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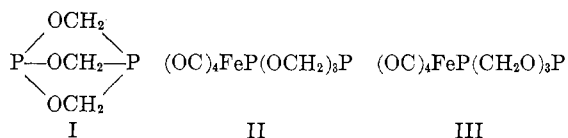
## Nuclear Magnetic Resonance and Molecular Structural Studies of *trans*-P(OCH<sub>2</sub>)<sub>3</sub>PFe(CO)<sub>3</sub>P(OCH<sub>2</sub>)<sub>3</sub>P

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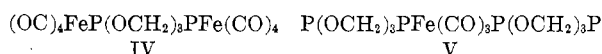
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That the title complex has the *trans* configuration and displays linkage isomerism of the ligand is strongly indicated by infrared and nmr evidence and is confirmed by a crystal-structure determination. The molecular structure was elucidated by single-crystal X-ray diffraction. The crystals belonged to the orthorhombic space group *Pnma* with  $a = 11.516$  (5),  $b = 9.780$  (4), and  $c = 17.065$  (6) Å. The Fe–P bond for the P(CH<sub>2</sub>)<sub>3</sub> bound ligand is substantially longer (2.190 (4) Å) than the Fe–P bond for the PO<sub>3</sub> bound ligand (2.116 (4) Å). Structural changes in the ligands upon coordination can be correlated with trends in the magnitudes and signs of the  $^2J_{\text{PH}}$  and  $^3J_{\text{PH}}$  coupling constants. The preparation of Fe(CO)<sub>4</sub>P(OCH<sub>2</sub>)<sub>3</sub>P, Fe(CO)<sub>4</sub>P(CH<sub>2</sub>O)<sub>3</sub>P, and (OC)<sub>4</sub>FeP(OCH<sub>2</sub>)<sub>3</sub>PFe(CO)<sub>4</sub> is also given. Evidence for a nonaxial isomer of Fe(CO)<sub>4</sub>P(OCH<sub>2</sub>)<sub>3</sub>P reported earlier (reference 1) is reinterpreted as arising from a mixture of ligand, the title complex, and the axial isomer.

A recent study of the coordination chemistry of the bicyclic phosphorus ligand I<sup>1</sup> showed that unlike most



difunctional phosphorus ligands, it is unable to chelate a metal atom because the opposed donor sites are fixed in a rigid geometry. It was further concluded from nmr studies that linkage isomerism of the ligand was possible in the case of Fe(CO)<sub>4</sub>L (II and III) as well as bridging of two iron atoms by I in the case of IV. The



appearance of the infrared spectra of II–IV in the carbonyl region was consistent with substitution by I in the axial position of a trigonal bipyramid.<sup>1</sup>

In this paper we report the preparation of the new complex V. Nmr spectroscopy and X-ray crystallographic studies are shown to be particularly complementary tools in elucidating the structural changes which occur upon coordinating the different phosphorus donor sites of I. Infrared and nmr evidence is also presented which denies the existence of the nonaxial isomer of II reported earlier.<sup>1</sup>

### Experimental Section

Nmr data were obtained on Varian A-60 or HR-60 machines. A description of the instrumentation used to carry out the double resonance experiments appears elsewhere.<sup>1</sup> A Beckman IR-12 spectrometer afforded the infrared spectra and an Atlas CH-4 single-focusing spectrometer gave the mass spectral results.

*trans*-P(OCH<sub>2</sub>)<sub>3</sub>PFe(CO)<sub>3</sub>P(OCH<sub>2</sub>)<sub>3</sub>P (V).—This compound was prepared by irradiating a quartz tube containing 600 ml of a dry hexane solution of 4.6 g (30 mmol) of I and 40 ml (30 mmol) of Fe(CO)<sub>5</sub> with a 673-A Hanovia lamp. After 4.5 hr of irradiation, the hexane solution was decanted and the solid which had formed was extracted with benzene. After the benzene was removed under reduced pressure, the residue was eluted on a silica-gel column. With a 9:1 benzene–hexane eluant, unreacted I was eluted first, followed closely by the complex which produced a parent-ion peak at 444 in its mass spectrum. Elemental analyses were not deemed reliable owing to moisture, air, and light sensitivity. The infrared spectrum of the complex in CH<sub>2</sub>Cl<sub>2</sub> revealed a single band at 1927 cm<sup>-1</sup> in the carbonyl region.

The <sup>1</sup>H nmr spectrum of the title compound in acetonitrile using TMS as the internal standard consists of eight lines of equal intensity; each ligand contributing a doublet of doublets owing to coupling to phosphorus. For one of the ligands δ<sub>H</sub> is 4.95 ppm ( $^2J_{\text{PH}} = 8.7$ ,  $^3J_{\text{PH}} = 6.2$  Hz). The signs of  $^2J_{\text{PH}}$  and  $^3J_{\text{PP}}$  (9.0) relative to  $^3J_{\text{PH}}$  were obtained by means of indor experiments (see Figure 1) and the absolute sign of the last coupling was assumed to be positive in determining the absolute signs of  $^2J_{\text{PH}}$ (+) and  $^3J_{\text{PP}}$ (+).<sup>2</sup> The indor experiments also yielded <sup>31</sup>P chemical shifts for this ligand with respect to 85% phosphoric acid by the procedure described earlier<sup>1</sup> (δ<sup>31</sup>P<sub>O3</sub> – 161.3, δ<sup>31</sup>P<sub>(CH2)3</sub> + 68.0 ppm), the magnitude of the <sup>31</sup>PFe<sup>31</sup>P coupling ( $^2J_{\text{PP}} = 38.0$  Hz), as well as a check on the value of  $^2J_{\text{PH}}$  obtained from the <sup>1</sup>H spectrum. The <sup>1</sup>H spectrum of the other ligand showed that δ<sub>H</sub> is 4.60 ppm while  $^2J_{\text{PH}} = 0.9$  and  $^3J_{\text{PH}} = 2.8$  Hz. Insufficient resolution and solubility prevented <sup>31</sup>P irradiation since the outer pairs of peaks were separated by less than 1 Hz. Assignment of the  $^2J_{\text{PH}}$  and  $^3J_{\text{PH}}$  couplings in both ligands is discussed later.

