(CF_3)_2AsCl$	1.69	1.53	0.77
$(CF_3)_2AsBr$	1.70	1.55	0.77
$(CF_3)_2AsI$	1.72	1.56	0.77

Bis(pentafluoroethyl)halogenoarsines $(C_2F_5)_2AsX$ (X = F, Cl, Br, I)

Pentafluoroethyltrifluoromethyliodoarsine $C_2F_5(CF_3)AsI$

For the last compound no preparation is given. For photolysis of the iodide see p. 172. The preparation of the other compounds, $(C_2F_5)_2AsX$, is described in Part 3, p. 204.

The ^{75}As, ^{79}Br, and ^{81}Br nuclear quadrupole resonance spectra of $(C_2F_5)_2AsF$ and of $(C_2F_5)_2AsBr$ at 77 K showed following frequencies [5]:

	$(C_2F_5)_2AsF$	$(C_2F_5)_2AsBr$
Nucleus ^{75}As	148.77 MHz	170.06 MHz
Nucleus ^{81}Br		200.12 MHz
Nucleus ^{79}Br		239.55 MHz

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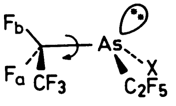
The ^{75}As frequencies are substantially higher than those for symmetrically substituted As compounds as $(C_2F_5)_3As$ (see p. 174). This shows a remarkable distortion of the trigonal pyramid around the trivalent As atom. Also, the ^{81}Br signal is at higher frequencies than that of $AsBr_3$. Evidently, a rearrangement of the electron system of the molecule during the unsymmetric substitution leads to an increase in the covalent nature of the As-Br bond [5].

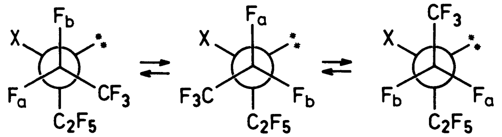
The chemical shifts δ (in ppm) in the ^{19}F NMR spectra (negative shifts mean highfield from the external standard CF_3COOH) are given in the following [6]:

	$(C_2F_5)_2AsF$	$(C_2F_5)_2AsCl$	$(C_2F_5)_2AsBr$	$(C_2F_5)_2AsI$
$\delta(CF_3)$	−5.58	−4.16	−3.47	−2.76
$\delta(CF_2)$	−42.47	−36.32	−32.0, −34.5	−24.7, −31.2
$\delta(AsF)$	−150.47			

The chemical shifts and the multiplicities of the CF_2 signals depend considerably on X. When X = Br or I the spectrum consists of an AB quartet with the parameters $\Delta\delta_{AB}$ = 6.5 ppm for X = I and 2.5 ppm for X = Br. The spin-spin coupling constant J(F-F) is found to be 283 Hz (I) and 287 Hz (Br). In the other compounds there are only weak signs of a fine structure of the CF_2 signals. In the bromine and iodine compounds, the F nuclei of the CF_2 groups are diastereotopic. The cause of this lies in the different configurational environment of the F_a and F_b nuclei on averaging over the three rotational isomers A, B, and C under condition of rapid rotation around the As-C bond (structure I) [6].



I



I_a I_b I_c

Bis(1-chlorotetrafluoroethyl)halogenoarsines $(CF_3CFCl)_2AsX$, X = F, Cl, Br, I

$(CF_3CFCl)_2AsCl$ is formed in 14% yield as a by-product when $(CF_3CFCl)_2AsF$ (58% yield) is prepared by reaction of AsF_3 with $F_2C{=}CFCl$ in presence of SbF_5 at 20°C (6 h) [7], see also Part 3, p. 204. The compounds $(CF_3CFCl)_2AsX$ are formed by nucleophilic replacement reactions of the fluoride according to [6]:

$$(CF_3CFCl)_2AsF \xrightarrow{X^-} (CF_3CFCl)_2AsX$$

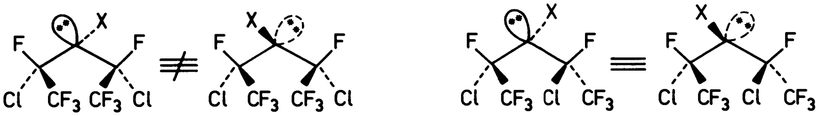
References p. 173

Physical properties:

$(CF_3CFCl)_2AsF$: Boiling point 117°C. Mass spectrum: m/e = 344, 366, 368, M^+ (0.25); 229, 231, $CF_3CFClAsF^+$; 135, 137, $C_2F_4Cl^+$; 116, 118, $C_2F_3Cl^+$ (100) [7].

$(CF_3CFCl)_2AsCl$: Boiling point 142°C. Mass spectrum: m/e = 380, 382, 384, 386, M^+ (0.15); 245, 247, 249, $CF_3CFClAsCl^+$; 135, 137, $C_2F_4Cl^+$ (31.3); 129, 131, $AsFCl^+$ (100); 116, 118, $C_2F_3Cl^+$ (67.8) [7].

The compounds $(CF_3CFCl)_2AsX$ have two chiral and one prochiral centers. As a result, they may exist as three diastereoisomeric forms, the symmetric forms A and B and the unsymmetrical form C, see below [6].



A B C

In the isomers A and B both CFCl groups, as well as both CF_3 groups are enantiotopic. In form C, both CFCl and both CF_3 groups are diastereotopic. This is shown by the investigation of ^{19}F NMR spectra. The resulting four signals of the CFCl groups as well as the CF_3 signal for the three compounds with X = F, Cl, I are given below (δ in ppm, external standard CF_3COOH) [6]:

X	$\delta(CF_3)$	δ(CFCl) forms A and B	form C
F*)	0.3	−58.83, −63.6	−60.7, −62.3
Cl	1.6	−52.55, −56.3	−54.2, −55.2
I	3.0	−44.0, −49.0	−45.4, −46.9

*) δ(AsF) = 108.78

Bis(heptafluoropropyl)iodoarsine $(C_3F_7)_2AsI$

Heptafluoropropyltrifluoromethyliodoarsine $(C_3F_7)(CF_3)AsI$

No preparation is given in the literature. For chemical reactions see p. 172.

Tris(pentafluorophenyl)dichloroarsorane $(C_6F_5)_3AsCl_2$

Tris(pentafluorophenyl)chloronitratoarsorane $(C_6F_5)_3AsCl(NO_3)$

Tris(pentafluorophenyl)chloroperchloratoarsorane $(C_6F_5)_3AsCl(ClO_4)$

Dropwise addition of a solution of Cl_2 in CCl_4 to a solution of $(C_6F_5)_3As$ in chloroform and stirring for 5 h at room temperature produces $(C_6F_5)_3AsCl_2$ (yield 92%). The compound can also be obtained, in 80% yield, by adding diethyl ether to a mixture of $(C_6F_5)_3As$ and $TlCl_3$ and stirring at room temperature for 12 h under nitrogen. The nitrato and perchlorato compounds are formed by addition of the corresponding silver salts ($AgNO_3$ or $AgClO_4$ in benzene) to $(C_6F_5)AsCl_2$ in benzene. The yield is about 50 to 60% [8].

References p. 173

Physical Properties [8].

$(C_6F_5)_3AsCl_2$: Melting point 190°C. Conductivity (in $\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$, 5×10^4M acetone solutions) $\Lambda = 1.64$.

$(C_6F_5)_3AsCl\ (NO_3)$: melting point 205°C; $\Lambda = 5.12$; IR: ν(As-Cl) = 300 (s), $\nu_{as}(NO_2)$ = 1450 to 1500 (vs), $\nu_s(NO_2)$ = 1260 (s), $\delta(NO_3)$ = 800 cm^{-1} (s).

$(C_6F_5)_3AsCl\ (ClO_4)$: melting point 225°C; $\Lambda = 160.08$; IR: ν (As-Cl) = 300 (s), ClO_4 vibrations ν_1 = 1150 (vs), ν_3 = 625 (m), ν_5 = 635 cm^{-1} (m).

5.3.5.2 Chemical Reactions

$(CF_3)_2AsF_2$ reacts in benzene with $(CH_3)_3SiNR_2$ (R = CH_3, C_2H_5, n-C_3H_7) at 80°C (30 h, sealed ampule) forming $(CF_3)_2AsNR_2$ and $(CH_3)_3SiF$ [9]. The reaction of $(CF_3)_2AsCl_2$ with $Re_2(CO)_{10}$ at 130°C (18 h) or at 185°C (10 h) yields $Re_2(CO)_8[As(CF_3)_2]_2$, $Re_2(CO)_8As(CF_3)_2Cl$ and an unidentified polynuclear complex [10]. Heating of $(CF_3CFCl)_2AsF$ with a 50% solution of $(C_2H_5)_3N$ in methanol gives only CF_3CFClH in quantitative yield [7].

Reactions of Perfluoroalkyliodoarsines

The photolysis of the iodides $(CF_3)_2AsI$, $C_2F_5(CF_3)AsI$, $C_3F_7(CF_3)AsI$, $(C_2F_5)_2AsI$, and $(C_3F_7)_2AsI$ was investigated in view of the iodine photodissociation laser. The absorption band near 290 nm (for all compounds) is responsible for the laser action of the iodine atoms according to the transition $5^2P_{1/2}$-$5^2P_{3/2}$. Above a certain pumping energy the compounds decompose thermally, for details see [11, 12]. Kinetic investigations of the quenching of the excited I atoms ($5^2P_{1/2}$) according

$$I + (CF_3)_2AsI \xrightarrow{k_1} (CF_3)_2As + I_2$$
$$I + (CF_3)_2AsI \xrightarrow{k_2} (CF_3)_2AsI + I$$

gave $k_2 = 1.7 \times 10^{-13} cm^3 \cdot molecule \cdot s^{-1}$ and $k_1 \ll k_2$ [13]. The recombination of $I(^2P_{3/2})$ atoms in presence of $(CF_3)_2AsI$ has been investigated by [14].

The iodides CF_3AsI_2 and $(CF_3)_2AsI$ are excellent starting compounds for the synthesis of CF_3AsH_2 and $(CF_3)_2AsH$, respectively. The reaction, especially with $(CH_3)_3SnH$ [15] is described on p. 163. The reaction of CF_3AsI_2 with Hg and HI gives $CF_3AsHAsHCF_3$ (p. 176), CF_3AsH_2 (p. 163) and $(CF_3As)_n$, n = 4, 5 (p. 162). $(CF_3)_2AsI$ reacts with $(CH_3)_3SnAsH_2$ at −78°C in toluene forming $(CF_3)_2AsAsH_2$ [16] (p. 176) and with F_3SiPH_2 at room temperature in 5d forming $(CF_3)_2AsPH_2$ (p. 177) and SiF_3I [17].

The reaction of $(CF_3)_2AsI$ with $CoMn(CO)_9$ proceeds at 0°C (24 h, sealed ampule, with or without pentane as solvent) according to [18]:

$$CoMn(CO)_9 + (CF_3)_2AsI \rightarrow Mn(CO)_5I + (CF_3)_2AsCo(CO)_4$$

The latter compound decomposes according [18]:

$$n(CF_3)_2AsCo(CO)_4 \rightarrow [Co(CO)_3As(CF_3)_2]_n + nCO$$

On raising the temperature to 110°C $Mn_2(CO)_8As(CF_3)_2$, $(CF_3)_2AsI$, and $As_2(CF_3)_4$ are formed. Heating for several days at 100°C produces the heteronuclear compound $MnCo(CO)_7[As(CF_3)_2]_2$ [19]. Heating of $(CF_3)_2AsI$ with $Re_2(CO)_{10}$ at 120°C to 170°C for 27 to 57 h in a sealed ampule results in the formation of a mixture of $Re_2(CO)_8As(CF_3)_2I$, $Re_2(CO)_8[As(CF_3)_2]_2$, $Re(CO)_5I$ and an unidentified polynuclear complex [10].

Reactions of $(C_6F_5)_3AsCl_2$

Refluxing (5 h) a solution of $(C_6F_5)_3AsCl_2$ and CH_3COOAg in acetone containing a few drops of anhydrous acetic acid gives $(C_6F_5)_3AsClOCOCH_3$. Stirring of $(C_6F_5)_3AsCl_2$ in methanol or in ethanol at room temperature for 12 h results in the formation of $(C_6F_6)_3AsClOR$ ($R = CH_3$, C_2H_5). With phenol, using acetone as solvent, $(C_6F_5)_3AsClOC_6H_5$ is obtained. The physical properties of the compounds are given in **Table 62** [8].

Table 62
Physical Properties of the Products of Reactions of $(C_6F_5)_3AsCl_2$ [8].

Compound	Melting point in °C	Conductivity[a] in $\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$	IR in cm^{-1}
$(C_6F_6)_3AsClOCOCH_3$	210	5.74	$\nu(As\text{-}Cl) = 300$, $\nu_{as}(OCO) = 2635$ (s), $\nu_s(OCO) = 1290$ (s)
$(C_6F_5)_3AsClOCH_3$	215	2.81	$\nu(As\text{-}Cl) = 300$, $\nu(C\text{-}H) = 2920$ (m)
$(C_6H_5)_3AsClOC_2H_5$	210	2.52	
$(C_6F_5)_3AsClOC_6H_5$	220	0.54	$\nu(As\text{-}Cl) = 300$

[a] Measured in 5×10^{-4} M solution, solvent acetone.

$(C_6F_5)_3AsCl_2$ oxidizes $ClAuP(C_6H_5)_3$ to $Cl_3AuP(C_6H_5)_3$ and is reduced to $(C_6F_5)_3As$. On heating $(C_6F_5)_3AsCl_2$ with a suspension of an excess of LiBr or NaI in acetone the following reaction takes place [8]:

$$(C_6F_5)_3AsCl_2 + 2\,X^- \rightarrow (C_6F_5)_3As + 2\,Cl^- + X_2 \qquad (X = Br, I)$$

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5.3.6 Tris(perfluorohalogenoorgano)arsines

Tris(trifluoromethyl)arsine $(CF_3)_3As$

Tris(pentafluoroethyl)arsine $(C_2F_5)_3As$

Tris(pentafluorophenyl)arsine $(C_6F_5)_3As$

The compounds have been already described in Part 3, p. 213.

The vibrational spectra of gaseous, liquid and solid $(CF_3)_3As$ were recorded and assigned to the molecular vibrations [1]. The result is in fair agreement with the investigation reported in Part 3, p. 214. The arsine reacts with $(CH_3)_3SnH$ at room temperature forming $(CH_3)_3SnAs(CF_3)_2$ and CF_3H. No reactions occur with $(CH_3)_3SiH$ and $(CH_3)_3GeH$. The reason is the H-M bond strength which increases with decreasing H-M distance (M = Sn, Ge, Si) [2]. Unlike $(CH_3)_3As$, $(CF_3)_3As$ forms no addition compounds with B_2H_6 [3].

The ^{19}F NMR spectrum of $(C_2F_5)_3As$ shows the chemical shifts $\delta = -5.85$ (CF_3) and -27.46 ppm (CF_2) with reference to the external standard CF_3COOH. The haloform decomposition reaction (with a 50% solution of $(C_2H_5)_3N$ in CH_3OH) leads to CF_3CF_2H [4]. The ^{75}As signal in the NQR spectrum is found to be at 108.92 MHz [5].

$(C_6F_5)_3As$ reacts with $AgClO_4$ in benzene producing $(C_6F_5)_3AsAgOClO_3$ (p. 177) and $Ag^+[As(C_6F_5)_3]_2ClO_4^-$ (p. 177). The reduction of ethanol solutions of $NiCl_2$ with a stoichiometric amount of $NaBH_4$ in the presence of the arsine gives metallic nickel, indicating that the arsine is unable to stabilize nickel(I) under these conditions [6]. For the reaction of $(CF_3)_3As$ with $(CF_3)_2NON(CF_3)_2$ see p. 166.

Bis(pentafluoroethyl) (1-chlorotetrafluoroethyl)arsine $(C_2F_5)_2AsCFClCF_3$

Bis(pentafluoroethyl) (2-chlorotetrafluoroethyl)arsine $(C_2F_5)_2AsCF_2CF_2Cl$

A mixture of the isomers $(C_2F_5)_2AsCFClCF_3$ (70%) and $(C_2F_5)_2AsCF_2CF_2Cl$ (30%) is obtained in an overall yield of 63% by reacting $(C_2F_5)AsF$ with $F_2C{=}CFCl$ in presence of SbF_5 for 6 h at 20°C in a steel ampule, followed by fractional distillation. The mixture boils at 115 to 116°C. The mass spectrum shows peaks at m/e = 448/450, M^+ (13); 329/331, $M^+ - C_2F_5$ (13.0); 135, 137, $C_2F_4Cl^+$ (100); 119, $C_2F_5^+$ (50) [7]. The ^{19}F NMR spectrum (negative shifts upfield from external standard CF_3COOH) shows the shifts $\delta = -5.31$ (CF_3) and -27.10 (CF_2) for the C_2F_5 groups and $\delta = -1.10$ (CF_3) and -46.35 (CF_2) for the first and -21.06 (CF_2) and 9.56 (CF_2Cl) for the second compound [4]. The treatment of the mixture with a 50% solution of $(C_2H_5)_3N$ in CH_3OH gave CF_3CF_2H, CF_3CFClH, and $F_2C{=}CF_2$ in quantitative yields [7].

