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Metal Carbonyl–Trifluorophosphine Systems. XIIB. Methylbutadienetricarbonyliron(0) Systems—Temperature-Dependent Nuclear Magnetic Resonance Studies

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An extensive fluorine nmr study has been made on the methyl-substituted (butadiene)Fe$(PF_3)_x(CO)_{3-x}$ complexes described in the previous paper. The results confirm the vibrational analysis and show that the PF_3 ligand exhibits a strong preference for the apical position over either of the two basal sites. In the diphosphines of asymmetric dienes PF_3 exhibits a secondary preference for the basal position *trans* to the methyl group on the butadiene ligand. Intramolecular exchange of the PF_3 groups occurs in the di- and triphosphines of both asymmetric and symmetric dienes. The limiting spectra are generally well developed by −100°. Comparison of the limiting and time-averaged parameters provides information concerning the general nature of the nonrigid process.

Introduction

The nmr technique is particularly suited for the study of the dieneiron carbonyl–trifluorophosphine systems since both proton and fluorine nuclei are present. The general appearance of the ^{19}F spectrum is very useful for determining the number of PF_3 groups substituted into the parent tricarbonyl, while the appearance of the ^1H spectrum can be used to assign a structure to the diene ligand.[1]

In addition to this information, an examination of the temperature dependence of the ^{19}F spectra of the butadiene[2] and cyclohexadiene[3] systems has revealed an intramolecular exchange of the phosphine groups. This exchange makes all PF_3 groups completely equivalent in the di- and triphosphine complexes. Since the methylbutadiene complexes appear to have the same square-based pyramidal structure, they are also expected to exhibit nonrigid behavior.

Of particular interest will be the complexes of the asymmetric dienes, isoprene, *trans*-1,3-pentadiene, etc. In the symmetric (C_s) complexes of butadiene and cyclohexadiene, two of the three coordination sites are equivalent. An asymmetric ligand such as isoprene will make the two basal sites nonequivalent and may yield additional information about the exchange process.

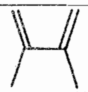
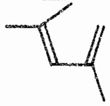
Spectra of the PF_3 derivatives of the following methylbutadieneiron tricarbonyls were examined: 2,3-dimethylbutadiene, *trans,trans*-2,4-hexadiene, isoprene, *trans*-1,3-pentadiene, *cis*-1,3-pentadiene, and 2,4-dimethyl-1,3-pentadiene. The preparation and isolation of these complexes, as well as the nmr spectrometer and operating conditions, have been previously described.[1]

Results

Symmetric Diene Complexes. The Monophosphines. Assuming a square-based pyramidal structure for these complexes, of the three possible isomers for the symmetric (C_s) diene monophosphines (Figure 1A) only two can be detected since isomers 2 and 3 form an enantiomeric pair. In this representation the lower positions denote the basal sites of the square-based pyramid, and the upper position denotes the apical site.

Vibrational analysis has already suggested that isomer 1, the species with PF_3 in the apical position, exists essentially to the exclusion of all other species in both the 2,3-dimethylbutadiene and *trans,trans*-2,4-hexadiene monophosphines.[1] At room temperature the ^{19}F nmr spectra of these monophosphines show only one fluorine resonance each. The chemical shifts and $^1J_{PF}$ coupling constants are given in Table I. The coupling constants agree well with the value of 1300 Hz found for apical PF_3 groups in both the butadiene[2] and cyclohexadiene[3] monophosphines. (Values of $^1J_{PF}$ for basal PF_3 ligands are expected to be about 20 Hz larger.[3]) The spectra remained unchanged over a temperature range of +27 to −123°.

Table I. Chemical Shifts and $^1J_{PF}$ Coupling Constants for Several (methylbutadiene)Fe$(PF_3)(CO)_2$ Complexes at +27° [a]

Diene	δ, ppm	$^1J_{PF}$, Hz
	73.234 (73.736)	1307.6 (1305.6)
	70.815 (71.226)	1303.6 (1301.4)
	73.825 (74.275)	1307.0 (1304.0)
	72.531 (72.866)	1305.2 (1302.4)
	73.031 (74.137)	1310.6 (1302.1)
	70.770 (71.050)	1308.9 (1306.2)

[a] Spectra were measured in a solution of isopentane, $CHFCl_2$, and $CFCl_3$. Chemical shifts are relative to the high-field peak of the $CHFCl_2$ fluorine doublet. Values in parentheses are for −103°. A positive value of δ represents a downfield shift. δ($CHFCl_2$) (upfield peak) = δ($CFCl_3$) + 81.206.

For a time-averaged spectrum, the averaged chemical shift $\langle\delta\rangle_T$ will be a function of the δ values of the individual isomers and the mole fraction (x) of each isomer existing at the particular temperature T according to the equation

$$\langle\delta\rangle_T = x_1(\delta)_1 + x_2(\delta)_2 + x_3(\delta)_3 \qquad (1)$$

Although the chemical shifts of isomers 2 and 3 should be the same, they are not expected to equal δ_1 for isomer 1. If δ_1 and δ_2 are sufficiently different, the loss of one or more of the isomers could be indicated by a break in the plot of chemical shift *vs.* the temperature T.[4]

For (2,3-dimethylbutadiene)Fe$(PF_3)(CO)_2$ a plot of δ *vs.* T is essentially linear suggesting that the depopulation of an isomer is very unlikely. The plot of δ *vs.* T for (*trans,trans*-2,4-hexadiene)Fe$(PF_3)(CO)_2$ is markedly curved (Figure 2).

It is not certain whether this curve indicates a loss of one or more of the possible isomers or whether the temperature dependence of δ for the preferred monophosphine isomer is simply nonlinear. If Figure 2 does indicate that some of isomer

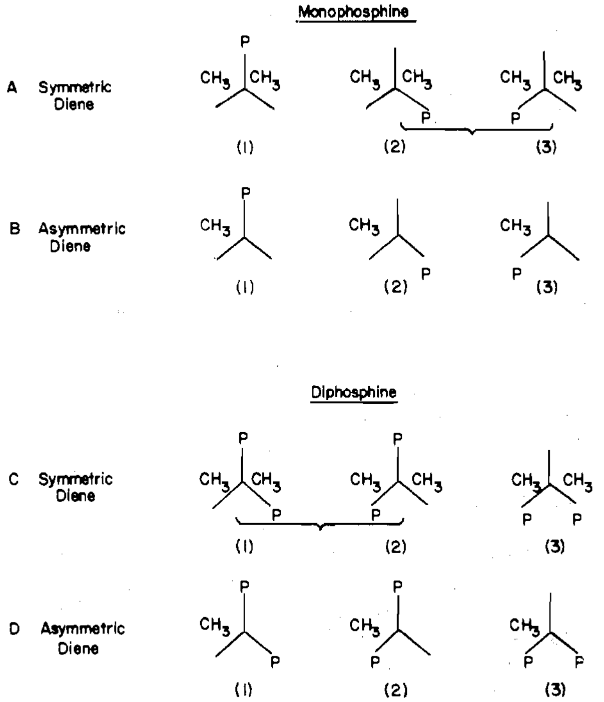


Figure 1. Possible isomers of the dieneiron carbonyl-trifluorophosphine complexes. Species in brackets are enantiomers.

