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Synthesis and Reactions of Cationic Perfluoropropyliron Carbonyl Acetonitrile Complexes

DOUGLAS W. HENSLEY and ROBERT P. STEWART, Jr.*

The reaction of n-$C_3F_7Fe(CO)_4I$ with silver hexafluorophosphate, $AgPF_6$, in acetonitrile at room temperature affords $[C_3F_7Fe(CO)_2(CH_3CN)_3]PF_6$ in almost quantitative yield. A characteristic feature of the $[C_3F_7Fe(CO)_2(CH_3CN)_3]^+$ cation is the extreme lability of its *unique* CH_3CN ligand; the two mutually equivalent CH_3CN groups are much less labile. This is illustrated by the selective exchange of only the unique CH_3CN ligand with free CD_3CN and by reactions of $[C_3F_7Fe(CO)_2(CH_3CN)_3]PF_6$ with group 5 Lewis bases (L). The latter reactions afford only *monosubstituted* $[C_3F_7$-$Fe(CO)_2(CH_3CN)_2L]PF_6$ derivatives even in the presence of excess L. The reactivity of the $[C_3F_7Fe(CO)_2(CH_3CN)_3]^+$ cation is compared with that of the isoelectronic *fac*-$[Mn(CO)_3(CH_3CN)_3]^+$ cation.

Introduction

The chemistry of the $Mn(CO)_5$ group has been investigated in great detail.[1-3] The isoelectronic relationship between $Mn(CO)_5$ and $RFe(CO)_4$ (R = alkyl) would suggest that an analogous extensive chemistry might be based upon the $RFe(CO)_4$ group. This has been realized in part with the use of *perfluoroalkyl* R substituents, particularly n-C_3F_7, on the iron moiety. Known analogues in the isoelectronic C_3F_7-$Fe(CO)_4$ and $Mn(CO)_5$ series include the following: (1) mononuclear iodides, $C_3F_7Fe(CO)_4I^4$ and $Mn(CO)_5I^5$ and corresponding derivatives formed by substitution of one or two CO groups with phosphorus[6,7] and nitrogen[6,8] donor ligands; (2) dinuclear iodides, $[C_3F_7Fe(CO)_3I]_2^4$ and $[Mn(CO)_4I]_2;^9$ (3) hydrides, $C_3F_7Fe(CO)_4H^{10}$ and $Mn(CO)_5H;^{11}$ (4) perfluorocarbon derivatives, $(C_3F_7)_2Fe(CO)_4^4$ and C_3F_7-$Mn(CO)_5^{12}$ and $(C_3F_7)(C_4F_7)Fe(CO)_4^{13}$ and $C_4F_7Mn(CO)_5;^{13}$ (5) mercury derivatives, $[C_3F_7Fe(CO)_4]_2Hg^{10}$ and $[Mn(CO)_5]_2Hg;^{14}$ (6) anions, $[C_3F_7Fe(CO)_4]^-$ [10,15] and $[Mn(CO)_5]^-;$[16,17] (7) cations, $[C_3F_7Fe(CO)_2(NH_3)_3]^+$ [8] and $[Mn(CO)_3(NH_3)_3]^+$.[18]

Although the preparation of cationic manganese carbonyl derivatives has received considerable attention,[19-21] cationic C_3F_7Fe analogues are limited to the single example cited above. In view of both the recent interest[20,21] in cationic derivatives of $[Mn(CO)_6]^+$ and our own interest[22] in the synthesis and reactivity of metal carbonyl cations, we have investigated the preparation of cationic carbonyls formally derived from the unknown $[C_3F_7Fe(CO)_5]^+$ cation. We report here the facile preparation of the $[C_3F_7Fe(CO)_2(CH_3CN)_3]^+$ cation, an isoelectronic analogue of the well-known[20,21] *fac*-$[Mn(CO)_3(CH_3CN)_3]^+$ cation, as well as a series of derivatives obtained from reaction of this iron cation with various Lewis bases. In addition to extending the isoelectronic analogy between $C_3F_7Fe(CO)_4$ and $Mn(CO)_5$, the complexes reported herein are further examples of the relatively limited class of *cationic* fluorocarbon–metal carbonyls.[23]

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of nitrogen. Microanalyses (Table I) were performed by Galbraith Laboratories, Knoxville, Tenn. Melting points (Table I) were taken in capillaries sealed under nitrogen and are uncorrected.