Tris(3,3,3-trifluoro-1-propynyl)arsine $(CF_3C{\equiv}C)_3As$

The preparation of the compound by the reaction of $CF_3C{\equiv}CLi$ and $AsCl_3$ as already described on the basis of a private communication, see Part 3, p. 214, has now been published [8]. The mass spectrum and the fragmentation scheme are also given in [8].

References:

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5.3.7 Perfluoroorganodiarsines, Bis(trifluoromethyl)phosphinoarsine, $(C_6F_5)_3$As-Ag Complexes

Tetrakis(trifluoromethyl)diarsine $(CF_3)_2AsAs(CF_3)_2$

For preparation and properties see Part 3, p. 222. — The IR spectra of the gaseous and solid compound between 1400 and 33 cm^{-1} and the Raman spectra of the liquid and the solid arsine have been recorded and analyzed [1]. A comparison of the IR and Raman bands shows that the mutual exclusion principle is operative, and it is concluded that $(CF_3)_4As_2$ exists in only the *trans*-structure(C_{2h}) in all three physical states. The molecule has 48 fundamental vibrations; 36 of these are motions due to the CF_3 groups. The remaining 12 skeletal vibrations are represented under C_{2h} symmetry by $4A_g + 3A_u + 2B_g + 3B_u$ and are assigned as follows from the Raman (Ra) and IR spectra of the solid, see **Table 63** [1]. The twelve CF_3 stretching modes give rise to extremely intensive IR absorption and rather weak Raman scattering between 1075 and 1175 cm^{-1}. The in-phase (A_g) component of the CF_3 symmetric deformation is a strong polarized Raman band at 733 cm^{-1}, the out-of-phase component (A_u or B_u) appears as an intense IR band at 733 cm^{-1}. The antisymmetric deformations are located at 533 (Ra), 536, 527 (IR), the rocking vibrations at 258, 226 (Ra), 277, 257, 246, and 227 (IR) cm^{-1} [1].

Table 63
Skeletal Vibrations of $(CF_3)_2AsAs(CF_3)_2$ [1].

Symmetry	Approximate description	ν (in cm^{-1})	Symmetry	Approximate description	ν (in cm^{-1})
A_g	AsC_2 stretching	337 (Ra)	B_g	AsC_2 stretching	324 (Ra)
	AsAs stretching	203 (Ra)		AsC_2 twisting	99 (Ra)
	AsC_2 wagging	124 (Ra)	B_u	AsC_2 stretching	335 (IR)
	AsC_2 deformation	99 (Ra)		AsC_2 wagging	—
A_u	AsC_2 stretching	313 (IR)		AsC_2 deformation	86 (IR)
	AsC_2 twisting	105 (IR)			
	torsion	—			

$(CF_3)_4As_2$ reacts with metal carbonyls and with compounds of the type HMR_3 (M = element of the main group 4, R = alkyl group). **Table 64**, p. 176, gives a survey of these reactions.

Table 64
Reactions of $(CF_3)_4As_2$ with $HM(CH_3)_3$ (M = Ge, Sn) and Metal Carbonyls.

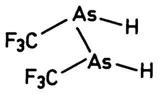
Starting compound	Conditions	Product	Ref.
$HGe(CH_3)_3$	20°C (98 d)	$Ge(CH_3)_3As(CF_3)_3$, $(CF_3)_2AsH$	[2]
$HSn(CH_3)_3$	20°C (1 h)	$Sn(CH_3)_3As(CF_3)$, $(CF_3)_2AsH$	[2]
$HMn(CO)_5$	20°C (10 min)	$Mn(CO)_5As(CF_3)_2$	[3, 4]
$HRe(CO)_5$	20°C	$Re(CO)_5As(CF_3)_2$	[4]
$CoMn(CO)_9$	0°C (4 d)	$Mn(CO)_5As(CF_3)_2$, $[Co(CO)_3As(CF_3)_2]_n$	[5]
	100°C (4d)	$MnCo(CO)_7[As(CF_3)_2]_2$, $[Co(CO)_3As(CF_3)_2]_n$	[6]
$MnRe(CO)_{10}$	160 to 190°C	$Mn_2(CO)_8[As(CF_3)_2]_2$, $Re_2(CO)_8[As(CF_3)_2]_2$, $MnRe(CO)_8[As(CF_3)_2]_2$	[6]
$Co_2(CO)_8$	–	$Co(CO)_4As(CF_3)_2$	[5]
$Re_2(CO)_{10}$	120/150/175/190°C (90/25/20/45 h)	$Re_2(CO)_8[As(CF_3)_2]_2$	[7]
$Re(CO)_5Cl$	90°C (62 h)	$Re_2(CO)_8As(CF_3)_2Cl$	[8]
$Re(CO)_5Br$	90°C (88 h)	$Re_2(CO)_8As(CF_3)_2Br$	[8]
$Re(CO)_5I$	90°C (108 h)	$Re_2(CO)_8As(CF_3)_2I$	[8]
$Mn(CO)_5Cl$	70°C (60 h)	$Mn_2(CO)_8As(CF_3)_2Cl$, $Mn_2(CO)_8[As(CF_3)_2]_2$, $Mn(CO)_5As(CF_3)_2$	[8]
$Mn(CO)_5Br$	60°C (108 h)	$Mn_2(CO)_8As(CF_3)_2Br$, $Mn_2(CO)_8[As(CF_3)_2]_2$	[8]
$Mn(CO)_5I$	50°C (110 h)	$Mn_2(CO)_8As(CF_3)_2I$	[8]

1,1-Bis(trifluoromethyl)diarsine $(CF_3)_2AsAsH_2$

1,2-Bis(trifluoromethyl)diarsine $CF_3AsHAsHCF_3$

On slowly warming (from −198 to −78°C) a mixture of $(CF_3)_2AsI$ and $(CH_3)_3SnAsH_2$ in a sealed glas ampule under nitrogen, a broad ^{19}F NMR signal with a chemical shift δ = −48.5 ppm (standard $CFCl_3$) is observed, which is assigned to $(CF_3)_2AsAsH_2$. The isolation of the compound was not successful [9].

$CF_3AsHAsHCF_3$ forms in 20 to 40% yield by the reaction of CF_3AsI_2 with Hg in presence of HI (molar ratio of 1:1 for CF_3AsI_2 to HI). The ^{19}F NMR spectrum of the diarsine in CH_3CN (negative shifts upfield from the internal standard $CFCl_3$) shows two $(AX_3)_2$ systems ($A = {}^1H$, $X = {}^{19}F$) of unequal intensity with $\delta = -39.26$ (J = 11 Hz) and −39.45 ppm (J = 10.5 Hz), which are assigned to the two diastereomers shown below in eclipsed configuration [10].



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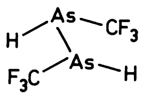

± form

The arsine decomposes in the liquid phase below room temperature to give CF_3AsH_2 and $(CF_3As)_n$, n = 4 and 5. The reaction with HI yields CF_3AsH_2 and CF_3AsI_2 [10].

Bis(trifluoromethyl)phosphinoarsine $(CF_3)_2AsPH_2$

The compound (Part 3, p. 222) forms quantitatively by the reaction of $(CF_3)_2AsH$ and F_3SiPH_2 at room temperature in 5d in a sealed ampule [11].

The Complexes $(C_6F_5)_3AsAgOClO_3$ and $Ag^+[As(C_6F_5)_3]_2ClO_4^-$

Addition of $(C_6F_5)_3As$ to a benzene solution of $AgClO_4$ (molar ratio 1:1) under nitrogen at room temperature results after 2 h in the formation of the neutral complex, electric conductivity (in $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$) $\Lambda = 175.59$ in acetone, 0.14 in benzene. On changing the molar ratio to 1:2 the cationic complex forms in 75% yield, melting point 213°C, $\Lambda = 187.4$ in acetone [12].

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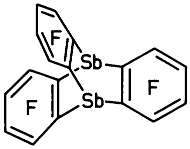
5.4 Perfluorohalogenoorgano Compounds of Antimony

5.4.1 Preparation and Physical Properties

Dodecafluoro-13,14-distibatriptycene



The triptycene forms in 12% yield on heating antimony powder with 1,2-diiodotetrafluorobenzene in an evacuated sealed tube at 300°C for three days [1] or at 250°C overnight; it can also be made by heating $(HgC_6F_4)_3$ and Sb [2]. The compound was recrystallized from 60 to 80 petroleum ether. The melting point is 258 to 259°C [2] (245 to 246°C is given in [1]). The ^{19}F NMR spectrum shows signals at δ (F^3,F^6) = −114.5 and δ (F^4,F^5) = −153.8 ppm (internal standard $CFCl_3$, THF solution) [2] (corrected values compared with those in [1]). The mass spectrum shows the parent peak at m/e = 685.7890; further main peaks due to the ions

$SbC_{12}F_8^+$, $SbC_6F_4^+$, SbF_2^+, SbF^+, and Sb^+ are observed [1, 2]. X-ray powder diffraction studies show that the distibatriptycene is isostructural with the diarsatriptycene [1]. IR spectra confirm this structure [1, 2].

The reaction of 1,2-dilithiumtetrafluorobenzene of $SbCl_3$ in THF at −78°C, followed by warming to 20°C after reaction had ceased, gives a product which is regarded to be the triptycene, melting point 155°C, ^{19}F NMR: $\delta = -112.8$ and -150.0 ppm [3]. The difference of these values from those in [2] is considered as an indication, that the compound prepared in [3] is not the triptycene [2].

Bis(trifluoromethyl)stibine $(CF_3)_2SbH$

Bis(trifluoromethyl)chlorostibine $(CF_3)_2SbCl$

Bis(trifluoromethyl)bromostibine $(CF_3)_2SbBr$

Bis(trifluoromethyl)iodostibine $(CF_3)_2SbI$

$(CF_3)_2SbH$ is formed by reaction of $(CF_3)_4Sb_2$ with $(CH_3)_3SnH$ [4]. Excess anhydrous HCl was reacted with $(CF_3)_2SbON(CF_3)_2$ yielding crude $(CF_3)_2SbCl$. Attempts to purify the compound were unsuccessful, since it disproportionated rapidly to $(CF_3)_3Sb$ and $SbCl_3$ at room temperature [5], for further details see Part 3, p. 226. $(CF_3)_2SbBr$ is formed by reacting $(CF_3)_2SbI$ with HgCl [4]. Beside chemical reactions, no new preparative and physical investigations on $(CF_3)_2SbI$, see Part 3, p. 226, are known.

Molecules and Spectra

The molecules $(CF_3)_2SbX$, X = H, Cl, Br, I belong to the C_s point group on the assumption of a symmetric orientation of the CF_3 groups. The fundamental modes of vibration comprise 13 vibrations of the species A′ and 11 of the species A″, see Table 59 (p. 168) for the analogous arsenic compounds. The vibrational spectra of the stibines are given in **Table 65**. A normal coordinate analysis was performed to support the assignment and to limit the force constants (see **Table 66**). For details see the original paper [6].

Table 65
Observed Vibrational Frequences and Approximate Assignment for $(CF_3)_2SbX$, X = H, Cl, Br, I [6].
The values (in cm^{-1}) are averages of IR and Raman measurements. The first quotation within the parentheses gives the IR intensity, the second one the Raman intensity (for abbreviations see p. 153). ν, δ, ϱ: valence, deformation, rocking vibration; s, as: symmetric, antisymmetric.

	$(CF_3)_2SbH$	$(CF_3)_2SbCl$	$(CF_3)_2SbBr$	$(CF_3)_2SbI$	Assignment
A′	1154 (vs, vw)	1175 (vs, vw)	1177 (vs, vw)	1170 (vs, vw)	$\nu_{as}(CF_3)$
	1094 (vs, vw)	1093 (vs, vw)	1089 (vs, vw)	1087 (vs, vw)	$\nu_s(CF_3)$
	714 (s, s, p)	719 (s, s, p)	719 (s, s, p)	717 (s, s, p)	$\delta_s(CF_3)$

Table 65 (continued)

	$(CF_3)_2SbH$	$(CF_3)_2SbCl$	$(CF_3)_2SbBr$	$(CF_3)_2SbI$	Assignment
A′	515 (w, w, dp)	523 (w, w, dp)	528 (w, w, dp)	524 (w, w, dp)	$\delta_{as}(CF_3)$
	245 (m, ms, p?)	226 (w, vs, p)	255 (w, s, p)	241 (w, ms, p)	$\varrho(CF_3)$
	273 (ms, m, p)	274 (ms, s, p)	276 (s, s, p)	272 (s, ms, p)	$\nu(SbC_2)$
	?	192 (–, w, p?)	195 (–, w)	182 (–, w)	$\delta(SbC_2)$
	1845 (s, s, p)	380 (s, s, p)	217 (m, vs, p)	189 (–, vs, p)	$\nu(SbX)$
	532 (m, w)	97 (–, w)	80 (–, w)	70 (–, w)	$\delta(CSbX)$
A″	1145 (vs, vw)	1111 (vs, vw)	1112 (vs, vw)	1112 (vs, vw)	$\nu_{as}(CF_3)$
	1083 (vs, vw)	1093 (vs, vw)	1089 (vs, vw)	1087 (vs, vw)	$\nu_s(CF_3)$
	714 (s, s, p)	719 (s, s, p)	719 (s, s, p)	717 (s, s, p)	$\delta_s(CF_3)$
	515 (w, w, dp)	523 (w, w, dp)	528 (w, w, dp)	524 (w, w, dp)	$\delta_{as}(CF_3)$
	221 (w, w, dp)	226 (w, vs, p)	217 (m, vs, p)	226 (m, w, dp)	$\varrho(CF_3)$
	253 (m, w)	256 (m, m, dp)	250 (m, m)	252 (m, m, dp)	$\nu(SbC_2)$
	617 (m, b, w)	113 (–, m, dp)	99 (–, w, dp)	81 (–, w)	$\delta(CSbX)$

Table 66
Internal Force Constants of $(CF_3)_2SbX$, X = H, Cl, Br, I [6].
Values in 10^2 N/m. *) Normalized to $r_{SbX} \cdot r_{SbC}$.

Molecule	f_{CF}	$f_{CF/CF'}$	f_{CSb}	$f_{CSb/CSb'}$	f_{SbX}	f_{CSbX}*)
$(CF_3)_2SbH$	5.76	0.76	1.84	0.24	2.10	0.15
$(CF_3)_2SbCl$	5.82	0.87	1.80	0.25	2.30	0.11
$(CF_3)_2SbBr$	5.82	0.87	1.67	0.22	1.55	0.09
$(CF_3)_2SbI$	5.80	0.90	1.60	0.25	1.00	0.07

Bis(trifluoroaminooxy)bis(trifluoromethyl)stibine $(CF_3)_2SbON(CF_3)_2$

Bis[bis(pentafluorophenyl)stibine]oxide $(C_6F_5)_2SbOSb(C_6F_5)_2$

Tris(trifluoromethyl)stibine $(CF_3)_3Sb$

Tris(3,3,3-trifluoro-1-propynyl)stibine $(CF_3C{\equiv}C)_3Sb$

Tris(pentafluorophenyl)stibine $(C_6F_5)_3Sb$

$(CF_3)_2SbON(CF_3)_2$ was prepared by the reaction of $(CF_3)_3Sb$ with $(CF_3)_2NO$ (molar ratio 1:2) at −74°C (1 h) and trapped at −30°C. The vapor IR spectrum shows bands characteristic of the CF_3 and $(CF_3)_2NO$ groups at 1885 (w), 1808 (s), 1466 (w), 1370 (s), 1325 (vs), 1280 (vs), 1240 (vs), 1190 (vs), 1145 (vs), 1125 (vs), 1095 (vs), 1070 (s), 970 (s), 800 (m), 710 (s) cm^{-1} [5].