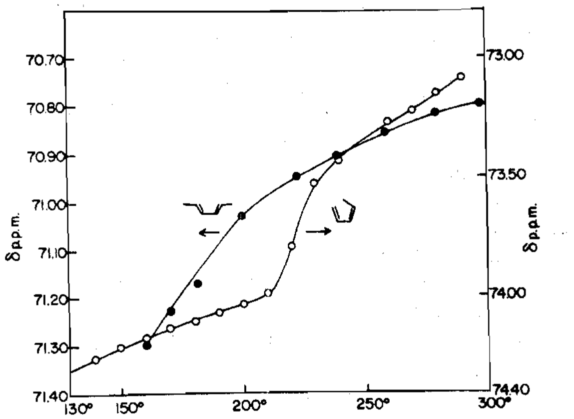


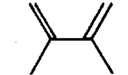
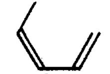
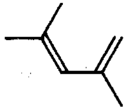
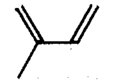
Figure 2. Plot of chemical shift *vs.* temperature for the monophosphine complexes of *trans,trans*-2,4-hexadiene (left) and *cis*-1,3-pentadiene (right).

2 (or 3) is present at room temperature, the amount must be too small to detect in the infrared spectrum.

The Triphosphines. The complex (*trans,trans*-2,4-hexadiene)$Fe(PF_3)_3$ was not studied. However, the ^{19}F spectrum of (2,3-dimethylbutadiene)$Fe(PF_3)_3$ shows a typical $AA'A''X_3X'_3X''_3$ pattern[5] indicative of a triphosphine with three equivalent PF_3 groups. The appearance of the room-temperature spectrum is almost identical with that of the butadiene- and cyclohexadiene triphosphine spectra[2,3] (Table II), suggesting, by analogy, that some kind of an exchange process is probably occurring, causing the nonequivalent PF_3 ligands to appear equivalent on the nmr time scale.

The Diphosphines. Assuming a square-based pyramidal structure for these complexes, of the three possible isomers for the symmetric diene diphosphines (Figure 1C), isomers 1 and 2 are mirror images and cannot be distinguished by nmr or infrared spectra. Vibrational analysis has suggested that of the distinguishable isomers, only one is present in detectable amounts at room temperature.[1]

Table II. Time-Averaged Chemical Shifts (ppm) and Coupling Constants[a] (Hz) for Several (diene)$Fe(PF_3)_3$ Complexes at 27° [b]

Diene	$\langle\delta\rangle$	$\langle ^2J_{PP'}\rangle$	$\langle ^1J_{PF}\rangle^c$	$\langle ^3J_{PF'}\rangle^c$
	76.360	63	1290	7
	74.668	~60	~1289	~7
	76.993	~60	~1291	~9
	75.369	55	1293	9
	75.725	~55	~1300	~10
	75.423	59.5	1290.4	7.8

[a] For this calculation $\langle ^4J_{FF'}\rangle$ was assumed to be zero. [b] Spectra were measured in a solution of isopentane, $CHFCl_2$, and $CFCl_3$. Chemical shifts are relative to the high-field peak of the $CHFCl_2$ doublet. [c] The constants $\langle ^1J_{PF}\rangle$ and $\langle ^3J_{PF'}\rangle$ have opposite signs.

Table III. Time-Averaged Chemical Shifts (ppm) and Coupling Constants[a] (Hz) for Several (diene)$Fe(PF_3)_2(CO)$ Complexes at +27° [b]

Diene	$\langle\delta\rangle$	$\langle ^2J_{PP'}\rangle$	$\langle ^1J_{PF}\rangle^c$	$\langle ^3J_{PF'}\rangle^c$
	74.609	~0	~1310	~10
	74.303[d]	~0[d]	~1304[d]	~13[d]
	72.908	~0	~1303	~10

[a] $^4J_{FF'}$ was assumed to be zero. [b] Spectra were measured in a solution of isopentane, $CHFCl_2$, and $CFCl_3$. Chemical shifts are relative to the high-field peak of the $CHFCl_2$ doublet. [c] $^1J_{PF}$ and $^3J_{PF'}$ have opposite signs. [d] Temperature of +67°, toluene solution, and α-trifluorotoluene reference.

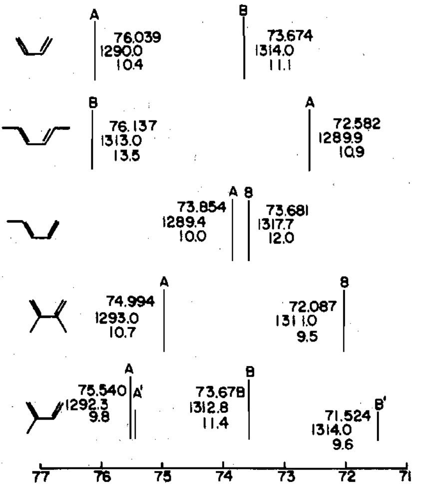


Figure 3. Schematic representation of the chemical shifts of the apical (A) and basal (B) PF_3 groups in the low-temperature limiting spectra of diphosphine complexes. The data are in order: chemical shifts (relative to upfield peak of $CHFCl_2$), $^1J_{PF}$, and $^3J_{PF'}$.

The appearance and temperature dependence of the ^{19}F spectra of (2,3-dimethylbutadiene)- and (*trans,trans*-2,4-hexadiene)$Fe(PF_3)_2(CO)$ are completely analogous to that of the butadiene diphosphine.[2] At high temperatures the spectra show an $AA'X_3X'_3$ pattern[6] indicative of a diphosphine with two equivalent PF_3 groups. However, as the temperature is lowered, the spectra broaden, collapse, and resharpen into two double doublets in a 1:1 ratio. This suggests an ABX_3Y_3 system arising from two nonequivalent PF_3 groups (isomers 1 and 2). The time-averaged nmr parameters are given in

Table IV. Approximate Chemical Shifts (ppm) and Coupling Constants (Hz) Obtained for the Limiting Spectra of Several (methyldiene)Fe(PF$_3$)$_3$ Complexes[a]

Diene	δ_1	δ_2	δ_3	$(^1J_{PF})_1$	$(^1J_{PF})_2$	$(^1J_{PF})_3$
 [b]	77.25	76.19	73.65	1275	1286	1292
 [c]	79.35	76.03	75.79	1287	1271	1303
 [d]	77.32	75.34	74.70	1275	1294	1294

[a] Spectra were measured in a solution of isopentane, CHFCl$_2$, and CFCl$_3$. Chemical shifts are relative to the high-field peak of the CHFCl$_2$ doublet. [b] At −113°. [c] At −93°. [d] At −133°.

Table III, while those of the limiting spectra at −103° are shown in Figure 3.

By analogy with the butadiene-[2] and cyclohexadiene[3] systems, the resonances at −103° with the larger $^1J_{PF}$ values are assigned to the basal PF$_3$ groups while the resonances with the smaller $^1J_{PF}$ values are assigned to the apical PF$_3$ groups. Averages of the $^1J_{PF}$ and $^3J_{PF'}$ values at −103° agree well with the time-averaged coupling constants at higher temperatures. This further suggests that only one apical and one basal PF$_3$ group are averaged by the exchange process and confirms the infrared data in suggesting that the concentration of isomer 3, even at room temperature, is negligible. The fluorine chemical shifts are sufficiently temperature dependent that an averaging of the shifts at −103° cannot be meaningfully compared to values at higher temperatures.

The activation energies for the exchange process were estimated for both diphosphine complexes by the method of Gutowsky and Holm.[7] For (2,3-dimethylbutadiene)Fe(PF$_3$)$_2$(CO) and (*trans,trans*-2,4-hexadiene)Fe(PF$_3$)$_2$(CO) these values are 9.28 ± 1.21 and 9.17 ± 0.32 kcal/mol, respectively. Within experimental error these values are equal to each other and to the activation energy found for the exchange process in the butadiene diphosphine (8.84 ± 0.27 kcal/mol, in a CHFCl$_2$–CFCl$_3$–isopentane solution).

