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Stereochemical Nonrigidity in Iron Carbonyl Fluorophosphine Compounds

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Compositions of the formula $\text{Fe}(\text{CO})_x(\text{PF}_3)_{5-x}$, obtained through the substitution of phosphorus trifluoride into iron pentacarbonyl, have been clearly shown to contain more than one isomer. The isomers of these compositions, which are presumably trigonal bipyramidal, have now been demonstrated to be stereochemically nonrigid and in facile equilibrium. The $\text{Fe}(\text{CO})_x(\text{PF}_3)_{5-x}$ compositions are originally basically random mixtures of isomers. Rapid isomerization results during alcoholic solvolysis reactions through which the lower phosphines are converted into products containing primarily one isomer. These isomerizations are brought about as the ligand is changed by an *in situ* replacement of F atoms by $-\text{OCH}_3$ groups. The isomeric composition of the higher phosphines is also changed through these reactions but to a lesser degree. The new ligands of the general composition $\text{PF}_x(\text{OCH}_3)_{3-x}$ show a strong preference for axial positions. When phosphines of the type $\text{PF}_x(\text{CF}_3)_{3-x}$ are substituted into iron pentacarbonyl, equatorial sites are favored by this ligand and the isomeric composition shifts toward the corresponding structures.

Introduction

Phosphorus trifluoride substitutes more extensively into pentacarbonyliron(0) than any other ligand.¹ All possible substitution products of the type $\text{Fe}(\text{CO})_x(\text{PF}_3)_{5-x}$ can be prepared and isolated. However, in contrast to the $\text{Mo}(\text{CO})_x(\text{PF}_3)_{5-x}$ system,² the various $\text{Fe}(\text{CO})_x(\text{PF}_3)_{5-x}$ compositions cannot be separated into isomers even under conditions of highly efficient gas-liquid partition chromatography. On the basis of the infrared spectra of these species in the carbonyl region, it was suggested that isomers are actually present in each composition, but that they are nonisolable owing to an intramolecular inversion process.³

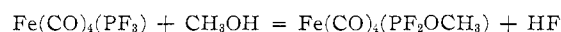
Tripathi and Bigorgne⁴ have studied these species somewhat more extensively. Through the use of infrared spectral studies of the various $\text{Fe}(\text{CO})_x(\text{PF}_3)_{5-x}$ compositions, they presented compelling arguments to show that the various compositions must contain isomers. These arguments were particularly strong for the higher substituted species.

Simultaneously with the study of Tripathi and Bigorgne,⁴ Haas and Sheline⁵ were making an extensive normal-coordinate treatment of the data of Clark.¹ This also produced compelling arguments for the existence of the various isomers. The per cent of the various isomers was calculated by Haas and Sheline.⁵ As an example, $\text{Fe}(\text{CO})_4(\text{PF}_3)$ was calculated to contain 33% axial and 67% equatorial isomers.

Still left unanswered is the question of the nonisolability of these isomers. Substitution experiments by Tripathi and Bigorgne⁴ are interpretable on some grounds by assuming that the various compositions contain stereochemically rigid isomers and on other grounds by assuming stereochemical nonrigidity.

Alcohol solvolysis reactions were carried out on all of the iron carbonyl species of the type $\text{Fe}(\text{CO})_x(\text{PF}_3)_{5-x}$.

These reactions which were carried out through several stages are represented in their simplest form by



Perfluoroalkylphosphine species of the general form $\text{Fe}(\text{CO})_x(\text{PF}_y(\text{CF}_3)_{3-y})_{5-x}$ were prepared by direct reactions between the phosphine and either iron pentacarbonyl or one of the phosphorus trifluoride substituents. Thus iron-fluorophosphine compounds were produced which contain various proportions of either alkoxy or trifluoromethyl groups. Infrared and other spectral studies were carried out on these compounds which gave an unequivocal demonstration of nonrigidity in these transition metal five-coordinate iron carbonyl complexes.

Experimental Section

The various compositions of the $\text{Fe}(\text{CO})_x(\text{PF}_3)_{5-x}$ species were prepared basically as before.¹ As suggested by Bigorgne,⁴ the temperature of the pressure reactions to prepare $\text{Fe}(\text{CO})_4(\text{PF}_3)$ -rich material should best be kept at 160° rather than a furnace temperature of 200° as reported earlier. In the ultraviolet approach, it has been found that the last two stages of substitution are greatly enhanced by the use of Vycor or quartz in both the reaction flasks and the lamp velocity tubes while simultaneously heating to 80°. Using this approach, one can prepare several grams of nearly pure $\text{Fe}(\text{PF}_3)_5$ in about 24 hr of irradiation time if the evolved CO is pumped off regularly at -196° . The various $\text{Fe}(\text{CO})_x(\text{PF}_3)_{5-x}$ species were isolated chromatographically pure on a 7.5×0.25 in. 40% DC-702 silicone column using a Varian-Aerograph A-700.

Methoxyfluorophosphines.—The solvolysis reactions were carried out basically as described in an earlier paper.⁶ For the lower solvolysis products where the species were to be isolated, quantities of chromatographically pure iron phosphine species were mixed with comparable volumes of dry methanol. After relatively short periods, usually 10–30 min, the samples were distilled through activated 4A molecular sieves to remove the methanol, and the iron complexes were then separated on 1–4-m 30% DC-702 silicone oil columns at temperatures between 50 and 100°. By varying the reaction conditions, one can easily determine the nature of the product by observing the sequential order of appearance.

