

Stereochemical Studies of Metal Carbonyl-Phosphorus Trifluoride Complexes

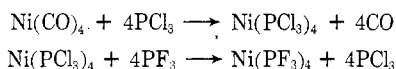
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Transition metal carbonyl chemistry originated with the discovery of Ni(CO)₄ in 1890. Since that time many other carbonyl complexes have been prepared, as well as a large number of compounds containing a variety of Lewis bases substituted for one or more of the carbonyl groups. As a general rule, the bonding properties of these other bases are quite different from those of CO, and the physical properties of the species formed by substitution of these bases are quite different from those of the parent carbonyl. Phosphorus trifluoride and its complexes are a striking exception.

The similarity of PF₃ and CO as ligands was first noted by Chatt.¹ In 1950, he suggested that phosphorus trifluoride should be capable of forming a complex with nickel, analogous to Ni(CO)₄. One year later Wilkinson² carried out the reactions



in which the final product, Ni(PF₃)₄, had properties quite similar to the carbonyl.

Chatt and Williams¹ at about the same time prepared a material of the approximate composition Ni(CO)₂(PF₃)₂. The properties of this material were so similar to those of the tetracarbonyl that it was not then possible to prove that the composition represented an actual intermediate substitution compound, as opposed to a mixture of Ni(CO)₄ and Ni(PF₃)₄. More recent work, however, has shown that, in addition to the tetracarbonyl and tetraphosphine, all possible intermediates do exist.³

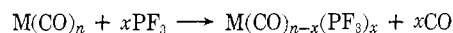
The similarity between the properties of metal carbonyls and their phosphorus trifluoride analogs has now been demonstrated for a large number of cases. This Account describes some of these studies, placing major emphasis on work with mixed carbonyl-phosphine complexes carried out in the authors' laboratory. The totally substituted species have been extensively reviewed by Kruck⁴ and more recently by Nixon.⁵

Work with these complexes has yielded considerable information on such subjects as bonding, stereo-

chemistry, and ligand site exchange. We believe that PF₃ can serve as an excellent model for CO, and, as such, produces compounds readily studied by fluorine nmr. Much of the information which this work has yielded would have been difficult, if not impossible, to obtain using ¹³C nmr.

Preparation

Most Lewis base substitution products of metal carbonyls are prepared by direct ligand replacement of carbon monoxide in the parent carbonyl. As applied to phosphorus trifluoride, the process is called trifluorophosphinedecarbonylation. With most lig-



ands the activation energy required to progress through successive stages of substitution increases markedly at each stage.⁶ Thus, through judicious control of time and temperature in a thermal substitution it is usually possible to obtain a product essentially composed of a single compound. A simple purification procedure such as recrystallization is frequently sufficient to yield the pure complex. However, this state of affairs does not exist in metal carbonyl-trifluorophosphine chemistry.

Although definitive data are lacking, the activation energies for each stage of PF₃ substitution appear to be nearly the same. As a result, the substituted compounds react with PF₃ almost as readily as the parent carbonyl, and complex mixtures are produced which are difficult to separate. With most monometallic carbonyls, M(CO)_n, these mixtures usually contain all possible compositions of the type M(PF₃)_x(CO)_{n-x}. If more than one isomer can result from each degree of PF₃ substitution, all possible isomers are usually present as well. By controlling the PF₃:CO ratio and the time of reaction, only limited control of the system composition is possible.

Reactions of PF₃ with metal carbonyls containing such readily replaceable ligands as amines or certain cyclic polyenes sometimes produce a limited number of products. Examples include the reaction of PF₃ with norbornadienemolybdenum tetracarbonyl⁷ to yield *cis*-Mo(CO)₄(PF₃)₂, with aminemolybdenum

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(1) J. Chatt, *Nature (London)*, **165**, 637 (1950); J. Chatt and A. A. Williams, *J. Chem. Soc.*, 3061 (1951).

(2) G. Wilkinson, *J. Amer. Chem. Soc.*, **73**, 5501 (1951).

(3) R. J. Clark and E. O. Brimm, *Inorg. Chem.*, **4**, 651 (1965).

(4) T. Kruck, *Angew. Chem., Int. Ed. Eng.*, **6**, 53 (1967).

(5) J. F. Nixon, *Advan. Inorg. Chem. Radiochem.*, **13**, 363 (1970).

(6) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967.

(7) C. G. Barlow, J. F. Nixon, and M. Webster, *J. Chem. Soc. A*, 2216 (1968); R. J. Clark, unpublished observations.

pentacarbonyl⁸ to yield $\text{Mo}(\text{CO})_5\text{PF}_3$, and with cycloheptatrienemolybdenum tricarbonyl to yield $\text{Mo}(\text{CO})_3(\text{PF}_3)_3$. In the last case, the *mer*, or a mixture of the *mer* and *fac*, isomers can be obtained, depending on the technique.⁷ (In the *mer* isomer three PF_3 ligands are planar, and in the *fac* isomer they are mutually perpendicular.) The factors controlling this isomer distribution have not been fully determined.