Since the exchange process in all these diphosphine complexes makes the PF$_3$ groups equivalent and since the activation energies for all three processes are essentially equal, it seems reasonable to assume that the actual mechanisms involved must also be identical. Therefore, the presence of methyl groups on the central and terminal carbons of butadiene does not appear to alter significantly the intramolecular exchange of PF$_3$ in these types of complexes.

Asymmetric Diene Complexes. The Monophosphines. For asymmetric diene monophosphines, the presence of the methyl groups makes the two basal sites nonequivalent, and all three isomers (Figure 1B) should be distinguishable by ^{19}F nmr. Vibrational analysis has already suggested that isomer 1 with PF$_3$ in the apical position should exist essentially to the exclusion of isomers 2 and 3.[1]

At room temperature the ^{19}F nmr spectra of the isoprene, *trans*-1,3-pentadiene, *cis*-1,3-pentadiene, and 2,4-dimethyl-1,3-pentadiene monophosphines show one fluorine resonance each. The nmr parameters are given in Table I. Other than a slight shift downfield and a small decrease in $^1J_{PF}$ the spectra of all complexes except the *cis*-1,3-pentadiene monophosphine remain unchanged down to temperatures of −120°. A plot of δ *vs.* T for the isoprene monophosphine is essentially linear, while those for the *trans*-1,3-pentadiene and 2,4-dimethyl-1,3-pentadiene complexes are somewhat curved.

The behavior of the *cis*-1,3-pentadiene monophosphine is completely different. At room temperature the ^{19}F nmr spectrum shows one fluorine resonance (Table I). At −13° the lines begin to broaden, at −53° they collapse, and by −103° they have resharpened into a limiting pattern. Only one fluorine resonance could be found at low temperatures. The $^1J_{PF}$ value of this resonance (Table I) is quite similar to others assigned to monophosphines with PF$_3$ in the apical site.

A plot of the chemical shift δ *vs.* the temperature T (Figure 2) shows a very pronounced break in the curve due to a sharp downfield shift in δ between −33 and −53°. A plot of $^1J_{PF}$ *vs.* T also shows a sharp decrease over the same temperature range. This suggests that any undetected species involved in the exchange process must have resonances with larger $^1J_{PF}$ values, upfield from the observed peaks. By analogy with previous systems, isomers 2 and 3 are expected to have $^1J_{PF}$ values larger than that of isomer 1.[2,3]

A low-temperature study of the ^{19}F nmr spectrum of the same *cis*-1,3-pentadiene monophosphine compound was also conducted in a CS$_2$–CFCl$_3$–CHCl$_3$ solution. The same spectral behavior was observed as the temperature was decreased showing that the behavior is solvent independent.

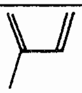
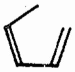
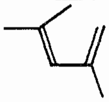
Broadening in the ^{1}H nmr spectrum of (*cis*-1,3-pentadiene)Fe(PF$_3$)(CO)$_2$ was also observed with decreasing temperature. By −73° J_{P-CH_3} in the methyl resonance had completely disappeared while proton–proton coupling in the same resonance remained unaffected. Due to the incompatibility of sample and solvent, the spectrum could not be studied below −93°. At this temperature a new splitting pattern resembling the room-temperature spectrum was just becoming evident. Since P–H but not H–H coupling is broadened, the most reasonable explanation involves an exchange of PF$_3$ ligands, analogous to that observed in the cyclohexadiene monophosphine.[3]

On the basis of the vibrational analysis and the value of $^1J_{PF}$, the ^{19}F resonance at −103° is assigned to isomer 1. Apparently observable quantities of isomer 2 and/or 3 exist at room temperature where the spectra are averaged but have essentially disappeared by −103°.

The Triphosphines. For asymmetric diene triphosphines three nonequivalent PF$_3$ groups are expected. The ^{19}F nmr spectra of the isoprene, *trans*-1,3-pentadiene, *cis*-1,3-pentadiene, and 2,4-dimethyl-1,3-pentadiene triphosphines all show a typical AA'A''X$_3$X'$_3$X''$_3$ pattern[5] with parameters similar to those of the other diene triphosphines (Table II). The appearance of the isoprene triphosphine spectrum broadens as the temperature is decreased, eventually collapsing and then resharpening into a limiting pattern at −113° (the lowest temperature at which the spectrum could be studied). This limiting pattern shows three types of resonances in an approximate ratio of 1:1:1 indicating three nonequivalent PF$_3$ groups. It was not possible to observe fine structure; however, approximate values of the chemical shifts and $^1J_{PF}$ coupling constants for the three resonances are given in Table IV.

Analogous behavior is observed in the spectra of the triphosphines of *trans*- and *cis*-1,3-pentadiene. In the case of the 2,4-dimethyl-1,3-pentadiene triphosphine, at the lowest temperature at which the spectrum could be studied, the lines were still too broad to determine the chemical shifts or coupling constants very accurately. However, three nonequivalent PF$_3$ groups could definitely be observed.

Table V. Chemical Shifts (ppm) and Coupling Constants (Hz) Obtained for the Time-Averaged Spectra of Several (methyldiene)Fe$(PF_3)_2$(CO) Complexes at +27° [a]

Diene	$\langle\delta_1\rangle$	$\langle\delta_2\rangle$	$\langle{}^1J_{PF}\rangle_1$	$\langle{}^1J_{PF}\rangle_2$	$\langle{}^3J_{PF'}\rangle_1$	$\langle{}^3J_{PF'}\rangle_2$
	74.310	73.763	1299.3	1308.5	9.9	10.8
	73.989	73.221	1301.5	1311.7	9.9	11.0
	74.196	73.118	1295.0	1313.5	10.9	13.0
	72.547	70.711	1297.0	1320.8	9.1	12.0

[a] Spectra were measured in a solution of isopentane, $CHFCl_2$, and $CFCl_3$. Chemical shifts are relative to the high-field peak of the $CHFCl_2$ doublet.

Although the $^1J_{PF}$ values of the limiting spectra are only approximate, an average of all three values at low temperature agrees fairly well with the time-averaged values $\langle{}^1J_{PF}\rangle$ at +27°. The change in spectral appearance with temperature and the manner of the averaging of the resonances suggest an intramolecular exchange of the PF_3 groups analogous to that existing in the other, previously studied triphosphine complexes.

The Diphosphines. In the asymmetric diene diphosphines, all possible isomers (Figure 1D) should be distinguishable by nmr. Each PF_3 group in each isomer (a total of six possible fluorine resonances) should appear as a double doublet pattern due to $^1J_{PF}$ and $^3J_{PF'}$ coupling.

The room-temperature spectrum of (isoprene)Fe$(PF_3)_2$(CO) shows two double doublets in a 1:1 ratio, indicative of two nonequivalent PF_3 groups. The chemical shifts and coupling constants are given in Table V. A high-temperature study of the spectrum from 27 to 90° (toluene solution with α-trifluorotoluene as a reference and lock) did not reveal any significant changes in the pattern. A plot of δ *vs.* T is linear over this range.

The results of a low-temperature study of this spectrum are shown in Figure 4. (Only the low-field half of the total spectrum is shown.) At −3° the downfield pair of doublets begins to broaden, followed by broadening of the upfield pair at −23°. By −73° both resonances had completely collapsed, and at −93° new structure begins to appear. The limiting spectrum consists of four pair of doublets. The chemical shifts and coupling constants of these resonances at −103° are shown in Figure 3.

Resonances 1 and 2 (Figure 4) overlap at −103° but are clearly distinguishable at −123°. Resonances 1 and 4 are of equal intensity as are resonances 2 and 3. The peaks of equal intensity must represent PF_3 groups in the same isomer. Since only four types of PF_3 groups are observed, only two of the three possible isomers must be present in detectable amounts at low temperatures.

