$\sim$-50, $J \cong 130$ Hz). While the general appearance of the spectrum is consistent with BH_2 groups in a polymeric structure, the chemical shift is at higher field than that of any other comparable species known to us. For comparison, the ^{11}B resonance of the cyclic $(H_2BNH_2)_3$ occurs at δ -11.[8,16]

The X-ray powder diffraction pattern of our $(H_2NBH_2)_x$ product (Table II) confirms its crystallinity, but the pattern clearly does not match those reported for the cyclic $(H_2NBH_2)_x$ (x = 2–5) oligomers.[8,13] The most intense band (3.76 Å) is similar to intense bands from 3.71 to 3.93 Å which appear in the patterns of the cyclic oligomers. Thus, the new product is distinct from both the known amorphous and crystalline forms of poly(aminoborane). The very low solubility of the product is consistent with either a cyclic or a linear polymer of relatively high molecular weight.[8] The evidence currently available does not permit a clear choice between these possibilities.

Some observations of the physical characteristics of the poly(aminoborane) were carried out by forming the substance on a polystyrene film and then dissolving the latter in toluene. The thin pieces of material thus formed were quite brittle and seemed to lack characteristics expected for high polymers.

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Registry No. $H_3N{\cdot}BH_3$, 13774-81-7; $(H_2NBH_2)_n$, 42208-67-3.

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Novel Iron Tetracarbonyl Fluorophosphine Complexes

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Fluorophosphine derivatives of iron carbonyl have been known for a number of years and have been prepared by several methods: direct substitution into iron pentacarbonyl,(1) cleavage of diiron enneacarbonyl by a fluorophosphine or reaction of a coordinated fluorophosphine with HCl or a nucleophile, which yielded a number of iron tetracarbonyl difluorophosphine derivatives containing a halogen or pseudohalogen on the phosphorus.(2) Interest in these compounds arises because of the possibility of fluxionality of the product. Clark showed that $(CO)_4FePF_3$ exists as a mixture of the axially and equatorially substituted isomers by infrared spectroscopy, although he was not able to confirm their presence by low-temperature NMR experiments nor was he able to separate them by chromatography. He concluded that the complex was fluxional. This behavior was also found for the other halofluorophosphine and pseudohalofluorophosphine complexes, $(CO)_4FeL$, where L = F_2PCl, $FPCl_2$, F_2PN_3, F_2PNCS, and $FP(NCS)_2$.(2)

On the other hand, if methoxy, dialkylamino, or phenyl groups are substituted for fluorine in the fluorophosphine complex $(CO)_4FeL$, where L = F_2POCH_3, $FP(OCH_3)_2$, $P(OCH_3)_3$,(3) $[(CH_3)_2N]_2PF$, $(CH_3)NCH_2CH_2N(CH_3)PF$,(4) $PhPF_2$,(2) and PPh_3,(5) only the axial isomers are observed.

While steric interactions are probably a factor in determining which isomer is formed under some circumstances, they are obviously not important here: trimethyl phosphite with a cone angle of 107° and triphenylphosphine with the larger cone angle of 145° both give the axial isomer whereas PF_3 with a cone angle of 104°(6) gives a mixture of the axial and equatorial isomers. Large cone angles would favor the formation of the equatorial isomer. Thus electronic effects must predominate in these cases. It was, therefore, of interest to prepare iron tetracarbonyl fluorophosphine complexes in which a group that was both bulky and highly electronegative had been substituted for fluorine on the phosphorus. Since $F_2P[OC(CF_3)_2CN]$ had been reported,(7) it was thought that this ligand would fill these requirements. In addition the related ligands $FP[OC(CF_3)_2CN]_2$ and $P[OC(CF_3)_2CN]_3$ were synthesized and used in the preparation of the series of iron tetracarbonyl complexes $(CO)_4FeF_{3-x}P[OC(CF_3)_2CN]_x$ (x = 1, 2, and 3).