The higher solvolysis products required more vigorous conditions in order to be produced in a reasonable length of time. A 1.7 M methanol solution of NaOCH_3 was used to produce solutions containing various stages of solvolysis. Increments of

(1) R. J. Clark, *Inorg. Chem.*, **3**, 1395 (1964).(2) R. J. Clark and P. I. Hoberman, *ibid.*, **4**, 1771 (1965).(3) A general review of five-coordination including stereochemical nonrigidity is given by E. L. Muetterties and R. A. Schunn, *Quart. Rev. (London)*, **20**, 245 (1966).(4) J. B. P. D. Tripathi and M. Bigorgne, *J. Organometal. Chem. (Amsterdam)*, **9**, 307 (1967).(5) H. Haas and R. K. Sheline, *J. Chem. Phys.*, **47**, 2996 (1967).(6) R. J. Clark and K. A. Morgan, *Inorg. Chim. Acta*, **2**, 93 (1968).

NaOCH_3 were added to the various chromatographically pure $\text{Fe}(\text{CO})_x(\text{PF}_3)_{5-x}$ species under nitrogen protection. After standing for about 10 min, the excess CH_3OH was pumped off at room temperature or below, hexane was added, and the infrared spectra were run. This reaction was quite rapid and mildly exothermic, requiring only a very short time for completion.

Ethanol and 2-propanol solvolysis reactions were also studied to a limited extent. The techniques were essentially the same except that the solvolysis reactions were slightly slower for these higher molecular weight alcohols.

Perfluoroalkylphosphines.—Trifluoromethylidophosphines were prepared from I_2 , $\text{Ag}(\text{CF}_3\text{COO})$ (or CF_3I), and red phosphorus by the basic reactions of Haszeldine⁷ and Mahler.⁸ The iodo compounds were converted to corresponding fluoro compounds by allowing them to stand over freshly sublimed SbF_5 at room temperature for several hours.

Substitution of these trifluoromethylphosphines into $\text{Fe}(\text{CO})_5$ or purified $\text{Fe}(\text{CO})_x(\text{PF}_3)_{5-x}$ species was accomplished by irradiating a mixture of the ligand and the iron complex with a General Electric AH-6 1000-W high-pressure mercury lamp using Pyrex vessels. Irradiations of 1–2 hr were used to produce small quantities (0.5 ml) of the lower substituted species and 3–4 hr to obtain more extensive substitution. At the completion of the reaction, the evolved CO was pumped off at -196° and the unreacted ligand was recovered by vacuum at -50° . The samples were chromatographed on a 7.5-m 40% DC-702 silicone column at 70° . The substitution obtained by these methods was not too extensive, and efforts to obtain higher substitution by longer irradiation resulted in excessive decomposition.

Infrared spectra were run in hexane on a Perkin-Elmer 521 spectrometer. The instrument was calibrated in the region of carbonyl absorptions using gaseous DCI .

Results

The results will be discussed in the order of increasing substitution with the methoxyphosphine and the perfluoroalkylphosphine studies being reported together for each basic degree of carbonyl replacement. As was done in the cobalt solvolysis paper,⁶ a special notation is used to simplify the problem of referring to a large number of closely related methanol solvolysis species. In this system, the letters A, B, C, D, and E determine whether the complex is a monophosphine, diphosphine, etc., and a following number designates how many stages of solvolysis have taken place. Thus A-2 represents the complex $\text{Fe}(\text{CO})_4(\text{PF}(\text{OCH}_3)_2)$, and C-3, $\text{Fe}(\text{CO})_2(\text{PF}_2\text{OCH}_3)_3$.

The species were identified by a series of approaches. The parent $\text{Fe}(\text{CO})_x(\text{PF}_3)_{5-x}$ compounds were isolated and identified by comparison with previous data on these species.^{1,4} For most of the reactions with these species, only subtle changes in the parent are to be expected. Therefore, the main tools to be relied on are the following.

(1) **Order of Formation.**—It is assumed quite logically that substitution or solvolysis will be stepwise; if a reaction is sampled frequently, the new species are easily identified in the order of their formation.

(2) **Infrared Spectra.**—A comparison of the spectra of the new products with those of the parents shows them to be closely related; thus it can be concluded that no new and unexpected products are formed.

(3) **Order of Elution.**—The order of elution and the systematics that result from the expected volatility decrease give a very good clue as to the nature of the species being formed.

(4) **Nmr Spectra.**—The ^{19}F nmr spectra have been run on some of the species and are totally consistent with the compositional assignments.

(5) **Mass Spectra.**—The parent ion molecular weights are also consistent with the compositional assignments for the lower solvolysis products.

Monophosphines.—The infrared spectra of the alkyloxy- and trifluoromethylphosphines of the iron tetracarbonyls are shown in Figures 1 and 2. At a

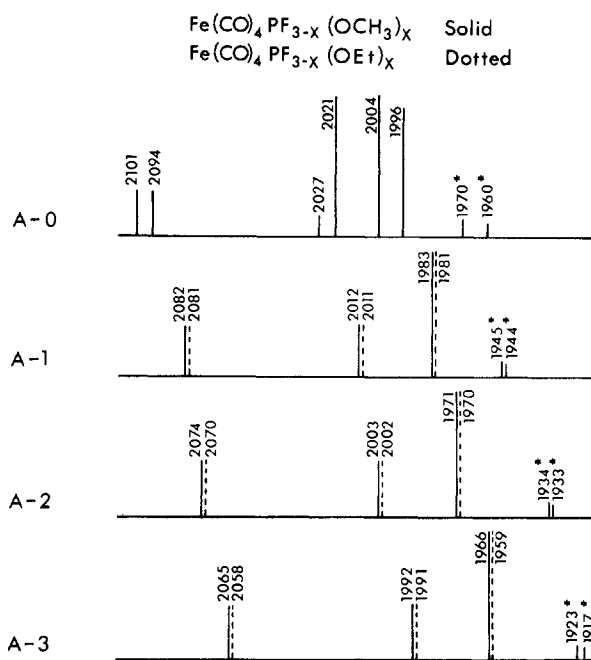


Figure 1.—Infrared spectra of the methanol (—) and ethanol (---) solvolyses products of $\text{Fe}(\text{CO})_4(\text{PF}_3)_3$ in the carbonyl region.

