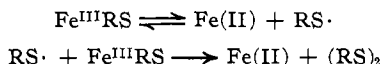
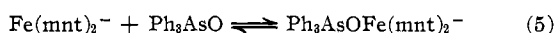
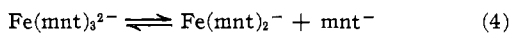


and in particular reaction 2 are similar to the well-known reactions of iron(III) salts of thiols such as cysteine: $2\text{Fe}^{\text{III}}(\text{RS})_n^{3-n} \rightarrow 2\text{Fe}(\text{II}) + \text{RSSR}^{2-}$. Reactions 2 and 3 involve a similar change in the formal oxidation state of both metal and ligand. The thiol reactions,²¹ in contrast to reaction 3, obey second-order kinetics ($d[\text{Fe}(\text{II})]/dt = k[\text{Fe}(\text{III})]^2$) which is attributed to the initial formation of iron(III) dimers. Second-order kinetics would, however, also be expected from the reaction scheme

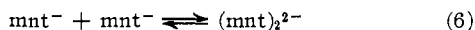


if the first reaction may be treated as a rapid preequilibrium. Since reaction 3 has been found to follow good first-order kinetics, mechanisms of the above type are not applicable to the dithiolate systems. In particular, initial dimerization either as the slow reaction in the mechanism or as a rapid preequilibrium is not consistent with first-order behavior.

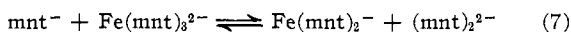
At first glance reactions 4–7 constitute a reasonable mechanism for reaction 3



and either



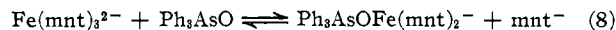
or



However, close analysis indicates that the first-order dependence on both $\text{Fe}(\text{mnt})_3^{2-}$ and Ph_3AsO concentra-

(21) D. L. Leussing and L. Newman, *J. Amer. Chem. Soc.*, **78**, 552 (1956).

tions is not realizable through this scheme. We consider the most plausible mechanism to involve direct attack of the nucleophiles on $\text{Fe}(\text{mnt})_3^{2-}$ or on a half-bonded intermediate (reaction 8). This reaction would



then be followed by either reaction 6 or 7 in a rapid second step. This mechanism is consistent with the observed first-order dependence on both $\text{Fe}(\text{mnt})_3^{2-}$ and Ph_3AsO concentrations provided that the reverse of reaction 8 can be ignored (*i.e.*, provided $k_6[\text{mnt}^-]^2 \gg k_{-8}[\text{Ph}_3\text{AsOFe}(\text{mnt})_2^-][\text{mnt}^-]$). In terms of this interpretation the value of k_a calculated from the slope of Figure 1 is the second-order rate constant for reaction 8. There are, of course, other possible reaction schemes consistent with the kinetic data. For example, a mechanism involving the elimination of mnt^{2-} from $\text{Fe}(\text{mnt})_3^{2-}$ in the first step is a possible alternative to the first reaction in the proposed mechanism, but we consider it less likely on thermodynamic grounds. We are unable at this time to assign a detailed mechanism to reaction 3 with any confidence.

Finally, another system in which iron in an oxidation state of 4 has been proposed is oxyhemoglobin.^{22,23} In terms of this oxidation state assignment the deoxygenation of oxyhemoglobin may be considered as a reductive elimination reaction in which ferroheme and molecular oxygen are formed. The deoxygenation reaction would then be analogous to reaction 3 for in each case a low-spin iron(IV) complex is postulated to undergo rapid reductive elimination.

(22) N. Sutin in "Oxidases and Related Redox Systems," T. E. King, H. S. Mason, and M. Morrison, Ed., Wiley, New York, N. Y., 1964, p 46.

(23) H. B. Gray, *Advan. Chem. Ser.*, **No. 100**, 365 (1971).

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Metal Carbonyl-Trifluorophosphine Systems. XI. The Fluxional Cyclohexadienetricarbonyliron(0) System

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1,3-Cyclohexadieniron tricarbonyl reacts with phosphorus trifluoride to yield a series of compounds of the general type $\text{C}_6\text{H}_8\text{Fe}(\text{PF}_3)_x(\text{CO})_{3-x}$. The individual species are separable by glpc and are light yellow solids of moderately low volatility. Both infrared and fluorine nmr show that the mono- and diphosphines contain two distinct isomers although these isomers are not separable by glpc. These isomers appear to exist owing to the ability of the CO and PF_3 ligands to occupy either apical or basal sites in the square-based pyramidal structure.