Materials. All solvents (reagent grade) were dried by appropriate methods and were saturated with nitrogen prior to use. The following compounds were purchased from the indicated commercial source and were used without further purification: n-C_3F_7I (PCR, Inc.);

Table I. Analytical Data and Melting Points

Complex	Mp, °C	Elemental analyses, calcd (found), %		
		C	H	N
$[C_3F_7Fe(CO)_2(CH_3CN)_3]PF_6$	112 dec	24.06 (23.82)	1.65 (1.61)	7.65 (7.53)
$[C_3F_7Fe(CO)_2(CH_3CN)_2$-$PPh_3]PF_6$	143 dec	42.10 (41.54)	2.75 (2.70)	3.64 (3.49)
$[C_3F_7Fe(CO)_2(CH_3CN)_2$-$AsPh_3]PF_6$	128	39.83 (39.24)	2.60 (2.47)	3.44 (3.32)
$[C_3F_7Fe(CO)_2(CH_3CN)_2$-$P(OMe)_3]PF_6$	143	22.80 (22.28)	2.39 (2.30)	4.43 (4.31)
$[C_3F_7Fe(CO)_2(CH_3CN)_2$-$P(OEt)_3]PF_6$	141	26.73 (26.92)	3.14 (3.14)	4.16 (4.00)
$[C_3F_7Fe(CO)_2(CH_3CN)_2$-$P(OPh)_3]PF_6$	96	39.63 (39.23)	2.59 (2.54)	3.42 (3.26)
$\{[C_3F_7Fe(CO)_2(CH_3CN)_2]_2$-$(diphos)\}(PF_6)_2$	139 dec	37.37 (37.30)	2.56 (2.59)	3.96 (3.81)
$C_3F_7Fe(CO)_2(CH_3CN)_2I$	125 dec	22.07 (21.98)	1.23 (1.32)	5.72 (5.59)

$Fe(CO)_5$, PPh_3, $Ph_2PCH_2CH_2PPh_2$ (Pressure Chemical Co.); $AgPF_6$ (Ozark-Mahoning Co.); $P(OPh)_3$, $AsPh_3$ (Aldrich Chemical Co.); $P(OMe)_3$, $P(OEt)_3$ (MC/B). Other chemicals were of reagent grade. The compound $C_3F_7Fe(CO)_4I$ was prepared from C_3F_7I and $Fe(CO)_5$ according to the method of King.[24]

Spectra. Infrared spectra (Table II) were obtained on a Perkin-Elmer 180 spectrometer calibrated with carbon monoxide, polystyrene, and indene. All spectra were run in KBr cells using dichloromethane as solvent.

Proton NMR spectra (Table II) were recorded at 60 MHz on a JEOL C-60-H instrument using internal TMS as reference and acetone-d_6, dichloromethane-d_2, or acetonitrile-d_3 as solvent. The ^{19}F NMR spectra (Table II) were obtained at 56.4 MHz on the same instrument and were recorded for <5 mol% solutions in dichloromethane or acetone. Hexafluorobenzene was used as internal reference and chemical shifts are presented relative to $CFCl_3$ using the conversion:[25]

$$\delta_{CFCl_3} = \delta_{C_6F_6} + 162.9 \text{ ppm}$$

Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6 mass spectrometer at 70 eV with a chamber temperature of 200 °C and a sample temperature of 95 °C.

