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Phosphorus Trifluoride Substitution Compounds of Iron Pentacarbonyl

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The reaction of $Fe(CO)_5$ and PF_3 at elevated temperatures and pressures results in the formation of mixtures of $Fe(CO)_{5-x}(PF_3)_x$ compounds where x has values of 1–5. The degree of replacement of carbon monoxide by phosphorus trifluoride is dependent upon the temperature of reaction with the average x in the above formula being 1 at 170° and 3–4 at 280° under pressures of 200–500 p.s.i. Higher temperatures lead to decomposition. Ultraviolet irradiation of mixtures with an average x of about 3 in the presence of PF_3 gas produces higher substitution without the problem of decomposition. The compounds were separated and isolated by means of vapor phase chromatography. They are yellow liquids except $Fe(PF_3)_5$ which melts to a yellow liquid at 44°. Infrared spectra of these compounds suggest some interesting structure anomalies but it is obvious that the structures are not simple trigonal bipyramids.

Introduction

Although iron pentacarbonyl undergoes substitution by a wide variety of ligands, comparatively few will replace carbon monoxide extensively to yield one for one substitution products. Frequently other types of compounds result such as $RFe(CO)_3$[1] where R is some polymerization product of the ligand or $[Fe^{II}A_6][Fe_3(CO)_{11}]$[2] where the polymeric carbonyl ferrate anion is produced by valency disproportionation. Substitution compounds of the type $FeL_x(CO)_{5-x}$ where L is a monodentate ligand are comparatively rare with the compounds in which $x = 3$, 4, or 5 being nearly nonexistent. Bidentate ligands such as diphosphines[3] and diarsines[4] are known to yield the tri- and monocarbonyls.

Phosphorus trifluoride seems like a ligand that will probably react more extensively than most ligands. Several compounds have been prepared in which phosphorus trifluoride replaces carbon monoxide, producing compounds much like the original carbonyl. Examples are $Ni(PF_3)_4$ prepared by Wilkinson and Irvine[5] and $(PF_3)_2PtCl_2$ prepared by Chatt and Williams.[6] Work by Clark and Brimm[7a] has further shown that the compounds intermediate between $Ni(CO)_4$ and $Ni(PF_3)_4$ can be prepared and isolated and that the properties of these compounds are similar to those of the two end members. A very recent example is the work of Kruck,[7b] who prepared molybdenum and chromium compounds of the type $M(PF_3)_6$ and $M(PF_3)_3(CO)_3$.

It has been concluded that PF_3 is capable of a high degree of π-bonding in its complexes in a manner related to the π-bonding in carbonyl complexes. Further, it appears that PF_3, like carbon monoxide, has little chance to form conventional σ-bonds. Phosphorus trifluoride, for example, does not form a complex with BF_3.[8] Other than a few borane compounds like $BH_3 \cdot PF_3$ there are no known complexes of PF_3 in which only σ-bonds are likely to be involved.

The apparent similarity between PF_3 and CO made it seem likely that extensive substitution between $Fe(CO)_5$ and this phosphine should occur. Further, its inability to polymerize and its seeming inability to form the σ-bonded cation portion of ionic iron carbonyls suggests the feasibility of the preparation of compounds like $Fe(PF_3)_x(CO)_{5-x}$.

The actual preparation of the entire series with x ranging from 1 to 5 has been accomplished. A description of the details follows.

Experimental

Phosphorus trifluoride was prepared by a modification of the procedure of Williams.[9] Instead of treating PCl_3 with dry ZnF_2 powder, the ZnF_2 was slurried in anhydrous tetrahydrofuran. After an induction period of up to 15 min., the reaction proceeded quite smoothly depending only upon the rate of PCl_3 addition. This technique serves to prevent the formation of intermediate chlorofluorides by allowing more intimate contact between the PCl_3 and ZnF_2. The yield was somewhat less than theoretical owing to a side reaction which resulted in the formation of a water-insoluble oil. The resultant PF_3 was purified by passing it through a 12-in. water tower packed with glass beads to remove impurities such as HCl. The PF_3 hydrolyzes slowly enough that this causes no problem. The PF_3 was dried by passing it through a −78° trap and then through a bed of activated Linde 4A Molecular Sieves. The PF_3 was trapped from the N_2 carrier gas at liquid nitrogen temperature. The ZnF_2 was obtained from Amend Chemical Co. and dried at 150°.

