solved in water and, on standing for several weeks, a blue crystalline solid precipitates with the composition $Fe(cp)_2 \cdot 2HgCl_2$. The ir spectrum of this material shows a large splitting in the ~1400-cm^{-1} band (see Figure 3 and Table III) this splitting is larger than that observed for either the red or the blue $Fe(cp)_2 \cdot 7HgCl_2$ compound. Addition of aqueous NH_4PF_6 solution to aqueous solutions of either the blue 1:7 or blue 1:2 ferrocene–mercuric chloride compounds gives $[Fe(cp)_2]PF_6$. Thus in solution the interaction between ferrocene and mercury halide is not stable.

In summary, it seems that ruthenocene forms simple 1:1 adducts with mercuric chloride and bromide, whereas the interaction of ferrocene with mercuric halides is complicated. It is reasonable to formulate the red $Fe(cp)_2 \cdot 7HgCl_2$ compound as a 1:1 iron–mercury bonded adduct with a large excess of "lattice" $HgCl_2$; however, conclusive evidence to support this formulation has not been found. Futher work on substituted ferrocenes and other metallocenes is in progress.

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Tricarbonyl-1,2-bis(dimethylphosphinoethane)iron(0). Synthesis and Nuclear Magnetic Resonance Study of a Stereochemically Nonrigid Molecule

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The new compound $Fe[(CH_3)_2PCH_2CH_2P(CH_3)_2](CO)_3$ (I) has been synthesized from $Fe(CO)_5$ and $(CH_3)_2PCH_2CH_2P(CH_3)_2$ (II). Its infrared spectrum is consistent with a trigonal-bipyramidal structure with a phosphorus atom at an axial and equatorial site. The ^{13}C nmr spectrum of the carbonyl groups in I is consistent with this molecule having a nonrigid structure down to −80° on the nmr time scale due to rapid intramolecular exchange. The temperature dependence of the second-order ^1H nmr spectra of I and II between +90 and −50° have been interpreted in terms of solvent effects. The ^{13}C spectra of the methyl and methylene groups of both I and II form the X part of typical ABX spectra. The ^{31}P nmr spectra of I and II are both complex. Values of chemical shifts, ^{13}C coupling constants with phosphorus, and a P–P coupling constant found for I and II are reported.

During recent years considerable interest has been shown in the study of stereochemically nonrigid molecules.[2-6] One important class of potentially stereochemically nonrigid molecules is those which may be considered as derivatives of $Fe(CO)_5$. Carbon-13 nmr studies of iron pentacarbonyl are consistent with a stereochemically nonrigid structure at temperatures down to −63°.[7] More recently ^{13}C nmr studies on $Fe[P(C_2H_5)_n(C_6H_5)_{3-n}](CO)_4$ (n = 1–3) have indicated that these molecules are also stereochemically nonrigid on the nmr time scale and undergo intramolecular carbonyl exchange at room temperature.[8] Infrared studies on $Fe(PF_3)(CO)_4$ and $Fe(PF_3)_2(CO)_3$ and other members of the $Fe(PF_3)_{5-x}(CO)_x$ series show that each compound consists of more than one isomer and that they are stereochemically nonrigid.[9] The ^1H nmr spectrum of the related compound $Fe[P(N(CH_3)_2)_3]_2(CO)_3$ has been reported to be temperature dependent.[10] Its infrared spectrum indicated that it consisted of only the trans isomer and it was therefore postulated that the temperature dependence of its ^1H nmr spectrum could not be due to cis–trans isomerization. This implied the molecule might be stereochemically rigid. It was suggested that the temperature dependence might have been related to hindered internal rotation of the phosphorus substituents in the ligand.

