

Preparation and Structure of the Fluxional Molecule (Tetraphenyldiphosphinomethane)heptacarbonyldiiron

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Abstract: The reaction of $\text{Fe}_2(\text{CO})_9$ with $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ in tetrahydrofuran for 3 hr at 23° followed by chromatography allows the isolation of a brown, crystalline compound. Infrared, nmr (^{13}C), and X-ray crystallographic data establish the structure to be as follows. Two iron atoms, each having three terminal CO ligands, are connected by a relatively long Fe-Fe bond, 2.709 (2) Å, and a symmetrical bridging CO ligand. Each of the phosphorus atoms of the $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ligand is attached to one of the iron atoms of this $\text{Fe}_2(\text{CO})_7$ moiety; the P-Fe bonds have a mean length of 2.253 (3) Å. The arrangement of the P and C atoms about each iron atom is roughly trigonal bipyramidal, with the phosphorus atom at an apical position. The entire molecule has an approximate plane of symmetry which passes through the center of the Fe-Fe bond, the bridging CO group, and the methylene carbon atom of the diphosphine ligand. The mirror symmetry is violated primarily by (1) a slight twist about the Fe-Fe bond so that the two halves are not precisely eclipsed, (2) differing rotational orientations of the phenyl groups about the P-C bonds, and (3) several other minor distortions. Crystal data: space group, $P2_1/c$; $a = 11.257$ (2), $b = 11.926$ (3), $c = 22.911$ (8) Å; $\beta = 100.22$ (2) $^\circ$; $V = 3026.9$ (12) Å 3 ; $Z = 4$. The structure was solved by direct methods. It was refined anisotropically, using 2388 counter-diffractometer-measured reflections for which $F_o^2 > 3\sigma(F_o^2)$, to $R_1 = 0.060$ and $R_2 = 0.077$. The infrared spectrum in methylcyclohexane has six terminal (from 2050 to 1935 cm^{-1}) and one bridge (1770 cm^{-1}) carbonyl stretching bands. The ^{13}C nmr spectrum in the CO region is a single 1-2-1 triplet ($J_{\text{P-C}} = 5.15$ Hz) at 25° showing that CO ligands are rapidly scrambled over all sites. Processes which might account for this scrambling are discussed.

The study reported here lies at the confluence of two streams of work currently in progress in this laboratory. One of these has dealt with the preparation of new iron carbonyl derivatives by reaction of $\text{Fe}_2(\text{CO})_9$ with various ligands using tetrahydrofuran as the reaction medium.^{1,2} The other is the investigation of fluxional polynuclear metal carbonyls.³⁻⁷ The former work has shown that new products, and new types of products, can be obtained when ligands such as amines and phosphines are allowed to react with $\text{Fe}_2(\text{CO})_9$ in the solvent THF, in which the nonacarbonyl is soluble with reaction. One of these new products, obtained by the reaction of $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ with $\text{Fe}_2(\text{CO})_9$, had the composition $(\text{Ph}_2\text{PCH}_2\text{PPh}_2)\text{Fe}_2(\text{CO})_7$. The infrared spectrum showed that there were both bridging and terminal CO ligands whereas the ^{13}C nmr spectrum showed that all CO groups are nmr equivalent at room temperature, thus identifying this as a fluxional molecule of the type where rapid scrambling of CO ligands is occurring. Before undertaking further nmr studies of the fluxional behavior of the molecule, it was decided to characterize it structurally by X-ray crystallography.

Experimental Section

Synthesis and Crystal Preparation of $\text{Fe}_2(\text{CO})_7(\text{Ph}_2\text{P})_2\text{CH}_2$. Di-iron nonacarbonyl was first dried *in vacuo* and then 5.0 g (0.0136 mol) was placed in a round-bottom flask with 3.0 g (0.0078 mol) of bis(diphenylphosphino)methane. Tetrahydrofuran (100 ml), which

was dried over molecular sieves, was added under an argon flush. The reaction mixture was stirred at 23° for 3 hr and then chromatographed on 100-200 mesh florisil. The large brown band eluted from the florisil column was evaporated to dryness *in vacuo* to give a brown solid. The solid was washed with dry pentane and then dried, yield 3.1 g, 56% based on $\text{Ph}_2\text{P}_2\text{CH}_2$. Large crystals were grown by dissolving the brown solid in hot methylcyclohexane and allowing the solution to cool slowly to room temperature. The ir spectrum in methylcyclohexane in the CO stretching region has strong bands at 2050, 2005, 1992, 1965, 1950, 1935, and 1770 cm^{-1} .

Collection of X-Ray Data. A crystal measuring approximately $0.18 \times 0.23 \times 0.35$ mm was selected for data collection and was mounted in a glass capillary to protect it from slow air decomposition.

