so small that this mechanism for tetrahalide formation is unlikely. It may well contribute to the formation of the tetrahalide initially present in SnX_2 samples, especially if the dihalide has been in contact with moist air for any length of time.

It is more likely that the dihalide disproportionates to form the tetrahalide and metallic tin. The reverse reaction occurs starting at about 520 K although it is inhibited by the production of a surface layer of $SnCl_2$ on the metal.[2]

We initially thought that we had attained equilibria for the reaction $2SnX_2(g) \rightleftarrows SnX_4(g) + Sn(l)$, and by measuring the variation of the appropriate ratios we obtained a ΔH for this reaction for both halides that agreed well with values calculated from the somewhat scanty data in the literature. We now believe that the "equilibria" we studied, certainly for the chloride, less certainly for the bromide, were due to some effect other than this reaction and that the numerical agreement was coincidental. Obviously great care must be exercised in interpreting what appear to be equilibria in this type of Knudsen cell.

Registry No. $SnCl_2$, 7772-99-8; $SnBr_2$, 10031-24-0.

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Iron Carbonyl Complexes of Some Perfluoromethyl-Substituted Polyphosphines

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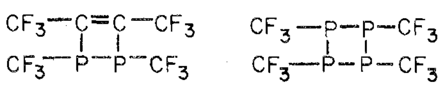
The purpose of the present note is to report the isolation of iron carbonyl complexes of the polyphosphine ligands 1,2,3,4-tetrakis(trifluoromethyl)-1,2-diphosphacyclobut-3-ene, **1**, and 1,2,3,4-tetrakis(trifluoromethyl)cyclotetraphosphine, **2**. The use of **1** as a ligand was suggested by its ob-



1 **2**

vious structural analogy to 1,2-bis(trifluoromethyl)dithietene, a compound which has yielded a variety of novel products by reaction with metal carbonyls.[2]

Alkyl and aryl cognates of **2** have elicited recent attention on account of their potentially varied coordination chemistry. At the present time three general categories of ligand behavior have been recognized, *viz.*, mono-, di-, and tridentate coordination of an intact cyclopolyphosphine ring,[3] coordination with ring cleavage,[3] and coordination with concomitant ring expansion.[4] However, very little attention has been devoted to the possibility of employing the perfluoroalkyl-substituted cyclopolyphosphines as ligands. In fact, the only previous report[5] in this area describes the reaction of **2** with $Ni(CO)_4$ which results in a presumably polymeric species of empirical composition $[Ni_{1.77}(CO)_{4.45}(PCF_3)_4]_n$.

Table I. Higher Mass Peaks in the Mass Spectra of Polyphosphine–Iron Carbonyl Complexes

m/e	Rel abund, %	Tentative assignment[a]
	$(CF_3)_2P_2C_2(CF_3)_2Fe(CO)_4$, **3**	
530	19.0	$(CF_3)_4P_2C_2Fe(CO)_4^+$
502	7.4	$(CF_3)_4P_2C_2Fe(CO)_3^+$
483	1.6	$(CF_3)_3(CF_2)P_2C_2Fe(CO)_3^+$
474	8.3	$(CF_3)_4P_2C_2Fe(CO)_2^+$
455	3.3	$(CF_3)_3(CF_2)P_2C_2Fe(CO)_2^+$
446	10.7	$(CF_3)_4P_2C_2Fe(CO)^+$
427	2.9	$(CF_3)_3(CF_2)P_2C_2Fe(CO)^+$
418	7.4	$(CF_3)_4P_2C_2Fe^+$
	$(CF_3)_2P_2C_2(CF_3)_2Fe_3(CO)_{10}$, **4**	
810	2.6	$(CF_3)_4P_2C_2Fe_3(CO)_{10}^+$
782	3.9	$(CF_3)_4P_2C_2Fe_3(CO)_9^+$
763	0.2	$(CF_3)_3(CF_2)P_2C_2Fe_3(CO)_9^+$
754	1.3	$(CF_3)_4P_2C_2Fe_3(CO)_8^+$
735	0.8	$(CF_3)_3(CF_2)P_2C_2Fe_3(CO)_8^+$
726	5.4	$(CF_3)_4P_2C_2Fe_3(CO)_7^+$
707	0.5	$(CF_3)_3(CF_2)P_2C_2Fe_3(CO)_7^+$
698	7.5	$(CF_3)_4P_2C_2Fe_3(CO)_6^+$
679	1.9	$(CF_3)_3(CF_2)Fe_3(CO)_6^+$
	$(CF_3P)_4Fe_2(CO)_6$, **5**	
680	54.9	$(CF_3P)_4Fe_2(CO)_6^+$
661	0.9	$(CF_3)_3(CF_2)P_4Fe_2(CO)_6^+$
652	28.2	$(CF_3P)_4Fe_2(CO)_5^+$
633	5.6	$(CF_3)_3(CF_2)P_4Fe_2(CO)_5^+$
624	15.0	$(CF_3P)_4Fe_2(CO)_4^+$
611	9.4	$(CF_3)_3P_4Fe_2(CO)_6^+$
605	1.4	$(CF_3)_3(CF_2)P_4Fe_2(CO)_4^+$
596	20.7	$(CF_3P)_4Fe_2(CO)_3^+$
583	0.5	$(CF_3)_3P_4Fe_2(CO)_5^+$
577	1.4	$(CF_3)_3(CF_2)P_4Fe_2(CO)_3^+$
568	0.2	$(CF_3P)_4Fe_2(CO)_2^+$
555	0.6	$(CF_3)_3P_4Fe_2(CO)_4^+$
549	0.5	$(CF_3)_3(CF_2)Fe_2(CO)_2^+$
540	3.3	$(CF_3P)_4Fe_2(CO)^+$
527	0.9	$(CF_3)_3P_4Fe_2(CO)_3^+$
512	15.0	$(CF_3P)_4Fe_2^+$