Single crystals of the title compound were obtained by cooling a saturated acetonitrile solution to –20°. Since the crystals decompose on prolonged exposure to the air, they were placed in thin-walled Lindemann glass capillaries. Rotation and Weissenberg photographs indicated the unit cell had orthorhombic symmetry. The systematic extinctions of *Ok*l (for  $k + l = 2n + 1$ ) and *h*k0 (for  $h = 2n + 1$ ) indicate either the space group *Pnma* (*D*<sub>2h</sub><sup>16</sup>) or *Pn*2<sub>1</sub>*a* (alternate setting of *Pna*2<sub>1</sub>, *C*<sub>2v</sub><sup>9</sup>).

A crystal of approximate dimensions 0.1 × 0.1 × 0.05 mm was then mounted on a fully automated Hilger-Watts four-circle diffractometer with a scintillation detector system, and accurate cell constants were determined to be  $a = 11.516$  (5),  $b = 9.780$  (4), and  $c = 17.065$  (6) Å. A density calculation indicated  $Z = 4$  (ρ<sub>calcd</sub> = 1.37). No density was measured owing to decomposition. The space group *Pnma* would require a molecular mirror plane. A similar situation was found for *N*-methyl-1,4-diazabicyclo[2.2.2]octonium trichloro-aquo-nickelate(II)<sup>3</sup> and for 1-oxo-4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane.<sup>4</sup> Data were collected in the *h*k*l* octant at room temperature using Zr-filtered Mo Kα radiation (0.7107 Å) for all reflections with 2θ < 60°. An ω–2θ scan technique was used, and backgrounds were measured at θ<sub>hkl</sub> ± (0.25 + 0.01 × θ<sub>hkl</sub>). Check reflections were monitored periodically to assess crystals and electronic stability. The intensities were corrected for Lorentz and polarization factors, and σ(*I*) was estimated from [(total count) + (background) + 5% (total count)<sup>2</sup> + 5% (background)<sup>2</sup>]<sup>1/2</sup>. The estimated deviation σ(*F*) of *F* was calculated from σ(*F*) = {[*I* + σ(*I*)]/Lp}<sup>1/2</sup> – (*I*/Lp)<sup>1/2</sup>.<sup>5</sup> All reflections with  $F \leq 3\sigma(F)$  were judged unobserved. A total of 1313 reflections were judged observed. No correction was made for anomalous dispersion or decomposition of the crystal. Also,

(2) R. D. Bertrand, F. B. Ogilvie, and J. G. Verkade, *J. Amer. Chem. Soc.*, **92**, 1908 (1970).

(3) F. K. Ross and G. D. Stucky, *Inorg. Chem.*, **8**, 2734 (1969).

(4) D. M. Nimrod, D. R. Fitzwater, and J. G. Verkade, *J. Amer. Chem. Soc.*, **90**, 2780 (1968).

(5) D. E. Williams and R. E. Rundle, *ibid.*, **86**, 1660 (1964).

(1) R. D. Bertrand, D. A. Allison, and J. G. Verkade, *J. Amer. Chem. Soc.*, **92**, 71 (1970).

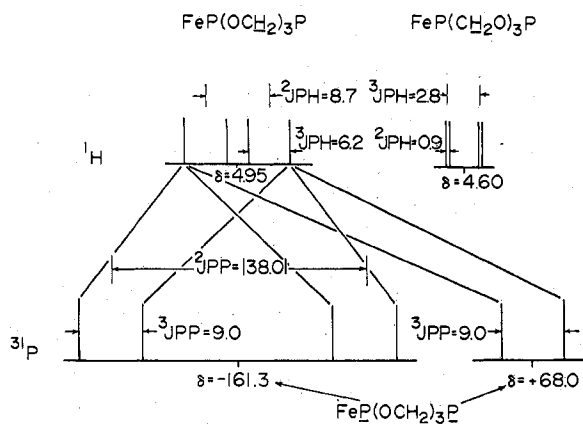


Figure 1.—Schematic representation of the entire <sup>1</sup>H nmr and the FeP(OCH<sub>2</sub>)<sub>3</sub>P portion of the <sup>31</sup>P nmr spectrum of *trans*-P(OCH<sub>2</sub>)<sub>3</sub>PFe(CO)<sub>3</sub>P(CH<sub>2</sub>O)<sub>3</sub>P. The <sup>31</sup>P spectrum was obtained by inductor studies on the outer lines of one segment of the <sup>1</sup>H spectrum as indicated. The connectedness of the lines indicates that all the couplings are of the same sign except <sup>2</sup>J<sub>PP</sub> for which only an absolute magnitude can be obtained.

the small calculated absorption coefficient,  $\mu = 11.7$ , indicated that no absorption correction was necessary.

A three-dimensional Patterson synthesis revealed the Fe position, and the remaining 22 non-hydrogen atoms were located subsequently from the Fe-phased electron density synthesis.<sup>6</sup> For the space group *Pnma*, full matrix least-squares refinements on  $\Sigma \omega(F_o - F_c)^2$ , where  $\omega = [1/\sigma(F)]^2$ , with anisotropic temperature factors reduced the conventional discrepancy index, *R*<sub>1</sub>, to the present minimum of 0.089 for the observed reflections.<sup>7</sup> The scattering factors were those of Hansen, *et al.*<sup>8</sup> A least-squares refinement was also examined in the space group *Pn2<sub>1</sub>a*, but a net lowering of only 0.1% for the net *R* factor was noticed. According to Hamilton's test, this decrease was not enough to justify the refinement in the lower symmetry space group *Pn2<sub>1</sub>a*.<sup>9</sup> In Tables I and II are listed the final positional and thermal parameters, respectively, along with their standard deviations. Tables III and IV list the final bond distances and bond angles, respectively, along with their standard deviations.<sup>10</sup> Figure 2 is a drawing of the final X-ray model of the molecule *trans*-P(OCH<sub>2</sub>)<sub>3</sub>PFe(CO)<sub>3</sub>P(OCH<sub>2</sub>)<sub>3</sub>P with the indicated labeling scheme. Figure 3 is a view of the unit cell down the *b* axis of one layer of complex and solvent molecules.<sup>11,12</sup>