Preliminary examination on the diffractometer of the red-orange crystal showed the crystal to be monoclinic. Cell constants at 22° and the orientation matrix for data collection were determined from least-squares refinement of the setting angles for 15 reflections. These dimensions and other crystal data are given in Table I. Sev-

Table I. Crystal Data for $\text{Fe}_2(\text{CO})_7(\text{Ph}_2\text{P})_2\text{CH}_2$

$a = 11.257$ (2) Å	Space group $P2_1/c$
$b = 11.926$ (3) Å	Mo $K\alpha$ radiation
$c = 22.911$ (8) Å	$Z = 4$
$\beta = 100.22$ (2) $^\circ$	$\mu = 11.4$ cm^{-1}
$V = 3026.9$ (12) Å 3	$d_{\text{calc}} = 1.52$ g cm^{-3}

eral strong reflections showed peaks with a width at half-height of 0.2° on ω scans. Data were collected at 22° with Mo $K\alpha$ radiation on a diffractometer equipped with a graphite-crystal incident-beam monochromator. The θ - 2θ scan technique with a variable scan rate from 4.0 to 24.0 $^\circ$ /min and a symmetric scan range from 0.8 $^\circ$ before Mo $K\alpha_1$ to 0.8 $^\circ$ after Mo $K\alpha_2$ was used to collect 3056 independent data up to a maximum 2θ value of 40° .

The intensities of three reflections were measured every 100 reflections as a check on crystal and electronic stability. These showed no significant variation relative to the standard deviations of the intensities based on counting statistics alone. A correction for Lorentz and polarization factors was applied to the data. See ref 5 for a listing of computer programs used in data reduction and in solving and refining the structure.

No correction for absorption was made in view of the small variation in transmission factors of $77.5 \pm 3.9\%$. No evidence for

(1) F. A. Cotton and J. M. Troup, *J. Amer. Chem. Soc.*, **96**, 1233 (1974).

(2) F. A. Cotton and J. M. Troup, *J. Amer. Chem. Soc.*, **96**, 3438 (1974).

(3) R. D. Adams and F. A. Cotton, *Inorg. Chim. Acta*, **7**, 153 (1973).

(4) R. D. Adams and F. A. Cotton, *J. Amer. Chem. Soc.*, **95**, 6589 (1973).

(5) R. D. Adams, M. D. Brice, and F. A. Cotton, *J. Amer. Chem. Soc.*, **95**, 6594 (1973).

(6) J. Evans, B. F. G. Johnson, J. Lewis, J. R. Norton, and F. A. Cotton, *J. Chem. Soc., Chem. Commun.*, 807 (1973).

(7) F. A. Cotton, L. Kruczynski, and A. J. White, *Inorg. Chem.*, **13**, 1402 (1974).

secondary extinction was observed in the data set. In the structural refinement only the 2388 reflections with $F_o^2 > 3\sigma(F_o^2)$ were used. The parameter p used in the calculation of standard deviations was set equal to 0.07.

Solution and Refinement of the Structure. Normalized structure factors were computed using the program FAME. The positions for the four heavy atoms were found by direct methods using the program MULTAN which combines the cyclic application of the tangent formula with multisolution techniques. The starting phase set chosen automatically by the program obtained phases for 231 reflections with E 's greater than 1.95. From the 32 phase sets generated one set showed the best figures of merit and was used to generate an E map. The positions of the two iron atoms and two phosphorus atoms were the top peaks on the E map and their positions were refined by two cycles of full-matrix least squares to give agreement factors of $R_1 = 0.358$ and $R_2 = 0.442$. Scattering factors were taken from the International Tables.⁸ Anomalous dispersion effects were included in the calculated structure factors for iron and phosphorus, using f' and f'' values given by Cromer and Liberman.⁹

A difference Fourier map then revealed the positions of all the remaining non-hydrogen atoms. The isotropic refinement was omitted on all atoms other than the phenyl ring carbon atoms. The 19 non-phenyl ring atoms were refined anisotropically (starting with isotropic temperature factors of 4.0 \AA^2) and the phenyl ring carbons were refined isotropically (starting with temperature factors of 4.0 \AA^2) in one large three-cycle full-matrix least-squares program. The end result was a completely converged refinement with no parameter shift exceeding 0.65 times the standard deviation in the parameter, giving final agreement indices of $R_1 = 0.060$ and $R_2 = 0.077$. The esd in an observation of unit weight was 1.54.