[a] The assignment of the parent peak was confirmed by high-resolution data in each case.

Experimental Section

Materials. The ligands $(CF_3)_2P_2C_2(CF_3)_2$,[6] **1**, and $(CF_3P)_4$,[7] **2**, were prepared and purified according to the literature methods. Diiron enneacarbonyl was procured commercially and used without subsequent purification. Olefin-free *n*-hexane was prepared by stirring the technical grade material with concentrated H_2SO_4. After decantation from the H_2SO_4 the *n*-hexane was dried by distillation from CaH_2. Reagent grade benzene was distilled from CaH_2 and stored over Linde 4A molecular sieves.

Mass Spectra. Low-resolution mass spectra were determined on a Du Pont-Consolidated Electrodynamics Corp. Model 21-491 spectrometer operating at an ionizing voltage of 70 eV. High-resolution spectra were measured on a Du Pont-Consolidated Electrodynamics Corp. Model 21-110 spectrometer operating at an ionizing voltage of 70 eV. Peak matching was accomplished by employing the appropriate perfluoroalkane fragmentation peaks.

Nmr Spectra. Proton spectra were determined on a Varian Associates A-60 or Perkin-Elmer R-12 spectrometer operating at a frequency of 60 MHz. ^{19}F spectra were measured on a Varian Associates HA-100 or a Perkin-Elmer R-12 instrument operating at spectrometer frequencies of 94.1 and 56.4 MHz, respectively. All ^{19}F

(1) To whom correspondence should be addressed.

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Table II. Some Spectroscopic Properties of Polyphosphine–Iron Carbonyl Complexes

Nmr δ_F,[a] ppm	Nmr δ_P,[b] ppm	Nmr J, Hz	Nmr Remarks[c]	Ir, ν_{CO}, cm^{-1}	Uv, λ_{max}, Å
			$(CF_3)_2P_2C_2(CF_3)_2Fe(CO)_4$, **3**		
−14.22		J_{PCF}, 62.6; J_{PPCF}, 13.5	d of d; CF_3(P) res	2015, 2025, 2099	1970, 2410
−2.80		J_{PCF}, 68.9; J_{PPCF}, 18.8	d of d; CF_3(P) res		
−1.34			s; CF_3(C) res		
0.0			s; CF_3(C) res		
	−45	J_{PCF}, 65	q		
	+17	J_{PCF}, 69	q		
			$(CF_3)_2P_2C_2(CF_3)_2Fe_3(CO)_{10}$, **4**		
−7.5			$X_3AA'X'_3$ type pattern; CF_3(P) res	1995, 2025, 2060, 2075, 2120	2700, 3850, 4900
−2.3			s; CF_3(C) res		
			$(CF_3P)_4Fe_2(CO)_6$, **5**		
−20.00			"Deceptively simple" t[d]	2005, 2035, 2060, 2095	2550, 3300, 3800
−18.20			"Deceptively simple" d[d]		

[a] Relative to external α,α,α-trifluorotoluene. [b] Relative to external 85% H_3PO_4. [c] Key: s, singlet; d, doublet; t, triplet; q, quartet. [d] R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, 39, 216 (1961); R. K. Harris, *ibid.*, **42**, 2275 (1964).

chemical shifts are referenced with respect to external α,α,α-trifluorotoluene. The ^{31}P spectra were run on a Varian Associates HA-100 spectrometer at a frequency of 40.1 MHz. ^{31}P chemical shifts are externally referenced to 85% H_3PO_4.