The species present are assigned to isomers 1 and 2 (Figure 1D) on the following bases. (1) The preference of PF_3 for the apical site, observed in the monophosphine, is expected to be present in the diphosphine as well. (2) Since local C_s symmetry is preserved in the $Fe(CO)_3$ group in isopreneiron tricarbonyl,[1] isomers 1 and 2 in the diphosphine will probably be infrared indistinguishable while isomer 3 should be different. Infrared distinguishes the presence of only one diphosphine isomer. (3) The two $^1J_{PF}$ values in isomer 3 should be fairly similar since both PF_3 groups occupy basal sites. However, $^1J_{PF}$ for the two downfield peaks compare well with 1293.0 Hz found for the apical PF_3 group in (2,3-dimethylbutadiene)Fe$(PF_3)_2$(CO), while the two upfield peaks have $^1J_{PF}$ values which compare well with 1311.0 Hz found for basal PF_3 groups in the same compound. Therefore, δ_1 and δ_4 must correspond to either isomer 1 or 2 with δ_1 assigned to PF_3 in the apical site and δ_4 assigned to PF_3 in the basal site. Likewise, δ_2 and δ_3 must correspond to the other diphosphine isomer with one PF_3 in the apical site (δ_2) and one PF_3 in the basal site (δ_3).

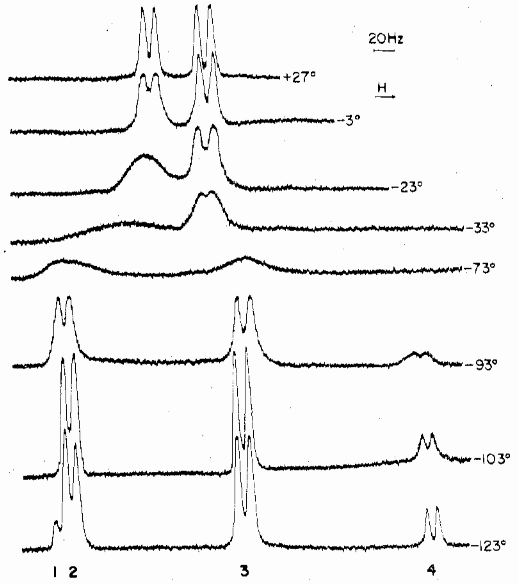


Figure 4. Representative tracing of the low-field half of the ^{19}F nmr spectra of (isoprene)Fe$(PF_3)_2$CO from +27 to −123°. Slight spectral shifts with temperature are not shown.

Careful determination of the equilibrium constant for the two isoprene diphosphine isomers according to the equation

$$K_{eq} = [\text{major species}]/[\text{minor species}] \qquad (2)$$

over the range −103 to −123° shows that the equilibrium constant increases as the temperature is lowered. For the conversion of the minor isomer to the major isomer, $\Delta G = -474 \pm 21$ and $\Delta H = -356 \pm 157$ cal/mol over the temperature range studied. The free energy was calculated from the equation $\Delta G = -RT \ln K_{eq}$ and the enthalpy was determined from the slope of the line produced from a plot of ($\ln K_{eq}$) *vs.* $(1/T)$.[8] Relative peak areas were determined by cutting and weighing. Each value of K_{eq} was calculated from an average of at least four measurements. The negative value of ΔH indicates that the major isomer is the more stable.

A comparison of chemical shift data at −103° (Figure 3) shows that the two apical PF_3 groups in the isoprene diphosphine isomers have resonances that fall about halfway between the apical PF_3 resonance in the butadiene diphosphine and the apical PF_3 resonance in the 2,3-dimethylbutadiene diphosphine. The basal PF_3 in the butadiene diphosphine has a shift value which corresponds very closely to a resonance assigned to the basal PF_3 in the most stable isoprene diphosphine isomer. However, the basal PF_3 in the second isoprene isomer has a shift which corresponds fairly well with the resonance assigned to the basal PF_3 in (2,3-dimethylbutadiene)$Fe(PF_3)_2(CO)$. On this basis, it seems reasonable to assign the isoprene diphosphine in major abundance to isomer 1 (basal PF_3 trans to the methyl group), with the isoprene diphosphine in minor abundance being assigned to isomer 2 (basal PF_3 cis to the methyl group). The relative stabilities of all three isomers appear to be $1 > 2 \gg 3$.

The room-temperature ^{19}F spectrum of (isoprene)$Fe(PF_3)_2(CO)$ shows two nonequivalent PF_3 groups. Since line-broadening at lower temperatures indicates that the pattern at +27° is definitely exchange-averaged, then PF_3 exchange in this complex must occur in such a way that the phosphine ligands never become completely equivalent.

Extrapolation of the straight-line equation obtained from a plot of ($\ln K_{eq}$) *vs.* ($1/T$) gives an equilibrium constant of $K_{eq} \approx 2.62$ with mole fractions $x(\text{major}) = 0.724$ and $x(\text{minor}) = 0.276$ at +27°. Assuming that the $^1J_{PF}$ values of the limiting spectrum do not change drastically between −103 and +27° and only two isomers are present, then averaging the coupling constants of δ_1 and δ_3 predicts a $\langle {}^1J_{PF} \rangle$ of 1307.9 Hz (1308.5 Hz observed) while averaging the coupling constants of δ_2 and δ_4 predicts a $\langle {}^1J_{PF} \rangle$ of 1298.3 Hz (1299.3 Hz observed). This suggests that the exchange mechanism averages the apical PF_3 of the major isomer with the basal PF_3 of the minor isomer, and likewise, the basal PF_3 of the major isomer is averaged with the apical PF_3 of the minor isomer. No other way of averaging the PF_3 groups gives as good a prediction of the $\langle {}^1J_{PF} \rangle$ constants at +27° and also produces time-averaged resonances of equal intensity. Early broadening of the downfield pair of time-averaged doublets (Figure 4) is now understandable since the downfield pair of doublets results from two resonances with a larger difference in chemical shifts (about 338 Hz) than the upfield pair of doublets (chemical shift difference of about 158 Hz).[9]

The room-temperature spectrum of (*cis*-1,3-pentadiene)$Fe(PF_3)_2(CO)$ also shows two pairs of doublets in a 1:1 ratio. Chemical shifts and coupling constants are given in Table V. As the temperature is lowered, both pairs of doublets broaden (−13°), completely collapse (−53°), and by −103° have sharpened into a limiting pattern of four pair of doublets of unequal intensity. The chemical shifts and coupling constants at −103° are $\delta_1 = 75.480$ ppm with $({}^1J_{PF})_1 = 1291.7$ and $({}^3J_{PF})_1 = 10.5$ Hz, $\delta_2 = 75.327$ ppm with $({}^1J_{PF})_2 = 1291$ and $({}^3J_{PF})_2 = 11$–12 Hz, $\delta_3 = 72.420$ ppm with $({}^1J_{PF})_3 = 1323.1$ and $({}^3J_{PF})_3 = 12.0$ Hz, and $\delta_4 = 72.185$ ppm with $({}^1J_{PF})_4 = 1323$ and $({}^3J_{PF})_4 = 10$ Hz.

On the basis of coupling constants and relative intensities, δ_1 and δ_3 represent either isomer 1 or 2 (Figure 1D) with δ_1 assigned to PF_3 in the apical site and δ_3 assigned to PF_3 in the basal site. The δ_2 and δ_4 resonances correspond to the other diphosphine isomer with one PF_3 in the apical site (δ_2) and one PF_3 in the basal site (δ_4).

Further assignment of the major and minor species to specific isomers cannot be made from chemical shifts because the *cis,cis*-2,4-hexadiene system was not available for study. Also the chemical shifts for the basal PF_3 groups are too similar for an unequivocal assignment by this method.