Experimental Section

General Methods. A standard Pyrex vacuum system was used for the transfer of volatile materials. Other manipulations of products were carried out under a nitrogen atmosphere. Purification was obtained either through trap to trap fractionation or by distillation with a variety of short-path stills or a Holzmann column.(8) Mercury manometers were covered with Kel F-10 oil. The compounds were prepared in 125-mL heavy-wall Pyrex pressure reactors fitted with Fischer-Porter Teflon valves (pressures were generally below 4 atm). All solid reactants were dried for 2 h on a vacuum line before volatile reactants were added. Since most compounds are moisture and oxygen sensitive, they were handled under vacuum or under a nitrogen atmosphere after preparation.

Materials. All the starting materials were prepared by literature methods; (i.e. $NaOC(CF_3)_2CN$,(7) $Fe_2(CO)_9$, F_2PCl, and $FPCl_2$,(7) $Fe(CO)_4PF_2Cl$ and $Fe(CO)_4PFCl_2$,(2) and $F_2POC(CF_3)_2CN$(7)). Hexafluoroacetone and iron pentacarbonyl were obtained from commercial sources and used without further purification.

Spectral and Analytical Characterization. NMR spectra were recorded on Hitachi Perkin-Elmer R-20 ($Cl_3C^{19}F$ as an internal standard) and Varian HR-100 ($^{31}P_4O_6$ as an external standard) instruments. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6 instrument. Infrared spectra were recorded on a Perkin-Elmer 621 grating spectrometer and calibrated with polystyrene. Analyses were performed at the University of Georgia, Meade Microanalytical Labs, Amherst, MA, and Galbraith Labs, Knoxville, TN.

Preparation of Bis(2-cyanohexafluoroisopropoxy)fluorophosphine, $FP[OC(CF_3)_2CN]_2$. A 4.30-g (0.020-mol) sample of the sodium cyanohydrin salt was placed in a pressure reactor. Pentane, 20.0 mL, and 1.21 g (0.010 mol) of dichlorofluorophosphine were condensed into the reactor. After the reaction mixture was warmed to 25 °C, it was stirred for 6 h. The excess $FPCl_2$ was removed under vacuum, and the residue was extracted with 50 mL of pentane. After the solution was filtered through filter aid, the filtrate was fractionated through traps maintained at -24, -78, and -196 °C. The product was retained in the -24 °C trap. Further purification was accomplished by distillation with a Holzmann column.

Preparation of Tris(2-cyanohexafluoroisopropyl) Phosphite, $P[OC(CF_3)_2CN]_3$. A 6.45-g (0.030-mol) sample of $NaOC(CF_3)_2CN$ was placed in a 300-ml round-bottom flask equipped with a magentic stirring bar. After the flask was flushed with dry nitrogen, 45 mL of pentane and 1.37 g (0.010 mol) of freshly distilled phosphorus trichloride were added. After the mixture was stirred for 6 h, the reaction solution was filtered and the filtrate was concentrated to about 10 mL in vacuo. After fractionation through traps maintained at -24, -78, and -196 °C, the product was obtained in the -24 °C trap.

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Further purification was accomplished by distillation using a Holzmann column.

Preparation of Tetracarbonyl((2-cyanohexafluoroisopropoxy)difluorophosphine)iron, $Fe(CO)_4F_2POC(CF_3)_2CN$. Method A. A 2.15-g (0.010-mol) sample of the sodium cyanohydrin salt was placed in a pressure reactor, and diethyl ether (20.0 mL) was condensed into the reaction vessel (pentane (30.0 mL) may also be used as a solvent). Then 0.010 mol of freshly distilled $Fe(CO)_4F_2PX$ (X = Br, Cl) was syringed into the reactor under a nitrogen blanket. The reactor was cooled to −196 °C, degassed, sealed, and allowed to warm to ambient temperature. After the reaction mixture was stirred for 6 h, it was fractionated through traps maintained at −24, −78, and −196 °C. The product was retained in the −24 °C trap.