Introduction

1,3-Cyclohexadieniron tricarbonyl, $\text{C}_6\text{H}_8\text{Fe}(\text{CO})_3$, was first prepared by Hallam and Pauson¹ and found to be closely related to butadieniron tricarbonyl, $\text{C}_4\text{H}_6\text{Fe}(\text{CO})_3$, prepared as part of the same investigation. Proton nmr clearly indicates a similarity between the two complexes.² X-Ray crystallographic data on the fluorine analog, $\text{C}_6\text{F}_8\text{Fe}(\text{CO})_3$, shows that the cyclo-

hexadiene and butadiene complexes are structurally related.³

Studies of phosphine substitution into $\text{C}_6\text{H}_8\text{Fe}(\text{CO})_3$ and into other dieneiron tricarbonyls are few. However, the coordination chemistry of the $\text{C}_4\text{H}_6\text{Fe}(\text{PF}_3)_x(\text{CO})_{3-x}$ system ($x = 1, 2, 3$) has been investigated in depth. This study included carbonyl force constant calculations and variable-temperature fluorine nmr.⁴

(1) B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 642 (1958).

(2) R. Burton, L. Pratt, and G. Wilkinson, *ibid.*, 594 (1961).

(3) M. R. Churchill and R. Mason, *Proc. Roy. Soc., Ser. A*, **301**, 433 (1967).

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

It was found that the PF₃ group preferred the apical position in the square-based pyramidal structure.⁵ All possible isomers were not produced. In the diphosphine one PF₃ group was in the apical position and the other in a basal position, but nmr nonequivalence was not observed until the temperature was lowered to -70°. Stereochemical nonrigidity was clearly evident.

Since the complexes C₆H₈Fe(CO)₃ and C₆H₈Fe(CO)₂ are structurally similar, it is important to compare their PF₃ chemistry, particularly with regard to the formation of isomers and the possibility of stereochemical nonrigidity. The two systems exhibit significant differences.

Experimental Section

1,3-Cyclohexadieneiron tricarbonyl can be prepared from either 1,3- or 1,4-cyclohexadiene.^{4,6,7} In this work, the 1,4 isomer was used because it is subject to less polymerization during the reaction.⁷

The compound C₆H₈Fe(CO)₃ was prepared by mixing approximately 6 ml of the diene (Aldrich), 5 ml of Fe(CO)₅ (Alfa Inorganics), and 10 ml of hexane in a 500-ml round-bottom flask equipped with a vacuum stopcock. Air was removed by vacuum at low temperatures and the flask was irradiated at room temperature for 2-8 hr by an AH-6 1000-W General Electric uv lamp. The solvent, excess diene, and Fe(CO)₅ were removed by vacuum distillation at 0° followed by recovery of the compound by vacuum at room temperature.

The PF₃ compounds were prepared by irradiating 0.5 ml of C₆H₈Fe(CO)₃ in 5 ml of hexane in a 500-ml round-bottom flask containing PF₃ at a pressure of about 600 Torr. The progress of the reaction as a function of reaction time was followed by periodically removing samples through a septum and examining the infrared spectrum of the solution in the carbonyl region. The bulk of the solvent was removed by vacuum distillation at -30°; then the products were isolated by glpc on a 2 m × 0.25 in. column of 15% DC-702 silicone oil on Chromasorb FB at 110° using a Varian Aerograph A-700 Autoprep chromatograph.

Infrared spectra of the complexes in hexane solution were recorded on a P-E 521 spectrometer calibrated with gaseous DCI.⁸ Proton and fluorine nmr were recorded on a Bruker HFX-90 spectrometer equipped with a variable-temperature unit and operating at 90 and 84.66 MHz, respectively. Chloroform and the high-field peak of the CHCl₂F fluorine doublet were used as lock signals. The temperature controller was calibrated by a thermocouple in a separate nmr tube. The temperature readings are accurate to at least ±3°. Chemical shifts were measured relative to lock signals. In measuring coupling constants and peak areas for equilibrium data, a mean of at least five observations was taken. Area measurements were made from the absorption lines by cutting and weighing. The temperature dependence of the nmr spectra was studied in solutions of isopentane with CFCl₃ as a secondary reference. Data taken in solutions of pentane or CS₂ did not differ significantly from those taken on solutions of isopentane. Mass spectra were determined at 70 eV on a Nuclide 12 90-G 1.5 instrument.

Results

Phosphorus trifluoride substitutes photochemically at room temperature into C₆H₈Fe(CO)₃ to yield all possible compositions of the type C₆H₈Fe(PF₃)_x(CO)_{3-x}. Replacement of the diene to yield the Fe(PF₃)_x(CO)_{5-x} species is not detected under the experimental conditions used. The compounds of the composition C₆H₈Fe(PF₃)_x(CO)_{3-x} (x = 1-3) can be identified by several techniques.