No systematic trends were found in the data as a function of $\lambda^{-1} \sin \theta$, $|F_o|$, Miller indices, or reflection number. The atomic coordinates and estimated standard deviations are given in Table II. The isotropic and anisotropic thermal parameters are given in Table III. Root-mean-square amplitudes of thermal vibration are given in Table IV. Structure factors for $\text{Fe}_2(\text{CO})_7(\text{Ph}_2\text{P})_2\text{CH}_2$ are given elsewhere.¹⁰

Spectroscopic Measurements. The infrared spectrum was measured with a Perkin-Elmer Model 457A spectrophotometer. The Fourier transform carbon-13 nmr spectra were recorded on a Jeol JNM-PS-100 spectrometer, equipped with a Nicolet computer package, at 24.920 MHz. The Fourier transform resulting from 3400 repetitive rf pulses of 10 μsec duration (corresponding to a 58° tilt angle) at intervals of 1.6 sec gave a fair (10/1 on the CO) signal to noise ratio. A 0.75 M sample with 0.05 M $\text{Cr}(\text{acac})_3$ ¹¹ was prepared using freeze-thaw-degassed toluene- d_8 (for ^1H lock) and 2% (v/v) CS_2 (chemical-shift reference). This solution was then transferred with a syringe to a 10-mm, serum-stoppered tube.

Results

The crystal structure consists of discrete molecules of $\text{Fe}_2(\text{CO})_7(\text{Ph}_2\text{P})_2\text{CH}_2$ with no unusual intermolecular contacts. Two views of the structure, one showing the near mirror plane symmetry of the molecule and the second showing the unusual iron carbonyl moiety, are given in Figures 1 and 2, respectively. A tabulation of bond lengths is given in Table V, and selected bond angles are given in Table VI. Important least-squares planes and dihedral angles are presented in Table VII.

The infrared and carbon-13 nmr spectra are shown in Figure 3.

Discussion

The Molecule in the Crystal. Although the molecule is stoichiometrically a substitution product of $\text{Fe}_2(\text{CO})_9$, in which two CO ligands are replaced by two tertiary phosphine ligands, its structure is qualitatively different

(8) D. T. Cromer, "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham, England, in preparation.

(9) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1971).

(10) See the paragraph at the end of the paper concerning supplemental material.

(11) O. A. Gansow, A. R. Burke, and A. N. LaMar, *J. Chem. Soc., Chem. Commun.*, 456 (1972).

Table II. Atomic Positional Parameters for Non-Hydrogen Atoms in $\text{Fe}_2(\text{CO})_7(\text{Ph}_2\text{P})_2\text{CH}_2$

Atom	x	y	z
Fe(1)	0.1319 (1)	0.5005 (1)	0.1909 (1)
Fe(2)	0.0678 (1)	0.3544 (1)	0.1002 (1)
P(1)	0.3055 (2)	0.4089 (2)	0.2240 (1)
P(2)	0.2385 (2)	0.2518 (2)	0.1212 (1)
O(1)	0.2051 (7)	0.5583 (6)	0.0764 (3)
O(2)	-0.0301 (8)	0.3732 (8)	0.2555 (4)
O(3)	-0.0573 (8)	0.6677 (8)	0.1552 (4)
O(4)	0.2497 (8)	0.6798 (7)	0.2643 (4)
O(5)	-0.1656 (7)	0.4676 (7)	0.0697 (4)
O(6)	0.0492 (8)	0.3060 (8)	-0.0261 (4)
O(7)	-0.0565 (10)	0.1704 (9)	0.1523 (6)
C(1)	0.1610 (9)	0.4987 (9)	0.1082 (5)
C(2)	0.0371 (10)	0.4190 (10)	0.2320 (5)
C(3)	0.0144 (10)	0.6004 (10)	0.1676 (5)
C(4)	0.2042 (10)	0.6087 (9)	0.2339 (5)
C(5)	-0.0733 (11)	0.4260 (10)	0.0826 (5)
C(6)	0.0596 (10)	0.3262 (9)	0.0233 (6)
C(7)	-0.0050 (11)	0.2441 (12)	0.1350 (6)
C(8)	0.2982 (9)	0.2596 (8)	0.2007 (4)
C(9)	0.3434 (8)	0.4005 (8)	0.3055 (4)
C(10)	0.4519 (10)	0.4403 (10)	0.3367 (5)
C(11)	0.4750 (11)	0.4336 (10)	0.3993 (5)
C(12)	0.3887 (10)	0.3880 (9)	0.4292 (5)
C(13)	0.2808 (10)	0.3475 (10)	0.3978 (5)
C(14)	0.2598 (9)	0.3533 (9)	0.3350 (5)
C(15)	0.4409 (9)	0.4647 (8)	0.2006 (4)
C(16)	0.5503 (9)	0.4016 (9)	0.2114 (5)
C(17)	0.6543 (10)	0.4453 (9)	0.1926 (5)
C(18)	0.6503 (10)	0.5501 (10)	0.1659 (5)
C(19)	0.5445 (10)	0.6136 (9)	0.1582 (5)
C(20)	0.4387 (9)	0.5698 (8)	0.1743 (4)
C(21)	0.3672 (8)	0.2798 (8)	0.0834 (4)
C(22)	0.4749 (10)	0.2193 (9)	0.1018 (5)
C(23)	0.5729 (11)	0.2387 (11)	0.0715 (5)
C(24)	0.5596 (11)	0.3135 (10)	0.0240 (5)
C(25)	0.4534 (11)	0.3668 (10)	0.0050 (5)
C(26)	0.3523 (9)	0.3538 (9)	0.0358 (5)
C(27)	0.2165 (9)	0.1013 (8)	0.1076 (4)
C(28)	0.1918 (11)	0.0672 (10)	0.0476 (5)
C(29)	0.1717 (12)	-0.0484 (11)	0.0348 (6)
C(30)	0.1807 (11)	-0.1277 (11)	0.0811 (6)
C(31)	0.2027 (12)	-0.0919 (11)	0.1397 (6)
C(32)	0.2215 (10)	0.0223 (9)	0.1547 (5)