$[(C_6F_5)_2Sb]_2O$ is formed by addition of small amounts of H_2O to a solution of $(C_6F_5)_3Sb$ in petroleum ether. After stirring at room temperature for a few minutes, evaporation of the solvent gives the compound as a crystalline solid in 80% yield, melting point 142°C, electrical conductivity $1.26\,\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ for a 5×10^{-4}M solution in acetone [7]. The compound shows IR absorptions found for $(C_6F_5)_3Sb$ by [8] and an additional absorption at 870 to 790 cm^{-1} which is assigned as Sb-O-Sb vibration [7].

The preparation and the properties of the stibines $(CF_3)_3Sb$ and $(C_6F_5)_3Sb$ are described in Part 3, p. 227. The preparation of $(CF_3C{\equiv}C)_3Sb$ given in Part 3, p. 227, as private communication has now been published [9]. The mass spectrum of the propynyl compound together with its fragmentation scheme is given in [9]. Solid-state IR and Raman spectra (400 to 40 cm^{-1}), including a discussion of the vibrational assignments, are given in [8]. For reactions of $(CF_3)_3Sb$ see p. 181.

Tris(pentafluorophenyl)dichlorostiborane $(C_6F_5)_3SbCl_2$

Tris(pentafluorophenyl)dibromostiborane $(C_6F_5)_3SbBr_2$

Tris(pentafluorophenyl)-bis[bis(trifluoromethyl)aminooxy]stiborane $(C_6F_5)_3Sb[ON(CF_3)_2]_2$

Tris(pentafluorophenyl)dinitratostiborane $(C_6F_5)_3Sb(NO_3)_2$

Tris(pentafluorophenyl)diperchloratostiborane $(C_6F_5)_3Sb(ClO_4)_2$

Bis[tris(pentafluorophenyl)chlorostiborane]oxide $Cl(C_6F_5)_3SbOSb(C_6F_5)_3Cl$

Bis[tris(pentafluorophenyl)nitratostiborane]oxide $NO_3(C_6F_5)_3SbOSb(C_6F_5)_3NO_3$

Bis[tris(pentafluorophenyl)perchloratostiborane]oxide $ClO_4(C_6F_5)_3SbOSb(C_6F_5)_3ClO_4$

$(C_6F_5)_3SbCl_2$ forms by direct chlorination of $(C_6F_5)_3Sb$ in ethanol [8] or by slowly adding a solution of Cl_2 in CCl_4 to a solution of $(C_6F_5)_3Sb$ in petroleum ether and stirring at room temperature for a few minutes [7]. The white crystals which precipitated were recrystallized from light petroleum ether, yield 78%. The dichloride is also formed on adding diethyl ether to a solid mixture of $(C_6F_5)_3Sb$ and $TlCl_3$ and stirring at 20°C for 48 h (yield 70%) or on adding $(C_6F_5)_3Sb$ to a solution of $CuCl_2\cdot2H_2O$ in acetone and stirring at 20°C for 1 h (80% yield) [7]. The melting point (m.p.) is 255 [7] or 255 to 257°C [8], the electrical conductivity of the dichloride (5×10^{-4}M solution) is found to be $\Lambda = 40.08$ in acetone and $16.06\ \Omega^{-1}\cdot cm^2\cdot mol^{-1}$ in nitromethane [7]. Direct bromination of $(C_6F_5)_3Sb$ in CCl_4 solution leads to the precipitation of $(C_6F_5)_3SbBr_2$, m.p. 207 to 209°C [8]. The solid-state IR and Raman spectra, including a discussion of the vibrational assignments, are given for the dichloride and for the dibromide [8].

$(C_6F_5)_3Sb[ON(CF_3)_2]_2$ is prepared by reaction of $(CF_3)_2NO$ and $(C_6F_5)_3Sb$ in Cl_2CFCF_2Cl as solvent in a sealed ampule within a few minutes at room temperature, yield 87%, m.p. 143 to 144°C, IR: 1643 (s), 1515 (s), 1495 (vs), 1395 (s), 1290 (vs), 1250 (vs), 1220 (s), 1205 (vs), 1192 (s), 1150 (vw), 1095 (vs), 1040 (vs), 980 (vs), 965 (vs), 801 (m), 735 (vw), 722 (vw), 710 (s), 680 (vw), 619 (vw), 540 (w) cm^{-1} [10].

Adding a solution of $(C_6F_5)_3SbCl_2$ in benzene to a solution of $AgNO_3$ in benzene and stirring under reflux for 2 h yield $(C_6F_5)_3Sb(NO_3)_2$, yield 40%, $\Lambda = 0.09\ \Omega^{-1}\cdot cm^2\cdot mol^{-1}$ in benzene, IR: $\nu_{as}(NO_2)$ = 1450 to 1500 cm^{-1}, $\nu_s(NO)$ = 1010 to 1040 cm^{-1} [7]. The same procedure using $AgClO_4$ gives $(C_6F_5)_3Sb(ClO_4)$, m.p. 95°C, $\Lambda = 260.43$ in acetone, and 178.35 in nitromethane, IR: 1140 (s), 925 (vw), 625 (m), 1010 to 1020 (vs), 635 (m) cm^{-1} (ClO_4 modes) [7].

$[(C_6F_5)_3SbCl]_2O$ forms on stirring $(C_6F_5)_3SbCl_2$, dissolved in hot aqueous ethanol, at 20°C for 1 h, yield 42%, m.p. 105°C, $\Lambda = 38.32\ \Omega^{-1} \cdot cm^2 \cdot mol^{-1}$ in acetone, IR: ν (Cl-Sb) $= 330\ cm^{-1}$ [7].

$[(C_6F_5)_3Sb(NO_3)]_2O$ is obtained in 43% yield on stirring a suspension of $(C_6F_5)_3Sb(NO_3)_2$ in water for 1 h at room temperature, m.p. 130°C, $\Lambda = 30.21$ in acetone and $12.86\ \Omega^{-1} \cdot cm^2 \cdot mol^{-1}$ in nitromethane.

The compound $[(C_6F_5)_3Sb]_2O(ClO_4)_2$ in 58% yield forms on adding dropwise a solution of $[(C_6F_5)_3SbCl]_2O$ in ethanol to a solution of $AgClO_4$ in benzene and stirring at 20°C for 2 h. Another procedure is to stir a solution of $(C_6F_5)_3Sb(ClO_4)_2$ in aqueous acetone for 1 h at 20°C, yield 76%, m.p. 110°C, $\Lambda = 257.34$ in acetone, $167.89\ \Omega^{-1} \cdot cm^2 \cdot mol^{-1}$ in nitromethane, IR (Sb-O-Sb) = 730 to 650 cm^{-1} [7].

5.4.2 Chemical Reactions

The distibatriptycene $(C_6F_4)_3Sb_2$ decomposes slowly at 400°C. After 15 h more than half of the compound is recovered [2].

The photolysis of $(CF_3)_2SbI$ with a xenon flash lamp yields excited iodine atoms. Thus this compound is discussed for use as photodissociation-iodine laser [11].

$(CF_3)_2SbON(CF_3)_2$ is thermally stable up to −30°C. At higher temperatures it decomposes forming perfluoroazapropene, trifluoromethylisocyanate and a white unidentified substance. The reaction with a 20% NaOH forms 2 mol CHF_3; with anhydrous HCl the reaction yields $(CF_3)_2NOH$ quantitatively [5].

$(CF_3)_3Sb$ reacts at −74°C with $(CF_3)_2NO$ in a molar ratio 1:2 forming $(CF_3)_2SbON(CF_3)_2$. Molar ratios of 1:4 and 1:6 yield perfluoro-2-azapropene, trifluoromethylisocyanate and white unidentified solids [5]. $(CF_3)_3Sb$ reacts with $(CF_3)_2NON(CF_3)_2$ on warming from −60°C to room temperature within 10 h forming SbF_3, $CF_3N{=}CF_2$ and $(CF_3)_2NOCF_3$ quantitatively [12]. Contrary to $(CF_3)_3P$, the stibine does not react in benzene with B_2H_6 forming an donor-acceptor complex [13].

$(C_6F_5)_3Sb[ON(CF_3)_2]_2$ is thermally stable up to 120°C. Heating at 160°C (18 h) leads to decomposition forming $(C_6F_5)_3Sb$, $(CF_3)_2NO$ and $F_2C{=}NCF_3$. It is not hydrolyzed by moist air and not decomposed at room temperature by anhydrous HCl. The reaction with HCl at 100°C (6d) leads to the decomposition of the compound giving $(CF_3)_2NOH$ and $(C_6F_5)_3SbCl_2$ [10].

$(C_5F_5)_3SbCl_2$ behaves as a halogenating agent. Thus, on reaction with $(C_6H_5)_3PAuCl$ both chlorine atoms are transfixed forming $(C_6H_5)_3PAuCl_3$ and $(C_6F_5)_3Sb$. It also oxidizes bromide and iodide ions in acetone to give free halogen. The dichloride reacts with $NaOCH_3$ at 20°C (4 h) forming $(C_6F_5)_3Sb(OCH_3)_2$, melting point 60°C. In chloroform the reaction with sodium acetylacetonate (acac) and sodium 8-hydroxyquinolinate (L) yields the monosubstituted octahedral compounds $(C_6F_5)_3SbCl$ (acac) and $(C_6F_5)_3SbCl$ (L), melting points 160 and 200°C, respectively [7].

References:

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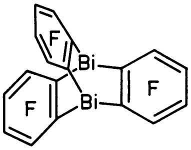
5.5 Perfluoroorgano Compounds of Bismuth

Dodecafluoro-13,14-dibismatriptycene



The triptycene is formed in 65% yield by the reaction of 1,1-dilithiumtetrafluorobenzene and $BiCl_3$ at −78°C in tetrahydrofuran. After reaction had ceased, the mixture was allowed to warm to room temperature. The obtained white solid was recrystallized from hexane. The compound decomposes above 300°C without melting. The ^{19}F NMR spectrum shows two signals at $\delta = -109.4$ and -154.0 ppm (negative shift upfield from the internal standard $CFCl_3$) [1].

Tris(trifluoromethyl)bismuthine $(CF_3)_3Bi$

The unsuccessful attempts to synthesize this bismuthine are reported in Part 3, p. 233. A successful route of preparation is the reaction of BiI_3 and C_2F_6 using the plasma technique. For this purpose, BiI_3 is converted by a radio frequency generator at 1 Torr into a plasma and then C_2F_6 is admitted continuously. After 100 h the contents of the −78°C trap and of the −196°C trap, in which the products are collected, are combined and the bismuthine purified by distillation at −55°C (yield 32%). The bismuthine is a colorless liquid, which fumes when exposed to air. At room temperature, it is hydrolyzed by base with the evolution of three equivalents of fluoroform. In sealed tubes, decomposition to metallic Bi occurs at 100°C with a half life of about 15 min, at 180°C in seconds. The ^{19}F NMR spectrum shows a singlet at $\delta = -45.9$ ppm (external standard CF_3COOH). The IR spectrum contains absorptions at 2135 (vw), 1235 (m), 1180 (vs), 1140 (s), 1120 (s), 1060 (vs), 1032 (w), and 718 (m). Peaks in the mass spectrum occur at m/e = 416, M^+ (6.8); 397, $Bi(CF_3)_2CF_2^+$ (1.6); 347, $Bi(CF_3)_2^+$ (62.0); 328, $Bi(CF_3)CF_2^+$ (0.7); 297, $BiCF_4^+$ (17.1); 278, $BiCF_3^+$ (14.5); 259, $BiCF_2^+$ (4.8); 247, BiF_2^+ (28.5); 228, BiF^+ (11.6); 209, Bi^+ (100); 69, CF_3^+ (32.5); 50, CF_2^+ (2.7) [2].

Tris(pentafluorophenyl)bismuthine $(C_6F_5)_3Bi$

In the presence of ytterbium, the bismuthine (see Part 3, p. 233) decomposes in tetrahydrofuran at 55°C (168 h) to low percentage yields of Bi and C_6F_5H [3].

References:

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6 Perfluorohalogenoorgano Compounds of Main Group 6 Elements

6.1 Preliminary Remarks

This chapter begins the treatment of the compounds of the Main Group 6 elements (without oxygen) and will be continued in the Supplement Volume 2. Up to the end of 1971, these compounds were covered in "Perfluorhalogenorgano-Verbindungen der Hauptgruppenelemente", Part 1 and 2, 1973. For further details see the preface of this Supplement Volume.

6.2 Perfluorohalogenoorgano Compounds of Sulfur

6.2.1 Perfluorohalogenosulfur(II) Compounds

6.2.1.1 Fluorothiocarbonyl Halides, Isothyocyanate and Amide FC(S)X (X = F, Cl, Br, NCS, NH_2)

6.2.1.1.1 Thiocarbonyl difluoride F_2CS

General Reference:

W. H. Sharkey, H. W. Jacobson, Preparation and Polymerization of Thiocarbonyl Fluoride, Macromol. Syn. **5** [1974] 25/33.

6.2.1.1.1.1 Preparation and Formation. Toxicity

The compound is prepared, as already described in Part 1, p. 1, in good yield by pyrolysis of tetrafluorothiirane or tetrafluoro-1,2,3-trithiolane at about 600°C. It is also formed as the only by-product in the preparation of the cyclic polysulfane [1]. The reaction of sulfur with tetrafluoroethylene at higher temperatures [1] as well as heating CS_2 with C_2F_4 at 700 to 900°C gives the thiocarbonyl fluoride [2]. Details for the preparation of F_2CS on a preparative scale from tetrafluoro-1,2-dithietane are described in [3].

F_2CS is formed on reacting $C_6H_5C(Cl){=}NC_6H_5$ with $AgSCF_3$ at 50°C (5 h) [4] and in the reaction of SF_6 with carbon in a Knudsen cell at 1500 K [5]. It is also presumably formed as an intermediate in the reaction of SF_6 with CS_2 [6, 7].

The enthalpy of formation of F_2CS has been determined by mass-spectrometric investigations of the reactions of gaseous SF_6 with carbon in a heated Knudsen cell to be $\Delta H_{f,298\,K} = -75.0 \pm 3.0$ kcal/mol [5].

Toxicity. Thiophosgene is very toxic. Since it can cause permanent injury by contact, ingestion, or inhalation, it should be used only in a forced-draft hood. If it comes into contact with skin, it should be immediately neutralized with ammonia, and affected areas washed with soap and water. If eyes are affected, they should be washed with sodium bicarbonate solution [3]. The acute toxicity on inhalation for 240 min is characterized by the value $LC_{50} = 2.5$ ppm V/V. F_2CS is three times as toxic as F_2CO [41].

6.2.1.1.1.2 The Molecule. Spectra

In the electronic ground state ($\tilde{X}^1A_1$), F_2CS is planar and has C_{2v} symmetry. From photoelectron spectra the following adiabatic and (in parentheses) vertical ionization energies E_i (in eV) are evaluated [8, 9]:

MO . . .	$4b_2$	$2b_1$	$5a_1$	$3b_2$	$1a_2$	Ref.
E_i . . .	10.52(10.69)	11.39(11.72)	14.91(15.06)	(16.48)	17.67(17.85)	[8]
E_i . . .	10.45	11.34	14.87		17.65	[9]

For assignments see Part 1, p. 2. The lowest ionization energy (10.53 eV) has been found in a mass spectrometric investigation of the reaction of SF_6 with C atoms which shows the appearance of F_2CS^+ [5]. Most of the photoelectron bands show a vibrational fine structure which enables one to identify the frequencies of the C=S stretch, C-F stretch and CF_2 deformation vibrations of F_2CS^+ ions [8, 9]. Calculations and the analysis of the spectra show that the F_2CS^+ ion has a greater C-S distance and F-C-F angle compared with the neutral molecule, independent from which orbital ionization occurs [9]. New investigations which confirm the earlier results permit comparisons between F_2CS and other thioketones which demonstrate the pronounced perfluoro effect of F_2CS. Fluorine acts as a σ acceptor and π donator (σ/π polarization) [10]. For CNDO/2 calculations of net charges see [38].

The value for the dipole moment, $\mu = 0.080 \pm 0.001$ D, results from the measurements of the Stark effect on two rotational lines of F_2CS [11]. Ab initio MO-SCF calculations give $\mu = +0.09$ D (S atom on the positive end of the dipole). Also reported are gross atomic charges, as well as σ, π, and overall electron densities [12]. CNDO calculations gave $\mu \approx -0.95$ D (S on the negative end of the dipole) [13]. Infrared intensity analysis reveals the dipole moment of the C-S and the C-F bond separately: $\mu_{C-S} = 0.2473$, $\mu_{C-F} = 0.2669$ D [14]. Using measured IR intensities, derivatives of the dipole moment with respect to the internal coordinates and bond moments have been calculated by CNDO calculations [13] and by a modified first-order approximation [15]. For the interpretation of IR intensities by polar tensors and on the resulting effective charges, mean dipole moment, derivatives, and anisotropies see [16, 17, 18]. The rotational contributions to the dipole moment derivatives are computed in [19].