Infrared Spectra. All ir spectra were measured on a Perkin-Elmer Model 337 grating spectrophotometer. Vapor samples were run in a 100-mm path length cell with KBr windows, oils were run as liquid films between KBr plates, and solids were run as Nujol mulls or KBr pellets.

Ultraviolet Spectra. All uv spectra were measured on a Cary Model 14 spectrophotometer in a quartz cell of 1-cm path length.

Reaction of $(CF_3)_2P_2C_2(CF_3)_2$ with $Fe_2(CO)_9$. In a typical reaction **1** (0.339 g, 0.936 mmol) was condensed *in vacuo* onto a slurry of $Fe_2(CO)_9$ (0.344 g, 0.945 mmol) and 10 ml of dry benzene at −196°. An atmosphere of argon was introduced as the flask warmed up and the mixture was stirred for ~16 hr at ambient temperature. The volatiles were then transferred to the vacuum line and separated by fractional condensation. Compound **3** (85 mg, 0.160 mmol) condensed in the 0° trap as a golden orange oil. *Anal.* Calcd for $(CF_3)_2C_2P_2(CF_3)_2Fe(CO)_4$: C, 22.67; P, 11.69. Found: C, 21.82; P, 12.20. The high-resolution mass spectrum of **3** exhibited a parent peak at 529.841 (calcd 529.843).

The nonvolatile material was chromatographed on a Florisil column using *n*-hexane as the eluent. Removal of the *n*-hexane from the reddish brown band afforded 72 mg (0.89 mmol) of **4**. *Anal.* Calcd for $(CF_3)_2C_2P_2(CF_3)_2Fe_3(CO)_{10}$: C, 23.74; P, 7.65. Found: C, 23.29; P, 8.20. The high-resolution mass spectrum of **4** displayed a parent peak at 809.683 (calcd 809.682). Some low-resolution mass spectroscopic data for **3** and **4** are presented in Table I. Additional spectroscopic data pertaining to compounds **3** and **4** are summarized in Table II.

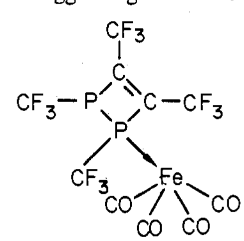
Reaction of $(CF_3)_2C_2P_2(CF_3)_2Fe(CO)_4$, 3, with $Fe_2(CO)_9$. The monoiron complex, $(CF_3)_2C_2P_2(CF_3)_2Fe(CO)_4$ (0.16 g, 0.30 mmol), and 10 ml of benzene were transferred *in vacuo* onto a slurry of $Fe_2(CO)_9$ (0.2136 g, 0.59 mmol) and benzene (8 ml) at −196°. The reaction mixture was warmed slowly to room temperature, placed under an argon atmosphere, and stirred for approximately 16 hr. The benzene was then stripped from the reaction mixture following removal of the unreacted $Fe_2(CO)_9$ by filtration through Celite. Chromatography of the nonvolatile material on a Florisil column using *n*-hexane as the eluant afforded 40.3 mg (0.049 mmol) of $(CF_3)_2P_2C_2(CF_3)_2Fe_3(CO)_{10}$, **4**. The triiron complex **4** was identified on the basis of its spectroscopic properties (*vide supra* and Table II).

Reaction of $(CF_3P)_4$ with $Fe_2(CO)_9$. The cyclotetraphosphine, **2** (0.52 g, 1.30 mmol), was treated with 0.95 g (2.61 mmol) of $Fe_2(CO)_9$ in 30 ml of benzene for approximately 14 hr using the procedure which was described in the foregoing experiments. The resulting reaction mixture was filtered in order to eliminate unreacted $Fe_2(CO)_9$ and chromatographed on a Florisil column using *n*-hexane as the eluent. Removal of the solvent from the reddish orange band afforded 0.24 g (0.35 mmol) golden yellow crystalline $(CF_3P)_4Fe_2(CO)_6$, **5**, which was recrystallized from benzene; mp 140° dec. *Anal.* Calcd for $(CF_3P)_4Fe_2(CO)_6$: C, 17.67; P, 18.23. Found: C, 17.90; P, 17.99. The high-resolution mass spectrum of **5** exhibited a parent peak at 679.716 (calcd 679.715). Some other spectroscopic properties of **5** are presented in Tables I and II.