The infrared spectrum of $Fe[P(C_6H_5)_3](CO)_4$ is consistent with a trigonal-bipyramidal molecule with the $P(C_6H_5)_3$ group in an axial position; similarly the infrared spectrum of $Fe[P(C_6H_5)_3]_2(CO)_3$ suggests that this molecule has a trigonal-bipyramidal configuration with the triphenylphosphine ligands occupying axial positions.[11] Infrared studies on $Fe[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2](CO)_3$ show three CO stretching bands.[12] This has been interpreted in terms of a trigonal-bipyramidal molecule with the phosphorus atoms occupying equatorial positions.[13]

The present study was undertaken in order to gain further information concerning the stereochemical behavior of substituted iron pentacarbonyl species. It

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[13] A trigonal-bipyramidal structure with one phosphorus at an axial position and one at an equatorial position would also be expected to give three bands in the ν_{CO} stretching region.[11]

was believed that the barrier to an intramolecular isomerization process might be increased if a bidentate ligand were used in a species such as $Fe(L{-}L)(CO)_3$ and, in order to simplify nmr studies, the ligand $(CH_3)_2PCH_2CH_2P(CH_3)_2$ was chosen in preference to $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$.

Experimental Section

All operations were carried out in dry nitrogen or *in vacuo* using standard high-vacuum techniques. Infrared spectra were recorded with a Perkin-Elmer 137B Infracord spectrophotometer and a Perkin-Elmer 521 double beam grating spectrophotometer using cells fitted with KBr windows. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Iron pentacarbonyl was obtained from Strem Chemicals, Inc. and 1,2-bis(dimethylphosphinoethane) was kindly donated by Dr. E. L. Muetterties, E. I. du Pont de Nemours and Company, Wilmington, Del.

Proton nmr spectra were recorded with a Varian HA 100D spectrometer using the HA mode at 100 MHz. The ^{13}C and ^{31}P spectra were obtained on a Varian XL-100-15 nmr spectrometer operating at 25.2 and 40.5 MHz, respectively. Approximately 10–20% by weight solutions in toluene-d_8 were employed for all spectra. The samples used for the ^1H spectra contained internal TMS as a standard. Phosphorus chemical shifts were measured with respect to external triphenylphosphine oxide.

The ^{13}C spectra were obtained in the Fourier transform mode of operation on the XL-100-15. The maximum errors in the measurement of the chemical shifts and coupling constants are 0.1 ppm and 0.4 Hz, respectively. All ^{13}C chemical shifts were measured with respect to the substituted carbon in toluene-d_8 and then converted to external TMS by using the conversion $\delta_{TMS} = \delta_{toluene} + 137.2$ ppm. The experimental details of a particular measurement are presented in the figure captions.

To prevent confusion in reproducing the spectra reported here, we present some definitions of certain experimental variables. Acquisition time (AT) is the time that the computer samples the free-induction decay; $1/AT$ is the maximum resolution for the experiment. Pulse delay (PD) is the time period between the end of acquisition and the beginning of the next pulse. The sampling frequency is twice the sweep width for the experiment. Pulse width (PW) is the time in microseconds that the pulse power amplifier is turned on.

Tricarbonyl-1,2-bis(dimethylphosphinoethane)iron(0), Fe[$(CH_3)_2PCH_2CH_2P(CH_3)_2$]$(CO)_3$.[12]—A solution of $(CH_3)_2PCH_2CH_2P(CH_3)_2$ (0.61 g, 0.40 mmol) in dry toluene (10 ml) was added dropwise with stirring to a solution of $C_8H_8Fe(CO)_3$[14] (0.98 g, 0.40 mmol) in dry toluene (20 ml). The reaction mixture was refluxed under nitrogen for 6 hr. The solvent was removed under vacuum and the dark gummy residue was chromatographed, using an alumina column and a 4:1 pentane–dichloromethane mixture. The solution thus obtained gave a yellow crystalline material (0.92 g, 80%) when the solvent was removed under vacuum. *Anal.* Calcd for $FeC_9H_{16}P_2O_3$ (mp, 54–55°): Fe, 19.25; C, 37.27; H, 5.56; P, 21.36. Found: Fe, 19.31; C, 37.01; H, 6.24; P, 21.05.