**Fe(CO)<sub>5</sub>P(OCH<sub>2</sub>)<sub>3</sub>P, Fe(CO)<sub>5</sub>P(CH<sub>2</sub>O)<sub>3</sub>P, and (OC)<sub>5</sub>FeP(OCH<sub>2</sub>)<sub>3</sub>PFe(CO)<sub>4</sub>.**—A solution of 2.0 ml (15 mmol) of Fe(CO)<sub>5</sub> and 2.3 g (15 mmol) of I in 60 ml of ethylbenzene in a quartz tube was irradiated for 2.5 hr with a 673-A Hanovia Lamp. The reaction mixture was filtered and the solvent removed under reduced pressure. The residue was separated by chromatography on a silica-gel column using a 1:1 hexane-benzene solution

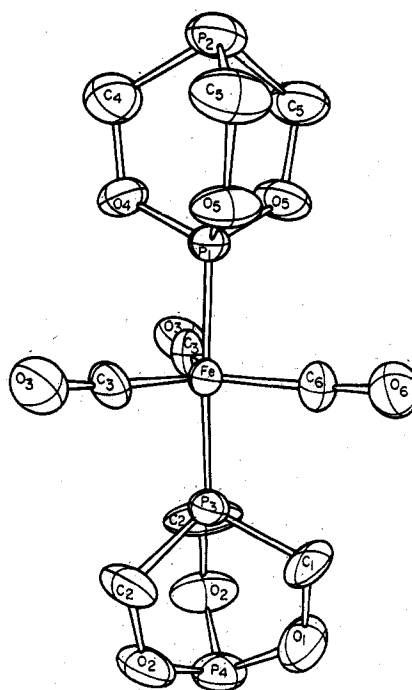


Figure 2.—Perspective drawing of the molecule *trans*-P(OCH<sub>2</sub>)<sub>3</sub>PFe(CO)<sub>3</sub>P(CH<sub>2</sub>O)<sub>3</sub>P indicating the atom labeling scheme. Hydrogen atoms are not shown. The ORTEP program of C. K. Johnson (U. S. Atomic Energy Commission Report ORNL-3794, Oak Ridge Laboratory, Oak Ridge, Tenn., 1965) was used to produce the figure.

TABLE I  
FINAL PARAMETERS<sup>a</sup> FOR  
*trans*-(OC)<sub>5</sub>Fe[P(OCH<sub>2</sub>)<sub>3</sub>P][P(CH<sub>2</sub>O)<sub>3</sub>P]

Atom	Positional parameters		
	<i>x</i>	<i>y</i>	<i>z</i>
Fe	0.0755 (2)	0.2500	0.0645 (1)
P(1)	0.0168 (3)	0.2500	0.1820 (2)
P(2)	-0.0679 (4)	0.2500	0.3497 (2)
P(3)	0.1476 (3)	0.2500	-0.0543 (2)
P(4)	0.2603 (4)	0.2500	-0.2142 (2)
O(1)	0.1210 (10)	0.2500	-0.2111 (6)
O(2)	0.2902 (7)	0.1202 (9)	-0.1567 (4)
O(3)	0.1906 (7)	0.5139 (8)	0.0990 (4)
O(4)	0.1166 (8)	0.2500	0.2445 (5)
O(5)	-0.0604 (6)	0.3788 (7)	0.2046 (3)
O(6)	-0.1700 (10)	0.2500	0.0198 (6)
N	0.4790 (20)	0.5490 (30)	0.0191 (20)
C(1)	0.0492 (12)	0.2500	-0.1380 (9)
C(2)	0.2421 (9)	0.1108 (9)	-0.0803 (6)
C(3)	0.1453 (11)	0.4132 (12)	0.0834 (5)
C(4)	0.0900 (13)	0.2500	0.3279 (9)
C(5)	-0.1082 (9)	0.3914 (13)	0.2832 (6)
C(6)	-0.0724 (10)	0.2500	0.0337 (8)
C(7)	0.4478 (18)	0.6441 (17)	0.0510 (10)
C(8)	0.4112 (11)	0.7676 (25)	0.0880 (10)

<sup>a</sup> Calculated using the ORFLS program of W. R. Busing, K. O. Martin, and H. A. Levy, U. S. Atomic Energy Commission Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

as eluant. The compounds were eluted in reverse order of the title heading of this paragraph. It should be pointed out that *trans*-P(OCH<sub>2</sub>)<sub>3</sub>PFe(CO)<sub>3</sub>P(OCH<sub>2</sub>)<sub>3</sub>P also appears in the second fraction as well as a large amount of unreacted ligand. Each fraction must be subjected to chromatography again to obtain compounds sufficiently pure to show no contaminants in the <sup>1</sup>H nmr spectra. All of the complexes appear to be air, light, and moisture sensitive. A parent-ion peak at 488 was observed in the mass spectrum of the bridged compound while each of the other two showed an analogous peak at 320. The infrared and nmr parameters of the monosubstituted and bridged complexes were reported previously.<sup>1</sup>

(6) J. Rodgers and R. A. Jacobson, "A General Fourier Program in PL1 for Triclinic, Monoclinic, and Orthorhombic Space Groups," U. S. Atomic Energy Commission Report 15-2155, Iowa State University of Science and Technology, Ames Institute for Atomic Research, 1969.

(7) W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Least-Squares Program," U. S. Atomic Energy Commission Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(8) H. P. Hansen, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).

(9) W. C. Hamilton, "Statistics in Physical Sciences," Ronald Press, New York, N. Y., 1964, pp 157-162; *Acta Crystallogr.*, **18**, 502 (1965).

(10) W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Function & Error Program," U. S. Atomic Energy Commission Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(11) C. K. Johnson, "ORTEP: A Fortran Thermal-Ellipsoid Plot Program For Crystal Structure Illustrations," U. S. Atomic Energy Commission Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(12) A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-2804. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