Preparation of $[C_3F_7Fe(CO)_2(CH_3CN)_3]PF_6$. A solution of $AgPF_6$ (6.31 g, 24.9 mmol) in 50 ml of acetonitrile was added dropwise to a solution of $C_3F_7Fe(CO)_4I$ (11.1 g, 23.4 mmol) in 40 ml of acetonitrile. Immediate precipitation of AgI occurred. The solution was stirred for 1.5 h at room temperature and AgI was removed by filtration. The bright orange filtrate was evaporated to dryness in

Table II. Infrared and NMR Data

Complex	ν(CO), cm^{-1} a	^{1}H NMR[b,c] τ(CH$_3$-CN)	J_{PH}, Hz	Other assignments	^{19}F NMR[c,d] α-CF$_2$	β-CF$_2$	CF$_3$	PF$_6^-$ e	$J_{F_\alpha F_\gamma}$, Hz
[C$_3$F$_7$Fe(CO)$_2$(CH$_3$CN)$_3$]PF$_6$	2099, 2058	7.51 s^f 7.56 s^f			76.9 q	117.4 s	79.4 t	73.3 d	11.7
[C$_3$F$_7$Fe(CO)$_2$(CH$_3$CN)$_2$-PPh$_3$]PF$_6$	2073, 2032	7.59 d	2.0	C$_6$H$_5$, 2.30 m	80.2 m	117.2 s	79.1 t	73.1 d	g
[C$_3$F$_7$Fe(CO)$_2$(CH$_3$CN)$_2$-AsPh$_3$]PF$_6$	2073, 2033	7.55 s		C$_6$H$_5$, 2.26 s	78.8 m	117.5 s	79.6 t	73.5 d	g
[C$_3$F$_7$Fe(CO)$_2$(CH$_3$CN)$_2$-P(OMe)$_3$]PF$_6$	2089, 2048	7.30 d	2.2	CH$_3$, 5.86 d; J_{PH} = 11.3 Hz	85.4 m	117.4 s	79.3 t	73.3 d	11.5
[C$_3$F$_7$Fe(CO)$_2$(CH$_3$CN)$_2$-P(OEt)$_3$]PF$_6$	2087, 2047	7.30 d	2.4	CH$_3$, 8.52 t; J_{HH} = 7.4 Hz CH$_2$, 5.51 qt; J_{HH} = 7.4 Hz^h	85.6 m	117.2 s	78.9 t	72.9 d	11.0
[C$_3$F$_7$Fe(CO)$_2$(CH$_3$CN)$_2$-P(OPh)$_3$]PF$_6$	2089, 2051	7.45 d	2.3	C$_6$H$_5$, 2.59 s	83.1 m	117.8 s	79.8 t	73.5 d	11.2
{[C$_3$F$_7$Fe(CO)$_2$(CH$_3$CN)$_2$]$_2$-(diphos)}(PF$_6$)$_2$	2075, 2034	7.68 s		C$_6$H$_5$, 2.20 m CH$_2$, 7.18 m	80.3 m^i	115.5 s^i	77.7 t^i	71.0 d^i	11.3^i
C$_3$F$_7$Fe(CO)$_2$(CH$_3$CN)$_2$I	2068, 2025	7.31 s			81.5 m	117.7 s	79.3 t		11.0

^{a} CH$_2$Cl$_2$ solution unless otherwise noted. ^{b} Acetone-d_6 solution unless otherwise noted. ^{c} Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; qt, quintet; m, multiplet. ^{d} Chemical shifts in ppm from CFCl$_3$; CH$_2$Cl$_2$ solution unless otherwise noted. ^{e} J_{PF} = 698 Hz. ^{f} CD$_2$Cl$_2$ solution. Relative areas of the τ 7.51 and 7.56 signals are 2:1, respectively. ^{g} Overlap with peak of PF$_6^-$ doublet prevented measurement of $J_{F_\alpha F_\gamma}$. ^{h} J_{PH} = 7.4 Hz. ^{i} Acetone-d_6 solution.

vacuo. Recrystallization of the resulting yellow solid from dichloromethane–hexane gave the pure yellow crystalline product in virtually quantitative yield.

