Table I. Appearance Potential Data (in eV) for the Positive Ions Formed by PF_2CN

Ion (X^+)	$A(X^+)$	Ion (X^+)	$A(X^+)$
PF_2CN^+	11.7 ± 0.2	PF^+	19.1 ± 0.2
$PFCN^+$	15.7 ± 0.2	CN^+	19.8 ± 0.3
PF_2^+	13.4 ± 0.2		

be 15.4 ± 0.1 eV. Since $D(\text{P-F}) = 4.5 \pm 0.1$ eV;[7,8] hence $D(PF_2\text{-F}) + D(\text{PF-F}) = 10.9 \pm 0.2$ eV. If we assume both bonds to have similar energies, then $D(PF_2\text{-F}) = 5.4 \pm 0.1$ eV, and since $D(PF_2\text{-F}) \leqslant A(PF_2^+) - I(PF_2)$, we may estimate that $I(PF_2) \leqslant 10.0 \pm 0.3$ eV. Substitution of this value for $I(PF_2)$ in $D(PF_2\text{-CN}) \leqslant A(PF_2^+) - I(PF_2)$ leads to a value of $\leqslant 3.4 \pm 0.5$ eV for $D(PF_2\text{-CN})$. No other value has been reported for this bond dissociation energy from which the heat of formation of the fluorocyanide molecule may be calculated to be $\sim -4.1 \pm 0.6$ eV.

(ii) CN^+

$$PF_2CN + e \rightarrow CN^+ + PF_2 + 2e \tag{2}$$

If the absence of excess energy in reactions 1 and 2 is assumed, then

$$A(PF_2^+) - I(PF_2) = A(CN^+) - I(CN) \tag{I}$$

From expression I a value of 16.4 ± 0.7 eV may be obtained for the ionization potential of the cyanide radical. This is in poor agreement with the reported value of 14.03 eV.[9] Application of Stevenson's rule[10] to reactions 1 and 2 would however suggest that the CN^+ ion is produced with excess kinetic energy and so expression I is invalid.

(2) Negative Ion Formation. The principal negative ions observed at 70 eV are PF_2CN^- (6.4), PF_2^- (10), FCN^- (1), F_2^- (1), CN^- (1000), and F^- (47); their relative intensities are shown in parentheses. The presence of F_2^- and FCN^- in the mass spectrum indicates the occurrence of rearrangement reactions, the ions presumably being formed by F atom migration.

In common with the formation of several ions in the PF_3 system[11] it was found that at relatively low electron energies the F^-, CN^-, FCN^-, and PF_2^- resonances at ~4 eV exhibited a vertical rise to their maximum cross section at threshold. This was shown by comparison of the ionization efficiency curves for these ions with that for O^--CO which is known[12] to exhibit the vertical onset effect. This result is interpreted to indicate that ion formation at this energy is due to the multichannel decay of an unstable excited state of the parent ion, *i.e.*

$$PF_2CN + e \rightarrow [PF_2CN^{-*}] \rightarrow PF_2^-, CN^-, \text{etc.}$$

A similar explanation has been advanced to account for ion formation in perfluoroolefins.[13]

(i) CN^-. This ion was formed abundantly particularly at ~0 eV. The major resonance peak onsets at 0.0 ± 0.1 eV; minor resonances were observed at 4.6 ± 0.1, 5.9 ± 0.2, and ~9 eV which have cross sections of 0.15, 0.07, and 0.10, respectively, relative to that of the initial resonance. The formation of CN^- is *via*

$$PF_2CN + e \rightarrow CN^- + PF_2 \tag{3}$$

$D(PF_2\text{-CN}) \leqslant A(CN^-) + E(CN)$, where $E(CN)$ is the electron affinity of the nitrile radical. Since $A(CN^-) = 0.0 \pm 0.1$ eV, then $D(PF_2\text{-CN}) \leqslant E(CN)$. A recent value of 3.8 ± 0.05 eV has been reported[9] for $E(CN)$, suggesting that $D(PF_2\text{-CN}) \leqslant 3.8 \pm 0.05$ eV. This bond strength is in reasonable accord with the value of $\leqslant 3.4 \pm 0.05$ eV deduced above in the positive ion study of the fluorocyanide.