Method B. The product, $Fe(CO)_4F_2POC(CF_3)_2CN$, may also be obtained by allowing $Fe_2(CO)_9$ to react with $F_2POC(CF_3)_2CN$. Diiron enneacarbonyl (3.63 g, 0.010 mol) was placed in a pressure reactor; pentane (15 mL) and 2.88 g (0.011 mol) of $F_2POC(CF_3)_2CN$ were condensed into the reactor. After the mixture was stirred for 12 h, the product was isolated in a manner analogous to that described above.

Preparation of Tetracarbonyl(bis(2-cyanohexafluoroisopropoxy)fluorophosphine)iron, $Fe(CO)_4FP[OC(CF_3)_2CN]_2$. Method A. Sodium 2-cyanohexafluoroisopropoxide (2.15 g, 0.010 mol) was placed in a pressure reactor, and diethyl ether (30.0 mL) was condensed into the reaction vessel. Then 1.55 g (0.005 mol) of freshly distilled tetracarbonyl(dichlorofluorophosphine)iron was added. The reactor was degassed at −196 °C, sealed, and allowed to warm to room temperature. After the mixture was stirred for 6 h, the solvent and excess $Fe(CO)_4FPCl_2$ were removed under vacuum. The residue was extracted with 100 mL of pentane. The extract was filtered and reduced in volume to about 5 mL. The product was isolated from the mother liquor with a short-path molecular still (the receiving section was cooled in an ice bath).

Method B. Tetracarbonyl(bis(2-cyanohexafluoroisopropoxy)fluorophosphine)iron may also be obtained by cleaving $Fe_2(CO)_9$ with $FP[OC(CF_3)_2CN]_2$. Diiron enneacarbonyl (3.63 g, 0.010 mol), diethyl ether (15 mL), and $FP[OC(CF_3)_2CN]_2$ (4.77 g, 0.011 mol) were combined at −196 °C. After the mixture was stirred for 12 h, the product was purified as described above.

Preparation of Tetracarbonyl(tris(2-cyanohexafluoroisopropyl) phosphite)iron, $Fe(CO)_4P[OC(CF_3)_2CN]_3$. Diiron enneacarbonyl (1.0 g, 2.8 mmol) was placed in a pressure reactor. A 20-mL amount of diethyl ether was added, and then 1.52 g (2.5 mmol) of $P[OC(CF_3)_2CN]_3$ was syringed into the reactor under a nitrogen blanket. The reactor was degassed and sealed at −196 °C and then allowed to warm to room temperature. The reaction mixture was stirred for 12 h, and then 20 mL of dry THF was added. The reaction mixture was filtered through filter aid and reduced in volume to about 10 mL. The residue was chromatographed, with use of a neutral alumina column (Woelm brand) and a 4:1 diethyl ether–THF mixture. The solution thus obtained gave a dark orange solid when the solvent was removed under vacuum.

Preparation of Tetracarbonyl(((2,2,5,5-tetrakis(trifluoromethyl)-4-oxazolinyl)oxy)difluorophosphine)iron, $Fe(CO)_4[F_2POCNC_2(CF_3)_4O]$. A 2.15-g (10.0-mmol) sample of $NaOC(CF_3)_2CN$ was placed in a pressure reactor, and 20 mL of diethyl ether was condensed into the reaction vessel. Then 2.15 g (5.0 mmol) of freshly distilled $Fe(CO)_4F_2POC(CF_3)_2CN$ was syringed into the reaction vessel under a nitrogen blanket. The reactor was degassed at −196 °C, sealed, and allowed to warm to room temperature. After the mixture was stirred for 24 h, the solvent and excess $Fe(CO)_4F_2POC(CF_3)_2CN$ were removed from the reaction vessel under vacuum. The residue was extracted with 100 mL of pentane. The filtrate was concentrated in vacuo, and the crude product was purified by distillation on a short-path molecular still.