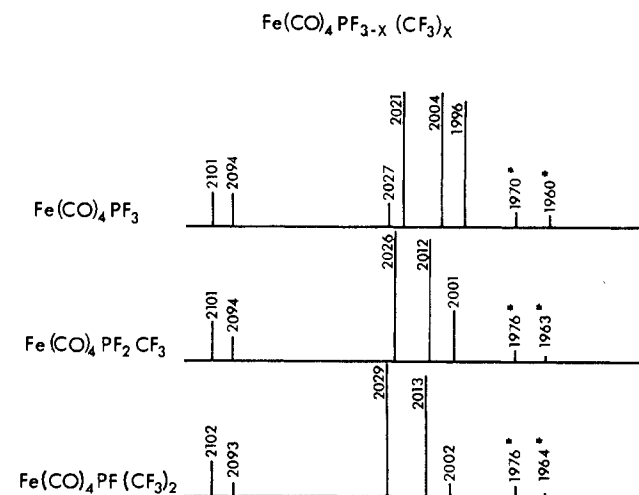


Figure 2.—Infrared spectra of the $\text{Fe}(\text{CO})_4(\text{PF}_{3-x}(\text{CF}_3)_x)$ compounds in the carbonyl region.

(7) F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 1565 (1953).

(8) W. Mahler, Dissertation Thesis, University of Southern California, University Park, Los Angeles, Calif., 1958.

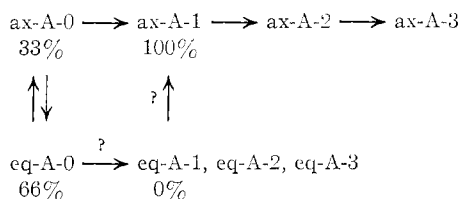
glance, it can be seen that seemingly subtle changes in the phosphine ligand make much more than a subtle change in the spectra. The solvolysis reaction creates the most dramatic change in the spectra of the parent

$\text{Fe}(\text{CO})_4\text{PF}_3$. The compound A-0 has five main carbonyl frequencies and a shoulder plus two ^{13}C O vibrations. These have been characterized by Haas and Sheline⁵ through their calculations using intensity factors as being due to 33% axial isomer and 67% equatorial isomer. During the first stage of methanol solvolysis in which A-1, $\text{Fe}(\text{CO})_4(\text{PF}_2\text{OCH}_3)$, is produced, the first spectrum of Figure 1 has radically changed. Three of the bands have disappeared and three others have shifted an average of 13 cm^{-1} to lower frequency. As one removes a fluorine atom and replaces it with a methoxide group, the π -bonding properties of the phosphine are changed so that such a shift would be expected. The rate of shift remains constant through the next two stages of solvolysis. The three bands that disappear are those assigned to the equatorial isomer. The carbonyl frequencies that remain after the three stages of solvolysis are the same as the ones assigned to the axial isomer of $\text{Fe}(\text{CO})_4\text{P}(\text{OCH}_3)_3$ which is prepared directly from the reaction of $\text{Fe}(\text{CO})_5$ and $\text{P}(\text{OCH}_3)_3$.⁹

The first stage of solvolysis appears to yield *quantitative* conversion of a mixture of ax-A-0 and eq-A-0 to exclusively ax-A-1. The quantity of A-1 produced roughly equals the amount of A-0 used, and, in addition, no decomposition, disproportionation, etc., products were seen. This appears to demand a mechanism for exchange between axial and equatorial isomers.

Further information was obtained by allowing the A-0 to A-1 conversion to go only halfway followed by a recovery of unreacted A-0. The spectrum of the A-0 recovered by the use of vacuum at room temperature or below was exactly the same as it was before the reaction was started. This further rules out the possibility of there being only a difference in rates of methanol solvolysis between ax-A-0 and eq-A-0.

These data are best explained on the basis of a set of equilibria



It seems quite clear that there must be a very facile equilibrium between ax-A-0 and eq-A-0. However, since there is no indication of the presence of any equatorial isomers of A-1, A-2, and A-3, one cannot say anything about any potential equilibrium between these species and the corresponding axial analogs. If such an equilibrium does exist, then it must be shifted sufficiently far in favor of the axial isomer that infrared evidence for the equatorial species is lacking.

The bands that disappear on solvolysis were attributed through the calculations of Haas and Sheline⁵ to the equatorial isomer and those that merely shifted were assigned as axial. If one assumes that the poorer

π -bonding ligands $\text{PF}_x(\text{OCH}_3)_{3-x}$ will seek the axial position, then this work strongly supports the assignment of Haas and Sheline.⁵

Solvolysis with ethanol rather than methanol produced qualitatively similar results. The equatorial isomer again disappears quantitatively. The actual shift of the carbonyl stretching frequencies to lower values is slightly greater as would be expected.