(ii) PF_2^-

$$PF_2CN + e \rightarrow PF_2^- + CN \tag{4}$$

$A(PF_2^-) = 4.6 \pm 0.1$ eV. The minimum enthalpy requirement for reaction 4 is $3.4 \pm 0.5 \text{ eV} - E(PF_2)$; since no ions are formed below 4.6 eV, clearly there is at least 1.2 eV of excess kinetic and/or excitation energy associated with reaction 4. We cannot attribute the reaction energy more specifically since we know of no reported value for the electron affinity of PF_2.

(3) Thermochemical Data. The following values for the heats of formation (in eV) at 298°K have been used in this paper: F, 0.8; P, 3.3; PF_2, −5.1 ± 0.1 (calculated from $D(PF_2\text{-F}) = 5.4 \pm 0.1$ eV); PF_3, −9.7; CN, 4.4.[14] Except where indicated all values have been taken from ref 15.

Registry No. PF_2Br, 15597-40-7; AgCN, 506-64-9; PF_2CN, 14118-40-2.

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Vaporization of Tin(II) Halides. I. Stannous Chloride and Stannous Bromide

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As part of a study of the reactions of tin halides with gases it was necessary to determine the composition of the gas in equilibrium with the molten salt. Brewer[2] has suggested on the basis of radius-ratio considerations that the dihalides of germanium and tin could be expected to dimerize in the gas phase. Vapor density measurements on stannous halides made without identifying the vapor species[3,4] show that at pressures in the 20–600 Torr range (1 Torr = 133.3 N m^{-2}) the number of molecules in the gas phase decreases and this effect has always been interpreted as a dimerization. Uy, *et al.*,[5] established that at the pressures used in Knudsen cell

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(1) (a) University of Melbourne. (b) CSIRO.

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studies, *ca.* 0.1 Torr, no association of $GeCl_2$ or $GeBr_2$ occurs up to 1000 K, although in the same apparatus they could observe polymers $(GeF_2)_n$ with n ranging from 1 to 4.

We have examined the vapor of $SnCl_2$ and $SnBr_2$ emerging from a Knudsen cell by a mass spectrometric method to gain more detailed knowledge of the reactions occurring. Tetrahalides were always observed in such systems and their formation will be discussed. The vapor over an $SnCl_2$-$SnBr_2$ mixture was also examined to see whether SnClBr was formed as in the analogous reaction of mixed lead halides.[6] Existing measurements of the vapor pressure[7-9] of these halides date from 1929-1939 and were made without a detailed knowledge of the constituents of the vapor phase over these salts.

Experimental Section

Initial measurements were made with the apparatus described previously,[10,11] a silica-lined Knudsen cell which discharged into a quadrupole mass filter. Some later measurements were made with an ion-focusing plate inserted between the ion source and the entrance aperture of the mass filter. This modification increased the sensitivity of the system. For some measurements on the $SnCl_2$ system an RF-DC generator (EA1 Model No. 969) replaced the homemade generator. This gave better resolution but did not have a wide enough mass range to be used for the bromide experiments.

The salts used were Hopkins & Williams $SnCl_2$ anhydrous and Alfa Inorganics $SnBr_2$ anhydrous. At first the salts were purified by heating at *ca.* 480°K under dynamic vacuum in the Knudsen cell for several hours. It was found that tetrahalides could not be completely removed by this procedure. For later measurements the salts were melted in a silica tube under dynamic vacuum and sublimed several times along the tube. Dry nitrogen was then admitted to the tube and the solid transferred to the Knudsen cell as quickly as possible.

For the pure salts, mass spectra were measured with 70-V electrons and corrections were made (never more than 5%) to the SnX_2^+ ion current due to dissociative ionization of any SnX_4 present. The mass spectra used for correction were of pure samples of SnX_4 measured in the same apparatus. For a 1:1 $SnCl_2$-$SnBr_2$ mixture, the 70-V mass spectrum was so complex that measurements were made with 20-V electrons to obtain a simpler spectrum. It was assumed that any correction to the SnX_2^+ current due to the dissociation of higher molecular weight ions could be neglected. The ion chamber temperature was 390 K. Knudsen cell temperatures were measured by a thermocouple calibrated at the boiling point of water and the melting points of lead and tin. Clapeyron plots were treated by the method of least squares. Confidence limits (95%) on ΔH determined by a single run were ±2 kcal mol^{-1} (1 kcal mol^{-1} = 4.184 kJ mol^{-1}), but replicate runs scattered more widely than this so that the overall deviation was about ±3 kcal mol^{-1}.