TABLE II  
ANISOTROPIC THERMAL PARAMETERS<sup>a,b</sup>

Atom	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Fe	0.0071 (2)	0.0097 (2)	0.00244 (7)	0.0	0.00013 (9)	0.0
P(1)	0.0072 (3)	0.0104 (4)	0.0026 (1)	0.0	0.0002 (2)	0.0
P(2)	0.0126 (5)	0.0171 (6)	0.0027 (1)	0.0	0.0011 (2)	0.0
P(3)	0.0076 (3)	0.0097 (4)	0.0024 (1)	0.0	0.0000 (1)	0.0
P(4)	0.0125 (5)	0.0174 (7)	0.0032 (2)	0.0	0.0015 (2)	0.0
O(1)	0.012 (1)	0.033 (3)	0.0032 (4)	0.0	-0.0010 (6)	0.0
O(2)	0.020 (1)	0.021 (1)	0.0043 (3)	0.009 (1)	0.0041 (5)	0.0026 (5)
O(3)	0.015 (1)	0.012 (1)	0.0051 (4)	-0.004 (1)	0.0006 (4)	-0.0005 (5)
O(4)	0.009 (1)	0.026 (2)	0.0023 (3)	0.0	-0.0012 (4)	0.0
O(5)	0.014 (1)	0.013 (1)	0.0035 (3)	0.004 (1)	0.0027 (4)	0.0006 (4)
O(6)	0.010 (1)	0.022 (2)	0.0047 (5)	0.0	-0.0021 (6)	0.0
N	0.013 (2)	0.014 (2)	0.0086 (10)	-0.004 (3)	-0.0015 (2)	0.0011 (15)
C(1)	0.011 (2)	0.036 (4)	0.0021 (5)	0.0	-0.0010 (8)	0.0
C(2)	0.023 (2)	0.021 (2)	0.0042 (5)	0.013 (2)	0.0063 (8)	0.0033 (8)
C(3)	0.008 (1)	0.011 (1)	0.0038 (4)	0.001 (1)	-0.0014 (5)	0.0011 (6)
C(4)	0.009 (2)	0.044 (5)	0.0031 (6)	0.0	-0.0005 (8)	0.0
C(5)	0.019 (2)	0.016 (2)	0.0038 (4)	0.005 (1)	0.0023 (7)	0.0002 (7)
C(6)	0.009 (1)	0.016 (2)	0.0035 (6)	0.0	0.0003 (8)	0.0
C(7)	0.008 (3)	0.009 (8)	0.0033 (20)	-0.0012 (20)	0.0011 (20)	0.0002 (20)
C(8)	0.008 (4)	0.006 (5)	0.0041 (15)	0.0034 (20)	0.0003 (20)	-0.0005 (15)

<sup>a</sup> The anisotropic temperature factor is of the form  $\exp(-B_{11}h^2 - B_{22}k^2 - B_{33}l^2 - 2B_{12}hk - 2B_{13}hl - 2B_{23}kl)$ . <sup>b</sup> See footnote a of Table I.

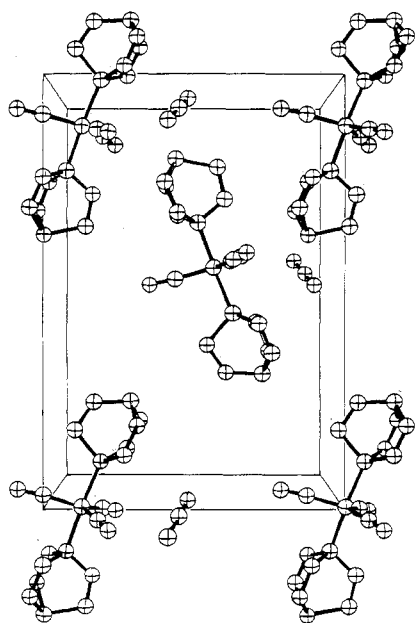


Figure 3.—View of the unit cell down the  $b$  axis of one layer of complex and solvent molecules. The ORTEP program of C. K. Johnson (U. S. Atomic Energy Commission Report ORNL-3794, Oak Ridge Laboratory, Oak Ridge, Tenn., 1965) was employed. Only one of the disordered pair of solvent molecules is shown for clarity.

### Discussion

Because the structure of I is conducive to polymer formation, optimum conditions for the preparations described here had to be found. In spite of the 1:1 ligand-metal ratios used, comparatively large amounts of I are left unreacted. Longer irradiation times tended to produce decomposition products and did not improve the yields of the desired products. The complexes are fairly air, light, and moisture sensitive and manipulations were carried out in a dry atmosphere of nitrogen and in the absence of light wherever possible.

The formulation of II-V as monomeric species is supported by the observation of a parent-ion peak in the mass spectrum in each case. The axial position of I in II and III and the trans orientation of the ligands

in V is strongly indicated by the three carbonyl stretching bands observed in the first two<sup>1</sup> complexes and the single band seen in the last. Although two sets of three bands might have been expected in IV owing to the presence of two different donor sites, only one set can be resolved.<sup>1</sup> This phenomenon has been observed before in complexes of the type  $(OC)_5MP-(OCH_2)_3PM(CO)_5$  ( $M = Cr, Mo, W$ ) wherein only one instead of two pairs of CO frequencies can be resolved.<sup>1</sup>

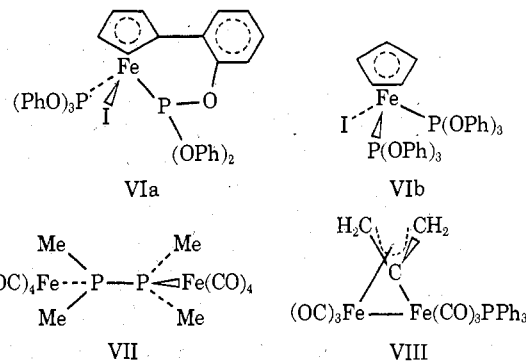
The basis for the assignment of the particular ligand linkage isomerism in II, III, and V lies in the comparison of the  $^{31}P$  chemical shifts with those obtained for the uncoordinated ligands and IV wherein both phosphorus atoms must be coordinated. These arguments have been put forth previously<sup>1</sup> for II and III and it remains only to show that the ligands in V are coordinated differently. The strongest indication that the ligands are not identically coordinated is the presence of two different proton chemical shifts exhibiting different  $^2J_{PH}$  and  $^3J_{PH}$  values (see Figure 1). Because the values of the  $^{31}P-^1H$  couplings for one of the ligands (+8.7 and +6.2 Hz) compares favorably with those found for  $(OC)_5MP(OCH_2)_3P$  ( $M = Cr, Mo, W$ ) complexes ( $^2J_{PH} = +8.5$  to +8.8 and  $^3J_{PH} = +5.3$  to +6.6 Hz),<sup>1</sup> the new couplings are assigned to  $^2J_{PH}$  and  $^3J_{PH}$ , respectively. Thus this particular ligand is coordinated through the  $PO_3$  phosphorus. That this ligand makes use of this coordination mode is also suggested by the  $^{31}P$  chemical shifts ( $\delta_{^{31}PO_3} -161.3$  and  $\delta_{^{31}P(CH_2)_3} +68.0$ ) which are similar to those found for  $(OC)_4FeP(OCH_2)_3P$  ( $\delta_{^{31}PO_3} -157.44$  and  $\delta_{^{31}P(CH_2)_3} +71.38$ ).<sup>1</sup> A comparison of the  $^{31}P-^1H$  couplings of the other ligand in V with those found for  $Fe(CO)_4P(CH_2O)_3P^1$  establishes that  $^2J_{PH} = 0.9$  and  $^3J_{PH} = 2.8$  Hz. Both of these couplings are likely to be positive by analogy with the positive signs determined for the model compound II.<sup>1</sup>