The speed of reaction between PF_3 and a metal carbonyl is variable, but, in general, the rate decreases as the coordination number of the metal increases. For $\text{Ni}(\text{CO})_4$, $\text{HCo}(\text{CO})_4$, and $\text{Co}(\text{NO})(\text{CO})_3$ reaction occurs at room temperature or below. For complexes of higher coordination number, either high-pressure-high-temperature or photochemical conditions are required.

Only limited work has been done on the substitution of PF_3 into polymetallic carbonyls.⁸ However, there appears to be a marked reluctance for simple replacement to occur, especially with complexes of the first-row transition metals.

Iron pentacarbonyl readily undergoes photochemical reaction to yield $\text{Fe}_2(\text{CO})_9$, but once PF_3 groups have been introduced, the $\text{Fe}(\text{PF}_3)_x(\text{CO})_{5-x}$ species do not yield dimers, even after extensive irradiation.⁹ The hydride $\text{HCo}(\text{CO})_4$ loses H_2 at -20° to yield $\text{Co}_2(\text{CO})_8$, but $\text{HCo}(\text{PF}_3)_4$ is stable to 200° . The $\text{HCo}(\text{PF}_3)_x(\text{CO})_{4-x}$ species have intermediate stabilities, but we have not been able to demonstrate¹⁰ simple loss of H_2 . Dimanganese decacarbonyl can have four CO groups replaced sequentially, but any attempt at further substitution produces $\text{Mn}_2(\text{PF}_2)_2(\text{PF}_3)_x(\text{CO})_{8-x}$ compounds with PF_2 bridges.¹¹ The $\text{Ru}_3(\text{CO})_{12}$ trimer can have up to six CO groups replaced sequentially before breaking down to yield the $\text{Ru}(\text{PF}_3)_x(\text{CO})_{5-x}$ species.¹²

Separation

The physical similarity of the $\text{M}(\text{PF}_3)_x(\text{CO})_{n-x}$ species makes their separation difficult. The solubilities and volatilities are too much alike for such techniques as recrystallization, sublimation, or pot-to-pot distillation to be completely successful. However, Bigorgne¹³ has claimed an enrichment of the $\text{Fe}(\text{CO})_x(\text{PF}_3)_{5-x}$ compounds by careful pot-to-pot distillation.

Distillation of the $\text{Mo}(\text{PF}_3)_x(\text{CO})_{6-x}$ species on a 24-in. spinning band column at reduced pressures has also yielded partial enrichment of the more highly substituted species, but only the monophosphine could be obtained pure. In general, however, fractional distillation is an unattractive separation technique. The compounds are quite toxic, some four-coordinate systems disproportionate readily, and, in general, the volatilities are simply too similar.

The separation technique that has proven most

generally useful has been gas-liquid chromatography on a small preparative scale. Columns packed with various silicon oils, phthalates, or squalene on firebrick are used. For the $\text{Ni}(\text{PF}_3)_x(\text{CO})_{4-x}$ and $\text{Co}(\text{NO})(\text{PF}_3)_x(\text{CO})_{3-x}$ species, disproportionation can still be troublesome. High column temperatures can also result in compound decomposition.

Elution chromatography from silica or alumina columns has not been particularly successful. The long retention times often result in extensive reaction with the basic alumina or with adsorbed water. However, a possible tool for the future, especially for systems with low volatility, is high-pressure liquid chromatography.

Characterization

The carbonyl-trifluorophosphine species can be characterized by a variety of techniques which have been found to be generally applicable from one group of complexes to another. *Sequence of formation* will generally provide the first clue in any new system. If replacement of CO by PF_3 is sequential, then the order in which the new species appear should be a function of the extent of PF_3 substitution. When prudently applied, an assignment based on this technique has never failed to be confirmed by other methods of characterization.

Sequence of elution is a consistent pattern in the glpc separations of these systems. The retention times of the species decrease as the degree of substitution increases. Thus, the parent carbonyl is always the last to be eluted, the monophosphine somewhat earlier, the diphosphine earlier yet, and so forth.

The matching of an experimental *infrared spectrum* with that predicted by group theory usually adds further confirmation to the identification of compounds containing one or more carbonyl groups.¹⁴ Frequently this method has also been useful in detecting the presence of isomers, and in determining possible structures for these species.

Fluorine nmr yields readily recognizable patterns. The typical pattern for a monophosphine consists of a doublet with $^1J_{\text{PF}}$ equal to about 1300 Hz. The patterns become more complex as the number of PF_3 groups increases, but they can be readily identified.⁵

Mass spectroscopy provides final confirmation. The parent ion peak is usually of strong intensity, and the high mass region is characterized by a pattern resulting from the successive loss of CO and PF_3 from the parent ion. Since mass spectroscopy became available, we have ceased doing elemental analysis as the formula obtained from an accurate analysis always agreed with that determined by other methods of characterization.