Evaluation of the equilibrium constant from eq 2 in the same manner used for the isoprene diphosphine yielded $\Delta G = -304 \pm 38$ and $\Delta H = -332 \pm 166$ cal/mol for the conversion of the minor isomer to the major isomer over the temperature range −93 to −123°. A value of $K_{eq} = 1.59$ with mole fractions $x(\text{major}) = 0.61$ and $x(\text{minor}) = 0.39$ was estimated at +27°. Averaging the apical PF_3 in one isomer with the basal PF_3 in the second isomer predicts $\langle {}^1J_{PF} \rangle$ values of 1303.9 Hz (δ_1 and δ_4) and 1310.6 Hz (δ_2 and δ_3). The observed values are 1301.5 and 1311.7 Hz at +27°. No other way of averaging the PF_3 groups gives as good a set of predictions and also produces time-averaged resonances of equal intensity. Broadening of the two averaged sets of doublets occurs at essentially the same temperature because δ_2 and δ_3 have a difference in chemical shifts of about 246 Hz, and the spread for δ_1 and δ_4 is nearly the same (about 279 Hz).

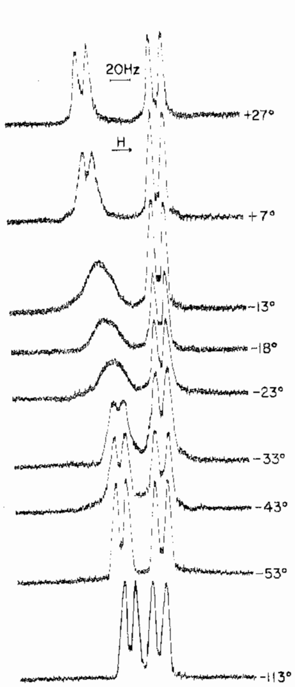


Figure 5. Representative tracings of the high-field half of the ^{19}F nmr spectra of (*trans*-1,3-pentadiene)$Fe(PF_3)_2CO$ from +27 to −113°. Slight spectral shifts with temperature are not shown.

The room-temperature spectrum of (*trans*-1,3-pentadiene)$Fe(PF_3)_2(CO)$ shows two pairs of doublets in a 1:1 ratio (Table V). A high-temperature study revealed no significant change in the spectrum. The results of the low-temperature study are shown in Figure 5.

At +7° the downfield pair of doublets begins to broaden and continues to broaden without showing total collapse until −38° when the pattern sharpens up again. Throughout this entire temperature range, the upfield pair of doublets remains almost unaffected. Some slight broadening may occur around −33°, but the doublet fine structure is never obscured. By −53° the limiting spectrum reveals only two pairs of doublets. The nmr parameters at −103° are shown in Figure 3.

A comparison of the chemical shifts and coupling constants of this spectrum at −103° with those of the butadiene and *trans,trans*-2,4-hexadiene diphosphines (Figure 3) suggests that the *trans*-1,3-pentadiene resonances are more similar to the butadiene than to the *trans,trans*-2,4-hexadiene resonances. On this basis the most stable diphosphine species is assigned to isomer 1 (Figure 1D) with the basal PF_3 group trans to the methyl. Since isomer 1 appears to exist to the exclusion of the other two isomers at −103°, preference for isomer 1 over isomer 2 is greater in the *trans*-1,3-pentadiene diphosphine than in the isoprene or *cis*-1,3-pentadiene diphosphines.

The changes in the spectrum of the *trans*-1,3-pentadiene diphosphine between +27 and −53° can be interpreted as resulting from the loss of a second isomer at temperatures too high for the exchange process to cause a total collapse of the time-averaged spectrum. A plot of δ *vs.* T for the upfield pair of doublets (which do not broaden significantly as the temperature is lowered) shows a break in the curve at about −28°, approximately the same temperature at which the downfield signal begins to sharpen up again. Because of the preference of PF_3 for the apical site in the monophosphine, it seems reasonable to assume that isomer 2 is most likely the species which is lost between +27 and −28°, and the relative stabilities of all three diphosphine isomers are $1 > 2 \gg 3$.

If the room-temperature ^{19}F spectrum of (*trans*-1,3-pentadiene)Fe$(PF_3)_2$(CO) is the result of exchange averaging between isomers 1 and 2, then the exchange of PF_3 must occur in such a way that the PF_3 groups never become chemically or magnetically equivalent. In the two previously studied asymmetric diene diphosphines, the apical PF_3 in one isomer was found to be averaged with the basal PF_3 in another isomer. A similar assumption leads to a self-consistent estimation of the relative populations of isomers 1 and 2 at room temperature from the equation

$$\langle {}^1J_{PF}\rangle = x_1({}^1J_{PF})_1 + (1 - x_1)({}^1J_{PF})_2 \qquad (3)$$

Assuming that the coupling constants $^1J_{PF}$ in the limiting spectrum do not change drastically over the temperature range −103 to +27° and that the values for the apical and basal PF_3 groups for isomer 2 are the same as the corresponding constants observed for isomer 1, then the time-averaged values $\langle {}^1J_{PF}\rangle$ of 1313.5 and 1295.0 Hz estimate the mole fraction x_1 for isomer 1 as 0.803 and 0.853, respectively.

The relative rates of broadening of the time-averaged resonances also support this method of averaging. Examining the positions of the three nonequivalent resonances in the triphosphine (Table IV) shows that two of the averaging species in the diphosphine could have a difference in chemical shifts of as much as 200–300 Hz, while, if the apical PF_3 resonances occur close together as they do in the isoprene and *cis*-1,3-pentadiene diphosphines, then the other two averaging species could have a difference in chemical shifts of as little as 20–30 Hz. This would cause a great difference in the temperature at which line broadening of the averaged resonances would be observed. Apparently broadening in the averaged downfield peak can be observed at temperatures where both isomers 1 and 2 exist. Isomer 2 is depopulated before broadening in the averaged upfield resonance becomes noticeable.

The room-temperature spectrum of (2,4-dimethyl-1,3-pentadiene)Fe$(PF_3)_2$(CO) shows two pairs of doublets in a 1:1 ratio. The behavior of the spectrum as the temperature is lowered closely resembles that of the *trans*-1,3-pentadiene diphosphine except that both averaged resonances show line broadening. At +7° the downfield pair of doublets begins to broaden, followed at −13° by the upfield pair. At −33° both resonances begin to sharpen up again without ever showing total collapse. The limiting pattern appears to be only two pair of doublets in a 1:1 ratio. The chemical shifts and coupling constants at −103° are $\delta_1 = 72.247$ ppm with $({}^1J_{PF})_1 = 1294.5$ and $({}^3J_{PF})_1 = 8.9$ Hz and $\delta_2 = 71.122$ ppm with $({}^1J_{PF})_2 = 1320.8$ and $({}^3J_{PF})_2 = 12.2$ Hz. On the basis of $^1J_{PF}$ coupling constants, δ_1 is assigned to a PF_3 in the apical site and δ_2 is assigned to a PF_3 in a basal site.

Only a tentative assignment of the −103° resonances to a specific isomer can be made. The basal PF_3 can be either cis or trans to the methyl on the central diene carbon. The chemical shift of the basal PF_3 in the 2,4-dimethyl-1,3-pentadiene diphosphine (71.122 ppm) agrees well with the chemical shift for the basal PF_3 cis to the methyl group in the minor isomer of the isoprene diphosphine (71.524 ppm). On this basis the preferred isomer may be the one with the basal PF_3 cis to the single methyl on the central diene carbon but trans to the two methyls on the terminal diene carbon.

The changes in the ^{19}F nmr spectrum from +27 to −113° can be explained if one or more of the three possible isomers is completely depopulated as the temperature is reduced.