The $Fe(CO)_{5-x}(PF_3)_x$ compounds were initially prepared as mixtures by the reaction of iron pentacarbonyl and excess PF_3 at elevated temperatures and pressures. A 150-ml. capacity stainless steel pressure bomb was used. The bomb was evacuated, cooled to −195°, and then $Fe(CO)_5$ and PF_3 were transferred into it by using vacuum techniques. In a typical run, 1.5 ml. of $Fe(CO)_5$ (11 mmoles) and sufficient PF_3 to create a pressure of 200–500 p.s.i. at room temperature were used. This quantity of PF_3 is estimated to be about 200 mmoles. The reaction vessel was heated to temperatures between 170 and 275° for 18 hr.

The reaction mixture was separated into fractions by trans-

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[1] See, for example, J. Chatt, "Organometallic Chemistry," H. Zeiss Ed., Reinhold Publishing Co., New York, N. Y., 1960, p. 487 and references therein.

[2] Reference 1, p. 491.

[3] T. A. Manuel, *Inorg. Chem.*, **2**, 854 (1963).

[4] H. Nigam, R. S. Nyholm, and E. V. R. Rao, *J. Chem. Soc.*, 1397 (1959).

[5] J. W. Irvine, Jr., and G. Wilkinson, *Science*, **113**, 742 (1951); G. Wilkinson, *J. Am. Chem. Soc.*, **73**, 5501 (1951).

[6] J. Chatt and A. A. Williams, *J. Chem. Soc.*, 3061 (1951).

[7] (a) R. J. Clark and E. O. Brimm, unpublished work; (b) Th. Kruck, *Z. Naturforsch.*, **19b**, 165 (1964).

[8] H. S. Booth and J. H. Walkup, *J. Am. Chem. Soc.*, **65**, 2334 (1943).

[9] A. A. Williams, *Inorg. Syn.*, **5**, 95 (1957).

ferring the contents of the bomb through a succession of traps at −78 and −195° *in vacuo*. The $Fe(CO)_{5-x}(PF_3)_x$ compounds were trapped at −78°, the PF_3 at −195° (for reuse), and the carbon monoxide was pumped out of the system. An alternate technique that was used frequently was to cool the bomb to −195° and pump off the carbon monoxide, warm the bomb to −78° and remove the PF_3, and finally vacuum distil the iron compounds from the bomb at room temperature.

In order to prepare mixtures rich in $Fe(PF_3)_5$, the following procedure was used. Several tenths of a milliliter of a mixture having the over-all composition of about $Fe(CO)_2(PF_3)_3$ was distilled into a 1-l. flask equipped with a vacuum stopcock and a joint for attachment to a high vacuum system. Phosphorus trifluoride was admitted to the flask until a pressure of $^2/_3$ atm. was reached. The flask was placed either in front of a 100-watt ultraviolet lamp or allowed to stand in the sunlight for several days. Several times during the irradiation, the flask was cooled to −195° and evacuated to remove the evolved carbon monoxide. Although this reaction was not studied in depth, it appeared that the nature of the glass container (Pyrex, Vycor, or Pyrex with a quartz window) was not of particular importance.

The compounds in the mixtures were separated by means of vapor phase chromatography, using either a ChromAlyzer-100 equipped with a series of glass traps at the gas outlet or an Autoprep-700. In the operation of the latter instrument, manual injection with automatic sample collection was used under isothermal conditions.

The best conditions that were found for separation were as follows: an 8-m. long $^3/_{16}$-in. dibutyl phthalate column (10% on Kromat FB), helium at about 60 ml./min., column temperature 60°, and injections of 10 μl. Good resolution could still be obtained with the carbonyl-rich compounds with 20-30-μl. injections, but with phosphine-rich material 3–5-μl. injections were the limit. When the $Fe(PF_3)_5$ content of the compounds was high enough to make the mixture solid, a small amount of Freon 113 (CCl_2FCClF_2) was added to lower the melting point below room temperature. The compounds were trapped from the carrier gas at −78°. The purified compounds were handled by high-vacuum technique, keeping exposure to the atmosphere and light reduced, and stored at −78° when being kept for prolonged periods of time.

Infrared spectra were run in cyclohexane on a Perkin-Elmer 221 in 0.1-mm. cells at concentrations of about 2 μl. of compound per 0.20 ml. of solvent. Rough density measurements were made by weighing the volume of a compound injected from a Hamilton syringe through a septum into a tared container.

The reactivity of these compounds toward various solvents was tested by adding the compound to the solvent, followed by injecting quantities of the mixture into a vapor phase chromatograph at various time intervals. The disappearance of the compound peaks was taken as evidence of reaction.