Results

Good yields of the new compound, tricarbonyl-1,2-bis(dimethylphosphinoethane)iron(0), $Fe[(CH_3)_2PCH_2CH_2P(CH_3)_2](CO)_3$, were obtained by the reaction of $C_8H_8Fe(CO)_3$ with $(CH_3)_2PCH_2CH_2P(CH_3)_2$. Its infrared spectrum showed the absorption maxima: (A) Nujol mull, ν_{CO} 1982 (s), 1911 (ms), 1895 (vs); other peaks, 1380 (s), 1285 (m), 1240 (w), 1125 (w), 1075 (w), 940 (w, br), 915 (w), 898 (m), 858 (m), 845 (s), 800 (w), 790 (w), 741 (s), 730 (s), 715 (s), 705 (s) cm^{-1}; (B) CH_2Cl_2 solution, ν_{CO} 1994 (s), 1925 (ms), 1910 (vs) cm^{-1}.

The ^1H nmr spectra of $(CH_3)_2PCH_2CH_2P(CH_3)_2$ at +80, +31, and −50° are given in Figure 1. The positions of the peaks (given in τ values for convenience) A, B, C, D, E, and F are, at 80°, τ 8.650, 8.690, 8.732, 9.120, 9.136, and 9.154; at 31°, τ 8.674, 8.710, 8.750, 9.120, 9.136, and 9.152; and at −50°, τ 8.760, 8.790, 8.824, 9.194, 9.208, and 9.222. Peaks A, B, C and D, E, F are assigned to the methylene amd methyl groups, respectively, on the basis of their relative intensities.

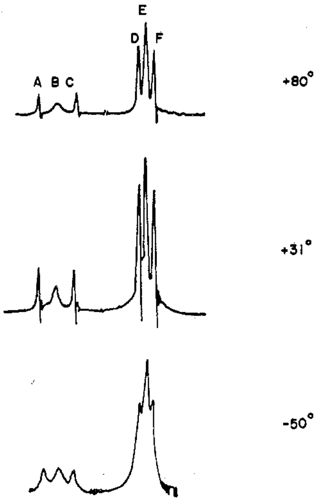

Figure 1.—^1H nmr spectra of $(CH_3)_2PCH_2CH_2P(CH_3)_2$ in toluene-d_8 at +80, +31, and −50°.

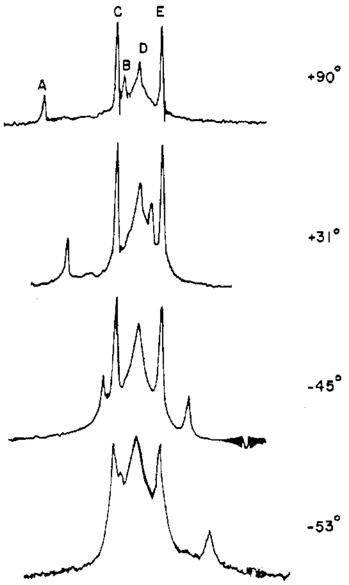

Figure 2.—^1H nmr spectra of $Fe[(CH_3)_2PCH_2CH_2P(CH_3)_2](CO)_3$ in toluene-d_8 at +90, +31, −45, and −53°.

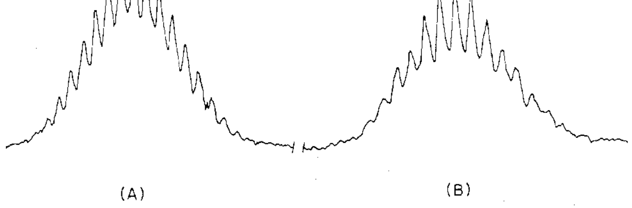

Figure 3.—^{31}P nmr spectra of (A) $(CH_3)_2PCH_2CH_2P(CH_3)_2$ and (B) $Fe[(CH_3)_2PCH_2CH_2P(CH_3)_2](CO)_3$ at 25° in toluene-d_8. Separations are in Hz.

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The ^1H nmr spectra of $Fe[(CH_3)_2PCH_2CH_2P(CH_3)_2](CO)_3$ at +90, +31, −45, and −53° are given in Figure 2. The positions of peaks (given in τ values for convenience) A, B, C, D, and E are, at 90°, τ 8.585, 8.752, 8.736, 8.781, 8.828; at 31°, τ 8.708, 8.882, 8.810, 8.788, and 8.906; at −45°, τ 8.898, 9.076, 8.924, 8.970, and 9.019; at −53°, τ 8.942, 9.136, 8.928, 8.976 and 9.026. Peaks A, B and C, D, E are assigned to the methylene and methyl groups, respectively, on the basis of their relative intensities.