Structural analysis of V by X-ray techniques confirmed the conclusions given above and also afforded some further insights into the coordination behavior of polycyclic phosphorus ligands. The crystal was found to contain acetonitrile of crystallization and the  $R$  factor descended to 0.089 when 0.4 molecule of solvent

per asymmetric unit was assumed to be present. Figure 2 shows the molecular structure of V without the H atoms while Figure 3 depicts the arrangement of these molecules and those of the solvent in the unit cell. There is some disorder in the solvent molecules, although the *R* factor is left unchanged by interchanging the methyl carbon and the nitrogen of the acetonitrile. The bond symmetry around the iron atom is a nearly idealized trigonal bipyramid. The mirror plane contains the C<sub>3</sub> axis and so a CO link in each ligand lies on this plane as well as a carbonyl group. The P(CH<sub>2</sub>)<sub>3</sub> bound ligand is eclipsed with respect to the trigonally arranged carbonyls and this configuration may be adopted to reduce steric interactions of the carbonyl groups with the methylene protons of the ligand. Thus models show more available space for the carbonyls between the two protons of

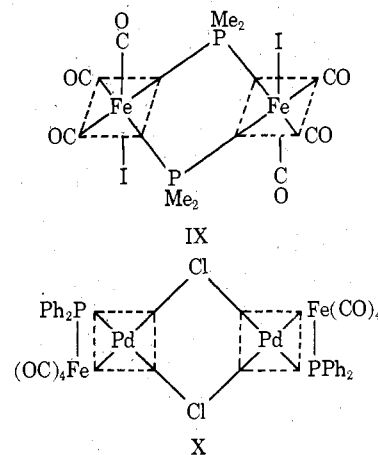
a methylene group than between two protons from different methylene carbons. In contrast, the PO<sub>3</sub> bound ligand is staggered relative to the carbonyl groups which is not unexpected if steric repulsions between the carbonyls and the oxygens of the ligands are to be minimized. Selected bond distances, bond angles and nonbonded distances are set forth in Tables III, IV, and V, respectively.

The Fe-P bond distance for the PO<sub>3</sub> bound ligand (2.116 (4) Å) is appreciably shorter than that found in VIa (2.14 (2) Å),<sup>13</sup> VIb (2.15 (2) Å),<sup>13</sup> and *cis*-FeH<sub>2</sub>[P-



(OEt)<sub>2</sub>Ph]<sub>4</sub> (2.128 (2) and 2.150 (2) Å).<sup>14</sup> The difference could be ascribed to the greater steric requirements of P(OPh)<sub>3</sub> and P(OEt)<sub>2</sub>Ph compared to I although differences in the nature of the Fe-P bond cannot be ruled out since P(OPh)<sub>3</sub> is apparently a poorer Lewis base toward a proton than is P(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>3</sub> which is closely related to I.<sup>15</sup> Moreover, there is structural and nmr evidence that substantial  $\pi$  back-bonding to phosphorus can occur from chalcogenide atoms<sup>4</sup> and transition metal carbonyl moieties<sup>16</sup> which exceeds that of open-chain phosphites.

The Fe-P bond distance for the P(CH<sub>2</sub>)<sub>3</sub> bound ligand (2.190 (4) Å) is also short compared to those found for VII (2.260 (5) Å),<sup>17</sup> VIII (2.25 Å),<sup>18</sup> IX



2.293 (6), (2.312 (6) Å),<sup>19</sup> and X (2.24 (2) Å).<sup>20</sup> Al-

TABLE III  
BOND DISTANCES<sup>a</sup> (Å) IN *trans*-(OC)<sub>3</sub>Fe[P(OCH<sub>2</sub>)<sub>3</sub>P][P(CH<sub>2</sub>O)<sub>3</sub>P]

Fe-P(1)	2.116 (4)	C(1)-O(1)	1.50 (2)
Fe-P(3)	2.190 (4)	C(2)-O(2)	1.42 (1)
		C(4)-O(4)	1.46 (2)
		C(5)-O(5)	1.46 (1)
P(3)-C(1)	1.82 (1)	Fe-C(3)	1.81 (1)
P(3)-C(2)	1.80 (1)	Fe-C(6)	1.78 (2)
P(2)-C(4)	1.86 (2)		
P(2)-C(5)	1.85 (1)		
P(4)-O(1)	1.600 (20)	C(3)-O(3)	1.15 (1)
P(4)-O(2)	1.642 (8)	C(6)-O(6)	1.15 (2)
P(1)-O(4)	1.568 (9)		
P(1)-O(5)	1.590 (7)	N-C(7)	1.14 (2)
		C(7)-C(8)	1.43 (3)

<sup>a</sup> Calculated using the ORFFE program of W. R. Busing, K. O. Martin, and H. A. Levy, U. S. Atomic Energy Commission Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

TABLE IV  
SELECTED BOND ANGLES<sup>a</sup> (DEG) IN *trans*-(OC)<sub>3</sub>Fe[P(OCH<sub>2</sub>)<sub>3</sub>P][P(CH<sub>2</sub>O)<sub>3</sub>P]

P(1)-Fe-P(3)	176.4 (2)	P(1)-O(4)-C(4)	120.8 (9)
P(1)-Fe-C(3)	88.4 (3)	P(1)-O(5)-C(5)	120.2 (6)
P(1)-Fe-C(6)	88.5 (4)	P(4)-O(2)-C(2)	121.2 (6)
P(3)-Fe-C(3)	89.8 (3)	P(4)-O(1)-C(1)	125.4 (9)
P(3)-Fe-C(6)	95.2 (5)		
C(3)-Fe-C(6)	118.4 (3)	Fe-C(3)-O(3)	176.7 (8)
		Fe-C(6)-O(6)	175.0 (10)
		N-C(7)-C(8)	177.0 (20)
C(1)-P(3)-C(2)	100.6 (5)		
C(4)-P(2)-C(5)	97.1 (5)		
O(4)-P(1)-O(5)	104.2 (4)		
O(1)-P(4)-O(2)	101.0 (4)		
P(2)-C(4)-O(4)	113.6 (9)		
P(2)-C(5)-O(5)	114.0 (7)		
P(3)-C(2)-O(2)	114.4 (7)		
P(3)-C(1)-O(1)	108.0 (10)		

<sup>a</sup> See footnote a of Table III.