Properties

The individual carbonyl-trifluorophosphine complexes are volatile and yellow, light-yellow, or colorless solids or liquids at room temperature. The thermal stability of these species seems to increase steadily as the degree of PF_3 substitution increases. Most are stable in nonpolar solvents, but undergo

(8) A. K. Wensky, Ph.D. Dissertation, Florida State University, 1970; D. J. Darensbourg and T. L. Brown, *Inorg. Chem.*, **7**, 1679 (1968).

(9) R. J. Clark, *Inorg. Chem.*, **3**, 1395 (1964).

(10) C. A. Udovich and R. J. Clark, *Inorg. Chem.*, **8**, 938 (1969).

(11) P. E. Brotman and R. J. Clark, unpublished observations.

(12) C. A. Udovich and R. J. Clark, *J. Organometal. Chem.*, **36**, 355 (1972).

(13) J. B. Tripathi and M. Bigorgne, *J. Organometal. Chem.*, **9**, 307 (1967).

(14) L. M. Haines and M. H. B. Stiddard, *Advan. Inorg. Chem. Radi-chem.*, **12**, 53 (1969).

solvolytic rather rapidly in hydroxylic solvents like alcohols or wet THF. However, they are sufficiently hydrophobic that the reaction with pure water is usually slow. Most compounds are not particularly sensitive to dry air and, once purified, can be stored for long periods of time in a deep freeze without noticeable decomposition, especially in sealed tubes from which water and air have been removed.

These compounds must be assumed to be quite toxic and should be treated with the same respect due the metal carbonyls themselves.

Bonding

Phosphorus trifluoride readily forms more extensive series of substitution products with more carbonyls than any other ligand. This has been attributed to a high degree of similarity in the bonding of PF_3 and CO groups to transition metals. Carbon monoxide is a weak σ donor, but has empty antibonding orbitals of the appropriate energy and symmetry to act as a π acceptor of electrons from filled metal d orbitals. The presence of the highly electronegative fluorine atoms on PF_3 also makes phosphorus trifluoride a weak Lewis base. However, these same fluorines also lower the energy of the empty phosphorus 3d orbitals and enhance the ability of PF_3 to accept electrons from filled metal orbitals. The stability of a PF_3 complex can thus be attributed to strong $d\pi$ - $d\pi$ bonding between the ligand and the metal, in contrast to $p\pi^*$ - $d\pi$ bonding between CO and the metal.

A considerable amount of physical evidence has accumulated which indicates that PF_3 has essentially the same π -bonding tendencies as carbon monoxide. Mass spectroscopic studies on certain mixed carbonyl-trifluorophosphine complexes have shown that, within experimental error, the metal-carbonyl and metal-trifluorophosphine bond energies are equal.¹⁵ Infrared and Raman studies also show that the CO stretching force constants change less on replacing CO by PF_3 than by any other ligand, except possibly NO which is not a conventional two-electron donor. There is little ^{19}F and ^{31}P chemical shift between the complexes as the number of PF_3 groups changes. It would also seem that only ligands of comparable bonding ability could be able to displace one another so readily. Additional evidence of this type has been reviewed by Nixon.⁵

Aside from bonding properties, the factor of size or cone angle¹⁶ is probably also important in determining the ability of PF_3 to coordinate so readily. Cone angle is a measure of how much crowding or steric interaction a ligand is likely to cause. A study of a series of complexes containing a variety of ligands suggests that, with the probable exception of CO itself (plus PH_3 and a caged phosphine), phosphorus trifluoride has the smallest cone angle. Thus, PF_3 would be expected to replace CO more readily than most other ligands since the presence of this group causes relatively little steric crowding around the metal.

In most metal carbonyls, PF_3 displays little site preference, and when isomers are possible, the relative isomer populations can often be approximately predicted from a simple statistical distribution of CO and PF_3 groups over all possible coordination sites. The slightly larger ligand $\text{P}(\text{OCH}_3)_3$ reacts to yield only the more crowded cis form of $\text{Mo}(\text{CO})_4\text{L}_2$. However, in $\text{Mo}(\text{CO})_4(\text{PF}_3)_2$ the cis:trans ratio is about 2.5:1 (compared to a 4:1 statistical distribution), suggesting that PF_3 has a slight trans-directing ability. These isomer abundances cannot be predicted from purely steric arguments and should still be attributed to the electronic similarity of CO and PF_3 .

A third factor which can also explain the large number of PF_3 derivatives of carbonyl complexes has to do with the physical properties imparted to the new compounds by PF_3 substitution. Generally, the introduction of some ligand other than CO results in a severe loss of volatility and solubility as compared to the parent. Frequently the materials are so intractable that only major products can be isolated and identified. In contrast, the presence of fluorine in the outer environment of PF_3 complexes yields materials of high volatility which can be subjected to gas-liquid chromatography, a technique ideally suited for the isolation of minor components and the separation of complex mixtures. It is interesting to speculate on the discovery of minor components in the carbonyl complexes of other Lewis bases, were these complexes also amenable to glpc separation.