The ^{31}P spectra of $(CH_3)_2PCH_2CH_2P(CH_3)_2$ and of $Fe[(CH_3)_2PCH_2CH_2P(CH_3)_2](CO)_3$ are given in Figure 3. Phosphorus chemical shifts of the free ligand and the complex are +75.2 and −42.9 ppm, respectively, with respect to external triphenylphosphine oxide. A plus sign in the chemical shift denotes higher shielding. In both cases this corresponds to the XX′ part of an $A_6A_6'B_2B_2'XX'$ spectrum. A summary of the pertinent spin-coupling constants and chemical shifts is presented in Table I.

TABLE I

^{13}C AND ^{31}P NMR PARAMETERS

	δ_C[a]	J_{CP}[c]	δ_P[b]	J_{PP}
$(CH_3)_2PCH_2CH_2P(CH_3)_2$				
$-CH_3$	−14.1	7.6		
$>CH_2$	−28.0	~1.0		
$>P-$			+75.2	~0
$Fe[(CH_3)_2PCH_2CH_2P(CH_3)_2](CO)_3$				
$-CH_3$	−20.2	13.4		
$>CH_2$	−31.0	25.1		
$>P-$			−42.9	~±1.1
$-CO$	−221.5	6.9		

[a] Chemical shifts are in ppm with respect to TMS. [b] Chemical shifts are in ppm with respect to external $(C_6H_5)_3PO$. [c] See text for a discussion of this coupling constant.

The ^1H noise decoupled ^{13}C spectra of the methylene and methyl carbons in the free ligand and complex at 25° are shown in Figures 4 and 5, respectively. Unambiguous peak assignments were made by examining the proton-coupled ^{13}C spectra. Under these conditions the methylene "triplet" became a triplet of triplets and the methyl "triplet" became a quartet of triplets. The ^{13}C spectrum of the carbonyl carbons is presented in Figure 6.

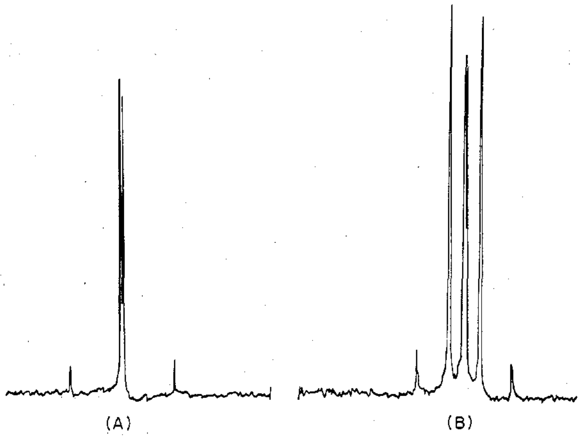

Figure 4.—^{13}C nmr spectrum of $(CH_3)_2PCH_2CH_2P(CH_3)_2$: (A) methylene region; (B) methyl region. 1000 pulses with $PW = 65\ \mu sec$, $AT = 3$ sec, and $PD = 0.0$.

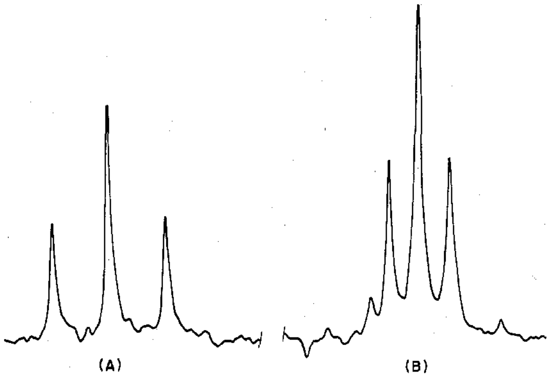

Figure 5.—^{13}C nmr spectrum of $Fe[(CH_3)_2PCH_2CH_2P(CH_3)_2](CO)_3$ at 25° in toluene-d_8: (A) methylene region; (B) methyl region. 500 pulses with $PW = 75\ \mu sec$, $AT = 2$ sec, and $PD = 0.0$.