The use of ligands of the type $\text{PF}_x(\text{CF}_3)_{3-x}$ further illustrates the ease with which the isomers of the iron carbonyl fluorophosphine systems shift their relative concentrations depending upon the electronic and stereochemical nature of the ligands. The infrared data of the $\text{Fe}(\text{CO})_4\text{PF}_x(\text{CF}_3)_{3-x}$ species are shown in Figure 2. Since these ligands have π -bonding abilities comparable to that of PF_3 ,¹⁰ no great shift in frequency is expected nor is it seen. However, the relative intensities of the bands for the two isomers shift quite noticeably. Neither isomer disappears as in solvolysis, but there is a decided enrichment of the bands for the equatorial isomer.

Diphosphines.—The infrared spectra for the diphosphines are shown in Figures 3 and 4. It can be seen that there is again a rather dramatic shift in the infrared spectra for these species as solvolysis takes place. The bands in general shift to lower frequencies by about 10 cm^{-1} . However, the bands originating at 2083 and 2018 cm^{-1} progressively weaken as solvolysis proceeds, and by the time B-3 is produced, these two bands are completely gone. The band originating at 2075 cm^{-1} weakens somewhat relative to the remaining strong band which originated at 1989 cm^{-1} .

It is clear that at least one and possibly two isomers have disappeared during the solvolysis reaction. However, the effect of solvolysis is not as dramatic as in the case of the monophosphine series. One stage of solvolysis for the monophosphines causes the composition to alter sufficiently so that one isomer disappears completely. In the present diphosphine case, it seems that since there are more P-F bonds, the effect of each stage of solvolysis on the isomer equilibrium is less. It is clear that at least the early solvolysis species in the diphosphine series are able to redistribute themselves rapidly. When the first stage of solvolysis is allowed to take place about halfway, the distribution of the B-1 isomers is quite different from the parent distribution. However, the infrared spectrum of the recovered B-0 is still identical with that of B-0 before any reaction was allowed to take place. Thus the species are seen to be stereochemically nonrigid.

A very interesting question arises as to which isomers remain after the solvolysis reaction proceeds. According to the calculations of Haas and Sheline,⁵ the composition of the mixture is approximately 23% *trans* with a band at 1986 cm^{-1} , 21% *cis* with bands at 1992, 2071, and 2019 cm^{-1} , and 56% *vic* with bands at 2012, 2081, and 2011 cm^{-1} . (The frequencies measured in this work are consistently about 3 cm^{-1} higher than those reported earlier.^{1,5}) As solvolysis takes place, the bands

(9) A. Reckziegel and M. Bigorgne, *J. Organometal. Chem.* (Amsterdam), **3**, 341 (1965).

(10) A. B. Burg and G. B. Street, *Inorg. Chem.*, **5**, 1532 (1966).

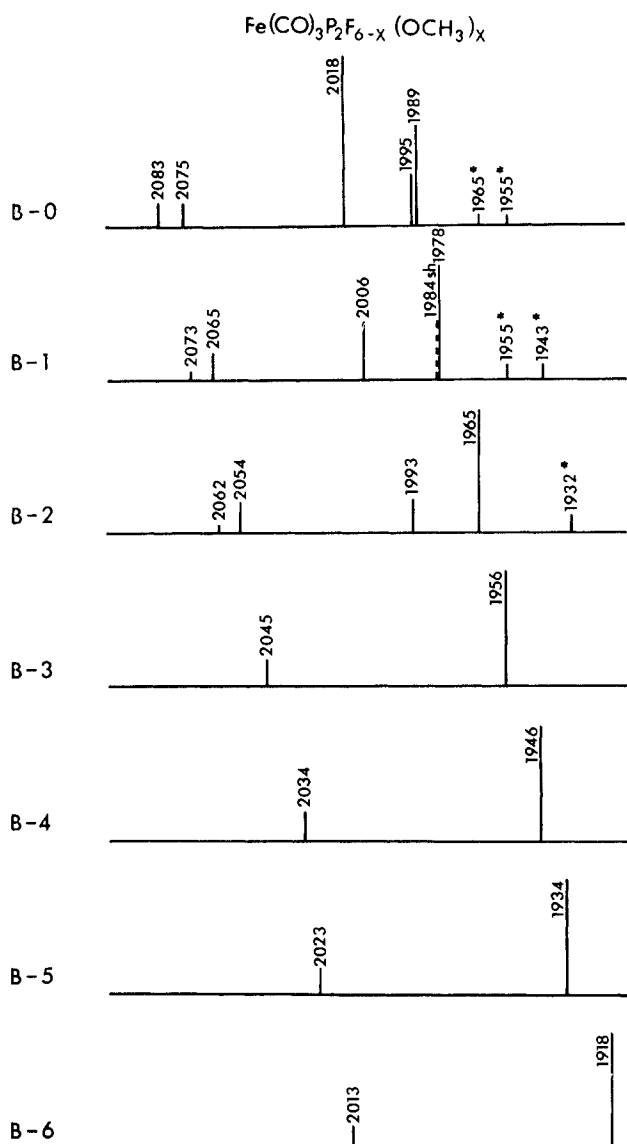


Figure 3.—Infrared spectra of the methanol solvolyses products of $\text{Fe}(\text{CO})_3(\text{PF}_3)_2$ in the carbonyl region.