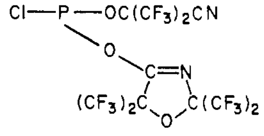
Results

A. Ligand Preparation. The preparation of the free ligands $F_{3-x}P[OC(CF_3)_2CN]_x$ was achieved by using the method reported for $F_2POC(CF_3)_2CN$:[7]

$$F_{3-x}PCl_x + xNaOC(CF_3)_2CN \xrightarrow{\text{pentane}} F_{3-x}P[OC(CF_3)_2CN]_x + xNaCl$$

$$x = 1, 2, \text{ or } 3$$

However, it was found that the choice of solvent and strict adherence to stoichiometry was critical. This was particularly true in the preparation of $P[OC(CF_3)_2CN]_3$. If a slight excess of the cyanohydrin salt $NaOC(CF_3)_2CN$ and/or a polar solvent such as CH_3CN was employed, the desired compound $P[OC(CF_3)_2CN]_3$ was found to be contaminated with other materials. Although it was not possible to separate and isolate the impurities, the principal impurity has tentatively been assigned the structure



on the bais of infrared ($\nu_{C=N}$ = 1669 cm^{-1}) and mass spectral data. A similar cyclization has previously been observed in the preparation of $NaOC(CF_3)_2CN$ in the presence of excess $(CF_3)_2C{=}O$, which yielded the sodium salt of 2,2,5,5-tetrakis(trifluoromethyl)-4-oxazolidone.[9] Alkylation of this ambident anion with ethyl sulfate gave a mixture of the O-alkylated product ($\nu_{C=N}$ = 1672 cm^{-1}) and the N-alkylated product ($\nu_{C=O}$ = 1771 cm^{-1}).[9] The O-alkylated product has the same ring as proposed for the major impurity. Although it has been reported that $NaOC(CF_2Cl)_2CN$ forms $P[OC(CF_2Cl)_2CN]_3$ in low yield[10] when allowed to react with PCl_3, a recalculation of the analytical data, the presence of chloride, and an infrared band at 1667 cm^{-1} suggest that the product reported is related to the major impurity observed here.

Both ligands were isolated by extraction of the crude mixtures with pentane followed by vacuum-line fractionation or vacuum distillation with a Holzmann column. The analytical and NMR data are given in Tables I and III, respectively. Bands attributable to a $\nu_{C\equiv N}$ stretch occurred at 2263 cm^{-1} for both $FP[OC(CF_3)_2CN]_2$ and $P[OC(CF_3)_2CN]_3$. The absence of a band around 1665 ± 5 cm^{-1} indicated that no ring formation had occurred. The ^{19}F NMR spectra demonstrated the presence of equivalent CF_3 groups in both ligands and the presence of a P–F bond in $FP[OC(CF_3)_2CN]_2$. A shift to lower field was noted in the ^{31}P spectra with increasing degree of substitution of the fluorine by the cyanohydrin group (for $F_2POC(CF_3)_2CN$ $\delta = -5.6$ relative to P_4O_6).[7]

B. Complex Preparation. The preparation of the iron tetracarbonyl complexes was achieved in a straightforward manner

$$Fe_2(CO)_9 + F_{3-x}P[OC(CF_3)_2CN]_x \xrightarrow{(C_2H_5)_2O} (CO)_4FeF_{3-x}P[OC(CF_3)_2CN]_x + Fe(CO)_5$$

$$x = 1, 2, \text{ or } 3$$

and the products could be isolated in good to moderate yields. Alternately two of the complexes, $(CO)_4FeF_2POC(CF_3)_2CN$ (**1**) and $(CO)_4FeFP[OC(CF_3)_2CN]_2$ (**2**), could be prepared by nucleophilic substitution of chloride ion from the corresponding chlorofluorophosphine complex by the $OC(CF_3)_2CN^-$ ion, in ether. The completely substituted phosphine complex $(CO)_4FeP[OC(CF_3)_2CN]_3$ (**3**) could not be prepared via this method presumably due to the instability of $(CO)_4FePCl_3$ in solution. The use of polar solvents and/or excess of the cyanohydrin salt led to the formation of side products similar to those observed in the preparation of the free ligands. It was possible to isolate another complex $(CO)_4FeF_2POCNC_2(CF_3)_4O$ (**4**), although in low yield, by reation of **1** with an additional equivalent of $NaOC(CF_3)_2CN$[11]

$$(CO)_4FeF_2POC(CF_3)_2CN + NaOC(CF_3)_2CN \rightarrow (CO)_4FeF_2POCNC_2(CF_3)_4O + NaCN$$