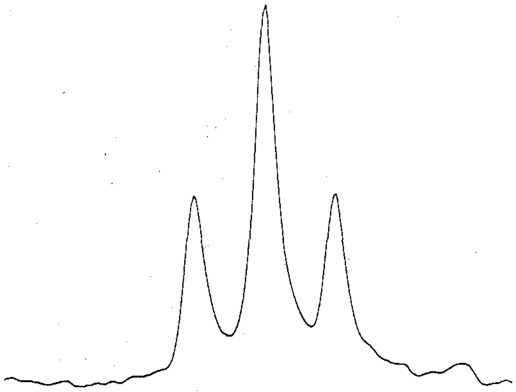

Figure 6.—^{13}C nmr spectrum of $Fe[(CH_3)_2PCH_2CH_2P(CH_2)_3](CO_3)$, carbonyl region, at −80° in toluene-d_8; 200 pulses with $PW = 75\ \mu sec$, $AT = 4$ sec, and $PD = 0.0$.

The ^1H coupled and decoupled ^{13}C spectra of the carbonyl carbons are identical. For the temperature range +25 to −80° the ^{13}C spectrum is independent of temperature. It is interesting to note that at room temperature it takes approximately 12 hr to observe the ^{13}C spectrum of the carbonyl carbons ($AT = 0.3$ sec and $PD = 4.7$ sec). However, if the temperature is lowered to at least −50°, the spectrum of the carbonyl carbons is obtained in about 5–10 min. This is believed to be caused by the increased viscosity of the solvent (toluene-d_8 in this case), which results in a much more efficient relaxation of the carbonyl carbons at the lower temperature. This point was further substantiated by observing the carbonyl carbons at the same temperature using CH_2Cl_2 as the solvent. Under these conditions *no* enhancement was noted. Because of this apparent enhancement in toluene, it was used as the solvent for the remainder of the experiments. It would appear that this procedure is preferable to the addition of paramagnetic "T_1 reagents" in order to diminish the spin–lattice relaxation time of the ^{13}C nuclei.[15] However, this technique has one disadvantage in that below −80° it is difficult to maintain a ^2H lock due to the increased viscosity of the solvent. Therefore, the temperature range which can be investigated is limited. Further studies of these intriguing results are in progress.

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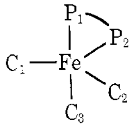
Discussion

No static polygon or polyhedron can exist having two adjacent vertices bridged by a bidentate chelating ligand with carbonyl groups at the other vertices, in which there are three equivalent carbonyl groups. The infrared spectrum of $Fe[(CH_3)_2PCH_2CH_2P(CH_3)_2](CO)_3$ is consistent with this fact in that it contains three strong CO stretching bands which are characteristic of structure **1**. Other structures consistent with the infrared spectrum are the following: **2**, a trigonal-bipyramidal molecule with P_1 and P_2 both occupying equatorial sites; **3**, a square pyramid with one phosphorus occupying an equatorial position and the other an axial position; and **4**, a square pyramid with both phosphorus atoms occupying equatorial positions.



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In view of the general preference especially for five-coordinate transition metal d^8 compounds to adopt trigonal-bipyramidal configurations,[2,3] and since $Fe(CO)_5$ itself has a trigonal-bipyramidal structure,[16] structure **1** or **2** is favored for this molecule. On the basis of previous experimental studies, structure **1** is preferred. For example, X-ray studies of five-coordinate metal complexes containing $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ ligands have indicated a preference for axial–equatorial rather than equatorial–equatorial coordination.[17,18] Steric considerations in pentagonal-bipyramidal alkyloxy phosphoranes involving a five-membered ring also favor axial–equatorial substitution which minimizes ring strain.[6] Ring strain is expected to be less in structure **1** as compared to **2**[5,6] although the geometry will not be precisely trigonal bipyramidal; the P_1–Fe–P_2 angle will probably be slightly larger (~100°) than the idealized 90°.