TABLE V  
NONBONDED DISTANCES<sup>a</sup> (Å) IN *trans*-(OC)<sub>3</sub>Fe[P(OCH<sub>2</sub>)<sub>3</sub>P][P(CH<sub>2</sub>O)<sub>3</sub>P]

P(1)-P(2)	3.025 (5)	O(3)-N	3.61 (3)
P(3)-P(4)	3.022 (5)	O(3)-C(7)	3.33 (2)
		O(3)-C(8)	3.55 (2)
C(1)-C(2)	2.79 (2)		
C(4)-C(5)	2.78 (2)	C(6)-C(1)	3.25 (1)
O(1)-O(2)	2.50 (1)	C(6)-O(5)	3.18 (1)
O(4)-O(5)	2.49 (1)	C(6)-C(3)	3.09 (2)
		C(3)-O(4)	3.19 (1)
		C(3)-C(2)	4.22 (1)

<sup>a</sup> See footnote a of Table III.

(13) V. G. Andrianov, Yu. A. Chupovskii, V. A. Semion, and Yu. T. Struchkov, *Chem. Commun.*, 282 (1968).

(14) L. J. Guggenberger, private communication.

(15) D. E. Morris and F. Basolo, *J. Amer. Chem. Soc.*, **90**, 2531 (1968).

(16) F. B. Ogilvie, J. M. Jenkins, and J. G. Verkade, *ibid.*, **92**, 1916 (1970).

(17) J. A. Jarvis, R. H. B. Mais, P. G. Owston, and D. T. Thompson, *J. Chem. Soc. A*, 622 (1968).

(18) E. Davis, *Chem. Commun.*, 248 (1968). No standard deviation was given.

(19) G. R. Davies, R. H. B. Mais, P. G. Owston, and D. T. Thompson, *J. Chem. Soc. A*, 1251 (1968).

(20) B. T. Kilbourn and R. H. Mais, *Chem. Commun.*, 1507 (1968).

though IX and X contain bridging phosphines, such ligands are formally similar to  $\text{PR}_3$  ligands in that they can be thought of as a coordinated  $\text{PR}_2\text{M}$  species. Again the low steric requirements of the  $\text{P}(\text{CH}_2)_3$  bound ligand I may be largely responsible for the short Fe-P distance but it should be realized that a rather electronegative  $\text{PO}_3$  group is attached to the carbons of the  $\text{P}(\text{CH}_2)_3$  coordinating site which would tend to decrease the  $\sigma$  basicity of the coordinated phosphorus but increase its  $\pi$  acidity. Infrared data have already been presented<sup>1</sup> which show that carbonyl stretching frequencies are not appreciably altered in a given complex by changing the site of phosphorus coordination in I. This may be an indication that the ligand properties of the two types of phosphorus atoms are somewhat more similar than a phosphite and a phosphine possessing ordinary alkyl groups. The Fe-C and carbonyl C-O distances are very close to those observed in VII,<sup>17</sup> VIII,<sup>18</sup> IX,<sup>19</sup> and X.<sup>20</sup>

Our observation that the Fe-P distance for the  $\text{PO}_3$  bound ligand is shorter by 0.074 (4) Å than the  $\text{P}(\text{CH}_2)_3$  coordinated bicyclic could be construed to reflect the somewhat larger steric bulk of the latter ligand. There is good reason to suppose, however, that the possibly better  $\pi$  acceptor properties of the  $\text{PO}_3$  bound donor may be partially responsible. Thus Grim and coworkers<sup>21</sup> have shown that the shorter Cr-P distance in  $(\text{OC})_5\text{CrL}$  when L is  $\text{P}(\text{OPh})_3$  (2.309 (1) Å) compared to  $\text{PPh}_3$  (2.422 (1) Å) is accompanied by longer Cr-C bonds trans and cis to the phosphite and shorter C-O lengths in the trans and cis carbonyls as expected if the phosphite is the better  $\pi$  acid. It was further shown more recently by Grim, *et al.*,<sup>22</sup> that the Cr-P distance in *trans*- $\text{Cr}(\text{CO})_4[\text{P}(\text{OPh})_3]_2$  is significantly shorter (2.252 (1) Å) than in  $\text{Cr}(\text{CO})_5\text{P}(\text{OPh})_3$ . This is expected since  $\text{P}(\text{OPh})_3$  competes more effectively for  $\pi$  bonding when trans to itself than when trans to a better  $\pi$  acceptor such as a CO group.

The bond parameters within the two independent polycycles of V feature some information on the nature of the behavior of ligands upon coordination. Interestingly all the bond lengths, the PCO and POC angles, and the intraligand P-P distances are quite constant. It does appear, however, that both the OPO and CPC angles open up about 3° upon coordination of the respective phosphorus atoms to the iron.<sup>23</sup> These observations are consistent with the expectation that s character will accrue in the PC and PO bonds as a result of donation of the phosphorus lone pair electrons. The  $^3J_{\text{PH}}$  and  $^2J_{\text{PH}}$  couplings are expected to increase positively and negatively, respectively, with the s character in the PO and PC bonds<sup>1</sup> and this prediction is confirmed from the nmr data for V. Thus  $^3J_{\text{PH}}$  and  $^2J_{\text{PH}}$  change from +2.8<sup>24</sup> to +6.2 Hz and from +8.7 to ( $\pm$ )0.9 Hz, respectively, upon coordination of the appropriate phosphorus atom. The sign and magnitude of  $^2J_{\text{PP}}$  (the