from that of $\text{Fe}_2(\text{CO})_9$ ¹² but similar to that suggested for $\text{Os}_2(\text{CO})_9$.^{13,13a} For molecules of composition $\text{M}_2(\text{CO})_9$, where M is Fe, Ru, or Os, as well as their derivatives in which one or more terminal CO groups have been replaced by other formally two-electron-donor ligands, the presence of an M-M single bond and an odd number of bridging CO ligands (one or three being the only practical possibilities) is required for the attainment of the usual 18-electron configurations at each metal atom. For $\text{Fe}_2(\text{CO})_9$, the structure with three CO bridges is preferred, while for $\text{Os}_2(\text{CO})_9$, where the M-M bond has to be longer, the structure with the minimum number of bridges is apparently preferred.

In the present case the singly bridged structure appears to be imposed by the diphosphine ligand. The

(12) (a) H. M. Powell and R. V. G. Ewens, *J. Chem. Soc.*, 286 (1939); (b) F. A. Cotton and J. M. Troup, *J. Chem. Soc., Dalton Trans.*, 800 (1974).

(13) J. R. Moss and W. A. G. Graham, *Chem. Commun.*, 835 (1970).

(13a) NOTE ADDED IN PROOF. We have just become aware of a paper describing $\text{Fe}_2(\text{CO})_7(\mu\text{-Ph}_2\text{CC})$ by O. S. Mills and A. D. Redhouse (*Chem. Commun.*, 444 (1966)). This molecule is closely related to the one described here. The small twist which slightly violates mirror symmetry in our case is quite advanced in this case. Presumably the $(\text{Ph}_2\text{P})_2\text{CH}_2$ ligand almost completely arrests the twisting distortion. It would also seem likely that in $\text{Ru}_2(\text{CO})_9$ the structure will be severely twisted.

Table III. Thermal Parameters for $\text{Fe}_2(\text{CO})_7(\text{Ph}_2\text{P})_2\text{CH}_2$

Atom	β_{11}^a	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe(1)	0.0054 (1)	0.0051 (1)	0.0014 (1)	0.0006 (1)	0.0008 (1)	0.0000 (1)
Fe(2)	0.0056 (1)	0.0052 (1)	0.0015 (1)	0.0002 (1)	0.0005 (1)	-0.0001 (1)
P(1)	0.0050 (2)	0.0044 (2)	0.0011 (1)	-0.0001 (2)	0.0006 (1)	0.0001 (1)
P(2)	0.0059 (2)	0.0045 (2)	0.0012 (1)	-0.0002 (2)	0.0006 (1)	-0.0001 (1)
O(1)	0.0103 (8)	0.0051 (6)	0.0019 (2)	-0.0006 (6)	0.0015 (3)	0.0003 (3)
O(2)	0.0080 (9)	0.0167 (12)	0.0042 (3)	-0.0019 (8)	0.0029 (4)	0.0032 (5)
O(3)	0.0156 (10)	0.0094 (9)	0.0038 (3)	0.0065 (8)	-0.0002 (4)	-0.0009 (4)
O(4)	0.0110 (9)	0.0078 (8)	0.0032 (3)	-0.0003 (7)	0.0014 (4)	-0.0015 (4)
O(5)	0.0078 (8)	0.0112 (9)	0.0033 (3)	0.0029 (7)	-0.0005 (4)	-0.0014 (4)
O(6)	0.0123 (10)	0.0133 (10)	0.0015 (2)	0.0006 (8)	-0.0003 (4)	-0.0018 (4)
O(7)	0.0180 (14)	0.0123 (12)	0.0072 (5)	-0.0017 (11)	0.0071 (7)	0.0024 (6)
C(1)	0.0049 (9)	0.0053 (9)	0.0020 (3)	0.0022 (8)	0.0001 (4)	-0.0002 (4)
C(2)	0.0067 (11)	0.0087 (11)	0.0020 (3)	0.0011 (9)	0.0004 (5)	0.0008 (5)
C(3)	0.0078 (11)	0.0076 (11)	0.0017 (3)	0.0002 (10)	0.0011 (5)	-0.0003 (5)
C(4)	0.0074 (11)	0.0058 (10)	0.0019 (3)	0.0006 (9)	0.0009 (5)	-0.0007 (4)
C(5)	0.0081 (12)	0.0080 (11)	0.0017 (3)	-0.0004 (10)	-0.0003 (5)	0.0002 (4)
C(6)	0.0083 (12)	0.0054 (10)	0.0022 (3)	-0.0003 (9)	-0.0004 (5)	-0.0009 (5)
C(7)	0.0084 (13)	0.0101 (13)	0.0034 (4)	0.0003 (11)	0.0023 (6)	0.0009 (6)
C(8)	0.0073 (10)	0.0045 (8)	0.0008 (2)	0.0001 (7)	0.0006 (4)	0.0002 (3)