The ^{13}C NMR chemical shift has been determined to be $\delta = 170.2$ ppm (-50°C; $CFCl_3$ as an internal standard, values recalculated to $(CH_3)_4Si$). The ^{13}C-^{19}F coupling constant was found to be 367 Hz [21]. The ^{19}F NMR chemical shift is 107.8 ppm (positive sign downfield from the standard $CFCl_3$) [22]. This value is not in line with previously published results (cf. Part 1, p. 3).

The analysis of the MW spectrum of F_2CS (11 rotational transitions of $^{19}F_2{}^{12}C^{32}S$, 6 of $^{19}F_2{}^{12}C^{34}S$) using the model of the rigid rotator yields the following constants [11] given in **Table 67**.

Table 67
Rotational Constants and Moments of Inertia of F_2CS [11].

Molecule		$F_2{}^{12}C^{32}S$		$^{19}F_2{}^{12}C^{34}S$	
Rotational constants	A_0 (MHz)	11892.57	± 0.5	11891.94	± 1.0
	B_0 (MHz)	5133.034	± 0.03	4959.011	± 0.05
	C_0 (MHz)	3580.316	± 0.03	3494.899	± 0.05
Asymmetry parameter	$\varkappa$	-0.62640	± 0.00003	-0.65128	± 0.00008

Table 67 (continued)

Molecule		$F_2{}^{12}C^{32}S$	$^{19}F_2{}^{12}C^{34}S$
Moments of inertia	I_A^0 ($\mu\cdot Å^2$)	42.4950 ± 0.002	42.4973 ± 0.004
	I_B^0 ($\mu\cdot Å^2$)	98.4554 ± 0.0006	101.9104 ± 0.0010
	I_C^0 ($\mu\cdot Å^2$)	141.1537 ± 0.0012	144.6036 ± 0.0021
Defect of inertia	Δ^0 ($\mu\cdot Å^2$)	0.203 ± 0.004	0.196 ± 0.007

Table 68 summarizes the geometric parameters (r and α) and the vibrational amplitudes (l) from microwave spectroscopy [11] and from an investigation of electron diffraction [23]. The last column shows the values of a joint analysis for both methods [23].

Table 68
Geometric Parameters (r, α) and Vibrational Amplitudes (l) of F_2CS obtained from MW Spectrum [11], from Electron Diffraction [23] and from a Joint Analysis of both Methods [23].
Error limits in columns 2 and 3 are three times the standard deviations.

Method	Microwave spectrum	Electron diffraction	Joint analysis for both methods
r(C-F)	1.315 (10) Å	1.315_5 (2_7) Å	1.316_5 (1_1) Å
r(C=S)	1.589 (10) Å	1.585_8 (4_8) Å	1.5894 (1_7) Å
α(FCF)	107.1 (1.0)°	106.9_4 (0.5_5)°	107.0_5 (0.1_6)°
l(C-F)		0.047 (5) Å	0.049 (2) Å
l(C=S)		0.043 (6) Å	0.040 (3) Å
l(F...F)		0.054 (8) Å	0.057 (4) Å
l(S...F)		0.056 (5) Å	0.059 (2) Å

Ab initio MO-SCF calculations of the geometric parameters are given in [12, 24], results of calculations by semiempirical methods are presented in [25, 26].

F_2CS has six fundamental vibrations, the symmetric C-F stretching $\nu_1(a_1)$, the C-S stretching $\nu_2(a_1)$, the symmetric CF_2 deformation $\nu_3(a_1)$, the antisymmetric C-F stretching $\nu_4(b_1)$, the antisymmetric SCF deformation $\nu_5(b_1)$ and the out-of-plane deformation $\nu_6(b_2)$. The analysis of the liquid-phase Raman spectrum and of the IR spectrum of a thin film at 77 K confirms the assignment of the molecular vibrations already reported in Part 1, p. 2 [27]. The gas-phase IR and liquid-phase Raman spectra have been reinvestigated in order to obtain exact gas frequencies for the fundamentals, the overtones, and the combination bands. Also matrix IR spectra in Ne and Ar at 4 and 15 K have been recorded and ^{13}C and ^{14}S satellites at natural abundance have been observed. Additionally a normal coordinate analysis has been performed [28]. In the following the fundamental vibrations ν_i and the anharmonicity constants x_{ij} (in cm^{-1}) are given [28] ($^{*)}$ = disturbed by Fermi resonance, not corrected):

$\nu_1 = 789.3$, $\nu_2 = 1365.2$, $\nu_3 = 526.2$, $\nu_4 = 1190$, $\nu_5 = 418$, $\nu_6 = 623.2$, $x_{11} = -3.3$, $x_{12} = -2.3$, $x_{13} = +1.8$, $x_{14} = -8^{*)}$, $x_{15} = -3.2$, $x_{22} = -1.1$, $x_{23} = -4.4$, $x_{24} = -9^{*)}$, $x_{25} = +10.7^{*)}$, $x_{26} = -2.2$, $x_{33} \approx 0$, $x_{34} = -1.8$, $x_{35} \approx 0$, $x_{44} = +2.2^{*)}$, $x_{45} = -9^{*)}$, $x_{55} = +1.4^{*)}$, $x_{66} = -1$

CNDO/2 calculations give $\nu_2 = 1418\ cm^{-1}$ [40].

The symmetry force constants (in 10^{-2} N/m) [28] are given together with those of [29] in the following:

F_{11}	F_{22}	F_{33}	F_{44}	F_{55}	F_{66}	F_{12}	F_{13}	F_{23}	F_{45}	
6.625	7.332	1.408	5.750	0.868	0.637	1.225	−0.315	+0.430	0.650	[28]
6.085	8.489	1.393	6.896	0.910	0.575	1.131	−0.318	+0.325	1.269	[29]

Experimentally determined Urey-Bradley force constants $K_{C\text{-}F} = 5.93$ and $K_{C\text{-}S} = 7.82$ have been evaluated, and these values were compared with $K_{C\text{-}F} = 5.93$ and $K_{C\text{-}S} = 7.93$, calculated by CNDO/2 methods. It is shown that this method does not reproduce quantitatively the experimental values but realizes the qualitative trend within the series of the homologous molecules $X_2C{=}Y$ (X = H, F, Cl, Y = O, S) [25]. Using the concept of kinetic constants, the potential constants for the general quadratic valence force field have been evaluated. From these constants vibrational mean amplitudes, Coriolis coupling constants, and centrifugal distortion constants have been calculated [30, 31]. Force constants and mean vibrational amplitudes calculated by use of the valence coordinate method are given in [32]. Mean amplitudes of vibration for molecules of the type ZXY_2, among them F_2CS, have been calculated by the method of characteristic vibrations [33].

Calculation of bond asymmetry parameters η connecting force constants along and perpendicular to a bond within a molecule for F_2CS leads to $\eta_{C\text{-}F} = 0.7529$ and $\eta_{C\text{-}S} = 0.3357$ [20].

Electronically Excited States. Electronic Spectra

The weak absorption which extends from about 4500 Å to shorter wavelengths in a series of well-defined bands has been assigned as $\pi^* \leftarrow n$ excitation of F_2CS from the ground state $\tilde{X}^1A_1$ to the $\tilde{A}^1A_2$ and $\tilde{a}^3A_2$ excited states, see Part 1, p. 3.

A new electronic transition in the near UV region has been photographed in the vapor phase at 25 and −78°C. The spectrum has a maximum at $49020\ cm^{-1}$ and an oscillator strength of f = 0.24. Progressions of several intervals in the vibrations $\nu_1 = 729$ [ν_s(C-F)], $\nu_3 = 400$ [δ_s(FCF)] and $\nu_6 = 544\ cm^{-1}$ (out-of-plane wagging mode) were identified in the vibrational fine structure. The electronic transition is identified as a transition between the planar ground state $\tilde{X}^1A_1$ to the nonplanar excited state $\tilde{B}^1A_1$ [34].

The intensities of low-energy electronic transitions for some carbonyls and thiocarbonyls, among them F_2CS, has been calculated from CNDO wave functions [35].

Experimental values for the geometry of the F_2CS molecule in the lowest excited triplet state $\tilde{a}^3A_2$ are not available. Ab initio SCF-MO calculations (STO-3G basis) of the equilibrium geometry and of portions of the potential energy surface for the triplet state yield r(C-F) = 1.355 Å, r(C-S) = 1.28 Å, α(FCF) = 109.1°. The deviation of the S atom from the F-C-F plane amounts to 42°. The height of the barrier for the inversion is predicted to be $E = 2707\ cm^{-1}$ in reasonable agreement with the experimental value of more than $3100\ cm^{-1}$ (see Part 1, p. 3) [24, 36]. E = 7.74 kcal/mol is cited in [37]. A comparative study on the suitability of the CNDO/2 method for the calculation of geometries, planar inversion barriers, excitation energies, electron densities of singlet and triplet excited states demonstrate pronounced deviations from the few experimental results [38]. Some photophysical parameters of small thioketones pertaining to excited singlet states are presented in [38].

6.2.1.1.1.3 Chemical Reactions

F_2CS adds HF forming CF_3SH [42]. Gaseous F_2CS reacts with sulfur atoms according to $F_2CS + S \rightleftharpoons CF_2 + S_2$. The third-law heat is found to be -4.0 kcal/mol [5].

The Diels-Alder reaction of the thiophosgene with cyclopentadiene was already described in Part 1, p. 5. Recently, the ^1H NMR spectrum of the reaction product has been published [43].

Irradiation of a liquid mixture of F_2CS and CF_3OF (volume ratio 1:10) with a 100 W-Hg/Xe lamp at -96°C shows the occurrence of the radical $(CF_3O)_2SF$ which is identified by its ESR spectrum. Similarly, the reaction of F_2CS and SF_5OF gives the radical $(SF_5O)_2SF$ (ESR values see the original literature) [44]. The reaction of F_2CS with $(CF_3S)_2CFSCl$ [45], FC(S)NCS [46] and XC(O)SCl (X = F, Cl) [47] gives by addition to the C-S double bond the title compounds $(CF_3S)_2CFSSCF_2Cl$, $CF_3SC(S)NCS$ and $XC(O)SSCF_2Cl$ (X = F, Cl).

Polymerization processes. Instructions for handling F_2CS in these reactions are reported in [3]. — F_2CS polymerizes in pentane at -78°C in presence of catalysts consisting of mixtures of $Ti(OR_4)$ and AlR_2X with R = iso-C_4H_9, X = Cl, H or iso-C_4H_9 [48]. The yield and the viscosity of the polymer can be influenced by varying the ligands on the Al atom and the ratio of the components of the catalyst. The polymer $(CF_2S)_x$ is characterized by the ^{19}F NMR signal at -38.6 ppm (standard CF_3COOH, 30% solution in CCl_4) and the nonresolved C-F IR absorptions at 1000 to 1300 cm^{-1} and the C-S stretching vibration at 849 cm^{-1}. Viscosity measurements on the material, which is soluble in chloroform and tetrahydrofuran, yield an average mole mass of 500000 to 1000000. For differential thermoanalysis, elasticity curves and X-ray analysis see the original paper [3]. The polymer is resistant against acids, but it is degraded on contact with amines [1]. Tris(N-methyl-N-octadecylamino)sulfonium-difluorotrimethylsilicate can be used also as a catalyst. After 2 h at -78°C the yield of the polymer amounts to 95% [32].

The radical-induced polymerization of F_2CS by UV irradiation in presence of C_2F_5I, CF_3OOCF_3 or CF_3SSCF_3 gives on addition of C_2F_4 colorless solid copolymers [50, 51]. They are insoluble in all usual solvents except hot Kel-F oil and perfluorokerosine and melt in the range between 240 and 325°C. They are used for coating razor blades [50, 52, 53]. The thermolysis gives the starting compounds and perfluorinated cyclic sulfanes [51]. The polymerization of F_2CS in an inert solvent at -78°C in the presence of perfluoroacetaldehyde or perfluoropropionalaldehyde forms an acid-resistant, low-molecular weight copolymer. A mixture of organoaluminiumhydride and complexes of phosphorous with rhodium and platinum is used as catalyst [28].

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6.2.1.1.2 Fluorothiocarbonyl chloride FC(S)Cl

6.2.1.1.2.1 Preparation

Since Part 1 (see p. 8) has been edited, no new methods of preparation have been published.

6.2.1.1.2.2 Molecule and Spectra

In the electronic ground state ($\tilde{X}\,^1A'$) the molecule is planar, symmetry group C_s as revealed from spectroscopic investigations (also see Part 1, p. 8) and from the electron diffraction measurements.

The NMR spectrum shows the chemical shifts (positive sign means downfield from the standard) $\delta(^{19}F)$ = 98.8 ppm (internal standard $CFCl_3$) and $\delta(^{13}C)$ = 174.4 ppm [internal standard $(CH_3)_4Si$)], coupling constant $J(^{13}C\text{-}^{19}F)$ = 389 Hz [1].

The analysis of the MW spectrum gives for $F^{12}C^{32}S^{35}Cl$ (for constants of the other isotopic molecules see [2]) the following rotational constants A, B, C, moments of inertia I (in u · Å^2), centrifugal distortion constants Δ and δ (in MHz), Cl quadrupole coupling constants χ (in Mz) [2], for coordinate system see **Fig. 3**:

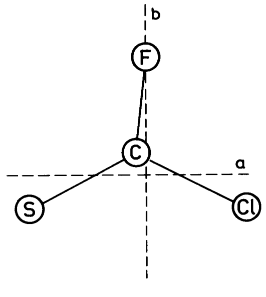
$A = 7984.462(2)$
$B = 3437.61(1)$
$C = 2400.047(1)$

$I_A = 63.29484(1)$
$I_B = 147.02413(3)$
$I_C = 210.56879(6)$

$\Delta_J = 0.6924$
$\Delta_{JK} = -0.5933(58)$
$\Delta_K = 10.991(6)$
$\delta_J = 0.2641(3)$
$\delta_K = 1.6766(4)$

$\chi_{aa} = -51.298(42)$
$\chi_{bb} = 23.587(58)$
$\chi_{cc} = 27.711(52)$

Fig. 3



Position of the axes of the principal moments of FC(S)Cl.

The asymmetry parameter, a quantity for the deviation of the charge distribution around the C-Cl axis from cylinder symmetry, is η = 0.24, this is interpreted in terms of a C-Cl double bond character of 10.8% [2]. For CNDO calculations of net charges see [3]. For the analysis of the MW spectrum in terms of the Watson's formula for the rotational energy, see [4].

The analysis of the MW spectrum of vibrationally excited $F^{12}C^{32}S^{35}Cl$ yields rotational constants and centrifugal distortion constants, for details see [5].

The following internuclear distances r (in Å) and angles are determined from MW measurements (r_0 and r_e structures) [2, 6] and from electron diffraction measurements (r_g structures) [7], the average values (r_{av}) obtained from both methods are included [7].

	r(C-S)	r(C-Cl)	r(C-F)	r(S-Cl)	α(SCCl)	α(SCF)
r_0 structure	1.5951(11)	1.7156(11)	1.3267(8)	2.9650	127.13°	123.84°
r_e structure	1.5927(11)	1.7133(11)	1.3216(11)		127.00°	123.99°
r_g structure	1.5940(12)	1.7162(15)	1.3385(19)			
r_{av} structure	1.5915(7)	1.7159(8)	1.3357(13)		127.50°	123.85°

An ab initio MO-SCF calculation of the equilibrium geometry is given in [8].

Reinvestigation of the gas-phase IR spectrum revealed the missing fundamental vibration ν_6 (see Part 1, p. 8) to be at 538.4 cm^{-1}. It was possible to obtain a full set of anharmonicity constants by exploring combination and overtone bands. In the following, data are given the measured fundamental vibrations ν_i (in cm^{-1}) and the harmonic frequencies ω_i (in cm^{-1}), calculated by use of the anharmonicity constants [9].

	i = 1	i = 2	i = 3	i = 4	i = 5	i = 6
ν_i	1257.4	1014.9	612.4	472.2	323.1	538.4
ω_i	1293.4	1049.4	632.7	419.4	323.1	570.4
assignment . . .	ν(C-S)	ν(C-F)	ν(C-Cl)	δ(SCF)	δ(SCCl)	δ(out-of-plane)

CNDO/2 calculations give 1301 cm^{-1} for the C-S stretching vibration [10]. Vibrational amplitudes are obtained by spectroscopic [9] and electron diffraction measurements [7].