Each resonance in the ^1H noise decoupled ^{13}C spectrum of the free ligand appears basically as a doublet of doublets, whereas, in the ^1H noise decoupled ^{13}C spectrum of the complex each resonance appears as a triplet. These splittings arise from spin coupling from the two chemically equivalent but magnetically nonequivalent ^{31}P nuclei. Since there is only one ^{13}C atom per molecule, the methyl carbons form the X part of an ABX spin system where A and B are the two ^{31}P atoms. A similar argument applies to the methylene carbons. The complete analysis of an ABX spin system has been carried out by Abraham and Bernstein.[19] Normally, one would consider the ^1H decoupled spin system in $(CH_3)_2PCH_2CH_2P(CH_3)_2$ as an AA'X system. However, because of a ^{13}C isotope effect on the phosphorus adjacent to the ^{13}C, that phosphorus will be chemically shifted with respect to the other phosphorus atom. Therefore, the system is actually of the ABX type. Under the conditions where A and B have nearly the same chemical shifts, Abraham and Bernstein have predicted that with sufficient resolution, the X portion should appear as a doublet of doublets, the separation between the doublets being related to the magnitude of the isotope shift. However, if the line width is broad as compared to the isotope shift, as is apparently the case in $Fe[(CH_3)_2PCH_2CH_2P(CH_3)_2](CO)_3$, then the spectrum will appear as a 1:2:1 triplet.

The separation between the lines of the triplet (or the doublet) is given by

$$d = {}^1/_2[J_{AX} + J_{BX}]$$

That is, only the average, J_{CP}, can be extracted from the ^{13}C resonances of the methyl and methylene carbons. The smaller outer resonances which are clearly observed in the spectrum of the ligand are "weak" combination lines.[19]

The ^{13}C doublet of doublets for the methylene region of $(CH_3)_2PCH_2CH_2P(CH_3)_2$ was unresolved whereas the methyl region consisted of a well resolved doublet of doublets (Figure 4). Under conditions of higher resolution (not shown in Figure 4) the methylene carbon doublet of doublets was barely resolved and yields a splitting of ~1.0 Hz. This implies that $^1J_{CP}$ and $^2J_{CP}$ for the methylene carbons are nearly equal, but opposite in sign. The magnitude of $^2J_{PP}$ in the complex was obtained by examining the ^{13}C satellites of the ^1H decoupled ^{31}P spectrum, *i.e.*, by observing the AB portion of the ABX spectrum.[19] The value of 1.1 Hz found for $^2J_{PP}$ is not unlike those reported for similar complexes.[10]

The triplet structure for the ^{13}C spectra of the carbonyl carbons can arise *via* two possible ways: (1) they can form the X portion of an ABX spectrum where the equatorial carbonyls have the same chemical shift and identical values of $^2J_{CP}$ as the axial carbonyl or (2) the carbonyl carbons are chemically equivalent *via* an intramolecular exchange process which is fast compared to the nmr time scale, and hence the two ^{31}P atoms become magnetically equivalent with respect to the carbonyl carbons. In view of the great sensitivity of ^{13}C chemical shifts with respect to their environment,[20,21] as demonstrated, for example, by the observation that the cis and trans chemical shifts of the carbonyl groups in $(C_6H_5)_3PMo(CO)_5$[20] differ by 4.5 ppm, we believe it is unlikely that accidental degeneracies of both chemical shifts and CP coupling constants are responsible for the carbonyl triplet. In this respect it may be noted that the resolution of our ^{13}C carbonyl spectra is approximately 2 Hz. The preservation of ^{13}C–^{31}P coupling in the ^{13}C nmr spectra of the carbonyl groups between +25 and −80° shows the exchange process occurring is of an intramolecular type and that it is not slowing down to any observable extent at −80°.