Atom	B_{iso}	Atom	B_{iso}	Atom	B_{iso}
C(9)	2.4 (2)	C(17)	4.0 (2)	C(25)	4.6 (3)
C(10)	4.2 (3)	C(18)	4.2 (2)	C(26)	3.6 (2)
C(11)	4.6 (3)	C(19)	3.7 (2)	C(27)	2.8 (2)
C(12)	4.2 (3)	C(20)	2.9 (2)	C(28)	4.6 (3)
C(13)	4.2 (2)	C(21)	2.6 (2)	C(29)	5.8 (3)
C(14)	3.5 (2)	C(22)	3.9 (2)	C(30)	5.3 (3)
C(15)	2.8 (2)	C(23)	5.1 (3)	C(31)	5.5 (3)
C(16)	3.4 (2)	C(24)	4.9 (3)	C(32)	4.0 (2)

Table IV. Root-Mean-Square Amplitudes of Thermal Vibration for $\text{Fe}_2(\text{CO})_7(\text{Ph}_2\text{P})_2\text{CH}_2$ (Å)

Atom	Min	Intermed	Max
Fe(1)	0.170 (3)	0.190 (2)	0.200 (2)
Fe(2)	0.185 (2)	0.193 (3)	0.202 (2)
P(1)	0.161 (5)	0.179 (4)	0.181 (4)
P(2)	0.172 (5)	0.180 (4)	0.192 (4)
O(1)	0.18 (1)	0.21 (1)	0.26 (1)
O(2)	0.16 (2)	0.29 (1)	0.40 (1)
O(3)	0.16 (2)	0.29 (1)	0.38 (1)
O(4)	0.21 (1)	0.26 (1)	0.31 (1)
O(5)	0.19 (1)	0.28 (1)	0.32 (1)
O(6)	0.17 (1)	0.28 (1)	0.33 (1)
O(7)	0.20 (2)	0.32 (1)	0.47 (1)
C(1)	0.14 (2)	0.21 (2)	0.24 (2)
C(2)	0.19 (2)	0.22 (2)	0.26 (2)
C(3)	0.20 (2)	0.23 (2)	0.24 (2)
C(4)	0.18 (2)	0.22 (2)	0.23 (2)
C(5)	0.19 (2)	0.24 (2)	0.25 (2)
C(6)	0.17 (2)	0.22 (2)	0.27 (2)
C(7)	0.20 (2)	0.26 (2)	0.31 (2)
C(8)	0.14 (2)	0.18 (2)	0.21 (2)

flexibility of this ligand, which arises from its ability to undergo internal rotation about each of the two methylene carbon to phosphorus bonds, allows it to function efficiently as a bidentate ligand in either of two ways, as shown in Figure 4. In **1a**, the entire $\text{C}_2\text{P}-\text{C}-\text{PC}_2$ skeleton (neglecting the rotational orientations of the phenyl groups) has C_{2v} (mm) symmetry, and the donor orbitals of the two phosphorus atoms are suitably oriented to form bonds to one metal atom. This possibility is well illustrated by $(\text{Ph}_2\text{PCH}_2\text{PPh}_2)\text{Fe}(\text{CO})_3$,¹⁴ where the mean P-Fe distance is 2.217 ± 0.008 Å and the P-Fe-P angle is $73.5 (1)^\circ$. However, if each PPh_2 group is rotated 60° (in directions which are

(14) F. A. Cotton, K. I. Hardcastle, and G. A. Rusholme, *J. Coord. Chem.*, 2, 217 (1973).