Results

$SnCl_2$. In the temperature range 400-600 K no ions containing two atoms of tin were detected (detection limit approximately 0.1% of the ion current due to $SnCl_2^+$). Even if the $Sn_2Cl_4^+$ ion were too unstable to be detected it would be expected that its major fragment would be $Sn_2Cl_3^+$ (*cf.* the fragmentation of Al_2Cl_6,[12] K_2Cl_2,[13] and most halides). Thus the evidence is strong that no significant amount of dimeric species is present in the gas phase at these temperatures at the Knudsen cell pressures (about 0.1 Torr).

When samples of $SnCl_2$ were heated in the Knudsen cell, quantities of $SnCl_4$ were evolved, but evolution ceased after a few hours of pumping at 450 K. The time taken to remove the $SnCl_4$ varied considerably with different stock samples of $SnCl_2$. After this treatment no further $SnCl_4$ was observed until 530 K above which a constant ion current due to $SnCl_4^+$ could be established at any given temperature; these ion currents were of the order of 10-20% of those due to $SnCl_2^+$. Andrews and Frederick[14] also found $SnCl_4$ initially present in a sample of $SnCl_2$ but claimed it could be removed by prolonged pumping at 463 K. They did not state the limiting amount of $SnCl_4$ that could be detected by their infrared technique.

It was first believed that this represented a true equilibrium of the disproportionation reaction $2SnCl_2 \rightleftarrows SnCl_4 + Sn$. However, the pressure of $SnCl_4$ is far higher than that calculated from the equilibrium constant.[15,16] Further examination revealed that different samples of $SnCl_2$ gave different pressures of $SnCl_4$ and that $SnCl_2$ purified by sublimation gave no indication of $SnCl_4$ until it was melted. However, it was never possible to eliminate $SnCl_4^+$ ion current from the $SnCl_2$ sample at temperatures above 530 K. These currents were about 1% of the current due to $SnCl_2^+$ and not sufficiently reproducible to study their variation with temperature.

It would seem that a minor reaction occurs producing $SnCl_4$ and probably Sn since a gray metallic film was always observed both on the Knudsen cell liner and the sublimation tube. Such a reaction could give an apparent false equilibrium if its rate was small enough to be comparable with the effusion rate through the Knudsen orifice. It was also observed that the ion $SnOCl_2^+$ was present over $SnCl_2$ and that purification by sublimation greatly reduced the amount but never entirely removed it.

We write the ion current of a given species X as $I(X^+)$, and it is assumed throughout this work that ionization cross sections are constant over the temperature intervals measured. Then from the slope of a plot of $\log [I(SnCl_2^+)T]$ against $1/T$, a value for the heat of sublimation of $SnCl_2$, $\Delta H_{subl}(SnCl_2(s))$, or the heat of vaporization, $\Delta H_{vap}(SnCl_2(l))$, can be obtained. For the salt purified by pumping only, an average of three determinations gave $\Delta H_{vap}(SnCl_2(l)) = 20.9 \pm 3$ kcal mol^{-1} (536-569 K). This was corrected to the melting point ($\Delta C_p(l \rightarrow g)$ assumed[17] equal to -10 cal K^{-1} mol^{-1}) to give $\Delta H_{vap,520}(SnCl_2(l)) = 21.2 \pm 3$ kcal mol^{-1}. For the salt purified by sublimation we measured $\Delta H_{subl}(SnCl_2(s)) = 26.6 \pm 3$ kcal mol^{-1} and corrected assuming $\Delta C_p(s \rightarrow v) = -5$ cal K^{-1} mol^{-1} to give $\Delta H_{subl,520}(SnCl_2(s)) = 26.4 \pm 3$ kcal mol^{-1}. These differ by 5.2 ± 4.2 kcal mol^{-1} which agrees within the error limits with the value of the latent heat of fusion,[18] 3.05 ± ? kcal mol^{-1} (this is an average of experimental determinations ranging in value from 2.4 to 3.4 kcal mol^{-1}). We prefer our sublimation value to our vaporization value and for consistency with the heat of fusion take $\Delta H_{vap,520} = 23 \pm 3$ kcal mol^{-1}.