Stereochemical Rearrangements

The preceding discussion of the similarities between the properties, bonding, and ligand sizes in the complexes of PF_3 and CO suggests why we consider phosphorus trifluoride to be such a good model for carbon monoxide in metal carbonyls. It therefore seems reasonable to assume that the presence or absence of ligand rearrangement in the carbonyl-trifluorophosphine complexes probably reflects analogous behavior in the parent carbonyl. We have carried out extensive work during recent years studying ligand rearrangement phenomena in many of these complexes. The rates of most of these processes fall conveniently within the "time scale" of high-resolution nuclear magnetic resonance. The importance of having a good model for CO can be appreciated by considering the difficulty of doing ^{13}C nmr, especially when spectra must be examined at frequent intervals over large temperature ranges. However, nmr is ideally suited for use with carbonyl-trifluorophosphine systems because of the presence of the more easily studied fluorine nuclei.

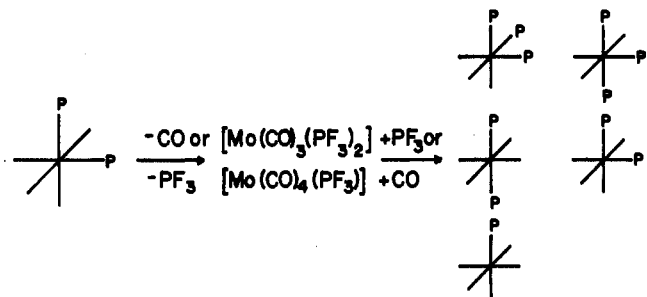
Among the simple $\text{M}(\text{PF}_3)_x(\text{CO})_{n-x}$ complexes, numerous cases of ligand rearrangement have been found. In most cases the processes appear to be intramolecular. However, some evidence for a process involving an intermolecular exchange has also been observed in several systems.

In general, six-coordinate systems appear to be completely rigid, while the five-coordinate systems frequently are not. Due to site equivalency in the tetrahedral four-coordinate complexes, it is quite difficult to find a technique to detect ligand rearrangements in these systems.

(15) F. E. Saalfeld, M. V. McDowell, S. K. Gondon, and A. G. MacDiarmid, *J. Amer. Chem. Soc.*, **90**, 3684 (1968).

(16) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2956 (1970).

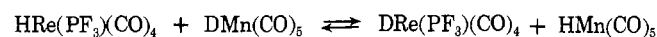
Six Coordination. Most six-coordinate systems like $\text{Mo}(\text{PF}_3)_x(\text{CO})_{6-x}$ are stereochemically rigid. We have found no case in which the isomerization of a compound like *cis*- $\text{Mo}(\text{CO})_4(\text{PF}_3)_2$ occurs without accompanying disproportionation,¹⁷ implying a general scrambling scheme as shown below. Complete



rigidity is also observed for such six-coordinate systems as $\text{Cr}(\text{PF}_3)_x(\text{CO})_{6-x}$,⁸ $\text{W}(\text{PF}_3)_x(\text{CO})_{6-x}$,⁸ $\text{CF}_3\text{-Mn}(\text{PF}_3)_x(\text{CO})_{5-x}$,¹⁸ and $\text{CF}_2\text{HCF}_2\text{Mn}(\text{PF}_3)_x(\text{CO})_{5-x}$.¹⁸ Rigidity in these latter systems implies only that the isomers are stable enough to be isolated by glpc at elevated temperatures and exist for lengthy periods of time without any indication of isomerization or disproportionation. What might occur under more forcing conditions has not been determined.

The $\text{HMn}(\text{PF}_3)_x(\text{CO})_{5-x}$ system is an exception.¹⁸ Irradiation of the parent carbonyl and PF_3 with uv light yields a mixture of complexes representing all possible compositions, $x = 1$ to 5. These can be readily isolated by glpc, but the individual isomers for each degree of PF_3 substitution cannot be separated from one another. The fluorine spectrum of $\text{HMn}(\text{CO})_4(\text{PF}_3)$ shown in Figure 1 indicates that both the *cis* and *trans* isomers are present, with relative populations of about 7:1.¹⁹ It can be inferred that the interconversion of the isomers is faster than glpc time (several minutes), but slower than nmr time (10^{-3} to 10^{-5} sec).

In the $\text{HRe}(\text{PF}_3)_x(\text{CO})_{5-x}$ system the individual isomers can be isolated if the column temperature is carefully controlled. The rate of the isomerization was found to be about the same as an intermolecular hydrogen-deuterium exchange reaction.



A similar, but faster exchange also occurs in the Mn system, suggesting that the isomerization of the CO and PF_3 ligands could be a result of this process.