Table V. Bond Lengths for $\text{Fe}_2(\text{CO})_7(\text{Ph}_2\text{P})_2\text{CH}_2$ (Å)

Fe(1)-Fe(2)	2.709 (2)	Ring 1	
Fe(1)-P(1)	2.250 (3)	C(9)-C(10)	1.39 (1)
Fe(1)-C(1)	1.98 (1)	C(9)-C(14)	1.37 (1)
Fe(1)-C(2)	1.82 (1)	C(10)-C(11)	1.41 (1)
Fe(1)-C(3)	1.79 (1)	C(11)-C(12)	1.39 (2)
Fe(1)-C(4)	1.74 (1)	C(12)-C(13)	1.38 (1)
Fe(2)-P(2)	2.257 (3)	C(13)-C(14)	1.42 (1)
Fe(2)-C(1)	2.01 (1)	Ring 2	
Fe(2)-C(5)	1.79 (1)	C(15)-C(16)	1.43 (1)
Fe(2)-C(6)	1.78 (1)	C(15)-C(20)	1.39 (1)
Fe(2)-C(7)	1.81 (1)	C(16)-C(17)	1.42 (1)
		C(17)-C(18)	1.39 (1)
P(1)-C(8)	1.86 (1)	C(18)-C(19)	1.39 (1)
P(1)-C(9)	1.84 (1)	C(19)-C(20)	1.42 (1)
P(1)-C(15)	1.83 (1)	Ring 3	
P(2)-C(8)	1.83 (1)	C(21)-C(22)	1.41 (1)
P(2)-C(21)	1.84 (1)	C(21)-C(26)	1.39 (1)
P(2)-C(27)	1.83 (1)	C(22)-C(23)	1.42 (2)
P(1)-P(2)	2.999 (4)	C(23)-C(24)	1.39 (2)
		C(24)-C(25)	1.36 (2)
C(1)-O(1)	1.19 (1)	C(25)-C(26)	1.45 (1)
C(2)-O(2)	1.14 (1)	Ring 4	
C(3)-O(3)	1.14 (1)	C(27)-C(28)	1.41 (1)
C(4)-O(4)	1.16 (1)	C(27)-C(32)	1.43 (1)
C(5)-O(5)	1.14 (1)	C(28)-C(29)	1.42 (2)
C(6)-O(6)	1.14 (1)	C(29)-C(30)	1.41 (2)
C(7)-O(7)	1.16 (1)	C(30)-C(31)	1.39 (2)
		C(31)-C(32)	1.41 (2)

opposite as each bond is viewed from P to C) to give **1b**, the donor orbitals can be made to lie parallel; thus, in **1b** the ligand is suited to forming bonds to two separate metal atoms which are about 2.5-3.0 Å apart and themselves able to form parallel bonds.

When this work was initiated, we had been hoping that the diphosphine ligand would behave in the first way, so that both phosphorus atoms would be bound to

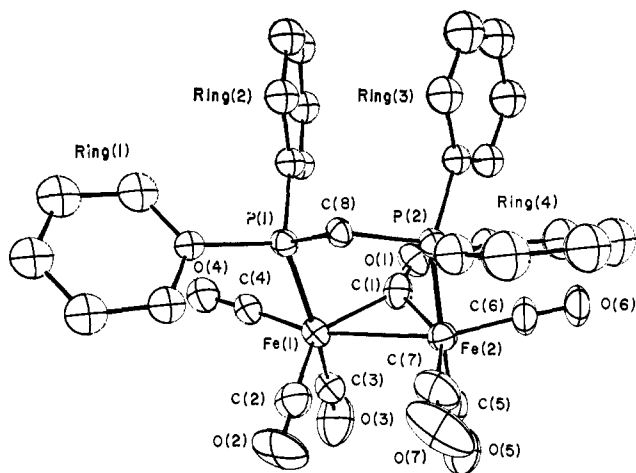


Figure 1. A view of $\text{Fe}_2(\text{CO})_7(\text{Ph}_2\text{P})_2\text{CH}_2$ showing the near mirror plane symmetry of the molecule.

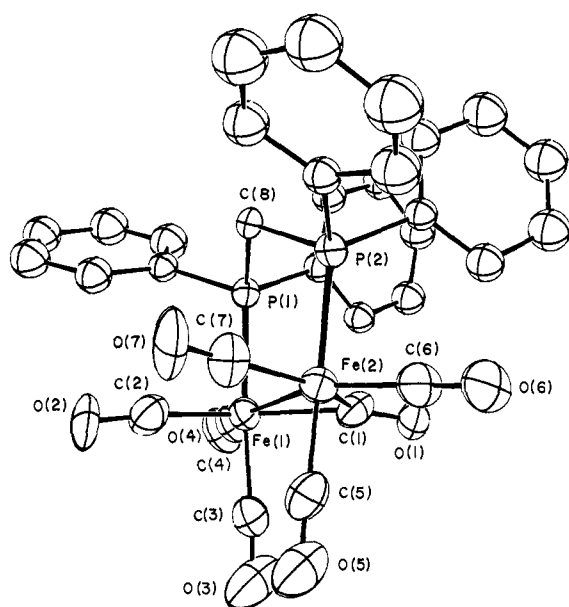


Figure 2. A view of $\text{Fe}_2(\text{CO})_7(\text{Ph}_2\text{P})_2\text{CH}_2$ showing the unusual $[\text{Fe}_2(\text{CO})_7]$ moiety.

one iron atom, thereby generating a product which could be informatively compared with $(\text{bipy})\text{Fe}_2(\text{CO})_7$, which we have recently described.¹ Probably because the second mode of coordination involves less strain (by giving rise to a five- rather than a four-membered ring), it is configuration **1b** which the diphosphine has adopted in this case.