The calculation of the general valence force field (in internal displacement coordinates) with the harmonic frequencies (see above) gives the following force constants (in mdyn/Å, mdyn · Å/rad^2 and mdyn/rad, respectively) [9], see also [5]:

	CS	CF	CCl	SCF	SCCl	out-of-plane
CS	6.838	0.845	0.197	0.726	0.365	0
CF		6.082	0.429	0.513	−0.378	0
CCl			4.141	−0.701	−0.250	0
SCF				2.136	1.144	0
SCCl					1.976	0
out-of-plane[a]						0.632

[a] Out-of-plane is characterized by the angle between r(C-Cl) and the plane SCF.

The diagonal elements of a force field given in [7] are (in mdyn/Å, $f_{out\text{-}of\text{-}plane}$ in mdyn/rad):

f_{CS}	f_{CF}	f_{CCl}	f_{SCF}	f_{SCCl}	$f_{out\text{-}of\text{-}plane}$
7.064	5.642	3.612	0.610	0.272	0.441

Electronically Excited States. Electronic Spectra

The visible and UV spectra of the molecule show three band systems: A band between 5000 and 4300 Å of weak intensity assigned to the forbidden transition $\tilde{A}\ {}^1A''$ (n, π*) ← $\tilde{X}\ {}^1A'$. The origin of the system is determined to be at ν_{00} = 21657.4 cm^{-1} [11] (in correction of the older value of 21096 cm^{-1}, quoted in Part 1, p. 8). The fundamental vibrations in this state are given in **Table 69**. The molecule is nonplanar, from the splitting of the out-of-plane vibration an inversion barrier of 1556.0 ± 45 cm^{-1} and an out-of-plane angle of 37° [11, 14], 38° [14] are determined. A comparative study of molecular properties of some carbonyls, among them FC(S)Cl, in excited singlet (and triplet) states by CNDO/2 calculations gives molecular geometries, inversion barriers, net charges and term energies [3].

Table 69
Fundamental Vibrations of FC(S)Cl in Electronically Excited States.

Term	$\nu_1(a')$	$\nu_2(a')$	$\nu_3(a')$	$\nu_4(a')$	$\nu_5(a')$	$\nu_6(a'')$	Ref.
$\tilde{A}$	745(913)	960	578	346	–	426	[12]
$\tilde{a}$	877.3	964.0	583.0	348.3	233.8	409.3	[11]
$\tilde{B}$	566	–	590	311	–	448	[13]

The absorption band system in the 495 nm region is assigned to the $\tilde{a}\ ^3A''\ (n, \pi^*) \leftarrow \tilde{X}\ ^1A'$ electronic transition with a band origin $\nu_{00} = 20191\ cm^{-1}$ [14]. The fundamentals are given in Table 69. The inversion barrier is estimated to be 1622 cm^{-1} [14], respectively, 5.80 kcal/mol [15]. An experimental value of 2675 cm^{-1} is given by [16]. Ab initio SCF-MO calculations result in a barrier height of 2041 cm^{-1} and in $\nu_6 = 466.8\ cm^{-1}$; the geometry parameters are calculated to be r(C-S) = 1.7805, r(C-F) = 1.3481, r(C-Cl) = 1.8126 Å, α(FCCl) = 112.1°, α(FCS) = 124.5°, and α(out-of-plane) = 38.4° [8]. For the results of CNDO/2 calculations see [3].

A third intensive absorption system starts at about 220 nm via longer wavelengths. It is assigned to the transition $\tilde{B}\ ^1A'\ (\pi, \pi^*) \leftarrow \tilde{X}\ ^1A'$ [11, 14, 26]. The origin is $\nu_{00} = 35277\ cm^{-1}$, the inversion barrier for the nonplanar molecule in the $\tilde{B}$ state is about 2000 cm^{-1} or more [13]. Along with the reduction of the C-S bond order from 2 (in the ground state) to 1 in the $\tilde{B}$ state [17] an increase of the C-S bond length of 0.60 ± 0.05 Å is predicted from the Franck-Condon profiles on $\pi \rightarrow \pi^*$ electron promotion [16]. Using the frequencies of ν_1 in the $\tilde{X}$ and $\tilde{B}$ states a value of 0.48 Å is obtained from Clark's empirical relationship [13, 18].

The molecule in the $\tilde{B}$ state shows appreciable fluorescence. Pumping single vibronic levels of this state with a tunable dye laser of narrow bandwidth, four well-resolved bands are observed and documented [18]. Life-times of excited states are measured [17, 19]. Excitation of low-lying vibrational levels of the $\tilde{B}$ state leads to fluorescent emission with high quantum yield ($\varphi \rightarrow 1$), whereas at higher energies of the levels a nonradiative decay, probably followed by dissociation, is the predominantly observed process [20].

6.2.1.1.2.3 Chemical Reactions

The reactivity of fluorothiocarbonylchloride is characterized by addition to the C-S double bond. The reactions of $Cl_2C{=}NSCl$ [21], $(CF_3S)_2CFSCl$ [22] and XC(O)SCl (X = F, Cl) [23] forming the title compounds $Cl_2C{=}NSSR_f$, $(CF{=}S)_2CFSSR_f$ and $X(CO)SR_f$ (X = F, Cl; $R_f = CF_2Cl$) are described in Supplement Volume 2.

For the Cl → Br metathesis on FC(S)Cl with PBr_3 resulting in the formation of FC(S)Br [24], see p. 192.

References:

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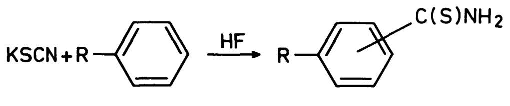
6.2.1.1.3 **Fluorothiocarbonyl bromide** FC(S)Br

The reaction of FC(S)Cl with PBr_3 at 125 to 130 °C (26 h) leads to a product which condenses at −90 °C. Fractional distillation gives 34% of a yellow liquid boiling at 4 to 8 °C/100 Torr which is 90% pure FC(S)Br. ^{19}F NMR (internal standard C_6F_5, value recalculated to $CFCl_3$, positive sign means lowfield): $\delta = 119.2$ ppm, mass spectrum m/e = 142, M^+, 123, $BrCS^+$, 91, CBr^+, 63, FCS^+, A. Haas, J. Mikolajczak (Chem. Ber. **114** [1981] 829/31).

6.2.1.1.4 **Fluorothiocarbonyl isocyanate** FC(S)NCS, **Fluorothiocarbonyl amide** $FC(S)NH_2$

For preparation and physical properties of the isocyanate see Part 1, p. 9. – In the presence of catalytic amounts of CsF the compound reacts with F_2CS forming $CF_3SC(S)NCS$ (see p. 198) [1, 2].

The amide is postulated as intermediate in the reaction



The formation is explained as HF addition to the C-N bond. But no direct proof is given [3].

References:

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6.2.1.2 Perfluorohalogenoorganothiocarbonyl Compounds

The compounds $CF_3SC(S)X$, X = F, Cl, SCF_3, are described on p. 198.

6.2.1.2.1 Preparation and Physical Properties

Trifluoromethylthiocarbonyl amide $CF_3C(S)NH_2$

The in-situ preparation is described in context with the reaction of the compound on p. 194.

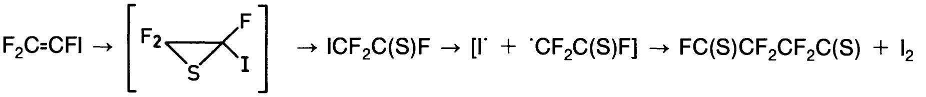
Trifluoromethylthiocarbonyl fluoride $CF_3C(S)F$

Pentafluoroethylthiocarbonyl fluoride $C_2F_5C(S)F$

For preparation and properties see Part 1, p. 10. Chemical reactions are covered on p. 194.

Tetrafluorodithiosuccinyl difluoride $FC(S)CF_2CF_2C(S)F$

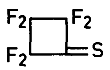
The compound forms on reaction of $F_2C{=}CFI$ with sulfur at 45°C in the gas phase. The yield is 60%. The following intermediate steps are postulated [1, 2]:



The compound is a red-brown liquid, boiling point 84 to 85.5°C. The ^{19}F NMR spectrum in $CFCl_3$ shows the chemical shifts $\delta(CF) = 66.2$ and $\delta(CF_2) = -109.1$ ppm (both multiplets). UV maxima are observed at 428 ($\varepsilon = 46.5$), 294 ($\varepsilon = 171$) and 220 nm ($\varepsilon = 11300$) [1].

Hexafluorothioacetone $(CF_3)_2CS$, **Radical Anion**

Hexafluorocyclobutanethione

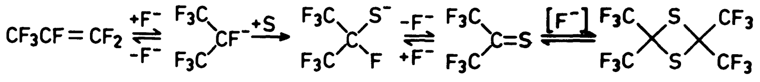


$(CF_3)_2CS$ is formed in the reaction of $(CF_3)_2C(OH)SH$ or of $(CF_3)_2C(OH)S_nC(OH)(CF_3)_2$ (n = 2, 3) with SF_4 at −78°C. In case of the polysulfanes as reactants this formation is accompanied by precipitation of sulfur [3]. The compound is also formed in a side reaction on reacting $CF_3Re(CO)_5$ with CS_2 at 130°C according to [4]:

$$CF_3Re(CO)_5 \leftrightharpoons CF_3^- + Re(CO)_5^+$$
$$4\,CF_3^- + 2\,CS_2 \rightarrow 2\,(CF_3)_2CS + 2\,S^{2-}$$

References p. 197

The reaction of perfluoropropene with sulfur and KF in tetramethylenesulfone at 120 °C in an autoclave yields as intermediate $(CF_3)_2CS$ [5] according to:



The catalytic effect of F^- ions on the equilibrium between $(CF_3)_2CS$ and its dimer, the tetrakis(trifluoromethyl)-1,3-dithietane, is used for the in-situ generation of the instable monomer from the stable dimer. Since unsolvated fluoride is useful for the reaction, aprotic, polar solvents like dimethylformamide are recommended [6 to 12]. The mechanism of the reaction is described by a nucleophilic attack of the fluoride anion on a sulfur atom of the dithietane followed by ionic fragmentation [6].

^{13}C NMR of $(CF_3)_2CS$ [standard $(CH_3)_4Si$]: $\delta = 194.4$ ppm [14].

The radical anion forms from $(CF_3)_2CS$ and lithium in a 1 : 3 mixture of hexamethyphosphoric amide and tetrahydrofuran at −95 °C. The ESR spectrum shows the hyperfine coupling constants (in G) $a^F = 22.56$, $a^C_{CS} = 18.6$ and $a^C_{CF_3} = 8.9$ [13].

A similar role, like $(CF_3)_2CS$ in the reaction system $CF_3CF{=}CF_2/KF$ and sulfur, is found for hexafluorocyclobutanethione as an intermediate in the reaction of perfluorocyclobutene with KF and sulfur [5].

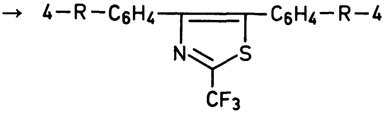
6.2.1.2.2 Chemical Reactions

Trifluoromethylthiocarbonylamide reacts with hexamethyldisilazene according to [14]:

$$2\,CF_3C(S)NH_2 + [(CH_3)_3Si]_2NH \rightarrow 2\,CF_3C(S)NHSi(CH_3)_3 + NH_3$$

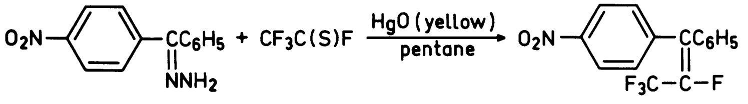
The product is characterized by IR and ^1H NMR data [14]. Several 2-bromo-1,2-diphenylethanone derivatives are reacted with $CF_3C(S)NH_2$ in CH_3CN as a solvent (reflux, 20 h) to form thiazole compounds [15, 16]:

$4\text{-}R\text{-}C_6H_4\text{-}CHBrC(O)\text{-}C_6H_4\text{-}4\text{-}R + CF_3C(S)NH_2 \rightarrow$



R = H (28% yield after chromatography on silica gel, melting point (m.p.) 94 to 97 °C) [15, 16]; R = Cl (m.p. 101 to 104 °C) [15], (m.p. 101 to 102 °C) [16], R = CH_3O (m.p. 51 to 54 °C) [15, 16]. Further derivatives (R = F, Br, $(CH_3)_2CHO$) are claimed but no characterization is reported [16]. Alternatively the thiazole (R = CH_3O) has been prepared by generating $CF_3C(S)NH_2$ "in situ" from $CF_3C(O)NH_2$ and freshly pulverized P_4S_{10} in benzene solution (reflux, 96 h) and adding the respective diphenylethanone (yield: 34%) [15, 16]. This method is extended to several other substituents R without presentation of any experimental details [16]. The resulting thiazole derivatives exhibit considerable activity as inhibitors of blood platelet aggregation [15, 16].

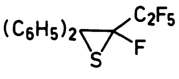
$CF_3C(S)F$ reacts with the following hydrazone compound according [17]:



Similarly the reaction with $(C_6H_5)_2C{=}NNH_2$ gives $(C_6H_5)_2C{=}CFCF_3$, boiling point 80°C/1.7 mmHg, ^{19}F NMR (negative sign means upfield from the standard $CFCl_3$): $\delta = -67.3$ (quartet, J = 10 Hz), and -64.4 ppm (doublet, J = 64.7 Hz), ^1H NMR see original [18].

$CF_3CF_2C(S)F$ reacts with $(C_6H_5)_2CN_2$ [18] forming a mixture of

$(C_6H_5)_2C{=}C(CF_2CF_3)F$ and



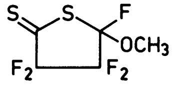
A B

^{19}F NMR (standard $CFCl_3$) [18]:

For compound A: $\delta(CF_3) = -83.6$ ppm [doublet of triplets (J = 9 Hz) of multiplets (J = 2.5 Hz) of quartets], $\delta(CF_2) = -113$ ppm [doublet of quartets (J = 13 Hz) of multiplets], $\delta(CF) = -127$ ppm (multiplet). For compound B: $\delta(CF_3) = -8.1$ ppm [doublet (J = 13 Hz) of multiplets], $\delta(CF_2) = -117$ ppm [ABX pattern: $\delta(F^A) = -114$, $\delta(F^B) = -119$ ppm, $J_{AX} = 9.5$ Hz, $J_{BX} = 12.5$ Hz, $J_{AB} = 277$ Hz], $\delta(CF) = -148$ ppm (multiplet).

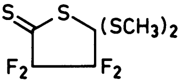
Tetrafluorodithiosuccinyldifluoride reacts with CH_3OH like an organic acid fluoride forming the diester and the dithiolactone [1] according:

$FC(S)-(CF_2)_2-C(S)F \xrightarrow{CH_3OH} CH_3OC(S)CF_2CF_2C(S)OCH_3 +$



The lactone which is formed by elimination of HF from an intermediate can only be isolated at low temperatures (−20°C). The reaction of the succinyldifluoride with ethanol or isopropanol gives only the corresponding diester. With CH_3SH the compound reacts as follows [1]:

$FC(S)-(CF_2)_n-C(S)F + 2\,CH_3SH \rightarrow$



The conditions of the reactions and the physical properties of the products are gathered in **Table 70**, p. 196.

$FC(S)(CF_2)_2C(S)F$ can be polymerized in wide ranges of pressure and temperature (−120°C to 0°C [2], for instance, by warming up from −78°C to 0°C [1]). Preferred conditions are temperatures between −50°C and −100°C and atmospheric pressure. In ethereal solvents with ionic initiators (amines, amides, quaternary ammonium salts, phosphines, CsF or metalalkyls) a pink polymer forms with the structure

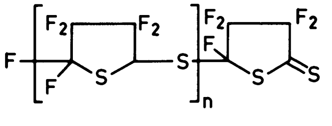
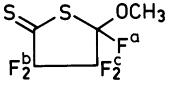
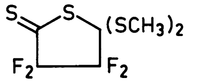
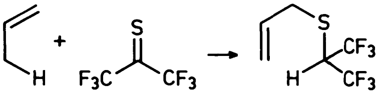


Table 70
Reactions of $FC(S)CF_2CF_2C(S)F$ and Physical Properties of the Reaction Products [1].
Refractive index n_D^{25}, boiling point (b.p.) in °C/pressure in Torr, NMR spectrum (chemical shift δ, spin-spin coupling constant J, standard $CFCl_3$ and $(CH_3)_4Si$, solvent $CFCl_3$), s = singlet, d = doublet, tr = triplet, qu = quartet, sept = septet, m = multiplet, UV absorption (wavelength λ, molar absorptivity ε).