Preparation of [C$_3$F$_7$Fe(CO)$_2$(CH$_3$CN)$_2$PPh$_3$]PF$_6$. A solution of [C$_3$F$_7$Fe(CO)$_2$(CH$_3$CN)$_3$]PF$_6$ (0.55 g, 1.00 mmol) and PPh$_3$ (0.52 g, 1.98 mmol) in 60 ml of dichloromethane was heated under reflux for 1.5 h. The solution was filtered and heptane was added to the yellow filtrate. Concentration on the rotary evaporator afforded a bright yellow crystalline solid (0.46 g, 60%).

Preparation of [C$_3$F$_7$Fe(CO)$_2$(CH$_3$CN)$_2$P(OR)$_3$]PF$_6$ (R = Me, Et, Ph). A typical procedure is outlined for R = Me. A mixture of [C$_3$F$_7$Fe(CO)$_2$(CH$_3$CN)$_3$]PF$_6$ (0.55 g, 1.00 mmol) and P(OMe)$_3$ (0.25 g, 2.02 mmol) in 80 ml of benzene was heated at 50 °C for 4 h. The solution was filtered and heptane was added to the filtrate. Concentration on the rotary evaporator gave an oil to which anhydrous ethanol was added. Recrystallization of the resulting solid from dichloromethane–heptane afforded an ivory crystalline solid (0.41 g, 65%).
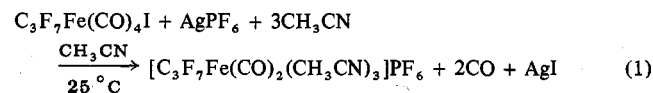
Preparation of [C$_3$F$_7$Fe(CO)$_2$(CH$_3$CN)$_2$AsPh$_3$]PF$_6$. A solution of [C$_3$F$_7$Fe(CO)$_2$(CH$_3$CN)$_3$]PF$_6$ (0.59 g, 1.07 mmol) and AsPh$_3$ (0.78 g, 2.55 mmol) in 75 ml of acetone was stirred for 3.5 h at room temperature. Solvent was removed in vacuo to give a green solid. Recrystallization from dichloromethane–heptane gave the product as a yellow crystalline solid (0.11 g, 13%).

Preparation of {[C$_3$F$_7$Fe(CO)$_2$(CH$_3$CN)$_2$]$_2$(diphos)}(PF$_6$)$_2$. A mixture of [C$_3$F$_7$Fe(CO)$_2$(CH$_3$CN)$_3$]PF$_6$ (1.69 g, 3.08 mmol) and Ph$_2$PCH$_2$CH$_2$PPh$_2$ (diphos) (0.74 g, 3.03 mmol) in benzene (100 ml) was heated at 50 °C for 6.5 h. Filtration gave a yellow solid which was washed with benzene and dichloromethane. Crystallization from dichloromethane–acetone gave the product as a bright yellow solid (1.67 g, 77%).

Preparation of C$_3$F$_7$Fe(CO)$_2$(CH$_3$CN)$_2$I. Solid KI (1.88 g, 11.3 mmol) was added to a solution of [C$_3$F$_7$Fe(CO)$_2$(CH$_3$CN)$_3$]PF$_6$ (0.64 g, 1.17 mmol) in acetonitrile (50 ml). The solution was stirred for 3 h at room temperature and was evaporated to dryness in vacuo. The solid was crystallized from dichloromethane–hexane to give a brown crystalline product (0.21 g, 37%).

Results and Discussion

Silver hexafluorophosphate, AgPF$_6$, readily reacted with C$_3$F$_7$Fe(CO)$_4$I in acetonitrile at room temperature to form the yellow crystalline solid [C$_3$F$_7$Fe(CO)$_2$(CH$_3$CN)$_3$]PF$_6$ in virtually quantitative yield (eq 1). Although the complex is insoluble in nonpolar solvents, it is quite soluble in di-

$$C_3F_7Fe(CO)_4I + AgPF_6 + 3CH_3CN$$
$$\xrightarrow[25\,°C]{CH_3CN} [C_3F_7Fe(CO)_2(CH_3CN)_3]PF_6 + 2CO + AgI \quad (1)$$

chloromethane, acetonitrile, and acetone. Decomposition of the solid compound in air at room temperature is negligible, but solutions decompose within a few hours.