As a result of the diphosphine functioning as it does, the $\text{Fe}_2(\text{CO})_9$ type structure is rendered unstable relative to the type postulated for $\text{Os}_2(\text{CO})_9$. This is because the two positions, on different metal atoms which the diphosphine would have to occupy, are so far apart in an $\text{Fe}_2(\text{CO})_9$ structure that either the $\text{Fe}_2(\text{CO})_7$ moiety or the diphosphine or, more likely both, would be subjected to severe strain. There is, however, a large amount of evidence, much of it coming from studies of CO scrambling in binuclear metal carbonyls,³⁻⁵ that structures which differ only in having either x bridging CO groups and y terminal ones or $(x - 2)$ bridging CO groups and $(y + 2)$ terminal ones generally differ in energy by 15 kcal/mol or less. Therefore, it is ener-

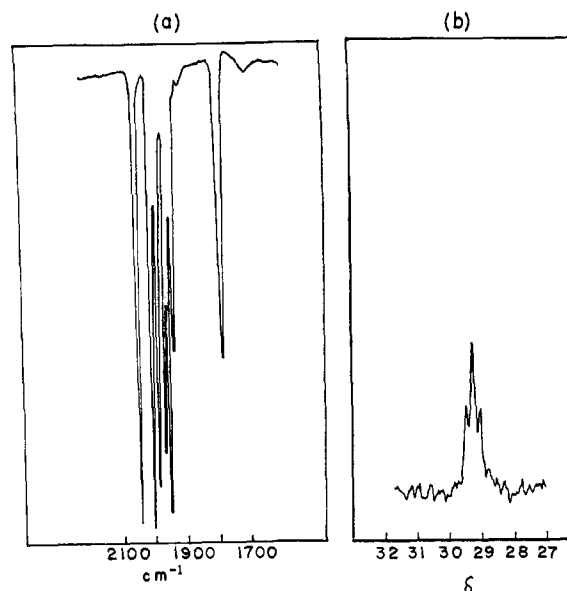


Figure 3. (a) The infrared spectrum of $\text{Fe}_2(\text{CO})_7(\text{Ph}_2\text{PCH}_2\text{PPh}_2)$ in methylcyclohexane. (b) The carbon-13 nmr spectrum of the compound in toluene- d_6 at 25°. The abscissa gives chemical shift values in ppm downfield from CS_2 .

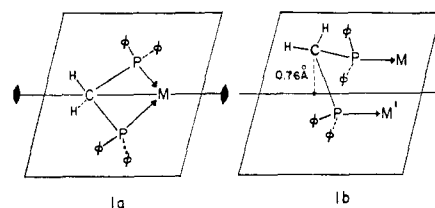


Figure 4. Diagrams showing how the $(\text{Ph}_2\text{P})_2\text{CH}$ ligand can adapt itself to function as a chelating bidentate ligand, **1a**, or as a bridging bidentate ligand, **1b**. The indicated displacement of 0.76 Å is that actually found in the compound under discussion.

Table VI. Selected Bond Angles for $\text{Fe}_2(\text{CO})_7(\text{Ph}_2\text{P})_2\text{CH}_2$ (deg)