Five Coordination. Within the last few years an ever-increasing number of molecules have been discovered which exhibit "nonrigid" or "fluxional" behavior. These molecules have more than one thermally accessible structure and pass rapidly from one of these structures to another by some kind of intramolecular rearrangement.²⁰

Our interest in this area began with the $\text{Fe}(\text{CO})_5$ problem. Both Cotton²¹ and the late Sir Ronald Nyholm²¹ with their coworkers attempted to determine

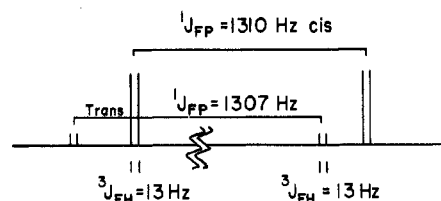


Figure 1. ^{19}F spectrum of $\text{HMn}(\text{CO})_4(\text{PF}_3)$.

the solution structure of $\text{Fe}(\text{CO})_5$ by ^{13}C (^{13}CO) nmr. A 3:2 or 4:1 ^{13}C environment should distinguish between the trigonal-bipyramid or square-based pyramid, respectively. Each research group reported only a single ^{13}C frequency, unchanged to -60° (more recently to -110°).²² Equivalence of CO groups was attributed to a rapid intramolecular process, postulated as the Berry pseudorotation.²³

Due to the electronic similarity of PF_3 and CO, our group felt that the substitution of phosphorus trifluoride into $\text{Fe}(\text{CO})_5$ should yield species similar to the parent with PF_3 distributed over all possible coordination sites. It also seemed likely that the much heavier PF_3 might slow the inversion process sufficiently to observe the fluorine nmr spectrum of the limiting structures. Although the first hope proved to be well founded,⁹ the second was not.

All compositions of the general formula $\text{Fe}(\text{PF}_3)_x(\text{CO})_{5-x}$ can be readily isolated by glpc.^{9,24} However, efforts to isolate the individual isomers have failed. The infrared spectra of these stable compounds give clear evidence that, based on a trigonal-bipyramid structure, each composition contains significant amounts of every possible isomer. Complete assignments of the CO stretching frequencies have been made.²⁵ However, the nmr spectra of the different compositions show all PF_3 groups to be equivalent down to temperatures of -120° with no broadening of the spectral lines. Since intermolecular CO and PF_3 substitution is quite slow, except at much higher temperatures or under uv irradiation, the isomers of each composition are probably undergoing a rapid intramolecular rearrangement at speeds much faster than the nmr "time scale," but slower than the vibrational frequencies of the atoms within the molecule.

Some elegant studies by Udovich²⁴ gave additional evidence for intramolecular exchange in these compounds. Methanol causes the solvolysis of PF_3 ligands into $\text{PF}_x(\text{OCH}_3)_{3-x}$, with the latter preferring axial sites over equatorial sites. An isomerization occurs *via* an intramolecular process during the solvolysis, quantitatively converting equatorial $\text{Fe}(\text{CO})_4\text{-PF}_3$ into axial $\text{Fe}(\text{CO})_4(\text{PF}_2\text{OCH}_3)$.²⁵ The $\text{Mn}(\text{NO})\text{-}(\text{PF}_3)_x(\text{CO})_{4-x}$,²⁶ $\text{Ru}(\text{PF}_3)_x(\text{CO})_{5-x}$,¹² and $[\text{Mn}(\text{PF}_3)_x(\text{CO})_{5-x}]^-$ ²⁷ systems show similar behavior.

(21) F. A. Cotton, A. Danti, J. S. Waugh, and R. W. Fessenden, *J. Chem. Phys.*, **29**, 1427 (1958); R. Bramley, B. M. Figgis, and R. S. Nyholm, *Trans. Faraday Soc.*, **58**, 1893 (1962).

(22) O. A. Gansow, A. R. Burke, and W. D. Vernon, *J. Amer. Chem. Soc.*, **94**, 2552 (1972).

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

(24) C. A. Udovich, R. J. Clark, and H. Haas, *Inorg. Chem.*, **8**, 1066 (1969).

(25) H. Haas and R. K. Sheline, *J. Chem. Phys.*, **47**, 2996 (1967).

(26) C. A. Udovich and R. J. Clark, *J. Organometal. Chem.*, **25**, 199 (1970).

(17) R. J. Clark and P. I. Hoberman, *Inorg. Chem.*, **4**, 1771 (1965).

(18) W. J. Miles, Jr., and R. J. Clark, *Inorg. Chem.*, **7**, 1801 (1968).

(19) W. J. Miles, Ph.D. Dissertation, Florida State University, 1970.

(20) E. L. Muetterties, *Accounts Chem. Res.*, **3**, 266 (1970).

A second type of nonrigid system was observed in the $R_f\text{Co}(\text{PF}_3)_x(\text{CO})_{4-x}$ compounds^{27,28} where R_f represents CF_3 , C_2F_5 , or C_3F_7 , and $x = 1$ to 4. The species are expected to be trigonal bipyramids with the perfluoroalkyl ligand occupying an axial site. In the simplest system,²⁸ $\text{CF}_3\text{Co}(\text{CO})_3(\text{PF}_3)$, both the averaged and limiting spectra could be studied.

At slightly above room temperature, fluorine nmr shows only one type of PF_3 group and one type of CF_3 group. On cooling, the lines broaden and then sharpen into a more complex pattern indicative of two different species, each with spectra qualitatively similar to the room temperature pattern. A comparison of the averaged coupling constants at low temperatures with those observed at high temperatures suggests that the room temperature pattern is an average of about equal concentrations of the two isomers.