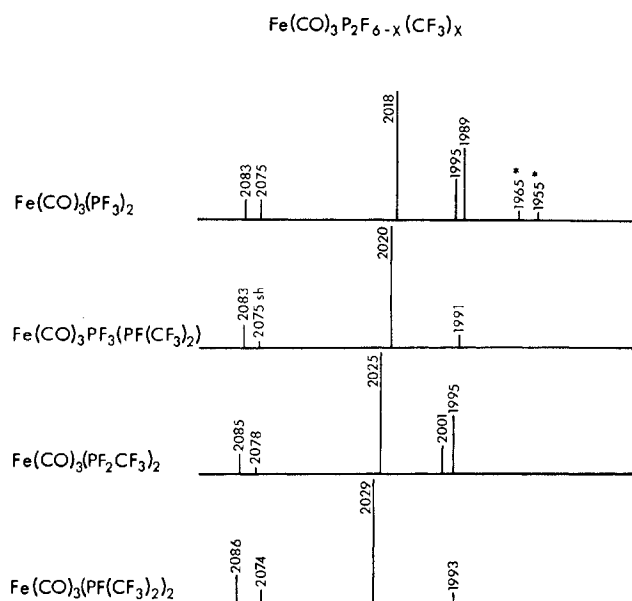


Figure 4.—Infrared spectra of the $\text{Fe}(\text{CO})_3\text{P}_2\text{F}_{6-x}(\text{CF}_3)_x$ compounds in the carbonyl region.

attributed to the *vic* isomer weaken and disappear by the third stage of solvolysis; the bands belonging to the *cis* isomer weaken and only the *trans* isomer remains strong. This assignment is quite consistent with the expected behavior. The $\text{PF}_x(\text{OCH}_3)_{3-x}$ ligands which are poorer at π bonding would be expected to favor strongly the axial position as have been observed in several cases.¹¹ This interpretation demands that the band originating at 2018 cm^{-1} weaken to about the same intensity as the one originating at 2075 cm^{-1} . The former band is not clearly seen in the mixture of species of B-3 to B-6 but it seems quite plausible that the band could be present.

The current interpretation of the bands in $\text{Fe}(\text{CO})_3(\text{PF}_3)_2$ has additional support. The frequency assigned to the *trans* isomer, extrapolated through the solvolysis series to B-6, yields a frequency identical with the band for $\text{Fe}(\text{CO})_3(\text{P}(\text{OCH}_3)_3)_2$ prepared from $\text{Fe}(\text{CO})_5$ and $\text{P}(\text{OCH}_3)_3$ and assigned as *trans*.⁹

The work with the perfluoroalkyl species is entirely consistent with this view. The data in Figure 4 show again a rather strong shift in the isomer mixture. As found earlier in the monophosphine system, the band positions do not shift appreciably. The 1989-cm^{-1} band for the *trans* isomer weakens. The bands that remain prominent are those originating at 2083 and 2018 cm^{-1} which correspond to the main bands of the *vic* isomer. With the $\text{PF}_x(\text{CF}_3)_{3-x}$ isomers which have π bonding comparable to that of CO or PF_3 ,¹⁰ steric factors should be of greatest importance. The equatorial position should give the most space and cause a predominance of the *vic* isomer as is seen by the spectra.

Triphosphine.—The triphosphine has been investigated in a manner analogous to the lower phosphines. The spectra of the solvolysis and the perfluoromethyl species are shown in Figures 5 and 6.

The intensity shift per stage of solvolysis is again less than that found with the preceding phosphine. Thus the information relative to stereochemical nonrigidity is less dramatic than that for the lower phosphines.

Calculations and assignments by Haas and Sheline⁹ indicate that $\text{Fe}(\text{CO})_2(\text{PF}_3)_3$ contains 67% of the *trans*- D_{3h} isomer, 18% of the *cis*- C_s isomer, and 15% of the *vic*- C_{2v} isomer. The arguments used earlier relative to the placement of the poorer π -bonding phosphine ligands would say that the *vic* isomer would be preferred over the *cis* isomer which in turn would be favored over the *trans* isomer. The frequencies assigned on this basis agree with the assignments made through the calculations of Haas and Sheline. The bands for the *vic* isomer increase in strength relative to those for the other two species.

In addition, the compound $\text{Fe}(\text{CO})_2(\text{P}(\text{OCH}_3)_3)_3$ assigned as *vic*⁹ has bands at about the same frequency as obtained when one extrapolates beyond C-6, the highest degree of solvolysis obtained thus far, to C-9.