The appearance of the ^{19}F nmr spectrum at room temperature suggests that the PF_3 groups are averaged in such a way that they never become equivalent. Using eq 3 and making the same assumptions as for the *trans*-1,3-pentadiene diphosphine, both of the averaged $\langle {}^1J_{PF}\rangle$ constants suggest that the preferred isomer comprises about 91% of the diphosphine population at +27°.

Discussion

Preferred Isomers. For a square-based pyramidal structure there are two possible geometric isomers in the mono- and diphosphine complexes of symmetric dienes. In the mono- and diphosphine complexes of the asymmetric dienes, three geometric isomers are possible because the basal sites are no longer equivalent.

The 2,3-dimethylbutadiene carbonyl– and *trans,trans*-2,4-hexadiene carbonyl–trifluorophosphine complexes resemble the butadiene system. Phosphorus trifluoride favors the apical site and only isomers based on this preference can be unequivocally detected by ^{19}F nmr. Intramolecular exchange of PF_3 groups is evident in the di- and triphosphines which were studied. The presence of methyl groups on the terminal and central carbons of the diene has no significant effect on the exchange mechanism. This mechanism is, therefore, assumed to be identical with that existing in the butadiene carbonyl–trifluorophosphine complexes.

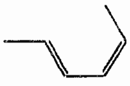
In addition to an apical site preference, PF_3 also exhibits a secondary preference for a basal position trans to methyl substituents on the diene ligand. This preference was observed in the diphosphines of isoprene and *trans*-1,3-pentadiene where the isomer in most abundance was identified by comparing the absolute ^{19}F chemical shifts of the diphosphine in question with the shifts observed in the totally unsubstituted butadiene diphosphine and the symmetrically substituted dimethyldiene diphosphine (2,3-dimethylbutadiene in the case of isoprene and *trans,trans*-2,4-hexadiene in the case of *trans*-1,3-pentadiene). These comparisons should be valid since the temperature and the solvent–reference system for each complex were the same.

For the 2,4-dimethyl-1,3-pentadiene diphosphine, chemical shift data seem to support an assignment of the most abundant isomer to that species in which the basal PF_3 is cis to the methyl on the central carbon and trans to the two methyls on the terminal carbon. A secondary site preference is also observed in the *cis*-1,3-pentadiene diphosphine, but an assignment of the preferred species based on ^{19}F chemical shifts is not possible.

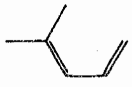
The relative values of the stretching force constants K_1 and K_2 in the tricarbonyl[1] appear to be a fairly reliable guide in predicting the most stable isomers of the trifluorophosphine derivatives. Except for the *cis*-1,3-pentadiene monophosphine, unless $K_1 \approx K_2$, only the isomer or isomers based on a preference of PF_3 for the apical site could be unequivocally detected.

Splitting in the lowest frequency ^{13}CO peak of the tricarbonyl also seems to be a fairly reliable guide in predicting the degree of secondary isomer preference in the asymmetric diene diphosphines. Splitting of this peak indicates loss of C_s symmetry, *i.e.*, that the two basal carbonyls are no longer equivalent. Both *cis*-1,3-pentadiene- and isopreneiron tricarbonyl retain local C_s symmetry.[1] Both isomers 1 and 2 (Figure 1D) are present in the diphosphines of these complexes. Local C_s symmetry is not retained for *trans*-1,3-pentadiene- and 2,4-dimethyl-1,3-pentadieneiron tricarbonyl.[1] At low temperatures in the diphosphine complexes of these dienes only one isomer exists to the exclusion of all the other possible species.

If the degree of secondary isomer preference can be predicted by the retention or loss of C_s symmetry in the infrared spectrum of any of these dieneiron tricarbonyls, it can be used to make a tentative identification of the most abundant isomer in (*cis*-1,3-pentadiene)Fe$(PF_3)_2$(CO). The infrared spectra of *cis,trans*-2,4-hexadieneiron tricarbonyl (**a**) and of 4-methyl-1,3-pentadieneiron tricarbonyl (**b**) were examined in part A of this study. The lowest frequency ^{13}CO band for



a



b

complex **b** is split by about 5.0 cm^{-1}, while that for complex **a** is only slightly broadened. If the relationship between loss of C_s symmetry and the degree of PF_3 preference for basal sites is valid for these complexes, then the diphosphine of **b** should show a greater preference for one single isomer than the diphosphine of **a**. This will occur if the effect of the two methyl groups on the diphosphine isomer preference is such as to reinforce each other in **b** but to oppose each other in **a**. Therefore, in both the *cis-* and *trans*-1,3-pentadiene diphosphines the isomer in major abundance should be the species with a basal PF_3 trans to the methyl group on the terminal diene carbon.

Electronic Effects. Isomer preferences in these complexes can be due to electronic and/or steric differences between the CO and PF_3 ligands. The preference of PF_3 for the apical site has been attributed primarily to electronic factors[1-3] with PF_3, a weaker π-bonding ligand than CO, occupying the coordination site with the poorer π-bonding potential.

Some idea of the electronic effects of methyl substitution on the two basal sites in the $Fe(PF_3)_x(CO)_{3-x}$ group can be obtained from the inductive model[10,11] which has already been fairly successful in showing the relationship between the carbonyl force constants and the position and number of methyl substituents on the diene ligand.[1] Calculation of the electron density function ψ^2 allows an examination of the effect of the methyl group on the entire π-electron network of the diene.

The π-electron network of the diene is often graphically symbolized in terms of its molecular orbitals, ψ_i (i = 1–4). In the HMO method, the four molecular orbitals for butadiene consist of linear combinations of the carbon 2p orbitals[10]

$$\psi_i = \sum_{r=1}^{4} C_r\varphi_r \qquad (4)$$

The Slater orbital for a carbon 2p electron[12] was chosen for φ_r. In accordance with the X-ray structure of butadieneiron tricarbonyl,[13] the distance between successive carbon atoms within the π network was chosen to be 1.45 Å. It was assumed that this distance remained constant throughout the entire series of compounds. To facilitate the calculation, it was further assumed that the carbon atoms lay on a straight line.

After calculating[10] the coefficient C_r, a program was written in Single User Basic[14] to determine the maximum value of ψ_i^2 at any point along the bond axis. The input parameters consisted of the coefficients C_r for any particular molecular orbital ψ_i. The program determined a ψ_i^2(maximum) in 0.1-Å steps along the bond axis and printed out the numeric results or a plot of ψ_i^2(maximum). Some representative plots of ψ_3^2(maximum) for butadiene and several of the methyldienes are shown in Figure 6.

A purely qualitative comparison of these plots suggests that a methyl on a central carbon of the diene appears to affect the electron density somewhat less drastically than substitution on the 1- or 4-carbon positions. The compounds with the most seriously affected electron densities are 1,3-pentadiene, 4-methyl-1,3-pentadiene, and 2,4-dimethyl-1,3-pentadiene. It is interesting that these are precisely the diene complexes which showed loss of C_s symmetry in the infrared spectrum of the tricarbonyl. The sole exception is the *cis*-1,3-pentadiene complex. Since this model does not distinguish between cis and trans isomers, it is possible that the two configurations affect the electron densities in slightly different ways.

Any distortion of the π-electron density relative to butadiene could have the effect of making the two basal coordination sites less equivalent. A more serious distortion of the π-electron density, represented by ψ_3^2(maximum), is indicated for those dienes whose diphosphine complexes show the greatest degree of secondary isomer preference. Again, the only exception involves (*cis*-1,3-pentadiene)$Fe(PF_3)_2(CO)$. If PF_3 is a weaker π-bonding ligand than CO and isomer populations in the diphosphine complexes are determined solely by electronic effects, then the basal site trans to the methyl on the diene ligand must have the poorer π-bonding potential.