Analysis.—Iron analysis was done spectrophotometrically with the *o*-phenanthroline method[10] using a Spectronic 20. Phosphorus, fluorine, and carbon analyses were carried out by the Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Because of the great similarity between the compounds, it was felt necessary to have the molecular weight determined for only one compound. Owing to the great difficulty in isolating large quantities of $Fe(PF_3)_5$, its analysis was not repeated in order to obtain better agreement. Calcd. for $Fe(CO)_4(PF_3)$: C, 18.78; Fe, 21.83; P, 12.10; F, 22.27. Found: C, 18.90; Fe, 21.8; P, 12.58; F, 21.66; *d* 1.53 g./cc. Calcd. for $Fe(CO)_3(PF_3)_2$: C, 11.41; Fe, 17.68; P, 19.61; F, 36.09. Found: C, 11.80; Fe, 17.5; P, 19.76; F, 35.56; *d* 1.66 g./cc. Calcd. for $Fe(CO)_2(PF_3)_3$: C, 6.39; Fe, 14.86; P, 24.72; F, 45.50; mol. wt., 376. Found: C, 6.26; Fe, 14.8; P, 24.04; F, 45.72; mol. wt., 388; *d* 1.80 g./cc. Calcd. for $Fe(CO)(PF_3)_4$: C, 2.76; Fe, 12.82; P, 28.43; F, 52.32. Found: C, 2.78; Fe, 12.5; P, 27.97; F, 51.97; *d* 1.92 g./cc. Calcd. for $Fe(PF_3)_5$: Fe, 11.27; P, 31.24; F, 57.49. Found: Fe, 9.8; P, 30.46; F, 57.30.

Results

The reaction of phosphorus trifluoride and iron pentacarbonyl at elevated temperatures and pressures results in mixtures of all the anticipated compounds of the formula $Fe(CO)_x(PF_3)_{5-x}$ where x has the values of 0 through 5. The ultraviolet irradiation of PF_3-enriched iron carbonyl in the presence of PF_3 is used to produce mixtures containing high percentages of $Fe(PF_3)_5$.

The reaction between $Fe(CO)_5$ and PF_3 at pressures of 200–500 p.s.i. becomes appreciable at temperatures of about 150° (for 18-hr. reaction times). As the temperature is raised, the degree of substitution becomes greater. Thus at a temperature of about 275° the product mainly consists of the tetra- and triphosphine with much smaller amounts of the penta- and diphosphine and almost no tetra- and pentacarbonyls. Efforts to extend the reaction to temperatures above 275–300° in order to obtain greater enrichment of PF_3 failed owing to decomposition with the simultaneous formation of a black solid.

Table I shows the composition (retention time times peak height) of the reaction between $Fe(CO)_5$ and PF_3 at various temperatures for 18 hr. Also included in this table are typical retention times for the compounds under the conditions mentioned in the Experimental section. Equilibrium was most probably not reached, thus no effort was made to obtain high accuracy in either the measurement of temperature or composition.

TABLE I

COMPOSITION (%) OF PF_3–$Fe(CO)_5$ REACTION MIXTURES

Compound	Retention time, min.	Reaction temperature			
		195°	225°	245°	290°
$Fe(PF_3)_5$	7.3	...	0.5	1.3	2.5
$Fe(PF_3)_4(CO)$	7.6	Trace	14.8	35.5	43.2
$Fe(PF_3)_3(CO)_2$	8.9	2.0	70.2	55.4	49.6
$Fe(PF_3)_2(CO)_3$	14.4	12.8	14.5	7.7	4.8
$Fe(PF_3)(CO)_4$	24.8	55.2	Trace	...	...
$Fe(CO)_5$	44.7	30.0	...	...	...

The yield of the mixtures appears to be nearly quantitative by any of the above approaches with no side reactions taking place until the obvious decomposition that takes place at 275–300°. It has not been possible to force the reaction to completion at lower reaction temperatures by frequently removing the evolved carbon monoxide with evacuation while keeping the other materials nonvolatile by cooling the vessel to −195°.

The injection of the various mixtures into a vapor phase chromatograph using a dibutyl phthalate column (the best of about 15 tried) resulted in six sharp peaks. This is the number of compounds to be expected with one-for-one substitution of phosphorus trifluoride for carbon monoxide. The sixth peak had the same retention time as iron pentacarbonyl.

These compounds can be separated and isolated in

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(10) L. M. Melnick, "Treatise on Analytical Chemistry," I. M. Kolthoff and P. J. Elving, Ed., Interscience Publishers, New York, N. Y., 1962, Part II, Vol. 2, p. 295.

substantially pure form by either manual or automatic sample collection from the v.p.c. The greatest difficulty was encountered with the first three compounds. Complete resolution required small samples of about 1 μl. Samples larger than 5 μl. caused such bad overlap that "heart cutting" would no longer yield pure compounds. A second purification would be necessary. A compromise between the need for large injections and high resolution was struck at 3–4 μl.