It seems likely that exchange occurs *via* a Berry or permutationally equivalent rearrangement such as Ugi's "turnstile rotation."[3,5,6,22,23] From the Berry rearrangement approach, the energetically most favorable exchange process is one that proceeds *via* a structure having a geometry identical with the ground-state geometry of **1** (one phosphorus axial and one phos-

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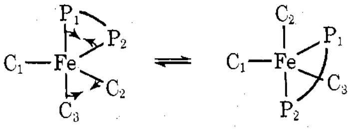
[23] I. Ugi, D. Marquarding, H. Klusacek, P. Gillespie, and F. Ramirez, *Accounts Chem. Res.*, **4**, 288 (1971).

phorus equatorial) but which still permits permutation of phosphorus environments and also carbonyl environments. For example, by holding the C_1–Fe bond fixed in space, structure **1** can be converted to structure **5** by bending the P_2–Fe–C_2 angle to 180° and decreasing the P_1–Fe–C_3 angle to 120°. A rotation of 90° about the C_1–Fe bond gives structure **5**.[5] This process equilibrates P_1 and P_2 and C_2 and C_3. If the process is repeated holding, this time, the C_2–Fe bond fixed in space, then C_1 and C_3 (as well as P_1 and P_2) will be equilibrated.



1 5

The proton nmr spectra of both the free and complexed ligand are complex (see Figures 1 and 2). This is undoubtedly due to the presence of short and long range coupling of the type described by Carty and Harris.[10,24,25] The type of spectrum obtained for Fe[$(CH_3)_2PCH_2CH_2P(CH_3)_2$]$(CO)_3$ has been stated by King, *et al.*,[26] to be that expected for a $(CH_3)_2PCH_2CH_2P(CH_3)_2$ complex with two magnetically equivalent phosphorus atoms; however, as already pointed out, the two phosphorus atoms cannot be magnetically equivalent.

Although the possibility of the previously reported iron pentacarbonyl derivative *trans*-Fe[$P(N(CH_3)_2)_3$]$_2$$(CO)_3$[10] having a stereochemically rigid structure at room temperature cannot be excluded, the mere absence of bands attributable to the cis isomer in the infrared spectrum does not preclude the possibility of a small, experimentally nonobservable amount of it being present. Even a small steady-state concentration of the cis isomer would be sufficient to permit intramolecular exchange. The temperature dependence of the proton spectra of $(CH_3)_2PCH_2CH_2P(CH_3)_2$ and Fe[$(CH_3)_2PCH_2CH_2P(CH_3)_2$]$(CO)_3$ is, in part, somewhat similar to that of *trans*-Fe[$P(N(CH_3)_2)_3$]$_2$$(CO)_3$.[10] Although the temperature dependence of the ^1H nmr spectrum of the above compound and of $(CH_3)_2PCH_2CH_2P(CH_3)_2$ might be due, at least in part, to rotational restrictions at lower temperatures, the small changes involved in both cases could well be due to temperature-dependent solvent effects. In the case of Fe[$(CH_3)_2PCH_2CH_2P(CH_3)_2$]$(CO)_3$ the somewhat larger temperature dependence is even more likely to be caused by temperature-dependent solvent effects since the reduction in freedom of motion of the complexed ligand will favor its interaction with the solvent.

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Electrochemical Investigation of Tris(1,10-phenanthroline) Complexes of Chromium[1,2]

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Tris(1,10-phenanthroline)chromium(III) undergoes a one-electron reduction at −0.50 V *vs.* the sce followed by a series of reactions which converts all unreduced tris(1,10-phenanthroline)chromium(III) into diaquobis(1,10-phenanthroline)chromium(III). This conversion parallels that previously observed for the tris(2,2′-bipyridine)chromium(III) complex; however, the rate of conversion is slower and is both pH and temperature dependent. The diaquobis(1,10-phenanthroline)chromium(III) complex is reducible at the mercury electrode to the corresponding Cr(II) complex. In the presence of excess 1,10-phenanthroline the diaquobis(1,10-phenanthroline)chromium(II) reverts to the corresponding tris chromium(II) complex. In the absence of excess 1,10-phenanthroline, the diaquobis(1,10-phenanthroline)chromium(II) is converted to equimolar amounts of tris(1,10-phenanthroline)chromium(II) and tetraaquomono(1,10-phenanthroline)chromium(II).

Introduction

The tris(1,10-phenanthroline) complexes of Cr(III), Cr(II), Cr(I), and Cr(0) have been prepared previously[4] and were found to be similar to the corresponding 2,2′-bipyridine complexes.[4,5] Information on the aqueous solution chemistry of these complexes is scarce and no studies of the electrochemical reduction behavior have been reported.

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