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Table I. Analytical Data

	% anal.							
	calcd			found				
compd	C	N	other	C	N	other	M_r[a] found[b] (calcd)	% yield
$FP[OC(CF_3)_2CN]_2$	22.12	6.44		22.10	6.34		434 (434)	54
$P[OC(CF_3)_2CN]_3$	23.72	6.92	56.34 (F), 5.11 (P)	23.79	6.93	56.32 (F), 5.21 (P)	607 (607)	71
$Fe(CO)_4F_2POC(CF_3)_2CN$	22.40	3.26	13.01 (Fe)	22.64	3.33	12.98 (Fe)	429 (429)	89
$Fe(CO)_4FP[OC(CF_3)_2CN]_2$	23.94	4.65		23.26	4.81		602 (602)	81
$Fe(CO)_4P[OC(CF_3)_2CN]_3$	24.79	5.42		24.39	5.07		735 (735)	51
$Fe(CO)_4PF_2OCNC_2(CF_3)_4O$	22.16	2.35		21.83	2.80		595 (595)	11.5

[a] Molecular weight determined by mass spectroscopy, based on ^{56}Fe, ^{12}C, ^{16}O, and ^{14}N. [b] All samples were run at low temperatures (110 °C chamber temperature).

Table II. Infrared Frequencies (cm^{-1})

compd	$\nu_{C\equiv O}$	ν_{P-F}	other
$Fe(CO)_4F_2POC(CF_3)_2CN$[a]	2102 w, 2094 w, 2028 vs, 2011 vs, 1998 s	875 m, 848 m	2267 vw (C-N)
$Fe(CO)_4FP[OC(CF_3)_2CN]_2$[a]	2109 w, 2095 w, 2041 sh, 2031 vs, 2017 vs, 2006 vs, 1996 sh	858 m	2266 vw (C-N)
$Fe(CO)_4P[OC(CF_3)_2CN]_3$[b]	2127 w, 2096 s, 2069 ms, 2045 ms		2260 vw (C-N)
$Fe(CO)_4PF_2OCNC_2(CF_3)_4O$[a]	2102 m, 2095 m, 2020 vs, 2003 vs, 1996 vs	878 m, 858 m	1676 w (C-N)

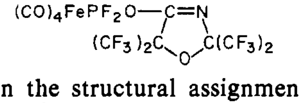
[a] In cyclohexane solution. [b] In KBr.

Table III. NMR Spectra

compd	nucleus	assignt	resonances, ppm[c]	J_{P-F}, Hz
$FP[OC(CF_3)_2CN]_2$	^{19}F[a]	CF_3	+74.7	
		PF	+46.0 (d)	1352
	^{31}P[b]	P	−22.4 (d)	1350
$P[OC(CF_3)_2CN]_3$	^{19}F	CF_3	+74.7	
	^{31}P	P	−36.1 (m)	6
$Fe(CO)_4F_2POC(CF_3)_2CN$	^{19}F	CF_3	+76.2	
		PF_2	+10.5 (d)	1300
	^{31}P	P	−54.3 (t)	1298
$Fe(CO)_4FP[OC(CF_3)_2CN]_2$	^{19}F	CF_3	+76.1	
		PF	+11.5 (d)	1304
	^{31}P	P	−95.8 (d)	1301
$Fe(CO)_4P[OC(CF_3)_2CN]_3$	^{19}F	CF_3	+75.0, +77.3	
	^{31}P	P	−134.3	
$Fe(CO)_4PF_2OCNC_2(CF_3)_4O$	^{19}F	CF_3	75.4	
		PF_2	11.6 (d)	1305
	^{31}P	P	−55.3 (t)	1302

