Laboratory and Mass Spectrometric Studies of Ligand Exchange Processes Involving $Fe(PF_3)_5$[1]

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Abstract: The ligand exchange reactivity of pentakis(trifluorophosphine)iron(0) in laboratory experiments is found to parallel the exchange behavior with the same ligands under the conditions of chemical ionization (CI) mass spectrometry in which the potential ligand is used as the reagent gas. Ligands that do not exchange with trifluorophosphine under CI conditions also fail to exchange in preparative reaction situations. These ligands included PCl_3, N_2, Ar, and Kr. The saturated hydrocarbons, isobutane and isopentane, produce ligand exchange ions with iron pentakis(trifluorophosphine) fragments. The appearance of these ions suggests that C–H bond breaking may occur under the influence of the iron species. The negative chemical ionization mass spectra of $Fe(PF_3)_5$ are universally dominated by $Fe(PF_3)_4^-$ ions regardless of the nature of the ligand reagent gas. Ligands that readily exchange with PF_3 give low-intensity $Fe(PF_3)_3L^-$ ions. General patterns of reactivity and the diagnostic value of chemical ionization mass spectra for investigations of potential homogeneous catalysts are discussed.

Introduction

Metal carbonyl–trifluorophosphine complexes are taking on increasing importance in the field of organometallic chemistry[2] and they show promise in the study of homogeneous catalysis.[3] The study of the substitution chemistry of these trifluorophosphine compounds is a hard and time-consuming operation. These difficulties result for a number of reasons which include isolation difficulties, the frequent absence of the carbonyl chemist's infrared spectroscopy tool, and the extreme complexity of the fluorine and phosphorus NMR when more than two PF_3 groups are present. On the other hand, chemical ionization data can be readily obtained. Studies with CI have shown that an analogy exists under the proper circumstances between mass spectral reactivity and thermal chemistry and photochemistry.[4] This has been demonstrated in several studies.[5] Thus, if chemical ionization data could be used to predict effectively the substitution chemistry of metal trifluorophosphines, the benefits would be substantial.

In this paper, correlations are reported between the thermal and photochemical substitution reactions of $Fe(PF_3)_5$ and the CI spectra of $Fe(PF_3)_5$ with various substrates. In general, it will be shown that ligands that do not undergo substitution reactions under CI conditions will not do so under normal preparative conditions and vice versa.

Experimental Section

The $Fe(PF_3)_5$ was prepared in a $Fe(PF_3)_x(CO)_{5-x}$ mixture as before[6] except that the photochemistry was done on a larger scale using a circulation apparatus.[7] In the final purification of the $Fe(PF_3)_5$ from lesser amounts of the various other carbonyls using a 12-m 40% dibutyl phthalate column, special care had to be taken to prevent traces of the carbonyls from being trapped with $Fe(PF_3)_5$. This could result from the use of too short a cycle time, and when it did traces of carbonyl groups had effects out of proportion to their concentrations.

The reactions of $Fe(PF_3)_5$ with acetone and acetonitrile were carried out under similar conditions. In a typical reaction, equal quantities (about 2 g each) of $Fe(PF_3)_5$ and the ligand were vacuum distilled into an irradiation vessel through P_4O_{10} drying traps. The outer Pyrex vessel was similar to Ace Glass 6515-25 and the inner quartz immersion well similar to Ace Glass 6515-34. The sample was then irradiated for approximately 20 min with a medium-pressure 450-W Hg lamp. The excess ligand and $Fe(PF_3)_5$ were removed at −30 °C. For acetonitrile, $Fe(PF_3)_4(CH_3CN)$ was sublimed high on the vessel upon gentle heating where it could be recovered. The acetone products were removed from the reaction vessel by heat and vacuum and then separated by chromatography on Varian-Aerograph Autoprep A700 on DC-702 silicone columns. Typically, 2 m × 0.6 cm columns, 30% DC-702 on Chromosorb P and 70–100 °C, were used. The products were characterized by electron impact mass spectrometry, infrared, and ^{19}F NMR spectroscopy. Ligand exchange reactions with acetone were also accomplished by vaporization cocondensation experiments. The details of the products obtained and the spectral properties are given in ref 7.

Chemical ionization and negative chemical ionization mass spectra of $Fe(PF_3)_5$ with a variety of ligands were obtained with an AEI Scientific Apparatus MS-902 mass spectrometer equipped with an SRIC chemical ionization source. Ionization was initiated by 490-eV (0.25 mA) electrons. The source temperature was monitored with a thermocouple detector. The relative pressures of the two reagents were estimated by use of an ionization gauge and checked with a Mensor quartz manometer attached to the chemical ionization source through a discharge suppression tube. In a typical experiment the relative pressures of $Fe(PF_3)_5$ and acetonitrile were maintained at 1:10 with a total pressure of 0.8 Torr.