Since in this compound each stage of solvolysis re-

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

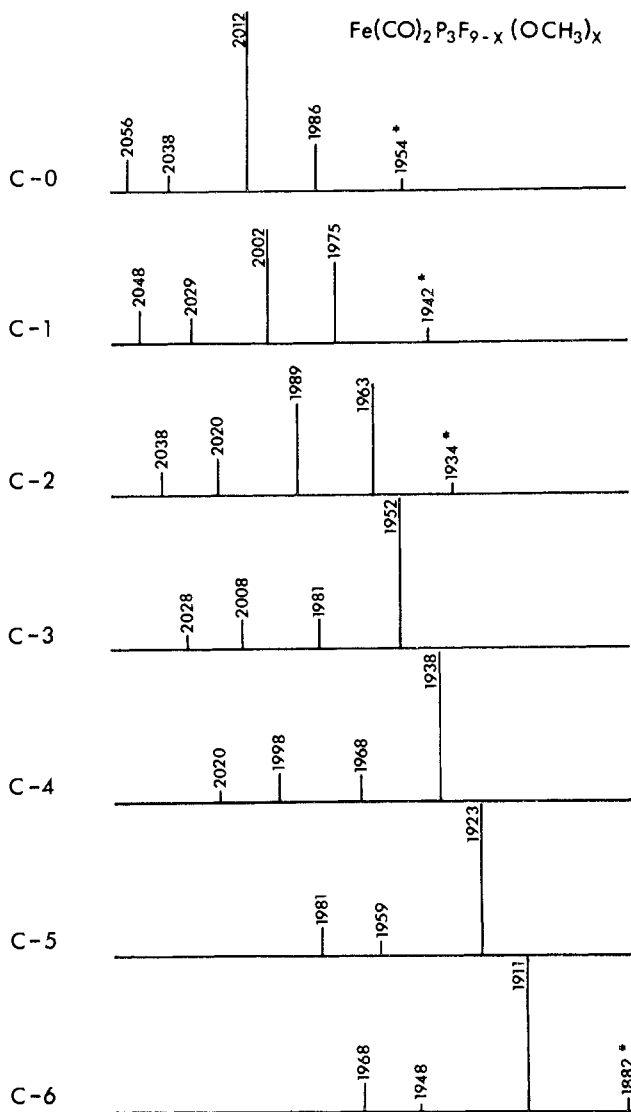


Figure 5.—Infrared spectra of the methanol solvolyses products of $\text{Fe}(\text{CO})_2(\text{PF}_3)_3$.

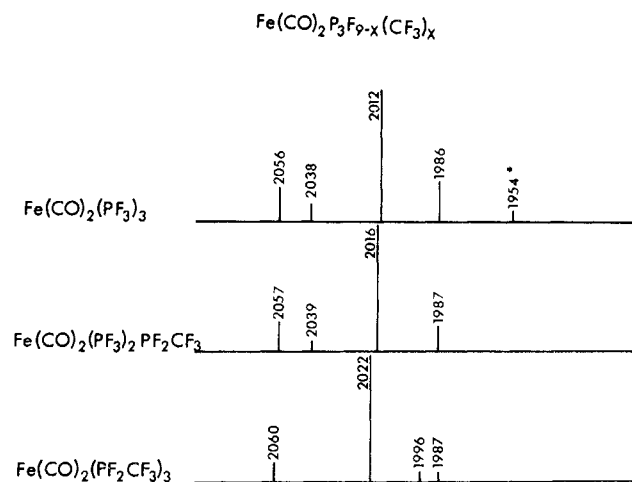


Figure 6.—Infrared spectra of the $\text{Fe}(\text{CO})_2\text{P}_3\text{F}_{9-x}(\text{CF}_3)_x$ compounds.

places only one-ninth of the P-F groups, one should expect an even further reduction of the change in composition per stage of solvolysis. Whereas in the monophosphine one stage made a complete change and three

stages in the diphosphine accomplished related results, in this compound five stages yield a spectrum which is comprised of two primary bands. These are the ones which originated at 1986 and 2038 cm^{-1} and have been assigned to the *vic* isomer. In the products of extensive solvolysis, only one other band is seen and that is a very weak remnant of the one that originated at 2012 cm^{-1} . This band could be assigned as arising from either the *trans* or the *cis* isomer, with the latter being expected. Its expected companion band was not clearly identified in the welter of peaks obtained from these mixtures.

As before, the partial solvolysis of C-0 to C-1 left recoverable C-0 with an unchanged spectra. Although a much smaller change in intensities of peaks occurs on going from C-0 to C-1 as compared to the previous A or B series, the change is still adequate to show that the C-0 isomers are reequilibrating themselves to the original composition. This shows that $\text{Fe}(\text{CO})_2(\text{PF}_3)_3$ like the tri- and tetracarbonyls must be stereochemically nonrigid.

The limited amount of work done with the perfluoroalkyl $\text{PF}_2(\text{CF}_3)$ is consistent with our present interpretation. The use of $\text{PF}(\text{CF}_3)_2$ as the ligand presented a problem owing to synthetic difficulties which were presumably due to steric effects. The spectra represented in Figure 5, however, are adequate to show a strong shift in isomer composition. The bands corresponding to parent frequencies 2038 and 1986 cm^{-1} weaken while bands corresponding to parent frequencies 2012 and 2056 cm^{-1} remain prominent. The former were assigned to the *vic* isomer and the latter to the *cis* and *trans* isomers. As judged by the relative intensities, the *trans* isomer is probably the predominant species as is expected.

Tetraphosphines.—The solvolysis reaction is of little use in determining whether internal rearrangement might be taking place in the monocarbonyl compound. Only four stages of solvolysis reaction take place even when a very large excess of sodium methoxide is present. The frequencies of the two carbonyl bands that originate at 2037 and 2008 cm^{-1} both shift about 10 cm^{-1} to lower frequency as expected for each stage of solvolysis. The relative intensities of the two bands do not change much through the various stages of solvolysis. The spectrum of D-0 recovered from a 50% conversion of D-0 to D-1 is identical with that of the original D-0. However, since the relative intensities of D-0 and D-1 are so similar, no conclusion can be reached concerning the facile rearrangement from these data.

The general trend of intensities is somewhat more revealing. As solvolysis proceeds, one would expect two of the now poorer π -bonding ligands to seek axial positions yielding an isomer with the carbonyl group in an equatorial position. The band that commences at 2038 cm^{-1} appears to weaken somewhat relative to the one starting at 2009 cm^{-1} . Thus one can tentatively assign the former to the axial and the latter to the equatorial positions. This agrees with the calculations made by Sheline and Haas.⁵

Steric problems have prevented any appreciable

synthesis of tetraferfluoroalkylphosphines although there is evidence for their existence.