(1) **Order of Formation.**—The new compounds are expected to be formed sequentially as a function of time. Thus, one identifies the monophosphine as the

first new compound produced followed by the di- and finally the triphosphine.

(2) **Order of Elution.**—In every metal carbonyl-phosphorus trifluoride system studied to date, the parent compound has always been the last to be eluted; the monophosphine, next to last with progressively shorter retention times as the degree of PF₃ substitution increases. The composition of the cyclohexadiene species identified in this way agrees with that determined by the order of formation.

(3) **Mass Spectroscopy.**—After isolation by glpc, the components of the reaction mixture were examined by mass spectroscopy. The parent ion molecular weight for each of the species agrees with that expected. Molecular ions corresponding to the loss of CO and PF₃ groups from the parent ion are the main features in the high mass region. The most intense peaks in the spectrum of the parent complex, C₆H₈Fe(CO)₃,⁹ as well as in the PF₃-substituted species, are due to C₆H₈⁺ and C₆H₆Fe⁺.

(4) **Proton Nmr.**—The proton nmr pattern for C₆H₈Fe(CO)₃ contains three basic resonances of relative intensities 2:2:4. These are complex due to second-order coupling. The PF₃-substituted species have very similar spectra, but are slightly more complex due to additional phosphorus coupling with some of the protons.

(5) **Fluorine Nmr.**—The room-temperature fluorine nmr spectra of the species identified as the mono-, di-, and triphosphines by the above techniques are characteristic of compounds containing one, two,¹⁰ or three¹¹ equivalent PF₃ groups, respectively. The low-temperature spectra are different and these will be discussed later.

(6) **Infrared Spectra.**—Generally, the matching of experimental infrared spectra with that expected on the basis of group theory adds further confirmation to the identification of carbonyl compounds. In a general way, the same is true here. However, under careful examination some of the bands are found to be split, which is interpreted in terms of the presence of isomers. As discussed later, the ¹³CO data for C₆H₈Fe(CO)(PF₃)₂ help confirm the assignment of two isomers for the one composition.

Force Constant Calculations.—The infrared spectrum in the carbonyl region for C₆H₈Fe(CO)₃ is shown in Table I. It consists of three strong ¹²CO bands and

TABLE I
OBSERVED INFRARED SPECTRA OF THE C₆H₈Fe(PF₃)_x(CO)_{3-x}
SPECIES IN THE CARBONYL REGION (cm⁻¹)

C ₆ H ₈ Fe(CO) ₃	C ₆ H ₈ Fe(CO) ₂ (PF ₃)	C ₆ H ₈ Fe(CO)(PF ₃) ₂
2048.1 s	2025.7 s	2002 sh
1980.7 s	2024.8 s	1996.2 s
1975.6 s	1976.0 s	1956 sh ^c
2038.1 w ^c	2012.0 w ^c	1950.5 w ^c
1945.1 w ^c	1946-1941 w ^{b,c}	
1941.3 w ^{a,c}		

^a The 1941.3-cm⁻¹ peak is twice as intense as the 1945.1-cm⁻¹ peak. ^b A broadish band containing two or more peaks. ^c ¹³CO vibration.

three weak ¹³CO bands. Based on the arguments⁴ used with C₆H₈Fe(CO)₃, and assuming C_s symmetry,

(9) R. E. Winters and R. W. Kiser, *J. Phys. Chem.*, **69**, 3198 (1965).

(10) J. F. Nixon, *Advan. Inorg. Chem. Radiochem.*, **13**, 363 (1970); R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).

(11) E. G. Finer and R. K. Harris, *J. Chem. Soc.*, 1972 (1969).

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

(6) J. E. Arnet and R. Pettit, *J. Amer. Chem. Soc.*, **83**, 2955 (1961).

(7) R. B. King, *Organometal. Syn.*, **1**, 129 (1966).

(8) IUPAC Commission on Molecular Structure and Spectroscopy, *Pure Appl. Chem.*, **1**, 582 (1961).

there are two stretching force constants and two interaction force constants to be calculated.¹² There are more than enough data for this calculation if proper assignments can be made. Three ¹²CO vibrations and one ¹³CO vibration can be used to predict the remaining four ¹³CO bands (two of which are clearly observable). As with the butadiene complex, there are four possible assignments for these frequencies. These four permutations and the results are shown in Table II. Both assignments I and III predict all ¹³CO peaks