coupling through the metal atom) is also of significance in discussing the metal-phosphorus bond. A previous paper<sup>16</sup> from our laboratories disclosed that in a wide variety of *cis*- and *trans*- $\text{M}(\text{CO})_4\text{L}_2$  complexes (where M = Cr, Mo, or W and L is a phosphorus ligand) the absolute magnitude of  $^2J_{\text{PP}}$  increases with the electronegativity of the substituents on phosphorus. Only two *trans*- $\text{Fe}(\text{CO})_3\text{LL}'$  complexes were reported at that time, namely where L = L' =  $\text{P}(\text{OCH}_2)_3\text{CMe}$  ( $^2J_{\text{PP}}$  = 183  $\pm$  1 Hz) and where L =  $\text{P}(\text{OCH}_2)_3\text{CMe}$  and L' =  $\text{P}(\text{NMe}_2)_3$  ( $^2J_{\text{PP}}$  = +65  $\pm$  10 Hz). The addition of the value of  $^2J_{\text{PP}}$  for V (38  $\pm$  10) suggests that a trend of this coupling with electronegativity of the phosphorus substituents exists which is very similar to the *trans*- $\text{M}(\text{CO})_4\text{L}_2$  series and reflects, therefore, an increase in the s character and s electron density in the phosphorus orbital attached to the iron. Inasmuch as one of the couplings is known to be positive in the iron series, it is likely that the highest one is of like sign. The sign of  $^2J_{\text{PP}}$  in V, however, is more open to question. Although the vast majority of  $^2J_{\text{PP}}$  values for *trans*- $\text{M}(\text{CO})_4\text{L}_2$  complexes are positive, they progress from negative to positive with increasing ligand electronegativity when M = chromium.<sup>16</sup>

No evidence for the two remaining isomers of V has been seen so far. Possibly the exclusive formation of V is dominated by dipolar considerations. The dipole moment of I is quite large (3.10 D in benzene<sup>25</sup>) and the  $\text{PO}_3$  portion of the molecule comprises the negative end of the molecular dipole.<sup>26</sup> The most favorable configuration of trans oriented dipoles would be the head-to-tail one as found in V.

Earlier<sup>1</sup> it was erroneously reported that evidence for a nonaxial isomer of  $\text{Fe}(\text{CO})_4\text{P}(\text{OCH}_2)_3\text{P}$  had been observed.<sup>27</sup> Chromatography of the reaction mixture from the preparation of II-IV produces another fraction appearing between those of II and III which contains 90% of V contaminated with II although the identity of V was then unknown. Attempts to separate this mixture of I, II, and V were not successful and a study of the mixture was initiated. The carbonyl infrared spectrum consisted of a very strong band with two shoulders and an additional weak band which is not inconsistent with the four bands expected for an equatorially substituted trigonal bipyramid or square pyramid. The <sup>1</sup>H nmr spectrum of the mixture revealed

(25) F. B. Ogilvie and J. G. Verkade, unpublished results.

(26) This postulate is based on the following argument. The direction of the dipole moment in  $\text{P}(\text{OCH}_2)_3\text{CMe}$  (4.13 D in benzene<sup>24</sup>) is toward the phosphorus (A. C. Vandenbroucke, E. J. Boros, and J. G. Verkade, *Inorg. Chem.*, **7**, 1469 (1968)). Subtraction of the  $\text{P}(\text{CH}_2)_3$  contribution (1.19 D) (J. W. Rathke, J. W. Guyer, and J. G. Verkade, *J. Org. Chem.*, **35**, 2810 (1970)) which also is in the phosphorus direction still leaves a calculated value of 2.94 D in the direction of the  $\text{PO}_3$  phosphorus of I which compares reasonably well with the observed moment.

(27) Monodentate ligands generally give axially substituted  $\text{Fe}(\text{CO})_5$  complexes and equatorial carbonyls are replaced only after both axial carbonyls have been substituted. Two important exceptions do occur, however, for complexes of the type  $\text{Fe}(\text{CO})_4\text{L}$  when L = olefin or  $\text{PF}_3$ . Although the olefin bond has been found to be in the equatorial plane (C. Pedone and A. Sirlu, *Inorg. Chem.*, **7**, 2614 (1968); A. R. Luxmore and M. R. Truter, *Acta Crystallogr.*, **15**, 1117 (1962)) these complexes involve an iron atom with six nearest neighbors and the distinction between a distorted trigonal bipyramidal and a distorted octahedral geometry becomes somewhat problematic. Spectroscopic studies of the  $(\text{OC})_5\text{-}\eta\text{-Fe}(\text{PF}_3)_n$  system indicate that a mixture of axial and equatorial trigonal-bipyramidal isomers is present (J. B. Pd. Tripathi and M. Bigorne, *J. Organometal. Chem.*, **9**, 307 (1967); E. A. Udovich, R. J. Clark, and H. Haas, *Inorg. Chem.*, **8**, 1066 (1969); and references therein).

(21) H. J. Plastas, J. M. Stewart, and S. O. Grim, *J. Amer. Chem. Soc.*, **91**, 4326 (1969).

(22) H. S. Preston, J. M. Stewart, H. J. Plastas, and S. O. Grim, *Inorg. Chem.*, **11**, 161 (1972).

(23) The lighter carbon and oxygen atoms are not refined as well as the iron and phosphorus atoms. The angle around C(1) has a particularly anomalous value, along with the C(1)-O(1) bond length. Although apparently some distortion occurs here, it is not felt to affect the measurement of the bridgehead angle, since the most important atom is the phosphorus which is well-behaved.

(24) Grounds for the assumption that this sign is highly likely to be positive is discussed in ref 1.

only the presence of the main components (I and V) but part of the absorption of I masked the presence of the  $P(\text{CH}_2)_3$  coordinated ligand in V. Moreover the couplings and chemical shifts for the  $\text{PO}_3$  coordinated ligand were indeed different from those reported for II or III.<sup>1</sup> They do, however, correspond within experimental error with those of V (see Experimental Section). A parent ion at 320 seen in the mass spectrum can now be attributed to II and the absence of a similar peak at 444 for V can be rationalized on the basis of its lesser

volatility under the conditions the spectrum was run. It was during the search for a better synthesis of the "nonaxial mono substituted isomer" that V was identified and found to be responsible (along with II as an impurity) for the spurious data.