[a] Cl_3CF is used as an internal standard. [b] P_4O_6 is used as an external standard. [c] Abbreviations: d = doublet; t = triplet; m = multiplet.

the product arising from the nucleophilic displacement of cyanide ion, followed by a concerted internal cyclization and a Chapman rearrangement.[12] The proposed structure of the ligand present in complex **4** is as follows:



This is based on the structural assignment made for the methoxy derivative.[9]

All of the complexes except **3** were liquids and isolated by vacuum distillation in a short-path still. Complex **3** was purified by liquid chromatography. The analytical, infrared, and NMR data for the complexes are given in Tables I, II, and III, respectively. All of the complexes exhibited parent molecular ions in their mass spectra as well as showed a stepwise loss of four carbonyl groups. The infrared spectra of complexes **1**, **2**, and **3** contained bands at 2267, 22668 and 2260 cm^{-1} respectively, which are attributable to a $\nu_{C\equiv N}$ stretch. Complex **4** had a band at 1676 cm^{-1} attributable to a $\nu_{C=N}$ stretch, which supports ring formation. The ^{19}F NMR spectra of the complexes deserve some comment. For complexes **1** and **2** the CF_3 groups appear to be equivalent, and the presence of F_2P and FP groups are clearly demonstrated. In addition the expected area ratios CF/PF were observed. However the CF_3 groups in complex **3** are nonequivalent and appear as a doublet. This is felt to arise because of steric crowding of the cyanohydrin groups around the coordinated phosphorus. However, the CF_3 groups in complex **4** are equivalent. This is attributed to the fact that the electronegativity of a –O–C unit and nitrogen are probably quite close so that the CF_3 groups appear to be in a similar environment.

Discussion

The most important question concerning these complexes is that of isomer distribution. Clark found that replacement of only one fluorine in $(CO)_4FePF_3$ by a methoxy group was sufficient to change the isomer distribution of 33% axial and 67% equatorial[13] to 100% axial in $(CO)_4FeF_2POCH_3$.[3] Further replacement of fluorine by methoxy groups did not alter the isomer distribution, but the $\nu_{C\equiv O}$ stretching frequencies were observed to shift to lower wavenumbers, indicating that the phosphorus was becoming a progressively weaker π acid. This was not the case when fluorine was substituted for by the cyanohydrin group, $OC(CF_3)_2CN$. Figure 1 presents a bar graph representation of the $\nu_{C\equiv O}$ stretching frequencies for the four new complexes. Included for comparison is the spectrum of $(CO)_4FePF_3$. It is obvious that for complexes **1**, **2**, and **4** a mixture of the axial and equatorial isomers exists. In fact, little difference in the spectra is observed between that of $(CO)_4FePF_3$ and those of complexes **1** and **4**. The infrared spectrum of complex **3** indicates that only the equatorial isomer is present. The 24-cm^{-1} difference between the two lowest frequency bands appears to be too large to be attributable to splitting of the E mode under C_{3v} symmetry as has been found for several axial isomers.[14]

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(11) For a preliminary report see D. P. Bauer, W. M. Douglas, and J. K. Ruff, *J. Organomet. Chem.*, **57**, C19, (1973).