Results and Discussion

The reaction of the diphosphacyclobutene ligand, $(CF_3)_2P_2C_2(CF_3)_2$, **1**, with $Fe_2(CO)_9$ yields polyphosphine–iron complexes of composition $(CF_3)_2P_2C_2(CF_3)_2Fe(CO)_4$, **3**, and $(CF_3)_2P_2C_2(CF_3)_2Fe_3(CO)_{10}$, **4**. In a separate experiment it was established that **4** is produced by the reaction of **3** with $Fe_2(CO)_9$. The above formulations for **3** and **4** are based on analytical and mass spectroscopic data. Compounds **3** and **4** exhibit parent peaks at 529.841 (calcd 529.843) and 809.683 (calcd 809.682) in their high-resolution mass spectra. The foregoing, together with the presence of the anticipated fragments in the low-resolution mass spectra of **3** and **4** (Table I), leaves little doubt about their composition.

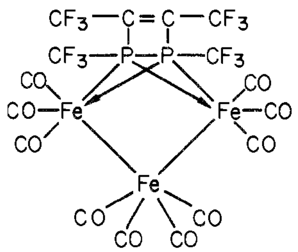
As indicated in Table II the ^{19}F nmr spectrum of the CF_3(P) groups of **3** consists of two doublets of doublets, one centered at −2.80 ppm and the other at −14.22 ppm. The implied nonequivalence of the phosphorus atoms is confirmed by the following additional facts: (a) two ^{31}P resonances of equal intensity are detected at +17 and −45 ppm and (b) two CF_3(C) ^{19}F singlet resonances are observed at 0 and −1.11 ppm. The nmr data therefore indicate that only one phosphorus atom of the diphosphacyclobutene moiety is coordinated, thus suggesting the structure shown for **3**.



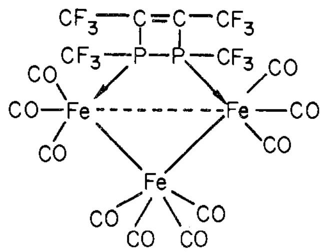
3

The presence of the diphosphacyclobutene ring is indicated (but not unequivocally established) by the fact that the electronic spectrum of **3** (Table II) is similar to that of free **1**.[6] The above structure is also consonant with the facile ambient temperature decomposition of **3** to yield free **1**.

The ^{19}F nmr spectrum of **4** consists of an $X_3AA'X'_3$ CF_3(P) resonance centered at −7.5 ppm. The CF_3(C) groups are also chemical shift equivalent since only one resonance is observed (−2.3 ppm). The ir spectrum of **4** indicates that there are no bridging carbonyl groups; hence the most reasonable structure is **4a**. However, it would also be possible to formulate the complex with a closed bidentate diphosphacyclobu-



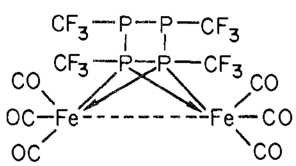
4a



4b

tene ring and an iron–iron bond as indicated in **4b**. The electronic spectrum of **4** (Table II) displays pronounced shifts compared with free **1**;[6] however, this evidence *per se* is not sufficient to establish the scission of the P–P bond. On the basis of these initial observations it would appear that the ligand behavior of **1** is quite different from that of 1,2-bis-(trifluoromethyl)dithietene since there are no sulfur analogs of **3** or **4**.[2] Compound **4** is also noteworthy from the standpoint that all previously reported $Fe_3(CO)_{10}$ complexes involve bridging CO groups.[8]