The room temperature spectra of the remaining trifluoromethyl²⁷ species, as well as those of all the ethyl and propyl compounds,²⁷ show that all PF_3 groups are equivalent for each substitution value x . In the methyl compounds, cooling to low temperatures causes broadening of the spectrum followed by the appearance of a pattern indicative of the individual isomers. Assuming that the CF_3 group occupies the axial position in a trigonal-bipyramidal structure, the time-averaged value of the $\text{CF}_3\text{-P}$ coupling constants suggested that roughly statistical amounts of each isomer are present.

For the ethyl and propyl compounds, cooling to temperatures as low as -100° revealed no sign of spectral broadening. Since accidental degeneracy of all the resonances is hardly likely, this could indicate that either the molecular structure of each isomer is such that all PF_3 groups are naturally equivalent or else the rearrangement process is too fast to observe by nmr.

The first suggestion seems unlikely since the infrared spectra in the carbonyl region as well as the fluorine nmr spectra (particularly the $^3J_{\text{CF}_2\text{-P}}$ coupling constants) suggest that the methyl, ethyl, and propyl species have similar structures at room temperature. The second suggestion requires the exchange process to be faster in the ethyl and propyl compounds than in the methyl complexes. However, since the ethyl and propyl groups are bulkier than the methyl, this possibility also seems unlikely, especially if the process occurs by the Berry mechanism which must involve the axial groups. A different rearrangement mechanism, however, might explain this phenomenon.

Other systems which show stereochemical nonrigidity are the dieneiron carbonyl-trifluorophosphine complexes, of which butadieneiron tricarbonyl is the prototype. These complexes have proven to be especially interesting not only because the phosphine groups undergo rearrangement but also because the investigation has revealed some significant differences between the CO and PF_3 ligands.

For butadieneiron tricarbonyl in the solid state, X-ray diffraction studies²⁹ have shown that the coordination

of the diene and carbonyl groups around the iron is in an approximately square-based pyramidal arrangement. The butadiene skeleton is cisoid and planar. Two carbonyl carbons and the two terminal carbons of the butadiene form the base and the third carbonyl group is at the apex.

For butadieneiron tricarbonyl in solution, three well-resolved ^{12}CO stretching vibrations are observed. Assuming a model requiring two of the three carbonyls to be equivalent, the close agreement of the observed ^{13}CO frequencies with those predicted from calculations based on a Cotton-Kraihanzel force field¹⁴ indicated that the structure of the complex in solution is essentially the same as that in the crystalline state.³⁰ Because of the similarity in size and bonding of the PF_3 and CO ligands, it was assumed that PF_3 substitution should not alter this structure.

In the butadienetrifluorophosphineiron dicarbonyl complex, the number and location of the ^{13}CO stretching vibrations indicated that the PF_3 group prefers the apical position in the square-based pyramidal structure. This preference is so great that only one of the two possible isomers could be detected by fluorine nmr.

In the butadienebis(trifluorophosphine)iron carbonyl complex, the infrared spectrum again indicated that only one of the two possible isomers is present, but could not determine the identity of the preferred species. The room-temperature fluorine nmr spectrum shows equivalent PF_3 groups, suggesting that both phosphines occupy basal positions. However, a temperature-dependent study of the spectrum revealed that the apparent PF_3 equivalence is actually due to a rapid intramolecular exchange of the phosphine groups. The limiting spectrum showed that the only isomer present has one PF_3 apical and one PF_3 basal.

Phosphine exchange was also evident in the butadienetrifluorophosphineiron complex. At room temperature, all fluorines are equivalent, while at -120° the limiting pattern shows two resonances with a 2:1 ratio of intensities.

There are several possible descriptions of the motion which could make the PF_3 groups nmr equivalent in the bis and tris phosphine complexes. One possibility is simple position exchange of the two PF_3 ligands. A more reasonable possibility is for all three ligands (three PF_3 groups in the tris phosphine and two PF_3 groups and one carbonyl in the bis phosphine) to undergo a sort of concerted rotation around the iron atom. The latter possibility is also suggested by a study³¹ of several diene $\text{Fe}(\text{PF}_3)_x(\text{CO})_{3-x}$ systems in which the two basal coordination sites are made nonequivalent by the presence of a group other than hydrogen on one of the diene carbons. Because the three sites are not mutually perpendicular, there must be some bending in addition to a rotation about the metal.

An examination of the metal orbitals appropriate for π bonding with each of the ligands in these com-

(27) C. A. Udovich, Ph.D. Dissertation, Florida State University, 1969.

(28) C. A. Udovich and R. J. Clark, *J. Amer. Chem. Soc.*, **91**, 526 (1969).

(29) O. S. Mills and G. Robinson, *Acta Crystallogr.*, **16**, 758 (1963).

(30) J. D. Warren and R. J. Clark, *Inorg. Chem.*, **9**, 373 (1970).

(31) M. A. Busch, Dissertation, Florida State University, 1972.