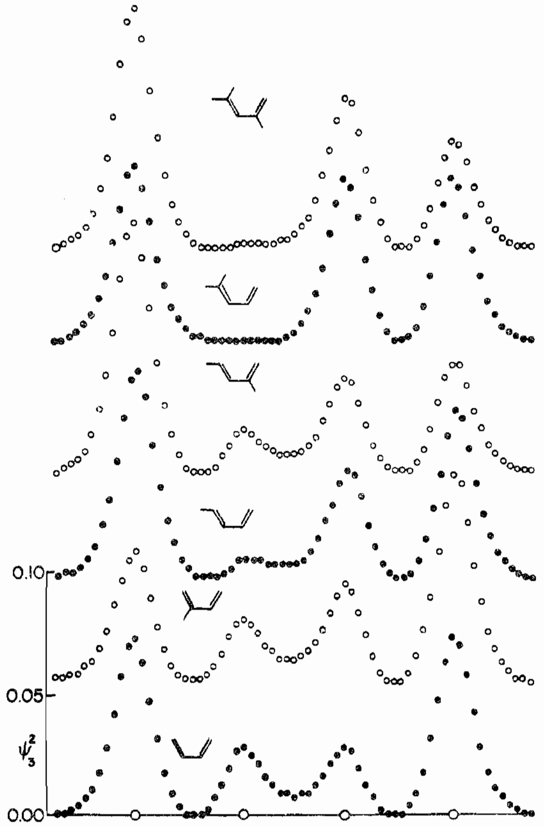


Figure 6. Electron density function ψ_3^2(maximum) for butadiene and several methylbutadienes. The vertical scale, shown only once, is the same for all plots.

Since methyl groups are electron releasing relative to hydrogen, it is more usual to consider that a coordination site trans to a methyl group will be the site with better π-bonding potential.[15] However, this argument greatly simplifies the effect of the functional group on the nature of the π bond.

Steric Effects. Steric interactions between methyl groups and CO ligands were found to be negligible in several methylbenzenechromium tricarbonyls in which a carbonyl was superimposed directly over the methyl group.[15] However, Clinton and Lillya[16] have been able to account successfully for the preferred conformations present in several dienoliron tricarbonyl compounds on the basis of steric interactions between the trans or outer substituents on the terminal carbons of the diene and the carbonyl occupying a basal position which is cis to the substituent on the diene.

All of the diene substituents[16] were considerably larger than a methyl group. However, a scale model[16] of these complexes, using the Mills and Robinson square-based pyramidal geometry[13] and bond lengths and angles typical of several dieneiron tricarbonyl complexes, suggests that, even for a methyl group, the interatomic distance between a trans methyl substituent and the basal CO cis to the methyl may be less than the sum of the van der Waals radii of the two groups.[16]

X-Ray data on trifluorophosphine derivatives of butadieneiron tricarbonyl are lacking. However, a study of nickel complexes containing a variety of phosphorus ligands suggests that the overall steric effect of a PF_3 group should be slightly greater than that of a CO ligand.[17] Thus, in (*trans*-1,3-pentadiene)Fe(PF_3)$_2$(CO), the PF_3 group may be preferentially located in the basal site trans to the methyl on the diene because less severe crowding from the trans methyl substituent occurs if the somewhat smaller carbonyl occupies the cis basal position.

The effects of substituents on the central carbons of the diene were not considered.[16] However, our models suggest that interaction of such groups with either basal carbonyl must be much less serious than the interaction involving the trans methyl on the terminal diene carbons. This is in agreement with the relative degree of secondary isomer preference observed in the diphosphine derivatives of these complexes with the order of preference being *trans*-1,3-pentadiene > isoprene ≈ *cis*-1,3-pentadiene.

The effect of the cis or inner methyl substituents in the complex is less clear. Our models indicate that an inner or cis methyl should be the least likely to interfere with any of the basal PF_3 groups, yet the degree of isomer preference in (*cis*-1,3-pentadiene)Fe(PF_3)$_2$(CO) and (isoprene)Fe(PF_3)$_2$(CO) is essentially the same. In the case of the *cis*-1,3-pentadiene system, this isomer preference must either be due to electronic effects or the result of a distortion in the molecule.

Cis substituents which are ring residues have been shown to be displaced away from the diene plane.[18] Other complexes of this type showing similar distortions have been discussed in the literature.[19] Our models also show that severe interaction between the cis methyl and the cis hydrogen on the two terminal diene carbons must occur if the diene remains planar. Thus, it seems likely that the cis methyl will distort the diene ligand in such a way that the methyl group will be twisted out of the diene plane, away from the other terminal carbon and probably also away from the iron atom and the apical carbonyl. Such distortion has been used to explain the greater stability of *trans*-1,3-pentadieneiron tricarbonyl as compared to *cis*-1,3-pentadieneiron tricarbonyl.[20]

Nonplanarity of the diene can be achieved by twisting either around the C_1–C_2 and C_4–C_3 bonds or around the C_2–C_3 bond. A comparison of J_{HH}(geminal) for (*cis*-1,3-pentadiene)Fe(CO)$_3$, (*trans*-1,3-pentadiene)Fe(CO)$_3$, and (isoprene)Fe(CO)$_3$ (2.9, 2.4, and 2.4 Hz, respectively), suggests only a very slight increase in the sp^3 character of the terminal diene carbons of *cis*-1,3-pentadiene.[21] Thus twisting about the C_1–C_2 and C_4–C_3 bonds is probably not very great.

Cais and Maoz[22] have suggested that considerable twisting about the C_2–C_3 bond can occur without an excessive loss of conjugation. This kind of distortion would probably not affect the geminal coupling constants very much as the double bonds of the diene would become more localized in character, but the hybridization on the carbons would remain essentially sp^2.

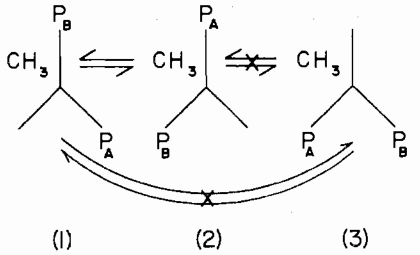
Twisting about the C_2–C_3 bond would probably occur so as to move the cis methyl away from the iron atom. This would force the hydrogen on the next diene carbon (a central carbon) up toward the ligand occupying the basal coordination site cis to the methyl substituent. The larger PF_3 group should then prefer the basal site opposite to the projecting hydrogen, *i.e.*, trans to the methyl. Tentative evidence in support of this species as the most stable isomer of (*cis*-1,3-pentadiene)Fe(PF_3)$_2$(CO) has been presented.

One final case in which steric strain must be present is found in the *cis*-1,3-pentadiene monophosphine. For every complex but this one, unless the stretching force constant K_1 is essentially equal to K_2 in the tricarbonyl, the only monophosphine isomer which could be unequivocally detected was the one with PF_3 in the apical site. The difference between K_1 and K_2 for (*cis*-1,3-pentadiene)Fe(CO)$_3$ is about +0.09 mdyn/Å.[1] Although only one monophosphine isomer could be found at low temperatures (identified as having PF_3 in the apical site), exchange broadening was definitely observed in the ^{19}F and ^{1}H nmr spectra. Changes in the $J_{\text{P-CH}_3}$ and $^1J_{\text{PF}}$ coupling constants suggest that a basal PF_3 group is involved. Destabilization of the isomer with PF_3 in the apical site as compared to PF_3 in a basal site is most likely the result of steric interaction between the cis methyl group (or hydrogen) and the apical PF_3.