Discussion

The fact that two or three isomers are present in the $\text{Fe}(\text{CO})_x(\text{PF}_3)_{5-x}$ compositions seems at this point unarguable. The eloquent arguments mounted by Tripathi and Bigorgne⁴ are quite convincing, the calculations of Haas and Sheline⁵ are equally strong, and the present work demands this interpretation.

The dynamics of stereochemical nonrigidity are being studied in various systems with increased intensity. Muettterties and Schunn³ have reviewed the stereochemistry of five-coordinate systems and discussed the earlier work dealing with some of these systems. For example, $\text{Fe}(\text{CO})_5$ has been studied by Bramley, Figgis, and Nyholm¹² and by Cotton¹³ using ^{13}C nmr. Both groups of workers found only one ^{13}C frequency for the trigonal-bipyramidal molecule rather than the expected two. The single line did not broaden at even low temperatures so it was postulated that the molecule was undergoing a rapid internal inversion. Other five-coordinate systems such as PF_5 ¹⁴ and a number of perfluoroalkylfluorophosphoranes¹⁵ have also been postulated as undergoing the same process. There are now a number of examples of phosphoranes where variable-temperature studies have clearly illustrated that such a process must be taking place.¹⁶ However, there has not been any such demonstration of the process for transition metal complexes except for that of $\text{CF}_3\text{Co}(\text{CO})_3(\text{PF}_3)$ just published by the authors.¹⁷ Figure 7 shows the general Berry mechanism¹⁴ for intramolecular inversion thought to be taking place.

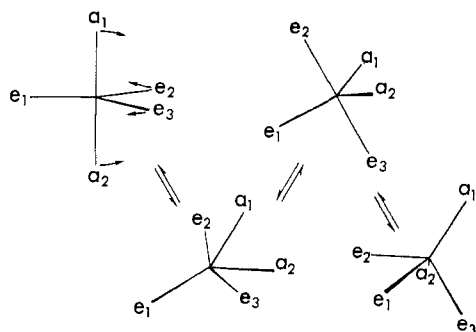


Figure 7.—Possible mechanism of the intramolecular exchange of ligands in the five-coordinate systems.

The experimental data on the lower phosphines seem to demand a rapid internal rearrangement among the individual $\text{Fe}(\text{CO})_x(\text{PF}_3)_{5-x}$ compositions. The mixture of axial and equatorial $\text{Fe}(\text{CO})_4(\text{PF}_3)$ shifts exclusively to axial $\text{Fe}(\text{CO})_4\text{PF}_2\text{OCH}_3$ on solvolysis. The shift is

quantitative. It has been argued^{12,13} that the mechanism which makes the ^{13}C of $\text{Fe}(\text{CO})_5$ equivalent in axial and equatorial positions cannot be intermolecular since the rate of CO exchange is far too slow. The same argument can be raised against an intermolecular exchange in $\text{Fe}(\text{CO})_x(\text{PF}_3)_{5-x}$ complexes. All evidence points to PF_3 or CO exchange on these complexes as being even slower than in iron pentacarbonyl.

The solvolysis argument pointing toward an internal rearrangement and isomer composition shift is strongest with the monophosphine and weakest with the tetraphosphine. In the former case, there are two separate indications of this shift: (1) the quantitative conversion of two isomers to only one in the solvolysis product and (2) the recovery of an unchanged isomer mixture in the unsolvolyzed portion from which a highly changed isomer mixture was isolated. The same arguments can be applied to the di- and triphosphines, but it is uncertain in the case of the tetraphosphine. The latter of the two arguments cannot be applied at all to the tetraphosphine since the isomer composition shifts so little. However, the relative intensity shifts over the course of four stages of solvolysis seem to imply that the relative amounts of the two isomers are changing.

Fluorine nuclear magnetic resonance studies are in progress and currently appear to be totally consistent with this interpretation of stereochemical nonrigidity through an intramolecular process.

The work with the ethanol and 2-propanol solvolyses (the latter not discussed earlier owing to its similarity to the former) gives results quite comparable with the methanol results. Since these increasingly bulky groups, like the methyl group, are also going into a sterically less favored axial location, one must conclude that the positioning of the solvolysis ligands is controlled by electronic rather than steric factors.

The spectra for A-3 and B-6 and the spectrum extrapolated for C-9 agree well with the spectra of $\text{Fe}(\text{CO})_4(\text{P}(\text{OCH}_3)_3)$, $\text{Fe}(\text{CO})_3(\text{P}(\text{OCH}_3)_3)_2$, and $\text{Fe}(\text{CO})_2(\text{P}(\text{OCH}_3)_3)_3$ prepared by Reckziegel and Bigorgne.⁹ These were assigned as axial, diaxial, and diaxial-equatorial and we concur in this assignment.