The reaction of the cyclotetraphosphine, $(CF_3P)_4$, with $Fe_2(CO)_9$ results in a product of empirical composition $(CF_3P)_2Fe(CO)_3$. If the intense mass spectral peak at *m/e* 680 (Table I) is assigned to the parent ion, the molecular formula of **5** is $(CF_3P)_4Fe_2(CO)_6$. The *m/e* 680 peak is considered to be the parent peak because West, *et al.*,[3,9] have demonstrated that several other compounds of the general type $(RM)_4Fe_2(CO)_6$ (M = P, As; R = alkyl, aryl) exhibit intense molecular ion peaks. The correctness of these mass spectral assignments was confirmed by a subsequent X-ray crystallographic study[10] of $(CH_3As)_4Fe_2(CO)_6$. One additional mass spectral feature which **5** shares in common with other $(RM)_4Fe_2(CO)_6$ compounds[3,9] is a fragment corresponding to the species $(RM)_4Fe_2^+$. Furthermore, like the compounds reported by West, *et al.*,[3,9] **5** exhibits four intense ir bands in the C–O stretching region. The latter observation appears to be a characteristic feature of phosphido and arsenido bridging[11] and may be due to coupling between the two $Fe(CO)_3$ groups. By analogy with the bis(arsenido)-bridged structure of $(CH_3As)_4Fe_2(CO)_6$ the most reasonable structure for **5** is



5

The above structure is also consistent with the fact that two equally intense resonances are observed in the ^{19}F nmr spectrum of **5**. The "deceptively simple" appearance[12] of these resonances is due to the second-order nature of the nuclear spin coupling within the $(CF_3P)_4$ moiety.

Registry No. $Fe_2(CO)_9$, 15321-51-4; $(CF_3)_2C_2P_2(CF_3)_2Fe(CO)_4$, 39262-37-8; $(CF_3)_2C_2P_2(CF_3)_2Fe_3(CO)_{10}$, 39153-36-1; $(CF_3P)_4Fe_2(CO)_6$, 39153-37-2.

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Displacement of Diborane from Pentaborane(9) by Strong Molecular Bases

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Received November 15, 1972

It has been demonstrated that the weak base dimethyl sulfide can act upon B_5H_9 to displace a BH_3 group as diborane or $(CH_3)_2SBH_3$.[1] It appeared that the driving force of the reaction was the attachment of $(CH_3)_2S$ to the remarkably strong Lewis acid B_4H_6 (through cleavage of two B–H–B bridges to remove one BH_3 from B_5H_9); then the resulting $(CH_3)_2S$-B_4H_6 complex would rapidly convert to unintelligible resins. The reaction thus was related to earlier work on the action of $(CH_3)_2NBH_2$ upon B_5H_9, whereby the displaced BH_3 group appeared as $(CH_3)_2NB_2H_5$.[2] More generally, it was assumed that any strong molecular base would capture each BH_3 group as soon as it was free, so that proof of the initial displacement of BH_3 from B_5H_9 would be more difficult than in the dimethyl sulfide case.

It now is found, however, that the relatively strong bases ammonia and methylamine, reacting with B_5H_9 during sudden heating at 160–180°, can displace as much as 0.25 B_2H_6 per B_5H_9 consumed. Thus we have interesting reactions in which strong bases act to liberate the strong Lewis acid diborane; that is, bases strong enough for irreversible attachment to BH_3 actually liberate this Lewis acid by action upon B_5H_9.

The final volatile products of these reactions included the borazine $(HNBH)_3$ or $(CH_3NBH)_3$ and the unstable μ-aminodiborane $H_2NB_2H_5$ or $CH_3NHB_2H_5$.[3,4] Thus steps such as the following may be suggested for all such reactions

$$n\mathrm{NH_3} + \mathrm{B_5H_9} \rightarrow \mathrm{BH_3} + \mathrm{B_4H_6}\cdot n\mathrm{NH_3} \rightarrow \text{resins} + \mathrm{H_2} \quad (1)$$

$$\mathrm{NH_3} + \mathrm{BH_3} \rightarrow \mathrm{H_3NBH_3} \rightarrow \mathrm{H_2} + \mathrm{H_2NBH_2} \quad (2)$$

$$\mathrm{H_2NBH_2} + \mathrm{BH_3} \rightarrow \mathrm{H_2NB_2H_5} \quad (3)$$

$$6\mathrm{H_2NB_2H_5} \rightarrow 3\mathrm{B_2H_6} + 2(\mathrm{H_2NBH_2})_3 \quad (4)$$

$$3(\mathrm{H_2NBH_2})_3 \rightarrow 3\mathrm{H_2} + (\mathrm{HNBH})_3 \quad (5)$$

Steps 1–3 would be fast and irreversible, leading to products known to be unstable in the sense of steps 4 and 5. On the assumption that these are the only processes which occur and that step 4 is complete, one would predict the formation of 0.25 B_2H_6 per B_5H_9 consumed, in good agreement with the results for the ammonia reaction. For methylamine, however, step 4 is far from complete (because the μ-aminodiborane is more stable), but the yield of diborane still can

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