Reactant (conditions)	Product (yield in %, color, n_D^{25})	b.p./Torr in °C	^{19}F NMR	^1H NMR	UV λ_{max} in nm (ε)
CH_3OH (10 to 20°C)	$CF_2C(S)OCH_3$ | $CF_2C(S)OCH_3$ (75%, orange-red, 1.4606)	97 to 98/96	$\delta = -109.2$ (s)	$\delta = 4.18$ (s)	$\lambda_{max} = 243$ (14000), 399 (31)
CH_3OH (−20°C)	 (19%, purple)	50 to 51/5.0	$\delta(F^a) = -97.4$ (m), $\delta(F^b) = -110.0$ (m), 110.9 (m) (AB spectrum), $\delta(F^c) = -131.3$ (m)	$\delta = 3.78$ [d (J = 1.2 Hz) of tr (0.4 Hz)]	$\lambda_{max} = 520$ (17), 302 (7500)
C_2H_5OH (15°C)	$CF_2C(S)OC_2H_5$ | $CF_2C(S)OC_2H_5$ (74%, orange, 1.4545)	76/0.55	$\delta = -109.7$ (s)	$\delta = 1.48$ (tr, J = 7 Hz, 6 H), $\delta = 4.68$ (qu, J = 7 Hz, 4 H)	$\lambda_{max} = 400$ (38.6), 308 (292), 244 (14100)
$(CH_3)_2CHOH$ (15°C)	$CF_2C(S)CH(CH_3)_2$ | $CF_2C(S)CH(CH_3)_2$ (orange)	77 to 80/0.75	$\delta = -107.2$ (s)	$\delta = 1.42$ (d, J = 6 Hz, 12 H), $\delta = 5.67$ (sept, J = 6 Hz, 2 H)	$\lambda_{max} = 400$ (54.8), 302 (410), 248 (13200)
CF_3SH (0°C, NaF)	 (21%, deep purple, 1.5896)	100 to 103/0.75	$\delta = -103.3$ (tr, J = 9.5 Hz, 2 F), $\delta = -116.8$ [tr (J = 9.5 Hz) of sept (J = 0.8 Hz) 2 F]	$\delta = 2.35$ (tr, J = 0.8 Hz)	$\lambda_{max} = 513$ (13.5), 320 (7300)

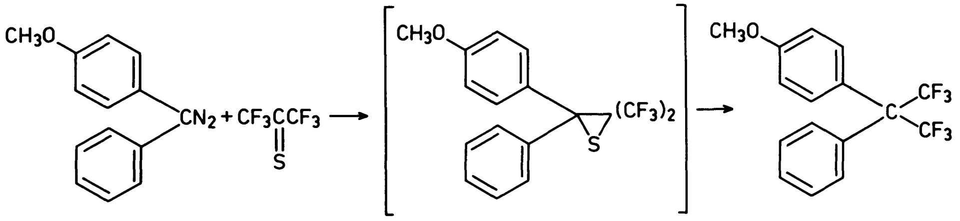
The polymer is insoluble in all common solvents and resistant against acids. At 242 to 267 °C the solid melts forming a viscous liquid [1, 2].

Hexafluorothioacetone reacts with olefins in an Ene fashion yielding exclusively products with C-S bonds.



This stereospecific reaction, which is in contrast to the behavior of the normal ketones (formation of an O-H bond), is interpreted on the basis of the HOMO-LUMO theory under consideration of the participation of the sulfur d orbitals [19].

$(CF_3)_2CS$ reacts with phenyl-4-methoxyphenyldiazomethane in CH_2Cl_2 according



The product (purity 87% after distillation) boils at 102 to 103 °C/0.2 Torr. It is used as antifertility drug [20, 21].

To avoid the quite difficult handling of $(CF_3)_2CS$ (tendency for dimerization, toxicity) preparative work performed with this compound is facilitated by capitalizing on the "in situ" generation from the cyclic dimer tetrakis(trifluoromethyl)-1,3-dithietane via fluoride ion catalysis. For such kinds of reactions therefore refer to the latter compound, see Suppl. Vol. 2.

Hexafluorothioacetone generated from its cyclic dimer by thermolysis (600 °C) has been reacted with diketene at 500 ± 10 °C to yield hexafluoroisobutylene (48%). Similar results, but varying yields, are obtained by substituting diketene by its monomer or by generating $(CF_3)_2CS$ from $CF_3CF{=}CF_2$ and sulfur at 380 to 425 °C and feeding it directly together with ketene or a ketene generating compound (diketene, acetone, acetic acid, isopropenyl acetate, or acetyl acetone) to a second reactor (reaction temperatures ranging from 300 to 800 °C) [22].

The ^1H NMR spectrum of thianorbornene, the product of the Diels-Alder reaction of $(CF_3)_2CS$ with cyclopentadiene (see the third compound in Table 4 in Part 1, p. 18) is given in [18].

The addition of ClF to $(CF_3)_2CS$ forming $(CF_3)_2CFSCl$ and the reaction of perfluorodialkylthiocarbonyls with HN_3 are covered in Suppl. Vol. 2.

References:

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[21] W. J. Middleton, E. I. Du Pont de Nemours & Co. (U.S. 3678117 [1972]; C.A. **77** [1972] No. 101125). — [22] M. van der Puy, L. G. Anello, B. Sukornick, R. F. Sweeney, R. A. Wiles, Allied Chem. Corp. (U.S. 4244891 [1979/81]; C.A. **94** [1981] No. 208337). — [23] M. S. Raasch (J. Org. Chem. **40** [1975] 161/72). — [24] W. Gombler (Spectrochim. Acta A **37** [1981] 57/61).

6.2.1.3 Trifluoromethylmercaptothiocarbonyl Compounds $CF_3SC(S)X$

($X = NH_2$, NCS, F, Cl, Br, SCF_3)

6.2.1.3.1 Preparation and Formation

Trifluoromethylmercaptothiocarbonyl amide $CF_3SC(S)NH_2$

CF_3SCN reacts with excess H_2S at 30 to 35°C (24 h) in a sealed tube forming $CF_3SC(S)NH_2$ (20% yield). The compound is thermally stable at 20°C only for about 24 h. The formation of the compound in the reaction of CF_3SH and NH_3 [1] could not be verified [2].

Trifluoromethylmercaptothiocarbonyl isothiocyanate $CF_3SC(S)NCS$

The compound (in 28% yield) forms by reacting F_2CS and FC(S)NCS in the presence of catalytic amounts of CsF at 20°C (shaking for 2 to 3 h). It is obtained as a by-product in the preparation of FC(S)NCS from FC(S)Cl and KSCN [2].

Trifluoromethylmercaptothiocarbonyl fluoride $CF_3SC(S)F$

The linear dimer of F_2CS is formed in small amounts during the addition of ClF to $(CF_3)_2CS$ [3].

Difluoro(isothiocyanato)methylmercaptothiocarbonyl fluoride $CF_2(NCS)C(S)F$

The compound is formed as by-product on reacting FC(S)Cl with KSCN at −25°C. It has been isolated as pure substance from some distillation residues [2].

Trifluoromethylmercaptothiocarbonyl chloride and bromide $CF_3SC(S)X$, X = Cl, Br

The chloride is obtained in 87% yield by reacting $CF_3SC(S)F$ with BCl_3 at 20°C for 20 h in a bomb tube [3]. The bromide (83% yield) forms similarly by F-Br exchange from $CF_3SC(S)F$ and BBr_3 at 35 to 40°C (0.5 h, open system), followed by warming to 60°C for some minutes [2].

Bis(trifluoromethylmercapto)thiocarbonyl $CF_3SC(S)SCF_3$

The compound forms as a by-product on reacting $FC(O)SCF_3$ with CsF, presumably according [4]:

$$FC(O)SCF \overset{CsF}{\rightleftharpoons} (CF_3SCF_2O)^-Cs^+ \xrightarrow{-F_2CO} (F_3CS)^-Cs^+ \rightleftharpoons F_2CS + CsF \xrightarrow{+\,2\,F_2CS} (CF_3S)_2CS$$

Small amounts of $(CF_3S)_2CS$ are obtained in the reaction of $(CF_3S)_3CSN(C_2H_5)_2$ with HCl [3].

Bis(trifluoromethyl)pentathiodiperoxycarbonate $(CF_3SS)_2CS$

On slowly introducing CF_3SCl into a rapidly stirred suspension of $Na_2CS_3 \cdot 3\,H_2O$ in petroleum ether at −30°C, 15% $(CF_3S)_2CS$ are formed [2, 5]. On replacing Na_2CS_3 by Tl_2CS_3 the yield is lowered to 10% [5].

1,2,3,4-Tetrakis(trifluoromethylmercapto)-2-butene-1,4-dithione

$CF_3SC(S)C(SCF_3)=C(SCF_3)C(S)SCF_3$

For details of this compound see Suppl. Vol. 2.

6.2.1.3.2 Physical Properties

Physical data of the compounds are compiled in **Table 71**. Additional information is presented below.

Table 71
Physical Data of Trifluoromethylmercaptothiocarbonyl Compounds, of $CF_2(NCS)C(S)F$ and of $(CF_3SS)_2CS$.
Boiling point (b.p.) in °C/pressure in Torr, melting point (m.p.) in °C (in parentheses), ^{19}F NMR spectrum (chemical shift δ in ppm, spin-spin coupling constant J in Hz, s, d, tr = singlet, doublet, triplet, internal standard C_6F_6, values refer to $CFCl_3$). UV spectrum (wavelength λ, molar absorptivity ε).

Compound	b.p./Torr (m.p.) in °C	^{19}F NMR (δ in ppm), IR spectrum (in cm^{-1}), UV spectrum (λ in nm)
$CF_3SC(S)NH_2$ colorless needles [2]	(63, decomposition)	^{19}F NMR: δ = −43.1 (s) IR: 3400 (s), 3260 (m), 3150 (s), 1604 (vs), 1417 (vs), 1218 (vs), 1177 (vs), 1166 (vs), 1138 (vs), 1098 (vs), 824 (vs), 751 (s)

Table 71 (continued)

Compound	b.p./Torr (m.p.) in °C	^{19}F NMR (δ in ppm), IR spectrum (in cm^{-1}), UV spectrum (λ in nm)
$CF_3SC(S)NCS$ red [2]	45/10	^{19}F NMR: $\delta = -44.5$ (s) IR: 1928 (vs, br), 1250 (s), 1220 (s), 1160 (s), 1105 (s), 1030 (s), 753 (m)
$CF_2(NCS)C(S)F$ orange [2]	40/10	^{19}F NMR: $\delta(CF_2) = -45$ (d), $\delta(CF) = -88.7$ (tr), J(F-F) = 19 Hz IR: 1964 (vs, br), 1228 (vs), 1210 (vs), 1181 (vs), 1105 (vs), 1074 (s)
$CF_3SC(S)Cl$ [3]	87	^{19}F NMR: $\delta = -47.7$ (s) IR: 1061 (s), 1038 (s), 1007 (s), 983 (s), 865 (s, br), 625 (m) UV (in isooctane): $\lambda_{max} = 212$ ($\varepsilon = 8750$), 237.5 ($\varepsilon = 10250$), 269 ($\varepsilon = 5250$), 288 ($\varepsilon = 5560$)
$CF_3SC(S)Br$ red [2]	67/150	^{19}F NMR: $\delta = -47.7$ (s) IR: 1181 (vs), 1131 (vs), 1082 (vs), 757 (s), 752 (m), 716 (s), 700 (s)
$(CF_3SS)_2CS$ [2, 5]	44/1	^{19}F NMR: $\delta = -44.7$ (s) IR: 1176 (vs), 1166 (vs), 1108 (vs), 1098 (vs), 1082 (vs), 815 (m), 755 (s) UV (in isooctane): $\lambda_{max} = 203$ ($\varepsilon = 14130$), 215 ($\varepsilon = 12870$), 258 ($\varepsilon = 12200$), 317 ($\varepsilon = 3800$)

The analysis of the photoelectron spectra of $CF_3SC(S)X$ (X = F, Cl, SCF_3) resulted in the following vertical ionization energies (in eV) and assignments [6]:

Peak	1	2	3	4	5	6	7	8	9
$CF_3SC(S)F$	10.12	10.45	12.45	13.3	13.8	15.8	17.3	–	–
	n_s	π_1	π_2	σ_{CS}					
$CF_3SC(S)Cl$	9.57	10.25	11.45	10.03	12.95	13.8	14.9	15.3	17.2
	n_s	π_1	n_{Cl}	$\pi_{2(Cl)}$	σ_{CS}				
$(CF_3S)CS$	9.25	10.00	10.50	12.7	13.2	14.6	15.4	16.4	17.2
	$n_s(b_2)$	$\pi_1(b_1)$	$\pi_2(a_2)$	$\sigma_{CS}(a_1)$					

The assignments are based on comparisons with other sulfur compounds and on the order of the orbitals calculated by the CNDO method.

A population analysis for the C=S group in $(CF_3S)_2CS$ shows no polarization [6].

6.2.1.3.3 Chemical Reactions

The chemical behavior of the CF_3S-thiocarbonyl compounds is characterized by the reaction of the C=S group. Electrophilic additions of halogens give sulfenyl chlorides. These chlorides react with the thiocarbonyl compounds on UV irradiation forming disulfanes; the reaction rate increases with the degree of the fluorination of the reaction components. For details see the Chapters on the sulfenyl chlorides and on the disulfanes in Suppl. Vol. 2.

The oxidation of the thiocarbonyl compounds by 3-chloroperbenzoic acid in absolute ether at 0°C yields the corresponding S oxides [2]:

$$XYC{=}S + 3\text{-}ClC_6H_4C(O)OOH \rightarrow XYC{=}SO + 3\text{-}Cl\text{-}C_6H_4COOH$$

In the following it is given for the investigated reactions the molar ratio perbenzoic acid/thiocarbonyl and the yield of the products [2]:

X	CF_3S	CF_3S	CF_3S	CF_3SS
Y	Cl	Br	CF_3S	CF_3SS
Molar ratio	1:1	2:1	1:1	1:1
Yield	64%	20%	76%	37%

In this reaction completely fluorine-substituted thiocarbonyls could not be oxidized, bromine-fluorine derivatives reacted only partially. The photochemically induced dimerization of the thiocarbonyls forming dithietanes is treated in Suppl. Vol. 2.

The compounds $CF_3SC(S)NH_2$ and $CF_3SC(S)Br$ hydrolyze on contact with water [2]. $(CF_3S)_2CS$ reacts with HgO forming $(CF_3S)_2CO$ and HgS, see Suppl. Vol. 2.

References:

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[6] H. Bock, K. Wittel, A. Haas (Z. Anorg. Allgem. Chem. **408** [1974] 107/14).

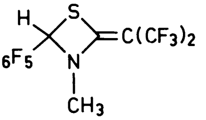
6.2.1.4 Bis(trifluoromethyl)thioketene $(CF_3)_2C{=}C{=}S$

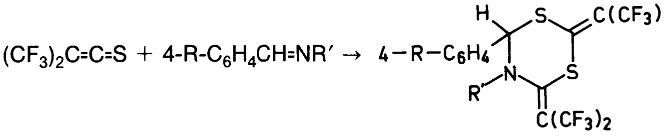
6.2.1.4.1 Preparation and Physical Properties

The ketene forms presumably as intermediate in the reaction of imidazolidinethiones with $(CF_3)_2CS$, which results by O-S exchange in the formation of the cyclic dimer of the ketene [1, 7], for preparation by pyrolysis of the dimer (1,3-dithietane) and for physical properties see Part 1, p. 30.

6.2.1.4.2 Chemical Reactions

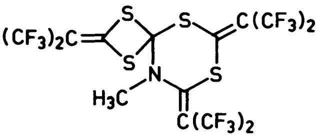
Bis(trifluoromethyl)thioketene yields both mono- and diadducts as a result of cycloaddition with Schiff bases depending on the type of the latter [6] (see **Table 72**, p. 203).

$(CF_3)_2C{=}C{=}S + C_6F_5CH{=}NCH_3 \rightarrow$ 

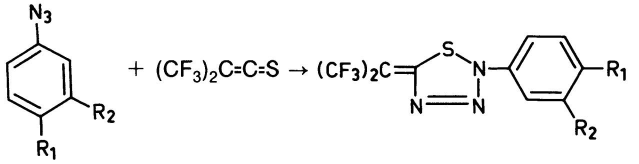


R = H, R′ = CH_3; R = H, R′ = $CH(CH_3)_2$,
R = Cl, R′ = CH_3; R = NO_2, R′ = CH_3,
R = CH_3O, R′ = 4-CH_3O-C_6H_4

With CH_3NCS the result of the reaction is a triadduct [6] (see Table 72).