Results and Discussion

The (positive) chemical ionization (CI) (Table I) and negative chemical ionization (NCI) (Table II) mass spectra of pentakis(trifluorophosphine)iron(0) ($Fe(PF_3)_5$) in the presence of an excess of acetonitrile are typical of the mass spectra obtained with the iron complex in the presence of other ligands that exchange readily with trifluorophosphine. The carbon monoxide containing ions in the CI spectrum are due to the presence of traces of iron-bound CO impurities in the $Fe(PF_3)_5$. The bulk of the ion current in this spectrum is carried by acetonitrile ligated iron species. In fact, only two of the prominent ions, *m/z* 267 and 496, contain the PF_3 ligand. This suggests that acetonitrile would readily exchange with trifluorophosphine in laboratory experiments, as it does (see below).

Since the general features of the chemical ionization mass spectra of $Fe(PF_3)_5$ in the presence of an excess of a series of other ligands do not differ markedly from each other, we have simply summarized the results of the examination of these spectra for the major ligand exchange reactions in Table III.

It will become clear from an examination of the data in Table III that the (positive) chemical ionization spectra correlate well with the laboratory substitution results. In these CI spectra, it is seen that carbon monoxide gives the greatest exchange with $Fe(PF_3)_5$. This is precisely what has been found in the laboratory results to be discussed later. It is also significant that, in addition to carbon monoxide, only tetramethylisobutyronitrile produces an ion corresponding to the pentacoordinate iron compound. These two contrast with other ligands such as acetonitrile, and this is in agreement with the known superiority of carbonyls and isonitriles to nitriles and

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Table I. Monoisotopic Chemical Ionization Mass Spectrum of $Fe(PF_3)_5 + CH_3CN$

m/z	probable formula	rel intensity, %	m/z	probable formula	rel intensity, %
127		16.1	220	$Fe(CH_3CN)_4$	100
136	$Fe(CH_2CN)_2$	82.0	221	$Fe(CO)_3(CH_3CN)_2$-H	13.0
138	$Fe(CH_3CN)_2$	28.2	238	$Fe(CH_3CN)_4(H_2O)$	2.3
142		7.5	248	$Fe(CO)(CH_3CN)_4$	3.5
151		3.1	267	$Fe(PF_3)(CH_3CN)_3$	11.9
157		3.0	317		7.2
168		5.0	423	$Fe(PF_3)_4(CH_3)$	2.0
174		12.5	496	$Fe(PF_3)_5$	56.1
179	$Fe(CH_3CN)_3$	38.1	535		2.0
180	$HFe(CH_3CN)_3$	17.2			
198	180 + H_2O	16.1			
207	$Fe(CO)(CH_3CN)_3$	4.0			
211		9.5			

Table II. Monoisotopic Negative Chemical Ionization Mass Spectrum[a]

m/z	probable formula	rel intensity, %
322	$H_2Fe(PF_3)_3$	21.6
361	$Fe(PF_3)_3(CH_3CN)$	0.32
408	$Fe(PF_3)_4$	100
409	$HFe(PF_3)_4$	27.8

[a] Ions with relative intensities less than 2% are not reported, with the exception of the ligand exchange ion at m/z 361.

related ligands as donors toward low-valent transition metals. The ligands isonitrile, CO, and PF_3 are the ones that π-back-bond more effectively than other types of ligands.[8]

The four ligands which we examined that showed no indication of ligand exchange ions are phosphorus trichloride, nitrogen, argon, and krypton. The spectrum of $Fe(PF_3)_5$ in the presence of phosphorus trichloride consists of a simple superposition of the high-pressure mass spectrum of each component taken individually.

Of the three hydrocarbons represented in Table III, isobutene was clearly the best ligand for iron, as would be expected for an olefin. The fact that isobutane and isopentane both associate with iron to give an observable complex is extremely interesting. It seems quite probable that association of these saturated hydrocarbons with iron to give stable ions must involve rupture of either carbon-carbon or carbon-hydrogen bonds.