Salts of the closely related [C$_3$F$_7$Fe(CO)$_2$(NH$_3$)$_3$]$^+$ cation have been reported by Behrens and co-workers.[8] In addition, we note that reaction conditions similar to eq 1 have previously been used to prepare [(η^5-C$_5$H$_5$)CoC$_3$F$_7$(CH$_3$CN)$_2$]ClO$_4$ from (η^5-C$_5$H$_5$)CoC$_3$F$_7$(CO)I.[23]

The ^{1}H NMR spectrum of [C$_3$F$_7$Fe(CO)$_2$(CH$_3$CN)$_3$]PF$_6$ in CD$_2$Cl$_2$ solution exhibited two signals at τ 7.51 and 7.56 with relative intensities of 2:1, respectively. For purposes of comparison, the methyl resonance of free CH$_3$CN was observed at τ 8.04 in CD$_2$Cl$_2$ solution. The downfield shift which accompanies coordination of CH$_3$CN in [C$_3$F$_7$Fe(CO)$_2$-(CH$_3$CN)$_3$]$^+$ is quite typical of related cationic metal–acetonitrile complexes.[21,26]

Additional ^{1}H NMR studies in CD$_3$CN solution show that the *unique* CH$_3$CN ligand in the [C$_3$F$_7$Fe(CO)$_2$(CH$_3$CN)$_3$]$^+$ cation undergoes rapid exchange with the solvent. Exchange is complete in less than 5 min at ambient temperature. Thus, immediate examination of freshly prepared solutions of [C$_3$F$_7$Fe(CO)$_2$(CH$_3$CN)$_3$]PF$_6$ in CD$_3$CN solution revealed only one sharp resonance (τ 7.48) attributable to coordinated CH$_3$CN.[27] A sharp resonance at τ 7.98, having half the intensity of the τ 7.48 signal, can be assigned to free CH$_3$CN by comparison with the ^{1}H NMR spectrum of an authentic sample in CD$_3$CN solution.[27] In contrast to these observations, exchange involving the two remaining *equivalent* CH$_3$CN ligands was not detected over a period of 40 min at ambient temperature. This type of *selective* exchange of free and coordinated CH$_3$CN has been recently observed in other cationic metal complexes which contain nonequivalent CH$_3$CN ligands.[28,29]

The marked difference in lability of CH$_3$CN ligands in [C$_3$F$_7$Fe(CO)$_2$(CH$_3$CN)$_3$]$^+$ is consistent with the reactivity of the cation toward Lewis bases. Thus, the complex [C$_3$F$_7$Fe(CO)$_2$(CH$_3$CN)$_3$]PF$_6$ reacted with an *excess* of the Lewis bases (L) PPh$_3$, AsPh$_3$, P(OMe)$_3$, P(OEt)$_3$, and P-(OPh)$_3$ in polar and nonpolar solvents to produce exclusively *monosubstituted* [C$_3$F$_7$Fe(CO)$_2$(CH$_3$CN)$_2$L]PF$_6$ derivatives (eq 2). The use of a stoichiometric amount of L led to

$$[C_3F_7Fe(CO)_2(CH_3CN)_3]PF_6 + L$$
$$\xrightarrow{40-50\,°C} [C_3F_7Fe(CO)_2(CH_3CN)_2L]PF_6 + CH_3CN \quad (2)$$
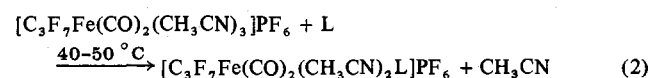
considerably longer reaction times for eq 2. It is significant to point out that even under more vigorous conditions (in the presence of excess L) substitution of more than one coordinated CH_3CN ligand could not be accomplished. Related to these observations is the reaction of $[C_3F_7Fe(CO)_2(CH_3CN)_3]PF_6$ with the bidentate ligand diphos (eq 3). Formation of the