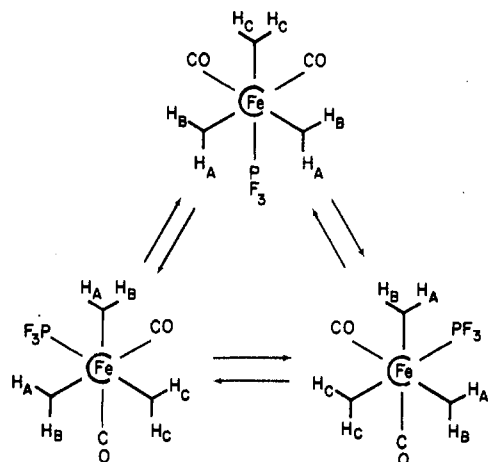


Figure 2. Schematic drawing of $\text{TMMFe}(\text{PF}_3)(\text{CO})_2$ rotamers.

plexes reveals a possible explanation for the site preference of PF_3 in the square-based pyramidal structure. The apical position appears to have a poorer potential for back-donation of electrons from the metal than the basal sites, resulting in a lower C-O bond order for the basal carbonyls than for the apical carbonyls. In agreement with this prediction, the carbonyl stretching force constant for the apical carbonyl in butadieneiron tricarbonyl was found to be at least 0.15 mdyne/Å larger than for the basal carbonyls. Therefore, site preference exhibited by PF_3 may be electronic in origin, with PF_3 , a slightly weaker π -bonding group, being forced into the apical site by the better π -bonding CO ligand.

An argument based on bonding differences is supported by the study of a second group of structurally similar complexes, the $(\text{C}_6\text{H}_8)\text{Fe}(\text{PF}_3)_x(\text{CO})_{3-x}$ (C_6H_8 , cyclohexadiene) system.³² In this case, the force constants for the two types of carbonyls in the parent compound are essentially equal, suggesting that the apical and basal sites are more nearly equivalent. All possible phosphine isomers are found to be present, although PF_3 substitution still favors the apical site. Temperature-dependent fluorine nmr shows that a rapid intramolecular process makes the PF_3 groups appear equivalent at room temperature.

When the two basal positions are made nonequivalent by an asymmetric diene, the PF_3 ligands exhibit additional site preferences.³¹ The possibility that such preferences can be generally predicted from the relative values of the CO stretching force constants is being investigated.

A final type of ligand rearrangement was discovered in the PF_3 -substituted complexes of trimethylenemethaneiron tricarbonyl, $(\text{TMM})\text{Fe}(\text{CO})_3$. The TMM ligand is an unstable organic intermediate, thought to be a diradical, stabilized by the $\text{Fe}(\text{CO})_3$ group.³³ Phosphorus trifluoride substitutes into the complex photochemically to yield all possible species of the type $(\text{TMM})\text{Fe}(\text{PF}_3)_x(\text{CO})_{3-x}$.³⁴

The high-resolution infrared spectrum as well as

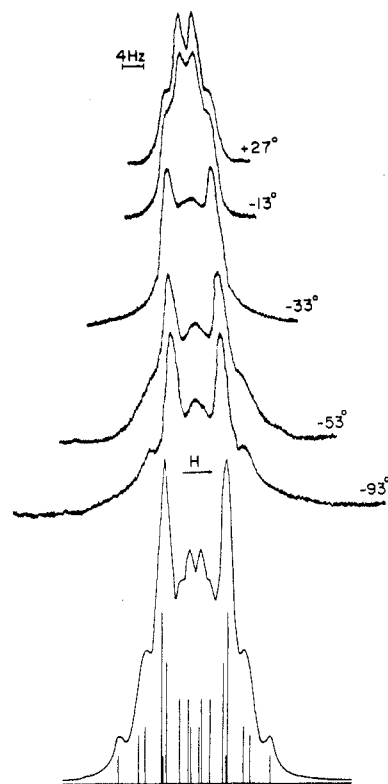


Figure 3. Variable-temperature ^{19}F spectra of $\text{TMMFe}(\text{PF}_3)_3$. Bottom spectrum: computer-simulated low-temperature limit at slightly different scale.

proton nmr suggests that all three carbonyls in $(\text{TMM})\text{Fe}(\text{CO})_3$ are equivalent. The fluorine spectra of the mono, bis, and tris phosphine complexes also show one, two, and three equivalent PF_3 groups, respectively. These patterns do not change with temperature.

The nonrigid character of the substituted $(\text{TMM})\text{Fe}(\text{CO})_3$ system is revealed by temperature-dependent proton nmr. At 100° , the spectrum of the monophosphine shows six equivalent protons coupled to a single phosphorus atom. At low temperatures, the spectrum broadens, then sharpens to a more complex pattern due to three types of protons in a 1:1:1 ratio.³⁴

The process most probably responsible for this behavior can be seen by viewing the molecule down the iron-methane carbon axis (Figure 2). It is apparent that the methylene protons have different positions relative to the PF_3 group, and hence are no longer chemically equivalent. If there is hindered motion of the PF_3 group relative to the TMM ligand, the resulting transformations through all three identical structures will allow each methylene proton to spend equal time in each of the three possible positions relative to PF_3 . If the rate of interconversion is fast enough, all protons will appear equivalent on the nmr time scale. The complex coupling pattern at low temperatures can be interpreted³⁴ in terms of these structures.