TABLE II
FORCE CONSTANTS (MDYN/Å) AND PREDICTED ¹³CO PEAKS (CM⁻¹) FOR CYCLOHEXADIENEIRON TRICARBONYL

	I	II	III	IV
Assignments				
A'(1)	2048.1	2048.1	2048.1	2048.1
A'(2)	1975.6	1980.7	1980.7	1975.6
A''	1980.7	1975.6	1975.6	1980.7
A'*(2)	1941.3	1941.3	1945.1	1945.1
Calcd Values				
K ₁	16.15	16.03	16.17	16.28
K ₂	16.19	16.25	16.18	16.13
K _{1,2}	0.39	0.29	0.36	0.41
K _{2,2'}	0.35	0.49	0.42	0.29
Predicted Values				
A'*(1)	2037.8	2043.1	2039.1	2033.8
Comment	Obsd 2038	Could be buried	Obsd 2038	4 cm ⁻¹ off
A*(1)	2038.0	2035.0	2037.3	2039.8
Comment	Obsd 2038	3 cm ⁻¹ off	Obsd 2038	Obsd 2038
A*(2)	1977.0	1980.0	1979.6	1977.3
Comment	Buried	Buried	Buried	Buried
A*(3)	1944.8	1944.6	1942.8	1942.7
Comment	Obsd 1945.1	Obsd 1945.1	Obsd 1941.3	Obsd 1941.3

to lie very near to observed peaks. However, a random distribution of the ¹³CO molecules should give twice as many species with ¹³CO in the equivalent, basal positions (the A*(3) vibration) as in the unique, apical position (the A'*(2) vibration). The relative intensities of the bands make assignment III superior to assignment I. This is the same assignment given to the butadiene complex.

The force constants for C₆H₈Fe(CO)₃, calculated from assignment set III, are K₁ = 16.17, K₂ = 16.18, K_{1,2} = 0.36, and K_{2,2} = 0.42 mdyn/Å. The interaction constants are almost equal to those found for C₄H₆Fe(CO)₃, but the force constants are lower and of the opposite relative magnitude (although they are essentially equal). Lower force constants are indicative of stronger metal-carbonyl π bonding and hence weaker metal-diene π bonding in the cyclohexadiene complex.¹²

Under low resolution the infrared spectrum of C₆H₈Fe(PF₃)₂(CO) shows two strong ¹²CO peaks and two weak ¹³CO peaks. Upon closer examination, the high-frequency ¹²CO band shows a slight splitting. The data are given in Table I. There are too many bands for a single isomer. Since the sample was purified by glpc and appears to be pure from its mass spectrum, it seems more likely that the extra band results from a second isomer rather than from an impurity. The low-frequency ¹²CO band must, then, be an unresolved combination of two bands, one from each isomer. Fail-

ure of glpc to separate such isomers has been observed in other PF₃-substituted systems.¹³

Force constant calculations were made for the two isomers. For the case of equivalent carbonyl groups, (C_s isomer), no ¹³CO data are required. Two possible assignments of the ¹²CO data are possible, and both predict quite reasonable ¹³CO frequencies as shown in Table III. Thus no firm conclusion is possible.

TABLE III
FORCE CONSTANTS (MDYN/Å) AND PREDICTED ¹³CO PEAKS (CM⁻¹) FOR CYCLOHEXADIENEIRON DICARBONYL-TRIFLUOROPHOSPHINE WITH EQUIVALENT CARBONYLS

¹² CO freq	K ₂	K _{2,2'}	¹³ CO predictions
2025.6, 1976.0	16.17	0.40	2011.7, 1945.4
2024.8, 1976.0	16.16	0.39	2011.0, 1945.2

To calculate the force constants of the isomer containing nonequivalent carbonyl ligands, one ¹³CO frequency is required. Since the ¹³CO peaks occur as an unresolved combination of bands, a different approach to the calculation was tried. Permutations of the two ¹²CO peaks were combined with a series of values for the ¹³CO peak ranging from 1941 to 1946 cm⁻¹. This calculation was unproductive because several combinations predicted ¹³CO frequencies close to measured peaks. No conclusion could be reached.

The infrared spectrum of C₆H₈Fe(PF₃)₂(CO) shows one ¹²CO peak with a shoulder and one ¹³CO peak with a shoulder. The data are given in Table I. Since the difference between the major ¹²CO peak and the major ¹³CO peak and the difference between the two shoulders were both 45 cm⁻¹, two diphosphine species are present, unseparated by glpc. The force constant for the major isomer is 16.09 mdyn/Å while that of the minor isomer is 16.18 mdyn/Å. The infrared data cannot be used to determine which band should be assigned to a particular isomer.

Variable-Temperature Fluorine Nmr.—As stated previously, at room temperature fluorine nmr spectra of the mono-, di-, and triphosphines are characteristic of one, two, and three equivalent PF₃ groups. Variable-temperature studies indicate that these are time-averaged spectra.