It is difficult to assess the accuracy of earlier vapor pres-

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sure measurements on this salt which were made without detailed knowledge of the vapor phase. The small quantities of $SnCl_4$ we detected over the dihalides would not be expected to have a marked effect on the high-temperature measurements. When $\Delta H_{vap,520}$ is calculated by extrapolation from higher temperature measurements (Σ-plot method),[17] reasonably concordant values were obtained. For $\Delta H_{vap,520}(SnCl_2(l))$, Fischer, Gewehr, and Wingchen's[8] results give 22.7 ± 1 kcal mol^{-1}; those of Fischer and Gewehr[9] give 23.5 ± 1.4 kcal mol^{-1}; and those of Maier[7] give 22.9 ± 0.9 kcal mol^{-1};[18] these are all our calculations with $\Delta C_p = -10$ cal K^{-1} mol^{-1}. The errors are 95% confidence limits on individual runs. True limits are difficult to assess both because replicate runs are not given and because the value $\Delta C_p = -10$ cal K^{-1} mol^{-1} is only an estimate.[17] If values of -5 and -15 cal K^{-1} mol^{-1} are used, for example, on Fischer, Gewehr, and Wingchen's results, ΔH_{520} becomes 21.5 and 24.0 kcal mol^{-1}, respectively. None of the experimental results available is precise enough to discriminate between these ΔC_p values.

Kelley[17] recalculated Maier's[7] value as 24.5 kcal mol^{-1}; in his calculation he discarded the two points with the largest deviation from the mean line through all the points. Whatever value of ΔC_p within the range -5 to -15 cal K^{-1} mol^{-1} is chosen, all the high-temperature results fall within our estimated range 23 ± 3 kcal mol^{-1}. It does not seem advisable to specify this value any more closely.

$SnBr_2$. The behavior of $SnBr_2$ was similar to that of $SnCl_2$. No dimer ions were detected up to 600 K and the $SnBr_4$ impurity always present initially could be removed by presublimation. However, at temperatures above the melting point, $SnBr_4$ appeared again, giving ion currents about 1-5% of the dihalide ion and apparent equilibrium could be established.

$\Delta H_{vap}(SnBr_2(l))$ was found to be 25.4 ± 3 kcal mol^{-1} (545-597 K) and corrected to give $\Delta H_{vap,505}(SnBr_2(l)) =$ 26.1 ± 3 kcal mol^{-1} at its melting point. A Σ-plot of the results of Fischer and Gewehr[9] (our calculation, ΔC_p assumed -10 cal K^{-1} mol^{-1}) gives $\Delta H_{vap,505}(SnBr_2(l)) = 27.5$ ± 2 kcal mol^{-1}; and a similar calculation from Karpenko's results[5] gives $\Delta H_{vap,505}(SnBr_2(l)) = 27.0 \pm 3.9$ kcal mol^{-1}. We select a mean value $\Delta H_{vap,505}(SnBr_2(l)) = 27 \pm 3$ kcal mol^{-1}.

Below its melting point the vapor pressure of $SnBr_2(s)$ was too small for its variation with temperature to be determined.

1:1 $SnCl_2$-$SnBr_2$ Mixture. The mass spectrum of the vapor over this mixture was complicated and unfortunately the mass filter could not distinguish between pairs like $SnCl_2Br_2$ and $SnBr_3$ or between fragments containing one bromine instead of two chlorines. (For example, in $SnCl_2Br_2$ there are 18 isotopic species ranging in molecular weight from 340 to 360 while in $SnBr_3$ there are 17 ranging from 349 to 367.) Some identifications were made by measuring appearance potentials (AP) by the techniques previously described.[11] $SnClBr_3^+$ was found to have an AP of 11.1 ± 0.3 eV and $SnClBr^+$ one of 10.3 ± 0.3 eV. These values are close enough to the ionization energies of $SnBr_4$, 10.6 eV, and $SnBr_2$, 10.0 eV, measured in the same apparatus[19] to establish that the molecules $SnClBr_3$ and $SnClBr$ are present in the gas phase since fragmentation processes would require 1 or 2 V more energy. On the other hand, the $SnClBr_2^+$ ion observed with AP = 12.0 eV must be a fragment which could come from $SnClBr_3$ or $SnCl_2Br_2$ as the parent.