The ligand exchange reactions of acetone with iron pentakis(trifluorophosphine) are unique both in the mass spectrometer and in laboratory experiments. Of all the ligands examined, only the acetone mass spectrum gives ions which correspond to iron bound to, among other things, fluorophosphine. The chemical process involving acetone which results in removal of fluorine from one of the trifluorophosphine ligands is obscure; however, the results of this process are clear both in the mass spectrum and in the laboratory. The chemical ionization mass spectrum of $Fe(PF_3)_5$ in the presence of excess acetone gives an ion at m/z 477 (4.4%, more than half the intensity of the molecule ion) which corresponds to removal of one fluorine from the coordinate molecule. If this intermediate were formed in the laboratory situation, it would be expected to be unusually reactive and could lead to diiron complexes with PF_2 bridging groups.

The fact that chemical ionization mass spectra are good predictors of ligand exchange can be further illustrated by a discussion of some laboratory results with these species.

The complete exchange found with carbon monoxide is as expected from the synthetic chemistry. Not only can one both thermally and photochemically exchange PF_3 readily into $Fe(CO)_5$ and vice versa, but Catral[9] has shown that the equilibrium constants for the reactions

$$Fe(PF_3)_x(CO)_{(5-x)} + PF_3 \rightleftarrows Fe(PF_3)_{(x+1)}CO_{(4-x)} + CO$$

are close to those based upon a statistical distribution of ligands. With irradiation times of up to a few hours, there is little evidence for polynuclear species, which is in agreement with what is found in the mass spectral work.

The laboratory results of the study of the photochemical reaction of $Fe(PF_3)_5$ with acetone are not complete, but they certainly confirm that it is unique among the ligands examined in this investigation. Gas chromatographic investigation of the species found in a photochemical reaction reveals no less than six low-volatility species (after removal of excess reactants). In addition, extremely low volatility material elutes from the column for many hours without any clear signs of resolution. Most prominent among the resolved peaks is the known compound[10] $Fe_2(PF_2)_2(PF_3)_6$. The molecular series $Fe_2(PF_2)_2(PF_3)_x(CO)_{6-x}$, in which the carbon monoxide presumably arose from the acetone, was produced with longer irradiation time. Long irradiation also produced $Fe(PF_3)_3(PF_2)_2C_3H_6O$. The fluorine NMR spectrum suggests that there are two different PF_2 groups present in this molecule but the broadness of the spectrum caused by all of the couplings has precluded a definitive structural assignment. Minor products from the acetone photolysis reaction include $Fe_2(P_2F_4)(PF_3)_x(CO)_{8-x}$ (x = 3, 4, 5) and $H_2Fe_2(P_2F_4)(PF_3)_6(CO)_2$. Presumably the iron atoms are bridged by a PF_2–PF_2 group in these compounds. The appearance of these molecules in the reaction mixture confirms the CI-based expectation of chemistry involving PF_2 when acetone is used as the exchange ligand.

Laboratory exchange of acetonitrile with $Fe(PF_3)_5$ yields only $Fe(PF_3)_4(CN_3CN)$ as stable, bright red crystals. The lack of products resulting from PF_2 chemistry is in agreement with expectations based on the CI reactivity of this same mixture.

Table III. $Fe(PF_3)_n(L)_m{}^+$ Ions Present in the Chemical Ionization Mass Spectra of $Fe(PF_3)_5$ + L:[a]

	CO	acetone	pyridine	CH_3CN	TMBI[b]	i-C_4H_8	i-C_5H_{12}	i-C_4H_{10}
n	m	m	m	m	m	m	m	m
0	1, 2, 3, 4, 5	2, 3, 4	2, 3, 4	2, 3, 4	3, 5	1, 2, 3	1	1
1		3	0, 3	3	1, 4		1	
2	0, 1, 3		1		3		0, 1	
3	0, 2		2, 3		0, 2	1	0	
4	0, 1	1	1		1	0, 1	0	0, 1

[a] See Experimental Section for details. [b] 2,2,3,3-Tetramethylisobutyronitrile.

The CI results with the other ligands examined (Table III) are in solid accord with data in the literature for laboratory experiments. The simple substitution found with isobutene has its laboratory analogy in studies by Kruck,[11] who has isolated a number of activated monoolefin complexes from the thermal or photochemical interaction of $Fe(PF_3)_5$ and the olefins. The noninteraction of $Fe(PF_3)_5$ and Ar, Kr, and N_2 fits the known facts. Turner, Polaikoff, et al.[12] have shown that, even under matrix isolation conditions, $Fe(CO)_4$ and Ar do not interact and the interaction with the heavier noble gases is very weak, and not to be expected at temperatures above 10-20 K. Although N_2 forms species of the type $Fe(N_2)_x(CO)_{5-x}$ under matrix isolation conditions, there is no evidence to suggest formation of the corresponding PF_3 complexes under laboratory conditions or in a mass spectrometer.