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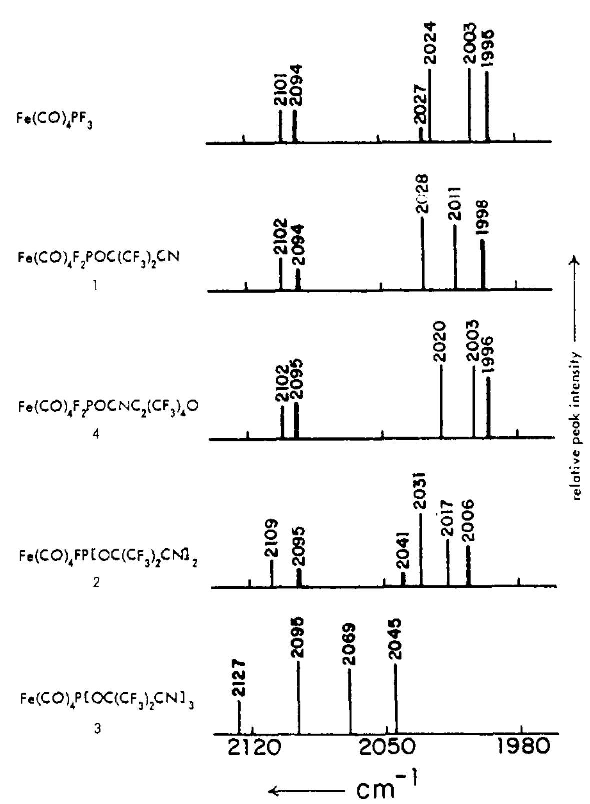

Figure 1. Metal carbonyl infrared stretching frequencies for iron cyanohydrin carbonyl complexes.

In Figure 1 the thick lines in the spectra of complexes **1**, **2**, and **4** as well as that of $(CO)_4FePF_3$ represent those $\nu_{C\equiv O}$ stretches assigned to the axial isomer by using the method of Haas and Sheline.[13] A calculation of the percent isomer distribution for complexes **1**, **2**, and **4** gave the following results: $(CO)_4F_2POC(CF_3)_2CN$, axial 22%, equatorial 78%; $(CO)_4FeF_2POCNC_2(CF_3)_4O$, axial 40%, equatorial 60%; $(CO)_4FeFP[OC(CF_3)_2CN]_2$, axial 15%, equatorial 85%. Only complex **4** exhibits a statistical distribution of isomers. Thus it is apparent that, as the degree of substitution of fluorine by the cyanohydrin group $OC(CF_3)_2CN$ increases, the equatorial isomer becomes more favored. This is in contrast with the results of methoxy substitution since $(CO)_4FeP(OCH_3)_3$ exists only as the axial isomer whereas $(CO)_4FeP[O(CCF_3)_2CN]_3$ exists only as the equatorial isomer.

It is tempting to attribute this difference to the difference in steric requirements of the axial and equatorial positions in the TBP arrangement. Since the cone angle of $Po[OC(CF_3)_2CN]_3$ must be considerably larger (an angle of at least 160°) than that of $P(OCH_3)_3$ (107°),[6] the cyanohydrin derivative would be expected to favor the equatorial position over $P(OCH_3)_3$. This would also explain the increasing amount of equatorial isomer formation as cyanohydrin groups are substituted for fluorine as illustrated by complexes **1** and **2**.

The importance of electronic effects is not clear, but steric factors alone can not explain why triphenylphosphine forms only the axial isomer[5] while $F_2POC(CF_3)_2CN$ forms predominantly the equatorial isomer. A comparison of the $\nu_{C\equiv O}$ stretching frequencies of the axial isomer of $(CO)_4FeFP[OC(CF_3)_2CN]_2$ with those of $(CO)_4FeFP(OCH_3)_2$ shows a shift to lower wavenumbers of about 20–35 cm^{-1} in the latter complex, suggesting that $FP(OCH_3)_2$ is a weaker π acid than $FP[OC(CF_3)_2CN]_2$. This could arise from the greater inductive effect of a $OC(CF_3)_2CN$ group over that of a OCH_3 group. An even more striking comparison is that of the $\nu_{C\equiv O}$ stretching frequencies of complex **3** with those of the equatorial isomer of $(CO)_4FePF_3$. The highest A_1 mode in the latter compound at 2101 cm^{-1} has been shifted to 2127 cm^{-1} in complex **3**. The other bands have also been shifted to higher wavenumbers. This suggests that the ligand $P[OC(CF_3)_2CN]_3$ is a very strong π acid. The $\nu_{C\equiv O}$ frequencies observed for complex **3** are higher than those observed for the complex cation $(CO)_4FeP[N(CH_3)_2]_2^+$, which contains the cationic ligand ${}^+P[N(CH_3)_2]_2$. This indicates an increased π acidity of the fully substituted PF_3 ligand when compared to that of PF_3 itself.