At room temperature, the spectrum of C₆H₈Fe(PF₃)₂(CO) shows a typical AA'X₃X'₃ pattern¹⁰ indicative of a diphosphine with equivalent PF₃ groups. The time-averaged coupling constants have been calculated and found to be ²J_{PP'} = 32.3 ± 0.2, ¹J_{PF} = 1302.4, and ³J_{PF'} = 9.8 Hz. ¹J_{PF} and ³J_{PF'} have opposite signs and ⁴J_{FF'} is assumed to be zero.

As the temperature is lowered, the spectrum of the diphosphine undergoes several changes, illustrated in Figure 1. First, the smaller side peaks shift positions; then the entire pattern broadens. Finally at our low-temperature experimental limit, initial sharpening of the low-field peaks reveals a broad doublet (the upfield portion has not yet begun to show limiting structure). Both components of this doublet appear to be further split into doublets suggesting an ABX₃Y₃ limiting spectrum arising from two nonequivalent PF₃ groups in a ratio of 1:1. This may be compared to the limiting spectrum of C₄H₆Fe(PF₃)₂(CO) in which nonequivalent PF₃ groups in a 1:1 ratio are also found.⁴ The limiting

(12) F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **84**, 4432 (1962), and other papers in this series.

(13) C. A. Udovich, R. J. Clark, and H. Haas, *Inorg. Chem.*, **8**, 1066 (1969); C. A. Udovich and R. J. Clark, *ibid.*, **8**, 938 (1969).

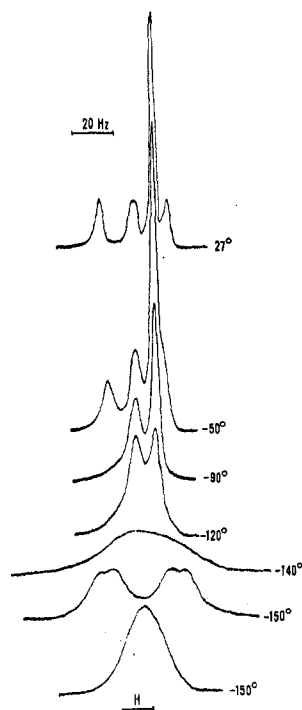
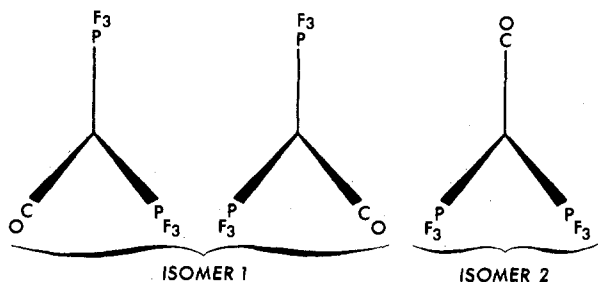


Figure 1.—Representative tracings of the low-field half of ^{19}F spectra of $\text{C}_6\text{H}_8\text{Fe}(\text{PF}_3)_2(\text{CO})$ from $+27$ to -150° . The bottom tracing represents the high-field half of the -150° spectrum. Slight spectral shifts with temperature are not shown.

spectrum of $\text{C}_6\text{H}_8\text{Fe}(\text{PF}_3)_2(\text{CO})$ is, therefore, interpreted to indicate that in cyclohexadiene-diphosphine, just as in the butadiene-diphosphine, isomer 1 is the more stable and at low temperatures exists to the exclusion of isomer 2. In this representation the lower positions denote equivalent basal sites on the square-pyramidal structure and the upper position denotes the apical site.



Since only the low-field peaks have begun to sharpen at our low-temperature experimental limit, it is not possible to obtain accurate coupling constants from the limiting spectrum. The $^1J_{\text{PF}}$ values are approximately 1300 Hz and the $^3J_{\text{PF}}$ values are on the order of 10 Hz. It is, therefore, not possible to determine from the nmr data alone whether the time-averaged spectrum observed at room temperature results from the presence of only isomer 1 or from an average of both isomers 1 and 2. However, the infrared data clearly show that both isomers exist in appreciable quantities at room temperature. Thus, from a combination of the infrared and nmr data, it appears that not only is the intramolecular process averaging out the nonequivalence of the PF_3 groups in isomer 1 but it is also averaging these with the PF_3 groups in isomer 2. The changes in the high-temperature spectra before

broadening occurs can, therefore, probably be attributed to a change in isomer population.

The spectrum of $\text{C}_6\text{H}_8\text{Fe}(\text{PF}_3)_2(\text{CO})_2$ at room temperature consists of a doublet with peaks separated by 1316 Hz. As the temperature is lowered, this spectrum undergoes the changes illustrated in Figure 2.