$$2[C_3F_7Fe(CO)_2(CH_3CN)_3]PF_6 + \text{diphos}$$
$$\rightarrow \{[C_3F_7Fe(CO)_2(CH_3CN)_2]_2(\text{diphos})\}(PF_6)_2 + 2CH_3CN \quad (3)$$
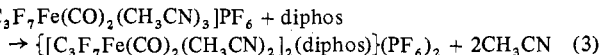
indicated product in preference to $[C_3F_7Fe(CO)_2-(CH_3CN)\text{diphos}]PF_6$ provides further evidence for the enhanced lability of the *unique* CH_3CN ligand in the $[C_3F_7Fe(CO)_2(CH_3CN)_3]^+$ cation.

It is appropriate to note that the behavior of the isoelectronic $[C_3F_7Fe(CO)_2(CH_3CN)_3]^+$ and *fac*-$[Mn(CO)_3(CH_3CN)_3]^+$ cations is strikingly different in several respects. Although the manganese cation undergoes facile exchange of its *three equivalent* CH_3CN groups in CD_3CN solution,[20] the qualitative rate of exchange appears to be significantly slower than that observed for $[C_3F_7Fe(CO)_2(CH_3CN)_3]^+$. Moreover, reaction of *fac*-$[Mn(CO)_3(CH_3CN)_3]PF_6$ with diphos under conditions similar to eq 3 afforded in our hands the known[20] complex $[Mn(CO)_3(CH_3CN)\text{diphos}]PF_6$. Substitution of two CH_3CN ligands in *fac*-$[Mn(CO)_3(CH_3CN)_3]^+$ has also been achieved with several monodentate phosphorus ligands.[21] Thus, it should be emphasized that the formal isoelectronic relationship between $C_3F_7Fe(CO)_4$ and $Mn(CO)_5$ groups, though useful for predicting or rationalizing stoichiometric and structural similarities, does not necessarily preclude quite different reactivity patterns for corresponding iron and manganese complexes.

Replacement of the unique CH_3CN group in $[C_3F_7Fe(CO)_2(CH_3CN)_3]^+$ could also be accomplished with iodide ion (eq 4). The neutral iodide complex $C_3F_7Fe(CO)_2(C-$

$$[C_3F_7Fe(CO)_2(CH_3CN)_3]PF_6 + \text{NaI}$$
$$\xrightarrow[25°]{CH_3CN} C_3F_7Fe(CO)_2(CH_3CN)_2I + \text{NaPF}_6 + CH_3CN \quad (4)$$
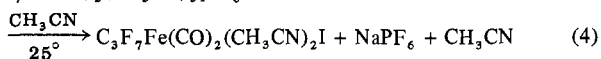
$H_3CN)_2I$ was isolated as a brown crystalline solid in moderate yield. Solutions of the complex readily decompose at room temperature in the presence of air. Attempted synthesis of the corresponding chloride and bromide by similar procedures proved futile.

Spectra. Proton NMR spectra (Table II) of the $[C_3F_7-Fe(CO)_2(CH_3CN)_2L]PF_6$ and $\{[C_3F_7Fe(CO)_2-(CH_3CN)_2]_2(\text{diphos})\}(PF_6)_2$ complexes indicated equivalent CH_3CN groups in all cases. For the phosphorus-ligand derivatives the CH_3CN signal was usually observed as a doublet with $^5J_{PH} \approx 2$ Hz in agreement with ^1H NMR data on related manganese complexes.[21] Unlike the $[C_3F_7Fe(CO)_2-(CH_3CN)_3]^+$ cation, the substituted cations exhibited no tendency to exchange coordinated CH_3CN with CD_3CN solvent. Similar conclusions have been noted concerning the relative lability of bound CH_3CN groups in the *fac*-$[Mn-(CO)_3(CH_3CN)_3]^+$ cation and its substituted derivatives.[20]

The ^1H NMR spectrum of $C_3F_7Fe(CO)_2(CH_3CN)_2I$ showed a single methyl resonance at τ 7.31. The mass spectrum exhibited the $[C_3F_7Fe(CO)_2I]^+$ and $[C_3F_7Fe-(CO)_2(CH_3CN)_2]^+$ ions as the only metal-containing ions which could be unequivocally assigned. The remainder of the mass spectrum was complicated by extensive fragmentation of fluorocarbon groups.