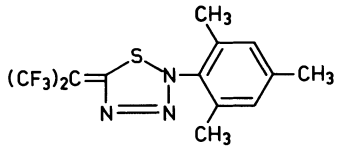


Aryl azides add to $(CF_3)_2C{=}C{=}S$ forming Δ^3-1,2,3,4-thiatriazolines [6] (see Table 72).



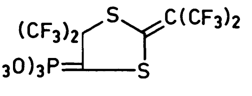
R_1 . . .	H	CH_3	OCH_3	Cl	Cl
R_2 . . .	H	H	H	H	Cl

Performing the same reaction with 2,4,6-trimethylphenylazide a similar product results [6]:

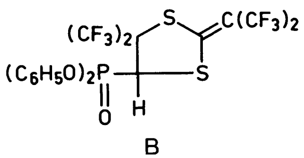


Beside these 1:1 $(CF_3)_2C{=}C{=}S$/azide adducts the formation of orange 2:1 adducts is observed, also accessible by adding excess thioketene to the 1:1 adducts. The structure of these compounds has not been established [6].

With $(CH_3O)_3P$, two molecules of thioketene react to form a water-sensitive product with structure (A). With $(C_6H_5O)_3P$ the reaction takes a similar course, but due to hydrolysis a different product (B) is isolated [6]:



A



B

Table 72

Physical Data[1] for the Products of the Reaction of $(CF_3)_2C=C=S$ with Schiff Bases, Methyl Isocyanate, Aryl Azides, Phosphite Esters, Methylbenzenes and Thiothiophthene [6].

Yield in %, boiling point (b.p.) in °C/pressure in Torr, melting point (m.p.) in °C, ^{19}F NMR (positive values of the chemical shift δ mean downfield from the standard, spin-spin coupling constant J), s, d, tr, qu, m = singlet, doublet, triplet, quartet, multiplet.

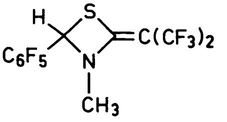
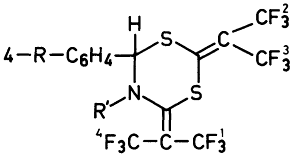
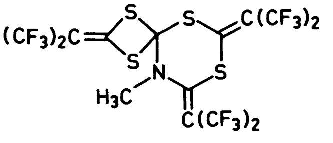
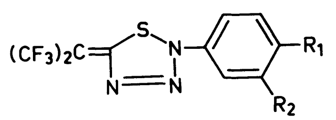
Compound (yield) reaction conditions	b.p./Torr (m.p.) in °C	^{19}F NMR[3] (δ in ppm, J in Hz)
 (79%), in hexane	(66.7 to 67.5)[2]	δ = 11.54 (qu of d of qu), 17.90 (qu of qu of d), $J(CF_3\text{-}CF_3)$ = 9.1, $J(CF_3^1\text{-}CH)$ = 1.2, $J(CF_3^1\text{-}CH_3)$ = 0.5, $J(CF_3^2\text{-}CH)$ = 1.3, $J(CF_3^2\text{-}CH_3)$ = 2.6
 R = H, R′ = CH_3 (78%), petroleum ether, 0°C	(162 to 162.8)[4]	δ = 9.30 (qu, CF_3^1), 10.3 (qu, CF_3^2), 11.4 (qu, CF_3^3), 13.5 (qu, CF_3^4), $J(CF_3^1\text{-}CF_3^4)$ = 8, $J(CF_3^2\text{-}CF_3^3)$ = 9, $J(CF_3^{2,3}\text{-}CF_3^{1,4})$ = 4.5, $J(CF_3^x\text{-}CH_3)$ = 1.3 (x = 1, 2, 3 or 4)
R = H, R′ = $CH(CH_3)_2$ (52%), petroleum ether, 0°C	(138 to 139)	δ = 10.13 (qu, 1 CF_3), 10.88 (qu, 1 CF_3), 11.47 (m, 1 CF_3), 14.44 (m, 1 CF_3)
R = Cl, R′ = CH_3 (60%), petroleum ether, 0°C	(143 to 144)	—
R = NO_2, R′ = CH_3 CH_2Cl_2, 0°C	(150 to 151)	—
R = CH_3O, R′ = 4-CH_3O-C_6H_4 (62%), CH_2Cl_2	(122 to 123)[6]	δ = 8.50 (qu, 1 CF_3), 10.7 (qu, 1 CF_3), 11.9 (m, 1 CF_3), 13.1 (m, 1 CF_3)
 (52%), occasional cooling	(121.5 to 122.5)	δ = 7.94 (qu of qu, CF_3^1), 8.92 (s, $(CF_3)_2C=$), 9.79 (qu, CF_3^2), 11.1 (CF_3^3)[7], 12.5 (CF_3^4)[7], $J(CF_3^1\text{-}CF_3^4)$ = 8.7, $J(CF_3^2\text{-}CF_3^3)$ = 9.3, $J(CF_3^1\text{-}CH_3)$ = 1.2
		
R_1, R_2 = H (26.5%), petroleum ether, 6 d	(125 to 125.5)[8,9]	δ = 10.20 (qu, 1 CF_3), 11.08 (qu, 1 CF_3)
adduct thioketene/azide (2:1), R_1, R_2 = H (22%)[12]	(80 to 81)[9,10]	δ = 0.21 (s, 2 CF_3), 9.54 and 9.98 (qu, $(CF_3)_2C=$)

Table 72 (continued)

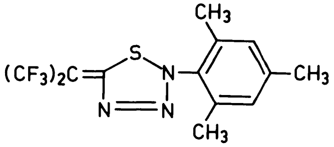
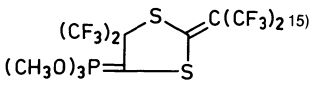
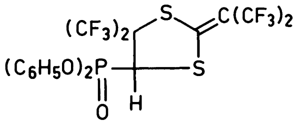
Compound (yield) reaction conditions	b.p./Torr (m.p.) in °C	^{19}F NMR[3] (δ in ppm, J in Hz)
$R_1 = CH_3$, $R_2 = H$ (35%), petroleum ether, 6 d	(124.5 to 125)[8]	δ = 9.66 (qu, 1 CF_3), 10.57 (qu, 1 CF_3)
adduct thioketene/azide (2:1), $R_1 = CH_3$, $R_2 = H$ (6%)	(77.5 to 78.5)[10]	–
$R_1 = OCH_3$, $R_2 = H$ (56%), hexane, 16 h	(113 to 113.7)[8,9]	δ = 10.21, 10.92 (A_3B_3 type)[11]
adduct thioketene/azide (2:1), $R_1 = OCH_3$, $R_2 = H$, (55%)[12]	(117.5 to 118)[9]	δ = 0.25 (s, 2 CF_3), 8.42 and 8.63 (qu, $(CF_3)_2C$=)
$R_1 = Cl$, $R_2 = H$ (14.4%), hexene, 4 d	(119 to 119.5)[6,8]	δ = 10.25 (qu, 1 CF_3), 10.57 (qu, 1 CF_3)
adduct thioketene/azide (2:1), $R_1 = Cl$, $R_2 = H$ (25%)[12]	(102.5 to 103)[9,10]	δ = 0.39 (s, 2 CF_3)[11], 9.52, and 9.89 (qu, $(CF_3)_2C$=)
R_1, $R_2 = Cl$ (4), hexane, 4 d	(116.5 to 117)[8,9]	δ = 10.25 (A_3B_3 type, 2 CF_3)[5,13], 10.76 (qu, 1 CF_3)[14], 11.65 (qu, 1 CF_3)[14]
adduct thioketene/azide (2:1), R_1, $R_2 = Cl$ (29%)[12]	(96.5 to 97)[9,10]	δ = 0.62 (s, 2 CF_3)[11], 9.75, and 10.07 (qu's, $(CF_3)_2C$=)
 (41%), hexane, 1 d	(126.7 to 127.2)[8,9]	δ = 10.28 (qu, 1 CF_3)[11], 10.78 (qu, 1 CF_3)
 [15] (59%), CH_2Cl_2, 0°C	–	δ = 0.89 [d, 5-$(CF_3)_2$, J(F-P) = 1.3], 9.68 (m, 2-$(CF_3)_2$)
 (62%), <30°C, moist air	(98 to 98.5)[6]	δ = 2.56 and 4.47 (qu, 5-$(CF_3)_2$), 9.95 (A_3B_3 type, 2-$(CF_3)_2C$=)

Table 72 (continued)

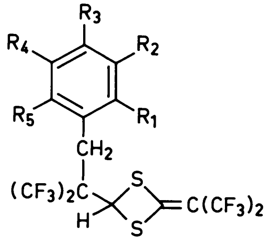
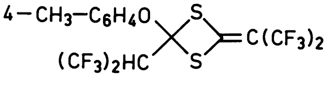
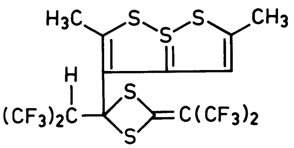
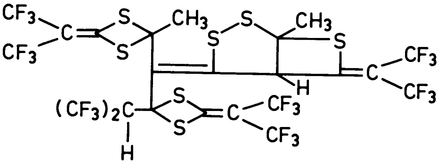
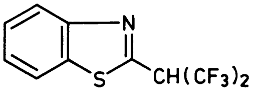
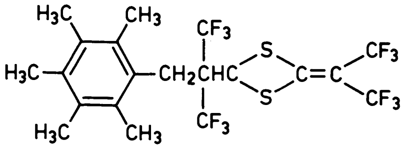
Compound (yield) reaction conditions	b.p./Torr (m.p.) in °C	^{19}F NMR[3] (δ in ppm, J in Hz)
		
R_1 to R_5 = CH_3 (45%), benzene, 100°C[16], 15 h	(120 to 120.2)[9]	δ = 2.73 (s, 2 CF_3), 9.26 (s, $(CF_3)_2C$=)
R_2, R_5 = H; R_1, R_3, R_4 = CH_3 (54%), 150°C[16], 6 h	(67 to 68)[9]	δ = 2.39 (s, 2 CF_3), 9.57 (s, $(CF_3)_2C$=)
R_1, R_2, R_4, R_5 = H; R_3 = OCH_3 (20%), 150°C[16], 8 h	(31.2 to 31.8)[9]	δ = 2.54 (s, 2 CF_3), 9.72 (($(CF_3)_2C$=)
R_1, R_2, R_4, R_5 = H; R_3 = OH (1.7%), 100°C[16], 15 h (by-product)	(102 to 104)[6]	δ = 2.66 (s, 2 CF_3), 9.61 (s, $(CF_3)_2C$=)
4-$CH_3C_6H_4OC(S)CH(CF_3)_2$ (35%), see above (main product)	(80 to 81)[7]	δ = 1.29 (d, J = 6)
 (18%), see above (main product)	(76 to 77)[6]	δ = 6.27 [d, $(CF_3)_2CH$, J(F,H) = 7], 8.87 (s, $(CF_3)_2C$=)
 (58%), CH_2Cl_2, 22 h	(151 to 152)[6],[17]	δ = 4.49 [d, $(CF_3)_2CH$, J(F,H) = 7], 9.84 (s, $(CF_3)_2C$=)
 (77%), CH_2Cl_2, 40 h	(134 to 135)[18]	δ = 3.03 [d, $(CF_3)_2CH$), J(F,H) = 6], 9.73 (s, $(CF_3)_2C$=CS_2), 9.84 (s, $(CF_3)_2C$=CS_2), 9.66 (A_3B_3, $(CF_3)_2C$=)

Table 72 (continued)

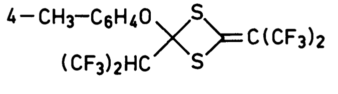
Compound (yield) reaction conditions	b.p./Torr (m.p.) in °C	^{19}F NMR[3] (δ in ppm, J in Hz)
 (39%), CH_2Cl_2	(101 to 103)[6]	δ = 2.30 [d, J(F,H) = 6]

[1] For further data (n_D, ^{1}H NMR, IR, mass spectrum) refer to the original publication [6]. — [2] Recrystallized from hexane/CCl_4. — [3] External standard $CFCl_2CFCl_2$. — [4] From CCl_4. — [5] In DCl_3. — [6] From hexane. — [7] Ten-line pattern. — [8] Yellow crystals. — [9] Recrystallized. — [10] Orange crystals. — [11] In CCl_4. — [12] Isolated from the filtrate of the 1:1 adduct. — [13] Room temperature. — [14] 0°C. — [15] Pale yellow oil. — [16] Sealed tube. — [17] Deep orange. — [18] White product from CH_3NO_2.

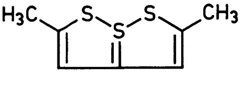
Hexamethylbenzene reacts with $(CF_3)_2C{=}C{=}S$ to form the following dithietane [6]:



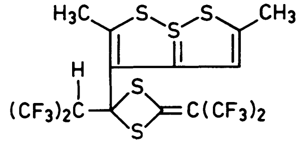
With 1,2,4,5-tetramethylbenzene and 4-methylanisole the analogous products are isolated. The same type of compound results from the reaction with 4-methylphenol; the yield is very small. Dominant are two other products, the ester $4\text{-}CH_3\text{-}C_6H_4OC(S)CH(CF_3)_2$ and another dithietane [6].



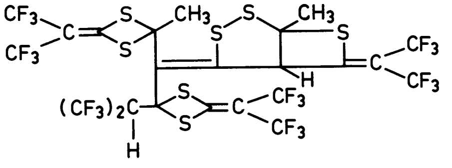
With toluene or xylene no reaction occurs. $(CF_3)_2C{=}C{=}S$ and thiothiophthene (A) yield in a reaction sequence first the 2:1 adduct (B), which can be isolated as an orange substance, and as a result of further thioketene addition the white 4:1 adduct (C). With 2-aminobenzenethiol the benzothiazole derivative (D) is formed [6].



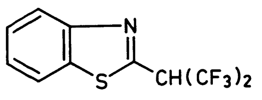
A



B

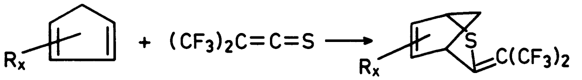


C

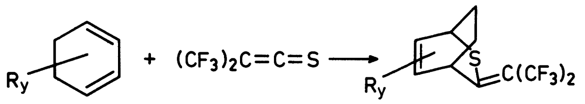


D

Bis(trifluoromethyl)thioketene reacts as dienophile in Diels-Alder reactions. The products with some of their physical properties are covered in **Table 73** [2, 5, 6]. It is remarkable that the reaction with 1,3-cyclohexadiene gives the Diels-Alder product and also the product of the Ene reaction (ratio 54.5:45.5). Many other compounds are formed in the reaction with cyclopentadiene derivatives (no physical properties are given) according [5]



Several cyclohexadiene adducts are produced from the thioketene and 1,3-cyclohexadiene [5]:



Dialkylsulfur diimides react with the thioketene forming N-alkylbis(trifluoromethyl)-keteneimines [3]:

$$2\ (CF_3)_2C{=}C{=}S + RN\text{-}S\text{-}NR \rightarrow 2\ (CF_3)_2C{=}C{=}NR + 3\ S$$

This procedure is applied to compounds with R = alkyl (C_1 to C_{18}, also branched) and with R = cycloalkyl (C_4 to C_7), see Part 1, p. 44. A characterization is given only for the keteneimines with R = CH_3, n-C_4H_9, t-C_4H_9. The reaction with diphenylsulfur diimide gives a compound, which is sensitive to UV irradiation. All substances can be used as antistatic agents for wool [3].

Table 73

Diels-Alder Reaction Products of $(CF_3)_2C{=}C{=}S$.

Yield in %, boiling point (b.p.) in °C/pressure in Torr, melting point (m.p.) in °C, ^{19}F NMR (values of the chemical shift δ are downfield from the external standard $CFCl_2CFCl_2$), spin-spin coupling constant J, (d, tr, qu mean doublet, triplet, quartet); for further properties (n_D, IR, ^1H NMR) see the original publications.