The bis and tris phosphines show comparable evidence of hindered rotation, and at high temperatures the proton spectra show a triplet and quartet respectively indicating equivalent protons coupled to two and three phosphorus atoms. As the temperature is

(32) J. D. Warren, M. A. Busch, and R. J. Clark, *Inorg. Chem.*, **11**, 452 (1972).

(33) G. F. Emerson, K. Ehrlich, W. P. Giering, and P. C. Lauterbur, *J. Amer. Chem. Soc.*, **88**, 3172 (1966).

(34) R. J. Clark, M. R. Abraham, and M. A. Busch, *J. Organometal. Chem.*, **35**, C33 (1972).

lowered, the spectrum of the tris phosphine undergoes the changes shown in Figure 3. In this case, as the rate of interconversion is slowed, the methylene protons remain chemically equivalent, but become magnetically nonequivalent due to different spatial relationships with each of the three PF_3 groups. A computer calculation of the low-temperature spectrum was found to agree quite well with the pattern observed at -93° . The proton spectrum of the bis phos-

phine also shows broadening at lower temperatures, and the limiting pattern is even more complex.

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Interlocked Deoxyribonucleic Acid Rings

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In an ordinary molecule, different parts of the molecule are held together by chemical bonds. The situation is different for two interlocked rings (a dimeric catenane), depicted diagrammatically in Figure 1. There is no chemical bond between the two component rings, yet the separation of the two rings requires the breakage of some chemical bonds, at least transiently, in one of the two rings. Therefore the two rings are said to be bonded by a topological bond or non-bond.¹ The possible existence of such a species was probably realized very early, after the discovery of cyclic compounds. The earliest known discussion of such a species was attributed to Willstätter in 1912,¹ although serious considerations on the formation of such a species were initiated only two decades ago when the formation of large polymeric rings was realized.

The first catenane was reported by Wasserman in 1960.² The formation of a cyclic acyloin from the linear molecule $\text{EtO}_2\text{C}(\text{CH}_2)_{32}\text{CO}_2\text{Et}$ by reduction with Na, in the presence of a high concentration of a 34-membered ring compound, $\text{C}_{32}\text{H}_{63}\text{D}_5$, was believed to give a catenane, depicted in Figure 2.

The formation of such a dimeric catenane is due to the threading of one ring by a linear chain which cyclizes subsequently. It is intuitively clear that the probability of interlocked ring formation is appreciable only when the sizes of both rings are sufficiently large. Steric consideration alone predicts that no interlocked rings would form if the number of carbon atoms in either ring is less than 20.¹

Interlocked DNA Rings

It was discovered by Hershey and his coworkers in 1963 that the DNA molecule of the bacteriophage λ (molecular weight 30.5×10^6) possesses two "cohesive ends" which can join to give a ring with a contour length of $\sim 170,000 \text{ \AA}$.³ It turned out that the cohesive ends are protruding single-stranded oligonucleotides with base sequences complementary (but not identical) to each other.⁴ Therefore the left end may join with the right end by the formation of a short segment of double-stranded DNA. If the ends are on the same molecule, a ring results. If the ends are on different molecules, a dimer or higher aggregate results. Since the discovery by Hershey, *et al.*, many other DNA molecules have been found to possess cohesive ends, some with sequences very similar to or identical with those of λ , and some with quite different base sequences.⁵

The physicochemical aspects of DNA ring formation were studied by Wang and Davidson.⁶ The DNA of λ is a fairly large molecule. In solution it resembles more or less a loose ball of thread with a root mean square radius of $\sim 5000 \text{ \AA}$. Since interpenetration of molecules can readily occur, the question whether a significant amount of interlocked rings are formed when the DNA molecules cyclize has been frequently raised.

The answer to the question is fairly straightforward. As long as one starts with a system of linear molecules, the fraction of interlocked rings which can

(1) H. L. Frisch and E. Wasserman, *J. Amer. Chem. Soc.*, **83**, 3789 (1961).

(2) E. Wasserman, *J. Amer. Chem. Soc.*, **82**, 4433 (1960).

(3) A. D. Hershey, E. Burgi, and L. Ingraham, *Proc. Nat. Acad. Sci. U. S.*, **49**, 748 (1963).

(4) For a recent review, cf. N. Davidson and W. Szybalski in "The Bacteriophage Lambda," A. D. Hershey, Ed., Cold Spring Harbor Laboratory, Cold Spring Harbor, N. Y., 1971, p 45.

(5) R. L. Baldwin, P. Barrand, A. Fritsch, D. A. Goldthwait, and F. Jacob, *J. Mol. Biol.*, **17**, 343 (1966).

(6) J. C. Wang and N. Davidson, *J. Mol. Biol.*, **15**, 111 (1966); **19**, 469 (1966).

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