The compounds have been unequivocally identified by means of complete chemical analysis. The data are given in the Experimental section. The compounds have been shown to be the following in the order of elution: $Fe(PF_3)_5$, pentakis(trifluorophosphine)iron(0); $Fe(CO)(PF_3)_4$, carbonyltetrakis(trifluorophosphine)iron(0); $Fe(CO)_2(PF_3)_3$, dicarbonyltris(trifluorophosphine)iron(0); $Fe(CO)_3(PF_3)_2$, tricarbonylbis(trifluorophosphine)iron(0); $Fe(CO)_4(PF_3)$, tetracarbonyl(trifluorophosphine)iron(0). Iron pentacarbonyl comes out last. The order of elution is opposite to the order of increasing molecular weight.

These compounds are all liquids except $Fe(PF_3)_5$ which is a solid that melts at 44° when pure. Of the remainder, only $Fe(CO)(PF_3)_4$ and the starting material $Fe(CO)_5$ solidify above −78°. These liquids are all yellow with the color becoming slightly lighter in shade as one progresses through the series from $Fe(CO)_5$ to $Fe(PF_3)_5$. The compounds, like their parent $Fe(CO)_5$, are all somewhat unstable toward water and oxygen. However, the stability toward these materials increases quite significantly as phosphorus trifluoride replaces carbon monoxide.

The compounds are stable in solvents like cyclohexane, benzene, and fluorocarbons and are attacked fairly rapidly by solvents like acetone and ethanol. They are immiscible with water and react with it only slowly.

These compounds are moderately volatile and readily handled in a vacuum system at room temperature. The vapor pressure has not been measured, but seems to be comparable to that of $Fe(CO)_5$ for all of the species.

The stability of the compounds toward light increases markedly as one replaces carbon monoxide groups by phosphorus trifluoride groups. The reactions that take place are highly complicated. Light induces disproportionation of any intermediate compound to mixtures of compounds. Decomposition is also evident. It is known that $Fe(CO)_5$, when formed, will decompose to give $Fe_2(CO)_9$ and CO, but it is not known if any of the intermediates can do so.

The infrared spectra of these compounds have been obtained and are reported in Table II. The only bands present are in the carbonyl and phosphorus–fluorine stretching regions.

Discussion

This appears to be the first case in which all possible substitution compounds of iron pentacarbonyl have been obtained for a monodentate ligand. The compounds are covalent, and it can be concluded that they are all monomeric like $Fe(CO)_2(PF_3)_3$. There is no evidence for the ionic or polymeric species so often found for iron carbonyl substitution compounds.

TABLE II

INFRARED SPECTRA (CM.$^{-1}$) OF $Fe(CO)_{5-x}(PF_3)_x$ COMPOUNDS

Compound	Carbonyl region	P–F region
$Fe(CO)_4(PF_3)$	2101 w	901 vw
	2094 w	889 m
	2021 vs	871 ms
	2004 vs	
	1996 vs	
	1970 vw	
	1960 vw	
$Fe(CO)_3(PF_3)_2$	2085 m	903 m
	2076 m	895 m
	2016 vs	875 m
	1990 vs	852 m
	1965 vw	
	1955 vw	
$Fe(CO)_2(PF_3)_3$	2058 m	926 w
	2039 w	896 w
	2011 vs	881 m
	1987 ms	853 m
$Fe(CO)(PF_3)_4$	2038 m	948 m
	2009 m	915 vs
		898 s
		886 s
		851 vs
$Fe(PF_3)_5$		920 vs
		900 vs
		852 vs

The volatility of these compounds is at first somewhat surprising. However, it has been observed that phosphorus trifluoride substitution into four carbonyls —$Ni(CO)_4$, $Fe(CO)_5$, $Mo(CO)_6$, and $Co_2(CO)_8$—causes little decrease in volatility compared to that which might be expected due to the large increase in molecular weight. In fact, qualitative data on PF_3–$Mo(CO)_6$ and PF_3–$Co_2(CO)_8$ systems[11] suggest that the volatility of some of the intermediate compounds is actually considerably greater than that of the parent compound. The explanation probably lies in the low polarizability of the fluoride that makes up the exterior environment in analogy with the volatility increase from hydrocarbons to fluorocarbons.

The physical similarity of these various substitution compounds again emphasizes the great similarity between carbon monoxide and phosphorus trifluoride as ligands.

The similarity is indicated further by the infrared carbonyl stretching frequencies of the various compounds. In most substituted carbonyl compounds, the CO stretching frequencies shift to lower and lower values as the degree of substitution increases.