The ^{19}F NMR spectra of all complexes showed the three resonances expected for the *n*-C_3F_7 group (Table II). The chemical shift of the α-CF_2 multiplet exhibited significant variation throughout the series of complexes. On the other hand, the ^{19}F chemical shifts of the β-CF_2 singlet and CF_3 triplet were relatively constant. The value of $^4J_{F_\alpha F_\gamma}$ ranged from 11 to 12 Hz. The ^{19}F NMR spectra are thus quite

similar to the spectra of other neutral[13,30,31] and ionic[21,31] perfluoropropyl–metal complexes.

The ^{19}F NMR spectra unambiguously supported the formulation of the ionic compounds. The PF_6^- resonance was observed as a sharp doublet centered at ~ 73 ppm with $^1J_{PF}$ = 698 Hz. These chemical shift and coupling constant values are in excellent agreement with literature values for the PF_6^- anion.[23]

The infrared spectra of all complexes prepared in this work exhibited two strong bands in the $\nu(CO)$ region (Table II). The $\nu(CO)$ frequencies of the $[C_3F_7Fe(CO)_2(CH_3CN)_2L]PF_6$ complexes appear to correlate with the generally acknowledged σ-donor and π-acceptor properties of the L groups.[32a] A notable exception is the unsubstituted cation (L = CH_3CN), which has *higher* $\nu(CO)$ frequencies than any of the substituted derivatives; this result is surprising in view of the relative electronic properties of the CH_3CN ligand.[32]

The infrared spectra also showed one or two weak bands in the 2300–2350-cm^{-1} region which can be attributed to coordinated CH_3CN.[21] Characteristic bands of the *n*-C_3F_7 group[23] were observed in the 1080–1340-cm^{-1} region. The infrared spectra of all ionic complexes also exhibited a strong band in the 825–855-cm^{-1} region due to the PF_6^- anion.[34]

Structures. The proton NMR results described earlier do not allow a distinction between the three possible structures for the $[C_3F_7Fe(CO)_2(CH_3CN)_3]^+$ cation (**1–3**). However, the observation of two intense $\nu(CO)$ bands in the infrared

1

2

3
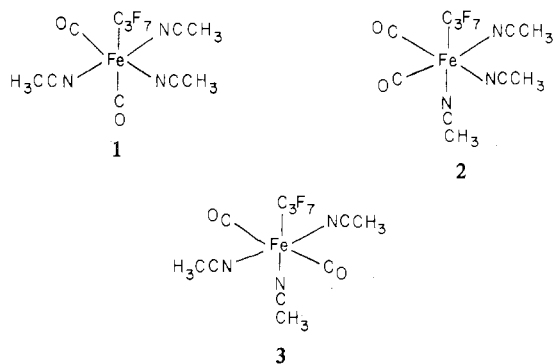
spectrum of $[C_3F_7Fe(CO)_2(CH_3CN)_3]PF_6$ is inconsistent with **3**. Structure **3** would be expected to give rise to the one weak and one strong $\nu(CO)$ band pattern observed for neutral $BrMn(CO)_2L_3$ complexes having this stereochemistry.[35] Infrared spectra of the other derivatives exhibited the same pattern in the $\nu(CO)$ region observed for the unsubstituted complex. Thus, it seems reasonable to conclude that substitution of the unique CH_3CN ligand in $[C_3F_7Fe(CO)_2-(CH_3CN)_3]^+$ does not lead to a change in stereochemistry. These considerations require that the geometry of the substituted derivatives be either **4** or **5** (X = L, I).