The work of Tripathi and Bigorgne⁴ in which they allowed various $\text{Fe}(\text{CO})_x(\text{PF}_3)_{5-x}$ species to react with $\text{P}(\text{CH}_3)_3$ is interesting. No products were isolated and only the infrared spectra were taken. Thus one cannot be certain what has occurred. However, the authors indicated that some bands weaken while others remain intense and we assume that no other new bands appear.⁴ If this latter interpretation is correct, then the results are quite difficult to understand. As an example, take the compound $\text{Fe}(\text{CO})_2(\text{PF}_3)_3$. On reaction with $\text{P}(\text{CH}_3)_3$, the bands at 2053 and 2009 cm^{-1} are said to diminish in intensity while the bands at 2035 and 1986 cm^{-1} remain strong. If carbonyl substitution took place on the isomer having bands at 2053 and 2009 cm^{-1} , then a new band for a monocarbonyl must appear somewhere in the spectrum. If the reaction is PF_3 replacement on the isomer having the 2053- and 2009- cm^{-1} bands, then the new dicarbonyl isomer would cer-

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

(13) F. A. Cotton, A. Danti, J. S. Waugh, and R. W. Fessenden, *J. Chem. Phys.*, **29**, 1427 (1958).

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

(16) See for example F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).

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

tainly not have bands at 2035 and 1986 cm^{-1} . The two bands would be shifted perhaps 20-30 cm^{-1} to lower frequency.

These substitution results of Tripathi and Bigorgne⁴ are quite interesting, but we do not see how they can be interpreted. They do not seem to be consistent with either a static or a dynamic model of isomers. Our results seem to require a dynamic model of isomerization.

The other point of disagreement between the work of Haas and Sheline⁵ and the work of Tripathi and Bigorgne⁴ is in the assignment of frequencies. The two sets of workers have different assignments for most of the isomers. Each group's assignments are based on certain assumptions and then the assignment for all isomers of the various compositions are internally consistent from this initial point of departure. Tripathi and Bigorgne⁴ have used as their starting point two principal points based on $\text{Fe}(\text{CO})(\text{PF}_3)_4$. One is a 3:2 ratio of intensities of the two bands, the more intense of which is assigned as equatorial. The other is the presence of PQR branching in the isomer of the monocarbonyl presumed to be the C_{3v} isomer. Haas and Sheline have as their initial assumptions: (1) the A_1 vibration

in axial $\text{Fe}(\text{CO})(\text{PF}_3)_4$ which will occur at higher frequency than in equatorial $\text{Fe}(\text{CO})(\text{PF}_3)_4$ as an analogy with the frequencies of the two A_1 vibrations in $\text{Fe}(\text{CO})_5$, (2) the internal consistency of the calculated and observed frequencies and intensities within their theoretical treatment, and (3) the preliminary solvolysis studies. The complete solvolysis studies and the study of the perfluoroalkyl compounds agree quite well throughout the series of compounds. The first point of Tripathi and Bigorgne⁴ assumes complete random positioning of ligands and equal absorptivities of the two A_1 bands. Our experience indicates that neither of these assumptions need be rigorously true.

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CONTRIBUTION FROM METCALF RESEARCH LABORATORIES, DEPARTMENT OF CHEMISTRY, BROWN UNIVERSITY, PROVIDENCE, RHODE ISLAND 02912

The Crystal and Molecular Structure of the Five-Coordinate Complex Chlorotris(*o*-methylthiophenyl)phosphenickel(II) Perchlorate

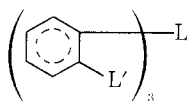
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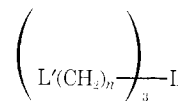
The crystal and molecular structure of chlorotris(*o*-methylthiophenyl)phosphenickel(II) perchlorate, $[\text{Ni}(\text{TSP})\text{Cl}][\text{ClO}_4]$, has been determined from three-dimensional single-crystal X-ray data collected by standard film techniques. The structure has been refined by least-squares methods to a conventional R factor of 0.090 for 1499 nonzero reflections. The complex crystallizes in space group $\text{C}2/c$ of the monoclinic system with a cell of dimensions $a = 22.93 \pm 0.04$, $b = 12.08 \pm 0.03$, $c = 18.21 \pm 0.03$ Å, $\beta = 102.4 \pm 0.1^\circ$, and $V = 4917$ Å³. An experimental density of 1.57 (4) g/cm^3 is in good agreement with a calculated value of 1.60 g/cm^3 for eight molecules in the unit cell. The $\text{Ni}(\text{TSP})\text{Cl}^+$ complex possesses a nearly regular trigonal-bipyramidal structure with the three S atoms located in the equatorial positions and the P and Cl atoms at the apices. The Ni-P and Ni-Cl distances are 2.113 (7) and 2.227 (7) Å, respectively. The Ni ion is displaced slightly but significantly out of the plane of the equatorial S atoms toward the apical halogen. The magnitude of this displacement is 0.061 (2) Å. The average Ni-S equatorial distance of 2.267 (7) Å is indicative of only slight metal-sulfur π bonding in the five-coordinate complex.

Introduction

One of the most successful methods employed to synthesize five-coordinate complexes of transition metal ions has involved the use of tetradentate "tripod-type" ligands of general forms I and II. This method has



- Ia, L = P, L' = $\text{P}(\text{C}_6\text{H}_5)_2$ (QP)
 b, L = As, L' = $\text{As}(\text{C}_6\text{H}_5)_2$ (QAS)
 c, L = P, L' = $\text{S}(\text{CH}_3)_2$ (TSP)
 d, L = As, L' = $\text{S}(\text{CH}_3)_2$ (TSA)



- IIa, L = As, L' = $\text{As}(\text{CH}_3)_2$, $n = 3$
 b, L = P, L' = $\text{As}(\text{CH}_3)_2$, $n = 3$ (TAP)
 c, L = N, L' = $\text{N}(\text{CH}_3)_2$, $n = 2$ (Me₂tren)

served to produce a number of five-coordinate Ni(II) complexes in which the metal ion is surrounded by a trigonal-bipyramidal array of donor atoms. The first

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