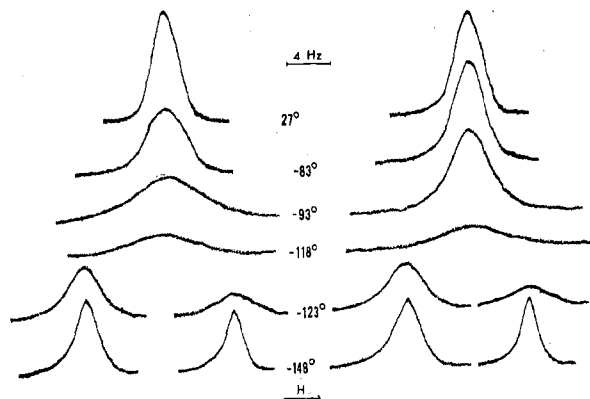
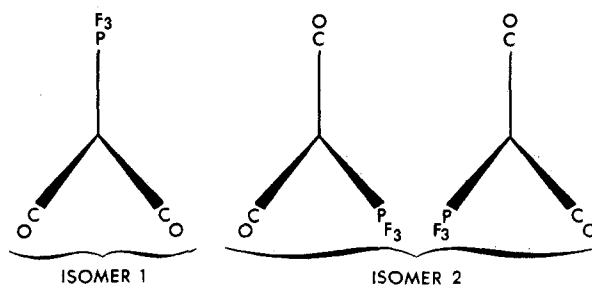


Figure 2.—Representative tracings of ^{19}F spectra of $\text{C}_6\text{H}_8\text{Fe}(\text{PF}_3)_2(\text{CO})_2$ from $+27^\circ$ to -148° . The low-field portion is shown on the left. In the 27° spectrum, the low- and high-field peaks are separated by 1316 Hz. In the -148° spectrum, the major and minor sets of peaks have $^1J_{\text{PF}}$ of 1324 and 1300 Hz, respectively, and a 66-Hz (0.73-ppm) chemical shift between them.

Between room temperature and -80° , the lines remain sharp. There is a slight downfield shift of the two peaks, but the time-averaged coupling constant $\langle J_{\text{PF}} \rangle$ remains constant to within 1.5 Hz. Between -80 and -120° both peaks broaden. Below -120° both the high- and low-field signals sharpen to yield two doublets of unequal intensity. This spectrum is indicative of two types of nonequivalent PF_3 groups and is interpreted as showing the presence of both isomer 1 and isomer 2.



At our low-temperature experimental limit, it is not certain whether the limiting spectrum has been reached. The peak widths do not narrow significantly over the last 10° , but the relative peak positions ($\delta_{\text{major}} - \delta_{\text{minor}}$) increase by approximately constant amounts per 5° intervals as the temperature is lowered. Since the lines do not narrow significantly, this change in the relative peak positions may be due to slight differences in the temperature dependence of the chemical shifts of the two isomers rather than to genuine time-averaging effects.

Coupling constants for the two isomers do not change significantly over the temperature range -123 to -148° . Values for these constants have been determined as $J_{\text{PF}}(\text{major}) = 1324$ Hz and $J_{\text{PF}}(\text{minor}) = 1300$ Hz. Assignments of the major and minor peaks to particular

isomers may be made using the following arguments.

In $C_4H_6Fe(PF_3)_2(CO)$ the value of $^1J_{PF}$ for the PF_3 group in the apical site was found to be less than $^1J_{PF}$ for the PF_3 group in the basal site.¹⁴ Since $J_{PF}(\text{minor})$ is less than $J_{PF}(\text{major})$ for $C_6H_8Fe(PF_3)(CO)_2$, the minor isomer appears to have PF_3 in the apical site (isomer 1).

Thermodynamic data lend additional support to this assignment. Previous work with the butadiene system suggested that PF_3 groups prefer to occupy the apical rather than the basal position. The low-temperature spectrum of $C_6H_8Fe(PF_3)_2(CO)$ suggests that the same is true for the cyclohexadiene system. Careful determination of the equilibrium constant K for the two $C_6H_8Fe(PF_3)(CO)_2$ isomers, $K = [\text{major}]/[\text{minor}]$, using relative peak areas over the range -123 to -143° shows that the equilibrium constant decreases as the temperature is lowered. A plot of $\ln K$ vs. $1/T$ gives a straight line over the region $T = -123$ to -143° as shown in Figure 3. A least-squares calculation on

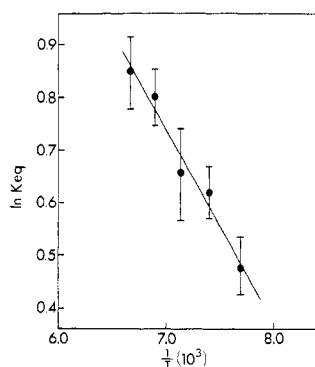


Figure 3.—Plot of $\ln K$ vs. $1/T$ from -123 to -143° for $C_6H_8Fe(PF_3)(CO)_2$.

all points gives $\Delta H = +725 \pm 200$ cal/mol from the slope of the line. The relative error in this value is about as small as can be expected from this kind of calculation.¹⁵ The positive value of ΔH indicates that the minor species is the more stable and is again assigned to isomer 1.