4

5
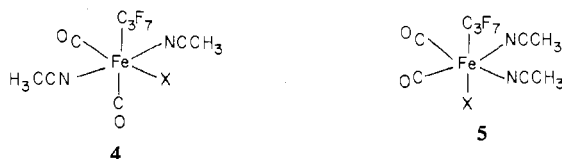
Further distinction between **1** and **2** or **4** and **5** is not possible from $\nu(CO)$ infrared data since both geometries are consistent with the observed infrared spectra. However, it should be pointed out that the magnitude of the $^3J_{PF_\alpha}$ coupling constant in $[C_3F_7Fe(CO)_2(CH_3CN)_2L]^+$ (L = phosphorus ligand) would in principle distinguish between the two structural alternatives **4** and **5**. In **4** the C_3F_7 and L groups are mutually cis while in **5** these groups have a mutual trans orientation. Related ^{19}F NMR investigations suggest that $^3J_{PF_\alpha}(\text{trans})$ should be substantially greater than $^3J_{PF_\alpha}(\text{cis})$.[36] Interpretation

of the results for $[C_3F_7Fe(CO)_2(CH_3CN)_2L]^+$ would be aided by comparison with $^3J_{PF_\alpha}$ in the corresponding $C_3F_7Fe(CO)_3(L)I$ derivative, in which the C_3F_7 and L groups have a mutual cis orientation.[37] Although the value of $^3J_{PF_\alpha}$ could not be obtained directly from the present ^{19}F NMR spectra due to the complexity of the α-CF_2 resonance, the use of ^{19}F spin decoupling techniques should allow a direct measurement of $^3J_{PF_\alpha}$ in corresponding $[C_3F_7Fe(CO)_2(CH_3CN)_2L]^+$ and $C_3F_7Fe(CO)_3(L)I$ complexes. It is anticipated that such spectroscopic studies, which are currently being pursued, will provide a distinction between the structural alternatives **4** and **5**.

At present we admittedly prefer structure **1** (and thus **4** for the monosubstituted derivatives) in which all three CH_3CN ligands are cis to the C_3F_7 group. This structural assignment is consistent with the mutual cis orientation of perfluoroalkyl[38] or alkyl[39] groups and phosphorus ligands in related $RMn(CO)_4L$ ($R = C_2F_5$, C_3F_7) and $CH_3Mn(CO)_{5-x}[P(OMe)_3]_x$ ($x = 1$–4) complexes. Furthermore, previous studies on a variety of six-coordinate cations have shown that mutually trans CH_3CN groups are extremely inert with respect to exchange.[28,29] These results also lend support to structure **1**. Thus, the enhanced lability of the unique CH_3CN ligand in $[C_3F_7Fe(CO)_2(CH_3CN)_3]^+$ might be attributed to the well-documented[40] trans-labilizing effect of CO.[41] Further speculation concerning the markedly different rates of CH_3CN exchange in $[C_3F_7Fe(CO)_2(CH_3CN)_3]^+$ must await detailed kinetic studies which are currently in progress.

Registry No. $[C_3F_7Fe(CO)_2(CH_3CN)_3]PF_6$, 59982-94-4; $[C_3F_7Fe(CO)_2(CH_3CN)_2PPh_3]PF_6$, 59982-96-6; $[C_3F_7Fe(CO)_2(CH_3CN)_2P(OMe)_3]PF_6$, 59982-98-8; $[C_3F_7Fe(CO)_2(CH_3CN)_2P(OEt)_3]PF_6$, 59983-00-5; $[C_3F_7Fe(CO)_2(CH_3CN)_2P(OPh)_3]PF_6$, 59983-02-7; $[C_3F_7Fe(CO)_2(CH_3CN)_2AsPh_3]PF_6$, 59983-04-9; $\{[C_3F_7Fe(CO)_2(CH_3CN)_2]_2(diphos)\}(PF_6)_2$, 59983-07-2; $C_3F_7Fe(CO)_2(CH_3CN)_2I$, 59983-05-0; $C_3F_7Fe(CO)_4I$, 22925-82-2; PPh_3, 603-35-0; $P(OMe)_3$, 121-45-9.

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