Chemical ionization studies with saturated alkanes present results that are intriguing and worth further study. The mass spectra indicate that there is an interaction between alkanes and $Fe(PF_3)_5$ or $Fe(PF_3)_4$. The precise nature of the bonding is not known. It may represent C-H or C-C bond breaking, which would be unusual for a homogeneous catalytic reaction. However, the intermediacy of such species in catalytic reactions has been postulated.[13] Further work is now underway.

It is, at first, surprising that, when hydrogen is the CI reagent gas, the abundance of $H_2Fe(PF_3)_4$-related ions does not significantly increase as compared to acetone or other reagent gases. The compound $H_2Fe(PF_3)_4$ is quite stable; however, our attempts to produce significant quantities of this compound by direct thermal or photochemical interaction of H_2 and $Fe(PF_3)_x(CO)_{5-x}$ have universally been unsuccessful. The hydride compound has been synthesized by photocatalytic interaction of H_2 and $Fe(PF_3)_5$ with platinum on asbestos.[14] The CI results are consistent with the requirements for catalytic activation of this reaction.

In contrast to the CI spectrum, the NCI spectrum of $Fe(PF_3)_5$ with CH_3CN as reagent gas shows very little influence of the reagent gas on the spectrum (Table II). Thus, in contrast to CI, the NCI spectrum is vastly dominated by PF_3-ligated iron ions. Of these, the prominent species is the iron tetrakis(trifluorophosphine) anion at m/z 408. There is generally a low-abundance ion in the spectrum corresponding to substitution of one of the trifluorophosphines by the available ligand. The intensity of this ion (m/z 361) in the acetonitrile spectrum was only 0.3%.

It is not very surprising that negative chemical ionization mass spectra offer little information about the bimolecular reactivity of $Fe(PF_3)_5$ with other ligands. The bimolecular exchange reactions that occur in the gas phase must be activated processes just as they are in laboratory experiments. In the case of positive ions it is possible for the reactive ion to contain a substantial amount of internal energy which can provide the necessary activation energy for a reaction. However, negative ions that contain substantial amounts of internal energy will have very short half-lives because of autoionization. The lack of ligand exchange reactions in the negative ion spectra is thus probably due to the fact that the half-lives of the reactive anions are less than the required time for detection. Another factor that contributes to the lack of exchange reactivity in the NCI spectra is the fact that the exchange reactions are nucleophilic processes, which will be strongly suppressed with anionic substrates.

In summary it appears that (positive) chemical ionization mass spectra can provide qualitatively reliable predictions of ligand exchange reactivity for transition-metal complexes. The further use of this technique for exploration of homogeneous catalytic reactivity is presently being explored. The negative chemical ionization spectra do not provide the correlation of the CI.

References and Notes

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(2) R. J. Clark and M. A. Busch, *Acc. Chem. Res.*, **6**, 246 (1973).
(3) G. L. Swartz and R. J. Clark, *J. Am. Chem. Soc.*, submitted.
(4) R. C. Dougherty, *Top. Curr. Chem.*, **45**, 93 (1974).
(5) W. N. Olmstead and J. I. Brauman, *J. Am. Chem. Soc.*, **99**, 4210 (1977); C. H. DePuy, V. M. Bierbaum, R. J. Schmitt, and R. H. Shapiro, *ibid.*, **100**, 2920 (1978); J. J. Solomon and F. H. Field, *ibid.*, **98**, 1567 (1976); P. F. Levonowich, H. P. Tannenbaum, and R. C. Dougherty, *J. Chem. Soc., Chem. Commun.*, 597 (1975).
(6) R. J. Clark, *Inorg. Chem.*, **3**, 1395 (1964).
(7) M. A. Krevalis, Ph.D. Dissertation, Florida State University, 1977.
(8) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed., Interscience, New York, 1972, Chapter 22.
(9) J. C. Catral, Masters Thesis, Florida State University, 1976.
(10) P. L. Timms, *J. Chem. Soc. A*, 2526 (1970).
(11) T. Kruck and L. Knoll, *Chem. Ber.*, **106**, 3578 (1973).
(12) J. Pollakoff and J. J. Turner, *J. Chem. Soc., Dalton Trans.*, 1351 (1973), and other papers in series.
(13) M. A. Schroeder and M. S. Wrighton, *J. Am. Chem. Soc.*, **98**, 551 (1976); G. Henrice-Olive and S. Olive, "Coordination and Catalysis", Verlag Chemie, Weinheim/Bergstr., Germany, 1976, p 119.