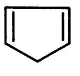
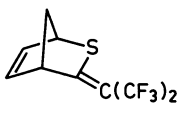
Reactant (conditions)	Product yield in %	b.p./Torr (m.p.) in °C	^{19}F NMR (δ in ppm)
 (15 to 20°C, CH_2Cl_2) [2, 5]	 96% [2], 89% [5]	69.7/7 [5], 196/760 (10) [2]	7.64 (qu)[1], 11.6 (q of d) [2, 5]

Table 73 (continued)

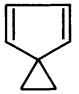
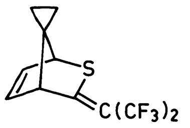
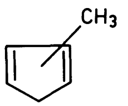
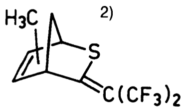
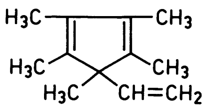
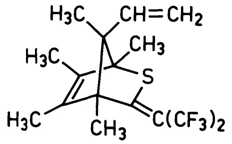
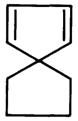
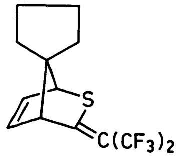
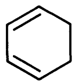
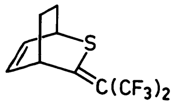
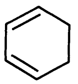
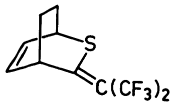
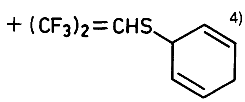
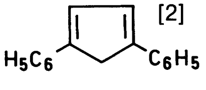
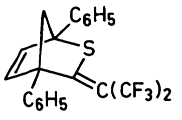
Reactant (conditions)	Product yield in %	b.p./Torr (m.p.) in °C	^{19}F NMR (δ in ppm)
	 91% [2]	45/0.4 [2], 45/0.05 [5]	11.75 (qu), 15.9 (qu of d, J = 1.8 Hz) [2]
 [5]		60 to 67/5	—
	 2 isomers, 81%	76/0.5 [6], 74/0.5 [5] (mixture of isomers) (50 to 52) for pure isomer$^{3)}$ [5, 6]	9.65 (qu), 17.9 [qu of tr, J(F-H) = 2.6 Hz], pure isomer [6]
 (0 °C, CH_2Cl_2)	 72% [5], 83% [6]	60/0.2 [5, 6]	8.13 (qu), 12.4 (qu) [6]
 [5] (0 °C, 16 h)		79 to 80/1.4	10.4 (qu), 14.1 (qu)
		78/5	9.65 (qu), 13.2 (qu)
		—	3.41 (qu of d), 6.33 (qu), J(F-F) = 6.4 Hz, J(F-H) = 1.5 Hz
 [2] (hexane, refluxing for 16 h)	 86%	(101, decomposition)$^{5)}$	7.91 (qu)$^{6)}$, 13.6 (qu)

Table 73 (continued)

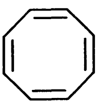
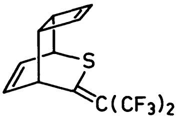
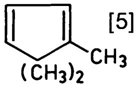
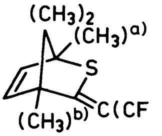
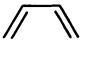
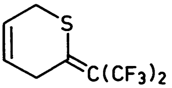
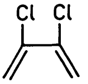
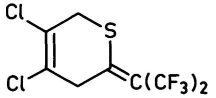
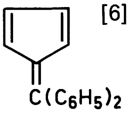
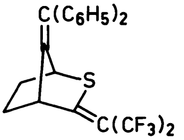
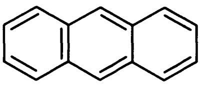
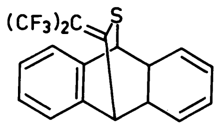
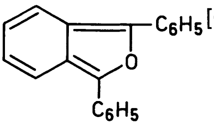
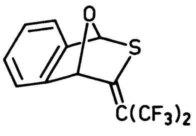
Reactant (conditions)	Product yield in %	b.p./Torr (m.p.) in °C	^{19}F NMR (δ in ppm)
 [5, 6] (100°C, bomb tube, 16 h)	 78%	(49 to 50)	10.3 (qu), 13.8 (qu)
 [5]	 isomers a) or b)	55/1.8	–
 [6] (0°C, 20 h, CH_2Cl_2)	 91%	72 to 73/8	9.79 (qu), 12.5 (qu)
 [6] (100°C, 2 h, bomb tube)	 72%	64/0.25	9.70 (qu of tr), 12.60 (qu)
 [6] (hexane)	 73%	(118.3 to 119)[7]	8.70 (qu), 12.6 (qu)
 [6] (18 h, 20%, C_6H_6, reflux)	 59%	(118.5 to 119)[8]	9.79 (qu), 14.9 (qu)
 [6] (0°C, CH_2Cl_2)	 83% [6]	(123)	6.84 (qu)[1], 13.9 (qu)

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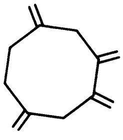
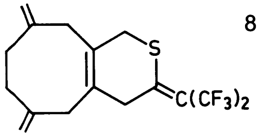
Table 73 (continued)

Reactant (conditions)	Product yield in %	b.p./Torr (m.p.) in °C	^{19}F NMR (δ in ppm)
 [6]		88/0.025	10.3 (qu), 13.5 [qu, J(F-F) = 11 Hz]

[1] Neat substance. — [2] CH_3 groups in position 1, 4, 5, 6 or 7. — [3] Fractional crystallization from CH_3OH gives a pure isomer. — [4] Not isolated, spectra from the mixture with the Diels-Alder product. — [5] Decomposition on reversal of the formation reaction. — [6] In $CDCl_3$. — [7] From hexane. — [8] From CH_3OH.

References

[1] H. Kohn, Y. Gopichand (Tetrahedron Letters **1976** 3093/6). — [2] M. S. Raasch (J. Org. Chem. **40** [1975] 161/72). — [3] E. I. Du Pont de Nemours & Co., M. S. Raasch (U.S. 3462489 [1969]; C.A. **71** [1969] No. 90831). — [4] M. S. Raasch (J. Org. Chem. **37** [1972] 1347/56). — [5] E. I. Du Pont de Nemours&Co., M. S. Raasch (Ger. Offen. 2118975 [1971]; U.S. 3752827 [1973]; C.A. **76** [1972] No. 59456).

[6] M. S. Raasch (J. Org. Chem. **43** [1978] 2500/8). — [7] H. Kohn, Y. Gopichand, P. Charumilind (J. Org. Chem. **43** [1978] 4955/61).

Table of Conversion Factors

Following the notation in Landolt-Börnstein [7], values which have been fixed by convention are indicated by a bold-face last digit. The conversion factor between calorie and Joule that is given here is based on the thermochemical calorie, $\mathrm{cal_{th\,ch}}$, and is defined as 4.184**0** J/cal. However, for the conversion of the "Internationale Tafelkalorie", $\mathrm{cal_{IT}}$, into Joule, the factor 4.1868 J/cal is to be used [1, p. 147]. For the conversion factor for the British thermal unit, the Steam Table Btu, $\mathrm{BTU_{ST}}$, is used [1, p. 95].

Force	N	dyn	kp
1 N (Newton)	1	10^{5}	0.1019716
1 dyn	10^{-5}	1	1.019716×10^{-6}
1 kp	$9.8066\mathbf{5}$	$9.8066\mathbf{5}\times10^{5}$	1

Pressure	Pa	bar	kp/m²	at	atm	Torr	lb/in²
1 Pa (Pascal) = 1 N/m²	1	10^{-5}	1.019716×10^{-1}	1.019716×10^{-5}	0.986923×10^{-5}	0.750062×10^{-2}	145.0378×10^{-6}
1 bar = 10^{6} dyn/cm²	10^{5}	1	10.19716×10^{3}	1.019716	0.986923	750.062	14.50378
1 kp/m² = 1 mm H_2O	$9.8066\mathbf{5}$	$0.98066\mathbf{5}\times10^{-4}$	1	10^{-4}	0.967841×10^{-4}	0.735559×10^{-1}	1.422335×10^{-3}
1 at = 1 kp/cm²	$0.98066\mathbf{5}\times10^{5}$	$0.98066\mathbf{5}$	10^{4}	1	0.967841	735.559	14.22335
1 atm = 76**0** Torr	$1.0132\mathbf{5}\times10^{5}$	$1.0132\mathbf{5}$	1.033227×10^{4}	1.033227	1	760	14.69595
1 Torr = 1 mm Hg	133.3224	1.333224×10^{-3}	13.59510	1.359510×10^{-3}	1.315789×10^{-3}	1	19.33678×10^{-3}
1 lb/in² = 1 psi	6.89476×10^{3}	68.9476×10^{-3}	703.069	70.3069×10^{-3}	68.0460×10^{-3}	51.7149	1

Work, Energy, Heat	J	kWh	kcal	Btu	MeV
1 J (Joule) = 1 Ws = 1 Nm = 10^7 erg	1	2.778×10^{-7}	2.39006×10^{-4}	9.4781×10^{-4}	6.242×10^{12}
1 kWh	$\mathbf{3.6}\times10^{6}$	1	860.4	3412.14	2.247×10^{19}
1 kcal	4184.**0**	1.1622×10^{-3}	1	3.96566	2.6117×10^{16}
1 Btu (British thermal unit)	1055.06	2.93071×10^{-4}	0.25164	1	6.5858×10^{15}
1 MeV	1.602×10^{-13}	4.450×10^{-20}	3.8289×10^{-17}	1.51840×10^{-16}	1

1 eV/mol = 23.0578 kcal/mol = 96.473 kJ/mol

Power	kW	PS	kp m/s	kcal/s
1 kW = 10^{10} erg/s	1	1.35962	101.972	0.239006
1 PS	0.73550	1	**75**	0.17579
1 kp m/s	$\mathbf{9.80665}\times10^{-3}$	0.01333	1	2.34384×10^{-3}
1 kcal/s	4.184**0**	5.6886	426.650	1

References:

[1] A. Sacklowski, Die neuen SI-Einheiten, Goldmann, München 1979. (Conversion tables in an appendix.)

[2] International Union of Pure and Applied Chemistry, Manual of Symbols and Terminology for Physicochemical Quantities and Units, Pergamon, London 1979; Pure Appl. Chem. **51** [1979] 1/41.

[3] The International System of Units (SI), National Bureau of Standards Specl. Publ. 330 [1972].

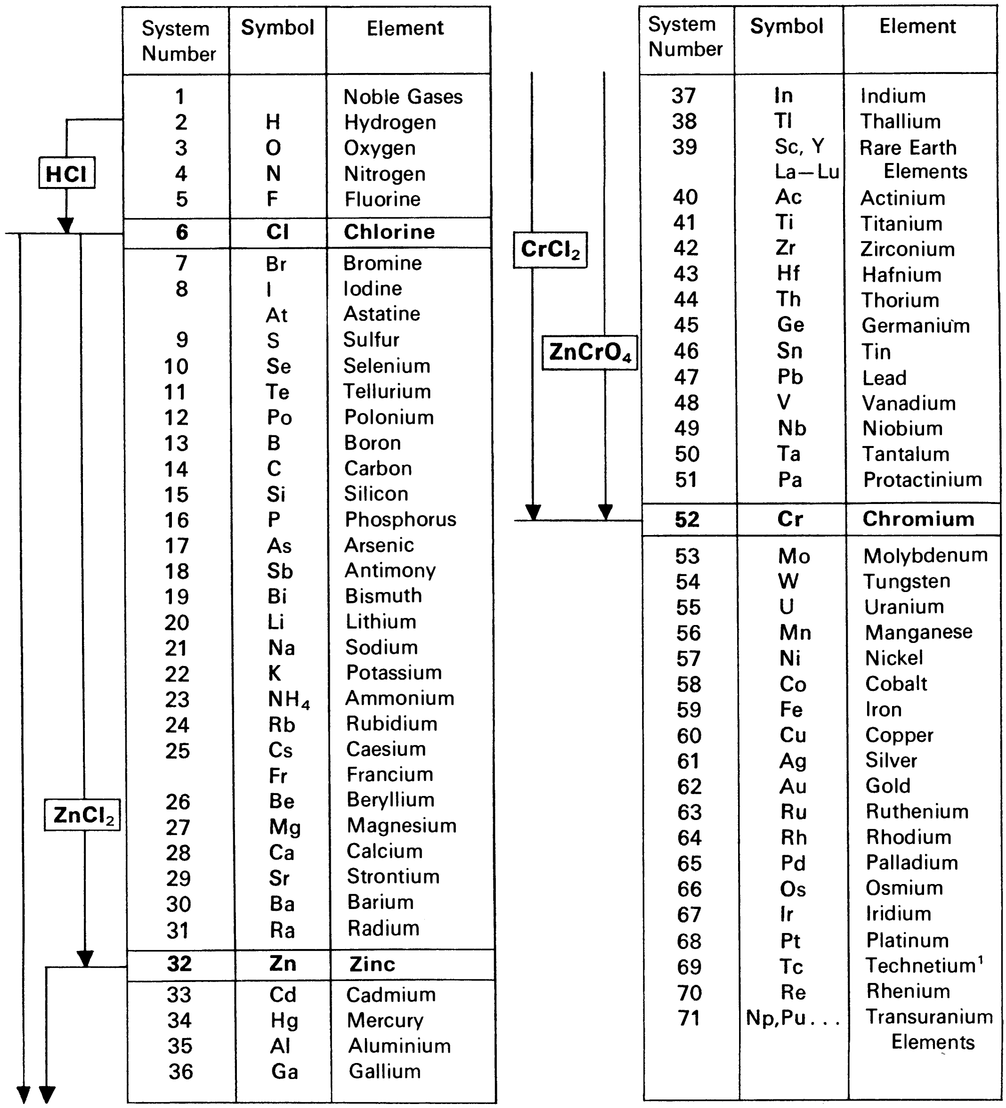
[4] H. Ebert, Physikalisches Taschenbuch, 5th Ed., Vieweg, Wiesbaden 1976.

[5] Kraftwerk Union Information, Technical and Economic Data on Power Engineering, Mülheim/Ruhr 1978.

[6] E. Padelt, H. Laporte, Einheiten und Größenarten der Naturwissenschaften, 3rd Ed., VEB Fachbuchverlag, Leipzig 1976.

[7] Landolt-Börnstein, 6th Ed., Vol. II, Pt. 1, 1971, pp. 1/14.

Key to the Gmelin System of Elements and Compounds



System Number	Symbol	Element
1		Noble Gases
2	H	Hydrogen
3	O	Oxygen
4	N	Nitrogen
5	F	Fluorine
6	**Cl**	**Chlorine**
7	Br	Bromine
8	I	Iodine
	At	Astatine
9	S	Sulfur
10	Se	Selenium
11	Te	Tellurium
12	Po	Polonium
13	B	Boron
14	C	Carbon
15	Si	Silicon
16	P	Phosphorus
17	As	Arsenic
18	Sb	Antimony
19	Bi	Bismuth
20	Li	Lithium
21	Na	Sodium
22	K	Potassium
23	NH_4	Ammonium
24	Rb	Rubidium
25	Cs	Caesium
	Fr	Francium
26	Be	Beryllium
27	Mg	Magnesium
28	Ca	Calcium
29	Sr	Strontium
30	Ba	Barium
31	Ra	Radium
32	**Zn**	**Zinc**
33	Cd	Cadmium
34	Hg	Mercury
35	Al	Aluminium
36	Ga	Gallium

System Number	Symbol	Element
37	In	Indium
38	Tl	Thallium
39	Sc, Y La–Lu	Rare Earth Elements
40	Ac	Actinium
41	Ti	Titanium
42	Zr	Zirconium
43	Hf	Hafnium
44	Th	Thorium
45	Ge	Germanium
46	Sn	Tin
47	Pb	Lead
48	V	Vanadium
49	Nb	Niobium
50	Ta	Tantalum
51	Pa	Protactinium
52	**Cr**	**Chromium**
53	Mo	Molybdenum
54	W	Tungsten
55	U	Uranium
56	Mn	Manganese
57	Ni	Nickel
58	Co	Cobalt
59	Fe	Iron
60	Cu	Copper
61	Ag	Silver
62	Au	Gold
63	Ru	Ruthenium
64	Rh	Rhodium
65	Pd	Palladium
66	Os	Osmium
67	Ir	Iridium
68	Pt	Platinum
69	Tc	Technetium[1]
70	Re	Rhenium
71	Np, Pu...	Transuranium Elements

Material presented under each Gmelin System Number includes all information concerning the element(s) listed for that number plus the compounds with elements of lower System Number.

For example, zinc (System Number 32) as well as all zinc compounds with elements numbered from 1 to 31 are classified under number 32.

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[1] A Gmelin volume titled "Masurium" was published with this System Number in 1941.

A Periodic Table of the Elements with the Gmelin System Numbers is given on the Inside Front Cover