This type of behavior is not observed at all with the iron complexes of phosphorus trifluoride. There is no consistent shift toward lower frequencies and some of the carbonyl stretching frequencies have actually shifted to slightly higher values. This type of behavior has also been observed with nickel complexes[7] and tends to suggest that PF_3 is able to π-bond to an extent which is comparable with carbon monoxide. The mechanism

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(11) P. I. Hoberman and R. J. Clark, work in progress.

is different, however. In one case the π-bonding is by the donation of a pair of electrons from the metal to antibonding π-orbitals on the carbon and in the other by the donation to empty 3d orbitals on the phosphorus.

One of the most intriguing aspects of this research has been the complex infrared spectra and their interpretation in terms of structures of these substituted iron carbonyls. The trigonal bipyramid structure of Fe(CO)$_5$ was to have been expected for each of these substitution products. However, a comparison of the spectra of the tetra- and tricarbonyl complexes with those calculated on the basis of group theory by Cotton and Parish[12] shows no similarity. For example, the monosubstituted phosphine Fe(CO)$_4$(PF$_3$) should show two to four peaks in the various trigonal bipyramid and square pyramid configurations. Five major peaks are observed. For the disubstituted compound, one or three should be observed. Four are seen.

Careful chromatographic purification of these compounds would seem to exclude impurities as an explanation. However, several possible explanations can be proposed, although none has yet been proven. It is possible that two or more stereoisomers exist with properties so similar that attempts to separate them have failed. The vapor phase chromatography peaks of all compounds were highly symmetrical, showing no indication of two compounds being present. Infrared spectra of two fractions of the most clearly resolved compound Fe(CO)$_4$(PF$_3$) after it had been separated into head and tail cuts were identical—still showing no evidence for separation into isomers. About 15 different types of columns have not allowed the separation of the various potential isomers.

The possibility of moderately rapid internal inversion between isomer forms is a potentially attractive explanation. This is similar to postulations made by several workers for compounds like Fe(CO)$_5$, PF$_5$, and VF$_5$.[13–15] In their work they postulated this form of inversion at a rapid rate to account for the lack of an n.m.r. chemical shift expected for two types of nonequivalent atoms attached to the central atom. If this is the case, then two isomers exist, but there would be no chance to isolate them through chromatography, although they would be clearly indicated by infrared spectroscopy. A phosphorus and fluorine n.m.r. study of the various compounds is in progress in an effort to clear up the matter.

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(12) F. A. Cotton and R. V. Parish, *J. Chem. Soc.*, 1440 (1960).

(13) R. Bramley, B. N. Figgis, and R. S. Nyholm, *Trans. Faraday Soc.*, **58**, 1893 (1962).

(14) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).

(15) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

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Dimethyl- and Diethyldithiocarbamate Complexes of Some Metal Carbonyl Compounds[1]

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The reactions of N,N-dialkyldithiocarbamate ions (alkyl = CH$_3$, C$_2$H$_5$) and tetramethyldithiuramyl disulfide [(CH$_3$)$_2$NC(S)S–]$_2$ with various metal carbonyl derivatives have been studied. The characteristic reaction of the former with metal carbonyl halides is displacement of the halide and one carbonyl group, while the dithiuramyl disulfide characteristically cleaves binuclear carbonyls displacing one CO from each metal atom at the same time. All compounds prepared evidently contain bidentate dithiocarbamato ligands. The infrared spectra show that there is partial double bond character in the CN bonds and that the dithiocarbamato groups have no marked effect on metal–CO multiple bonding.

Introduction

A number of transition metal dithiocarbamate complexes have been previously studied and characterized.[2] The dithiocarbamate group has been found to act as a uninegative bidentate ligand, coordinating through both sulfur atoms,[3] and both four- and six-coordinated complexes of a number of transition metal ions have been isolated.

A characteristic feature of the dialkyldithiocarbamate group is its infrared spectrum. The C–N single bond stretching frequencies in amines[4] fall in the region 1250–1350 cm.$^{-1}$, close to the C–H deformation bands, and the >C=N– stretching frequency in the region 1640–1690 cm.$^{-1}$. Chatt, Duncanson, and Venanzi[2] have found that dithiocarbamate complexes exhibit a band of medium intensity in the region 1480–1550 cm.$^{-1}$, that is between the ranges for C—N and C=N. This band has been assigned to a CN stretching mode,

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(1) Supported by the National Science Foundation.

(2) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Suomen Kemi*, 75 (1956).

(3) P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *J. Chem. Soc.*, 668 (1962).

(4) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958.