An apparent similar effect was noted for several nickel carbonyl fluorophosphine complexes in which the fluorine in PF_3 was replaced by CF_3 groups.[15] Thus for $(PF_3)_3NiCO$ the $\nu_{C\equiv O}$ occurred at 2085 cm^{-1} while for $(CF_3PF_2)_3NiCO$ it occurred at 2092 cm^{-1}. The suggested explanation was that the amount of F→P π bonding was decreased by substitution, making phosphorus a better π acceptor while it was also becoming a better σ donor. This decrease was not osberved upon disubstitution on phosphorus. Another example in which CF_3 groups were substituted for fluorine in PF_3 showed only a significant shift in the E mode between the compounds $Mo(CO)_5PF_3$ and $Mo(CO)_5P(CF_3)_3$[16] (e.g.: $Mo(CO)_5PF_3$, $A_1 = 2103$ cm^{-1}, $A'_1 = 2011$ cm^{-1}, and E = 1989 cm^{-1}; $Mo(CO)_5P(CF_3)_3$, $A_1 = 2104$ cm^{-1}, $A'_1 = 2009$ cm^{-1}, and E = 1996 cm^{-1}). Although the changes observed in the carbonyl stretching frequencies in the above two examples are smaller in comparison with those observed for compound **3**, it should be pointed out that the replacement of F by a CF_3 group is not completely analogous to the replacement of F by a $OC(CF_3)_2CN$ group, since the possibility of O→P π bonding exists in the latter case. Thus replacement of fluorine by the $OC(CF_3)_2CN$ group on phosphorus would be expected to decrease the π acidity of the phosphorus faster than replacement of fluorine by CF_3 groups if one assumes similar inductive effects (if the $OC(CF_3)_2CN$ group is less electronegative than the CF_3 group, an even faster lowering of the π acidity would be expected). This does not appear to be the case since the π acidity of the phosphorus in compounds **1**, **2**, and **3** apparently increases as substitution increases. The reason for this is not understood, and further studies are under way to shed some light on this problem.

Registry No. **1** (axial), 85185-65-5; **1** (equatorial), 85248-75-5; **2** (axial), 85185-66-6; **2** (equatorial), 85248-76-6; **3**, 85185-67-7; **4** (axial), 85185-68-8; **4** (equatorial), 85248-77-7; $FP[OC(CF_3)_2CN]_2$, 85185-63-3; $P[OC(CF_3)_2CN]_3$, 85185-64-4; $Fe(CO)_4F_2PBr$, 42886-00-0; $Fe(CO)_4F_2PCl$, 60182-92-5; $Fe_2(CO)_9$, 15321-51-4; $NaOC(CF_3)_2CN$, 6737-59-3; $F_2POC(CF_3)_2CN$, 20765-90-6; $FPCl_2$, 15597-63-4; PCl_3, 7719-12-2.

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(14) This splitting was found to be 10 cm^{-1} in $[(CH_3)_2N]_2PFFe(CO)_4$[4] and $[(C_2H_5)_2N]_2PFFe(CO)_4$,[2] 8 cm^{-1} in $(PhPF_2)Fe(CO)_4$,[2] and 12 cm^{-1} in $C_5H_{10}NPF_2Fe(CO)_4$.[2]

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Synthesis and Reactivity of Dicationic Diolefin Complexes of the Type $Me_2Si[\eta^5\text{-}C_5H_4Fe(CO)_2(\eta^2\text{-olefin})]_2[BF_4]_2$

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There is considerable attention being focused presently on the synthesis and study of dinuclear transition-metal com-