For the time-averaged spectra, the average coupling constant $\langle J_{PF} \rangle_T$ will be a function of the J_{PF} values of the individual isomers and the mole fraction (x) of each isomer existing at the particular temperature T according to the equation

$$\langle J_{PF} \rangle_T = x_1(^1J_{PF})_1 + x_2(^1J_{PF})_2$$

Calculation of x_1 and x_2 over the range $t = 27$ to -73° using $(^1J_{PF})_1$ and $(^1J_{PF})_2$ values determined at our low-temperature limit gives a second set of equilibrium values which also decrease as the temperature is lowered. Calculation of ΔH using the values determined from the coupling constants does not agree with the previous calculation. The lack of agreement between the two sets of values suggests that the temperature dependence of $\langle J_{PF} \rangle_T$ may be determined by other fac-

(14) At the time of the publication of the butadiene work,⁴ an assignment of the nmr spectra could not be made. Since then, the low-temperature fluorine nmr of $C_6H_8Fe(PF_3)_2$ has been obtained. At the limiting temperature, a 1:2 intensity ratio of peaks is seen which allows an unambiguous assignment of the relative chemical shifts of the apical and the basal PF_3 groups. Using these relative chemical shift values, the 1:1 relative intensity peaks of the apical and basal PF_3 groups in $C_4H_6Fe(CO)(PF_3)_2$ could be assigned with $^1J_{PF}$ values 1287 and 1310 Hz, respectively.

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tors in addition to the population changes of isomer 1 and isomer 2.

An attempt has been made to calculate the activation energy for this intramolecular process using data from the monophosphine in the exchange region. However, since it seems probable that the limiting spectrum has not been reached, even at our low-temperature experimental limit, only approximations could be made. Values ranging from 6 to 10 kcal/mol were obtained, depending on the assumptions made.

The room-temperature spectrum of $C_6H_8Fe(PF_3)_3$ shows an AA'A'X₃X'X''₃ pattern indicative of a triphosphine with three equivalent PF_3 groups.¹¹ The time-averaged coupling constants have been calculated and found to be $(^2J_{PP'}) = 59$, $(^1J_{PF}) = 1290$, and $(^3J_{PF'}) = 9$ Hz. $(^1J_{PF})$ and $(^3J_{PF'})$ have opposite signs and $(^4J_{FF'})$ is assumed to be zero. Some broadening is evident at low temperatures, but the limiting spectrum is expected at temperatures even lower than those required to see the limiting spectrum of the diphosphine. It appears that as the number of PF_3 groups increases, progressively lower temperatures are required to slow the intramolecular process. A similar situation has been found for the butadiene and other analogous systems.

Discussion

Phosphorus trifluoride substitutes photochemically at room temperature into cyclohexadieneiron tricarbonyl to yield all possible compounds of the type $C_6H_8Fe(PF_3)_x(CO)_{3-x}$. Replacement of the diene to yield the $Fe(PF_3)_x(CO)_{5-x}$ species did not occur under the experimental conditions used. The compounds were isolated by glpc and identified by a variety of techniques.

Isomers in the mono- and diphosphine species are possible for the square-pyramidal structure that is assumed to be present. There are two basal positions and one apical position that could be occupied by carbonyl or phosphorus trifluoride groups yielding a maximum of two isomers for both the mono- and diphosphines.

Neither the mono or diphosphine species can be separated into isomers by glpc, a technique operating on a very slow time scale. However, the presence of such isomers is definitely indicated by both infrared and ^{19}F nmr spectroscopy. Infrared spectroscopy, operating on the fastest time scale, shows the presence of isomers by the number and type of carbonyl vibrational bands present in the spectrum. Nmr operating on a time scale intermediate between those of infrared and glpc shows the isomers as individual entities at low temperatures, but as averaged species at room temperature. At intermediate temperatures, spectral broadening occurs for both compounds. At our lowest available temperatures, the nature of the limiting spectrum has just become evident for the diphosphine. The spectrum of the monophosphine, although more fully developed, appears to be shifting slightly, indicating that the limiting spectrum may not have been reached for this compound either.