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## The Crystal and Molecular Structure of Bis(6-*tert*-butyl-1,3,5-trimethylcyclohexadienyl)iron(II)

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The orange crystals of bis(6-*tert*-butyl-1,3,5-trimethylcyclohexadienyl)iron(II) are monoclinic with  $a = 7.606$  (9) Å,  $b = 12.332$  (12) Å,  $c = 12.956$  (14) Å, and  $\beta = 104.25$  (4)°. The space group is  $P2_1/c$  and with two molecules per cell,  $d_{\text{meas}} = 1.15$  g/cm<sup>3</sup> and  $d_{\text{calcd}} = 1.157$  g/cm<sup>3</sup>. Diffractometer data were measured using monochromatized Mo  $K\alpha$  radiation and a  $\theta$ - $2\theta$  scan technique. The structure was solved by the heavy-atom method and refined by least-squares methods to a final  $R$  of 0.056 for the 1598 observed reflections used in the analysis. The molecule is required to have  $C_2$  symmetry by the space group. The distances and angles are normal for a  $\pi$ -pentadienyl system. The final orientation of the  $\pi$ -pentadienyl system minimizes the steric interaction between the methyl groups while maximizing the number of bonds in the  $\pi$  system which are eclipsed. These results suggest that interligand interactions are important in  $\pi$  complexes. In addition, the methyl groups and hydrogen atoms appear to be bending inward toward the metal atom, an effect which is not observed frequently. Finally, the absence of the C-H stretch at 2730–2830 cm<sup>-1</sup> has been shown to indicate an endo hydrogen atom and suggests that this band can be a useful diagnostic tool.

### Introduction

Structural data on organometallic compounds containing cyclohexadiene as a ligand are limited to a few examples,<sup>1-4</sup> all of which have at least one carbonyl group bonded to the metal atom. Two controversial features of these cyclohexadiene compounds are (1) whether the symmetric nature of the  $\pi$ -pentadienyl group is an intrinsic property of the ligand and (2) the relative orientation of two cyclohexadienyl rings compared to the corresponding bis- $\pi$ -cyclopentadienide complexes.<sup>5-7</sup> These points have been resolved by our study of bis(6-*tert*-butyl-1,3,5-trimethylcyclohexadienyl)iron(II), the first example of a cyclohexadienyl complex containing no carbonyl groups.

### Experimental Section

Orange crystals of the compound were kindly supplied by Helling and Braitsch.<sup>8</sup> Preliminary precession photographs indicated monoclinic symmetry. The systematic absences of  $h0l$  if  $l = 2n + 1$  indicated that the probable space groups were

$Pc$  ( $C_2^2$ ) or  $P2_1/c$  ( $C_{2h}^4$ ). Although the intensity statistics were inconclusive, the space group  $P2_1/c$  was confirmed by the structure analysis.

The intensity crystal was made approximately spherical (0.25 mm in diameter) by rotation of the crystal in cyclohexane. The unit cell dimensions were obtained from a least-squares fit of  $2\theta$ ,  $\omega$ ,  $\varphi$ , and  $\chi$  values for nine reflections measured on the Syntex P1 diffractometer. The final values are  $a = 7.606$  (9) Å,  $b = 12.332$  (12) Å,  $c = 12.956$  (14) Å,  $\beta = 104.25$  (4)°. The density calculated for two molecules of  $\text{Fe}(\text{C}_{13}\text{H}_{21})_2$ , mol wt 410.47, per unit cell is 1.157 g/cm<sup>3</sup>, in good agreement with the value of 1.15 g/cm<sup>3</sup> measured by flotation.

The intensity data were measured on a computer-controlled Syntex P1 diffractometer, using graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda$  0.71069 Å). A  $\theta$ - $2\theta$  scan at 4°/min was used to measure all the independent reflections up to a  $2\theta$  limit of 50°. The background was measured for a time equal to one-quarter of the total scan time at a point 1° to each side of the  $\alpha_1$  and  $\alpha_2$  peaks. [The intensity,  $I$ , was equal to [total scan counts - (backgrounds/background to scan ratio)](scan rate), with a standard deviation equal to [total scan counts + (backgrounds/background to scan ratio)<sup>2</sup>]<sup>1/2</sup>(scan rate)]. Four standard reflections were measured after every 50 reflections and were used to correct for a small variation (maximum 2%) of the standard reflections with time. The 1598 reflections which had an intensity  $I \geq 1.3\sigma(I)$  were considered observed and the 422 reflections which failed to meet the criterion were considered unobserved and flagged with a negative sign. These data were reduced to a set of structure amplitudes on an arbitrary scale by the usual methods. Since the value of  $\mu r$  was only 0.08 ( $\mu$  is 6.3 cm<sup>-1</sup> for Mo  $K\alpha$  radiation) and the crystal was approximately spherical, no absorption corrections were applied.

### Structure Determination and Refinement

The position of the iron atom was determined from a sharpened three-dimensional Patterson function. A Fourier synthesis phased on only the iron atom contribution revealed the positions

(1) M. R. Churchill and F. R. Scholer, *Inorg. Chem.*, **8**, 1950 (1969).

(2) P. J. Van Vurren, R. J. Fletterick, J. Meimwald, and R. E. Hughes, *J. Amer. Chem. Soc.*, **93**, 4394 (1971).

(3) The complex  $[\text{C}_6(\text{CH}_3)_3\text{H}]\text{Re}(\text{CO})_3$  was studied by P. H. Bird and M. R. Churchill, *Chem. Commun.*, 777 (1967), but virtually no distances and angles were given.

(4) The structure of bis(1,3-cyclohexadiene)monocarbonyliron has the olefin acting as a 1,3-diene rather than as a pentadienyl system: C. Kruger and C. H. Tsay, *Angew. Chem., Int. Ed. Engl.*, **10**, 261 (1971).

(5) Data on the orientation of the cyclopentadienide rings in ferrocene derivatives can be found in ref 6 and 7.

(6) G. J. Palenik, *Inorg. Chem.*, **9**, 2424 (1970).

(7) M. R. Churchill and J. Wormald, *ibid.*, **8**, 716 (1969).

(8) J. F. Helling and D. M. Braitsch, *J. Amer. Chem. Soc.*, **92**, 7207 (1970).