Table I. Enthalpy Changes for Measured Reactions (kcal mol^{-1})

Reaction	Lit.	This work	Preferred
$SnCl_2(s) \rightarrow SnCl_2(g)$		26.4 ± 3 (520)[f]	26.4 ± 3
$SnCl_2(l) \rightarrow SnCl_2(g)$	22.9,[a] 24.5,[b] 22.7,[c] 23.5[d]	21.2 ± 3 (520)	23 ± 3
$SnBr_2(l) \rightarrow SnBr_2(g)$	27.5,[d] 27.0[e]	26.1 ± 3 (505)	27 ± 3
$SnBr_2(l) \rightarrow SnBr_2(g)$ in 1:1 $SnCl_2$-$SnBr_2$ mixture		25 ± 3 (505)	
$SnClBr(l) \rightarrow SnClBr(g)$ in 1:1 $SnCl_2$-$SnBr_2$ mixture		20 ± 3 (572)	

[a] Reference 7, our calculation. [b] Reference 7, Kelley's calculation.[17] [c] Reference 8. [d] Reference 9. [e] Reference 5. [f] Figures in parentheses are mean temperatures in degrees Kelvin.

Molecular SnClBr is presumed to be formed by the exchange reaction $SnCl_2 + SnBr_2 \rightarrow 2SnClBr$. Beattie and Perry[20] have recently found Raman bands in the vapor over a molten $SnCl_2$-$SnBr_2$ mixture which do not belong to either of the individual molecules. They assigned them to SnClBr formed by the same reaction as we postulate here.

A Clapeyron plot for $SnBr_2$ in the halide mixture gave the partial molar heat of vaporization as 24 ± 3 kcal mol^{-1} (550-594 K). A similar plot gave the partial molar heat of vaporization of SnClBr over the same mixture as 20 ± 3 kcal mol^{-1} (550-594 K).

Discussion

A summary of the results obtained is given in Table I. Agreement is reasonable with other experimental results. Although the difference is close to the estimated errors, we consider our preferred values for $\Delta H_{vap,520}(SnCl_2(l)) = 23 \pm$ 3 kcal mol^{-1} and $\Delta H_{vap,505}(SnBr_2(l)) = 27 \pm 3$ kcal mol^{-1} are more reliable than the values selected by Feber in his compilations,[21,22] namely, for $SnCl_2$, 22.67 kcal mol^{-1} (1963) and 24.5 kcal mol^{-1} (1965) and for $SnBr_2$, 29.0 kcal mol^{-1} (1965). Feber used these values to calculate heats of sublimation at 298 K, his corrections amounting to +4.39 and +2.7 kcal mol^{-1}, respectively. It should be emphasized that these corrections involve estimates of unknown ΔC_p values, that the magnitude of the error in them is unknown, and that the ΔH_{vap} values are uncertain to ±3 kcal mol^{-1}. Quotation of these $\Delta H_{sub,298}$ values to the first place of decimals gives an unwarranted impression of their accuracy.

We have no information about the state of the liquid system in the Knudsen cell. It is assumed that liquid $SnCl_2$, liquid SnClBr, and liquid $SnBr_2$ form a homogeneous phase. From Table I, the difference between the heat of vaporization of $SnBr_2(l)$ and the partial molar heat of vaporization of $SnBr_2(l)$ from the salt mixture is 1.3 ± 4 kcal mol^{-1}. Within these limits, then, there is little interaction between the liquids; and similarly it seems likely that the partial molar heat of vaporization of SnClBr in this mixture is not very different from the heat of vaporization of the pure salt.

It has not been possible to establish clearly how the tetrahalides are formed. It is conceivable that they result from $SnOX_2$, although this molecule was only observed in the chloride system, since Dehnicke[23] observed that $SnOCl_2$ decomposes to $SnCl_4$ and SnO_2 at temperatures above 457 K. We could never remove $SnOCl_2$ entirely by our purification methods, but the ion current due to this molecule was

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

1

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

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