The appearance and changes in the ^{19}F nmr spectra of the mono- and diphosphine species indicate that two isomers are present and that a rapid intramolecular process is occurring. This process makes all PF_3 groups

equivalent at room temperature. The mechanism of this process is assumed to be the same as that proposed for the butadieneiron tricarbonyl system.⁴

If PF₃ and CO are quite similar as ligands, the apical and basal positions should be occupied in a nearly random fashion. The cyclohexadiene system contrasts with the butadiene system with regard to the occupation of these sites. In the mono- and diphosphines of the butadiene system, PF₃ prefers to occupy the apical site and only the isomers based on that preference are observed. For the cyclohexadiene system, all possible isomers are detected. It is interesting that the carbonyl stretching force constants calculated for both systems predict this site preference. In butadieneiron tricarbonyl, K_1 is at least 0.15 mdyn/Å greater than

K_2 indicating that the two types of carbonyl sites are not equivalent. In cyclohexadieneiron tricarbonyl, where the two force constants are essentially equal, the two types of sites are more nearly equivalent. For these types of systems, PF₃ and CO are apparently not equal in their bonding ability. Other dieneiron tricarbonyl systems are currently being studied in an effort to determine (1) whether this type of prediction can be extended to other systems, (2) the reasons for the different behavior of different dienes, and (3) the effect of different dienes on the intramolecular process.

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Magnetic Spin Equilibria in Some New Five-Coordinate Schiff Base Complexes of Cobalt(II)

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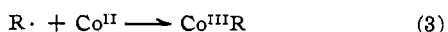
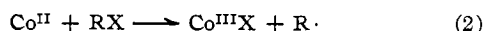
Solid-state, room-temperature magnetic susceptibility data for six new complexes of the type Co^{II}(salen)B (where salen = *N,N'*-bis(salicylidene)ethylenediamino and B = imidazole, 2-methylimidazole, benzimidazole, 5,6-dimethylbenzimidazole, 3-iodopyridine, and 3,5-lutidine) and one new complex of the type Co^{II}(saloph)B (where saloph = *N,N'*-bis(salicylidene)-*o*-phenylenediamino and B = imidazole) are reported. The room-temperature moments lie between 1.9 and 3.5 BM, and the results are interpreted as arising from ⁴A'' to ²A' spin equilibria. The anomalous temperature dependence of the magnetic susceptibility of Co^{II}(salen)(5,6-dimethylbenzimidazole) is that expected for such equilibria. This conclusion is also applicable to complexes of the type Co^{II}(saloph)B (where B = pyridine, 3,4-lutidine, and 1-methylimidazole) in methylene chloride solution. The results afford a reasonable explanation for the dependence on B of the "outer-sphere" reduction of nitrobenzyl halides by these complexes.^{2,3}

Introduction

Several low-spin, five-coordinate cobalt(II) d⁷ complexes have been shown⁴⁻⁶ to undergo the reaction with organic halides (RX)

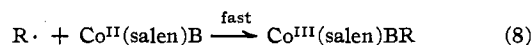
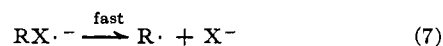
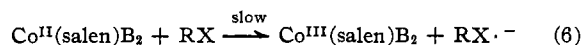
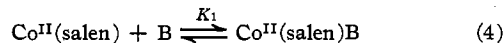


Rates of reaction 1 for a large variety of organic halides and several complexes (*e.g.*, Co^{II}(CN)₆³⁻ and Co^{II}-(DH)₂B, where B = pyridine, triphenylphosphine, etc., and DH₂ = dimethylglyoxime) have been studied by Halpern and coworkers.⁴⁻⁶ The mechanism (eq 2 and 3) advanced to explain the data involves halogen abstraction² as the rate-determining step.



Extension of these reactions to other cobalt(II) complexes, principally of the type *N,N'*-bis(salicylidene)-ethylenediamino(1-methylimidazole)cobalt(II) (Co^{II}-

(salen)(1-methylimidazole)) led to the discovery of a new class of reactions² involving "outer-sphere" electron transfer (eq 4-8) when RX is a ring-substituted nitrobenzyl halide. When 1-methylimidazole is re-



placed by pyridine, however, the reduction occurs *via* the more usual halogen atom transfer pathway.³ The reasons for the unusual difference in reaction mechanism for such apparently similar ligands are not clear.

Preliminary studies of the magnetic susceptibility of methylene chloride solutions of Co^{II}(salen) and Co^{II}-(saloph) (where saloph = *N,N'*-bis(salicylidene)-*o*-phenylenediamino) in the presence of ligands such as pyridine and 1-methylimidazole revealed magnetic moments intermediate between low spin (*ca.* 2 BM) and high spin (*ca.* 4-5 BM). Those complexes which reacted by the outer-sphere mechanism had higher moments than those which favored halogen abstraction.

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