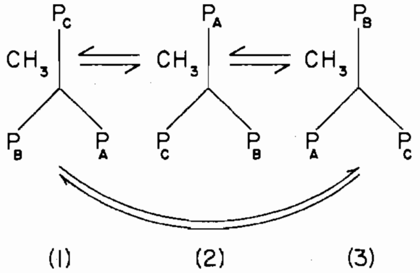
Intramolecular Exchange. Exchange of phosphine groups in the di- and triphosphine complexes of symmetric dienes and in the triphosphines of the asymmetric dienes makes all PF_3 groups appear equivalent at high temperatures. In the diphosphines of asymmetric dienes, the PF_3 groups never become equivalent. An examination of the coupling constants in the limiting and time-averaged spectra suggests that only isomers 1 and 2 (Figure 1D) are present in detectable amounts and that the apical PF_3 in isomer 1 is averaged with the basal PF_3 in isomer 2, while the apical PF_3 in isomer 2 is averaged with the basal PF_3 in isomer 1.

Several suggestions have been made to explain the motion that is responsible for the nmr equivalence of PF_3 groups in the ^{19}F spectra of the butadiene di- and triphosphine complexes.[2] Simple position exchange in which each PF_3 can occupy any coordination site is now definitely excluded as a possibility; otherwise the time-averaged PF_3 ligands in the asymmetric diene diphosphines would also appear equivalent. The movement of the PF_3 and CO groups must be concerted with the relative positions of the ligands remaining the same.

If the diphosphine PF_3 groups are labeled P_A and P_B, then the results of the exchange process can be illustrated as below. (The concentration of isomer 3 is assumed to be zero, although this is not required to produce nonequivalent PF_3 groups in the time-averaged patterns.)



Complete equivalency of the two PF_3 groups will occur only when the two basal sites are equivalent (as in the symmetric diene complexes). The process will always produce complete equivalency for PF_3 groups in triphosphine complexes because all instantaneous structures produced by the exchanging ligands are equivalent.



Nonequivalency of time-averaged nuclei has been observed in certain substituted ethanes where rotation occurs around the C–C axis because the relative positions of substituents on each carbon atom remain fixed.[23] Thus, the exchange motion in these phosphine complexes has the overall effect of a rotation of the CO and PF_3 groups about the iron atom. In the diphosphines, the effect becomes a rocking between isomers 1 and 2. The high activation energy for conversion between species 1 and 3 and between 2 and 3 can be attributed to a large positive ΔH for isomer 3.

If the interconversion of ligands in these complexes is a true rotation, some bending motion must also be involved. There is also the possibility that use is made of the empty site beneath the basal plane. For Berry pseudorotation to occur, the required trigonal-bipyramidal intermediate would be severely distorted due to the small bite size of the 1,3-diene ligand.[13] However, fluxional behavior has been observed in the ^{13}C nmr spectrum of (butadiene)Fe(CO)$_3$.[24] Since nonconjugated 1,4- and 1,5-dienes, which span axial-equatorial sites of a trigonal bipyramid more easily, show a dramatic increase in fluxionality,[24] pseudorotation may be the mechanism involved in the rearrangement observed for these dieneiron carbonyl-trifluorophosphine systems.

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Registry No. (2,3-Dimethyl-1,3-butadiene)Fe(PF$_3$)(CO)$_2$, 52950-83-1; (*trans,trans*-2,4-hexadiene)Fe(PF$_3$)(CO)$_2$, 52950-82-0; (isoprene)Fe(PF$_3$)(CO)$_2$, 52950-80-8; (*trans*-1,3-pentadiene)Fe(PF$_3$)(CO)$_2$, 52950-81-9; (*cis*-1,3-pentadiene)Fe(PF$_3$)(CO)$_2$, 52993-18-7; (2,4-dimethyl-1,3-pentadiene)Fe(PF$_3$)(CO)$_2$, 52950-84-2; (1,3-butadiene)Fe(PF$_3$)$_3$, 52993-22-3; (2,3-dimethyl-1,3-butadiene)Fe(PF$_3$)$_3$, 52993-23-4; (*cis*-1,3-pentadiene)Fe(PF$_3$)$_3$, 52993-24-5; (*trans*-1,3-pentadiene)Fe(PF$_3$)$_3$, 52993-25-6; (2,4-dimethyl-1,3-pentadiene)Fe(PF$_3$)$_3$, 52993-26-7; (isoprene)Fe(PF$_3$)$_3$, 52993-27-8; (1,3-butadiene)Fe(PF$_3$)$_2$(CO), 52993-20-1; (*trans,trans*-2,4-hexadiene)Fe(PF$_3$)$_2$(CO), 52950-87-5; (2,3-dimethyl-1,3-butadiene)Fe(PF$_3$)$_2$(CO), 52950-88-6; *trans*-(isoprene)Fe(PF$_3$)$_2$(CO), 52993-21-2; *cis*-(isoprene)Fe(PF$_3$)$_2$(CO), 52950-90-0; (*cis*-1,3-pentadiene)Fe(PF$_3$)$_2$(CO), 52993-19-8; (*trans*-1,3-pentadiene)Fe(PF$_3$)$_2$(CO), 52950-86-4; (2,4-dimethyl-1,3-pentadiene)Fe(PF$_3$)$_2$(CO), 52950-89-7; 1,3-butadiene, 106-99-0; isoprene, 78-79-5; *trans*-1,3-pentadiene, 2004-70-8; 2-methyl-*trans*-1,3-pentadiene, 926-54-5; 4-methyl-1,3-pentadiene, 926-56-7; 2,4-dimethyl-1,3-pentadiene, 1000-86-8.

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Iron(II) and Cobalt(II) Complexes of Boc-(Gly-L-Cys-Gly)$_4$-NH$_2$ as Analogs for the Active Site of the Iron–Sulfur Protein Rubredoxin

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Iron(II) and cobalt(II) complexes of Boc-(Gly-L-Cys-Gly)$_4$-NH$_2$ have been synthesized in dimethyl sulfoxide. Evidence is presented that the iron complex is the first rubredoxin model incorporating a polypeptide backbone demonstrated to have a tetrahedral FeS$_4$ core.

Introduction

The iron–sulfur proteins[1] function in biological electron-transfer reactions.[2] The simplest class of these proteins is the rubredoxins[3] (red redox proteins). Rubredoxins isolated from anaerobes have mol wt *ca.* 6000. They contain a single iron atom but unlike other iron–sulfur proteins no *inorganic* sulfide. The polypeptide backbone has 50–60 amino acid residues, *four* of which are cysteines. Sequencing studies on a number of rubredoxins from anaerobes show that they all contain two well-separated -Cys-X-X-Cys- (X = amino acid) units.[4,5]

The X-ray structural studies by Jensen, *et al.*,[5] on the oxidized form of rubredoxin from *Clostridium pasteurianum* show that the iron atom is coordinated to only the *four* cysteinyl sulfurs with approximately tetrahedral geometry. A large number of physical studies have been performed on rubredoxins, in both oxidation states, which are generally in accord with their formulations as Fe^{II} and Fe^{III} complexes.[2,3]

Although its biological function is unknown, rubredoxin is, nevertheless, of interest to inorganic chemists for a variety of reasons: (i) the apoprotein is a tetradentate tetrathiolato ligand; (ii) it forms high-spin d^6 (Fe^{II}) and d^5 (Fe^{III}) complexes with an approximately tetrahedral FeS$_4$ core; in fact, oxidized rubredoxin is the only example of an iron(III) complex with this structural feature; (iii) rubredoxins are the only known compounds containing iron tetrahedrally coordinated to four sulfurs that undergo reversible iron(II)–iron(III) redox behavior[6] ($E_0{}' = -0.057$ V for *C. pasteurianum* rubredoxin[6]); (iv) the 1.5-Å X-ray data show that the Fe–S distance of