P(1)-Fe(1)-C(1)	92.1 (3)	P(2)-Fe(2)-C(1)	91.9 (3)
P(1)-Fe(1)-C(2)	96.9 (3)	P(2)-Fe(2)-C(5)	175.7 (4)
P(1)-Fe(1)-C(3)	167.3 (4)	P(2)-Fe(2)-C(6)	90.0 (4)
P(1)-Fe(1)-C(4)	83.0 (3)	P(2)-Fe(2)-C(7)	87.0 (4)
P(1)-Fe(1)-Fe(2)	92.5 (1)	P(2)-Fe(2)-Fe(1)	94.9 (1)
C(1)-Fe(1)-C(2)	134.5 (5)	C(1)-Fe(2)-C(5)	92.3 (4)
C(1)-Fe(1)-C(3)	87.8 (4)	C(1)-Fe(2)-C(6)	100.8 (5)
C(1)-Fe(1)-C(4)	114.2 (5)	C(1)-Fe(2)-C(7)	148.7 (6)
C(1)-Fe(1)-Fe(2)	47.6 (3)	C(1)-Fe(2)-Fe(1)	46.8 (3)
C(2)-Fe(1)-C(3)	92.3 (5)	C(5)-Fe(2)-C(6)	88.8 (5)
C(2)-Fe(1)-C(4)	111.2 (5)	C(5)-Fe(2)-C(7)	89.6 (6)
C(2)-Fe(1)-Fe(2)	87.3 (4)	C(5)-Fe(2)-Fe(1)	88.3 (4)
C(3)-Fe(1)-C(4)	85.5 (5)	C(6)-Fe(2)-C(7)	110.5 (6)
C(3)-Fe(1)-Fe(2)	96.8 (4)	C(6)-Fe(2)-Fe(1)	147.2 (4)
C(4)-Fe(1)-Fe(2)	161.3 (4)	C(7)-Fe(2)-Fe(1)	102.1 (4)
Fe(1)-P(1)-C(8)	112.2 (3)	Fe(2)-P(2)-C(8)	109.4 (3)
Fe(1)-P(1)-C(9)	113.5 (3)	Fe(2)-P(2)-C(21)	120.8 (3)
Fe(1)-P(1)-C(15)	116.4 (3)	Fe(2)-P(2)-C(27)	114.3 (3)
C(8)-P(1)-C(9)	103.3 (4)	C(8)-P(2)-C(21)	106.1 (4)
C(8)-P(1)-C(15)	105.2 (4)	C(8)-P(2)-C(27)	103.5 (4)
C(9)-P(1)-C(15)	105.1 (4)	C(21)-P(2)-C(27)	101.1 (4)
P(1)-C(8)-P(2)	109.0 (5)	Fe(1)-C(1)-Fe(2)	85.6 (5)
Fe(1)-C(1)-O(1)	137.7 (9)	Fe(2)-C(1)-O(1)	136.5 (8)
Fe(1)-C(2)-O(2)	174.3 (10)	Fe(2)-C(5)-O(5)	176.8 (11)
Fe(1)-C(3)-O(3)	176.3 (10)	Fe(2)-C(6)-O(6)	176.9 (11)
Fe(1)-C(4)-O(4)	177.2 (10)	Fe(2)-C(7)-O(7)	173.9 (14)

getically preferable for the $\text{Fe}_2(\text{CO})_7$ moiety to open two CO bridges, thus making it possible for the diphos-

Table VII. Least-Squares Planes and Dihedral Angles for $\text{Fe}_2(\text{CO})_7(\text{Ph}_2\text{P})_2\text{CH}_2$

Plane	Atoms defining plane				Equation of mean plane ^a				
I	Fe(1), Fe(2), P(1), P(2)				$6.360x + 6.963y - 15.443z = 1.364$				
II	Fe(1), Fe(2), C(1)				$9.096x - 6.059y + 3.334z = -1.196$				
III	Fe(1), Fe(2), C(1), C(2), C(4), C(6), C(7)				$8.962x - 6.234y + 3.636z = -1.243$				
Displacement of Atoms from Mean Plane (Å)									
Plane I				Plane II			Plane III		
Fe(1)	0.012	C(3)	0.32	P(1)	2.25	Fe(1)	0.00	P(1)	2.25
Fe(2)	-0.013	C(4)	0.56	P(2)	2.25	Fe(2)	0.01	P(2)	2.25
P(1)	-0.033	C(5)	-0.14	C(2)	-0.23	C(1)	-0.03	C(3)	3.03
P(2)	0.035	C(6)	0.93	C(3)	-1.75	C(2)	-0.19	C(5)	-1.76
C(1)	1.46	C(7)	-1.78	C(4)	0.15	C(4)	0.13	C(8)	-1.77
C(2)	-1.79	C(8)	-0.76	C(5)	-1.78	C(6)	-0.17		
				C(6)	-0.16	C(7)	0.17		
				C(7)	0.12				
				C(8)	3.01				
Dihedral Angles between Planes (deg)									
	I-II	90.6		I-III	91.9		II-III	1.3	

^a Equations have the form $Ax + By + Cz = D$ where x , y , and z are fractional monoclinic coordinates.

phine ligand to occupy two coordination sites in an approximately strain-free way.

The present structure suggests that the details of the $\text{Os}_2(\text{CO})_9$ structure may differ in one respect from the drawing shown in ref 13. The five ligand atoms surrounding each metal atom have an approximately trigonal bipyramidal distribution. The result is that not only are the pairs of metal-ligand bonds perpendicular to the plane of the three-membered ring parallel to each other but also one pair of Fe-C-O groups in this plane is parallel, or nearly so.

Some of the dimensions of this molecule can be instructively compared to those in related molecules. The Fe-Fe distance, 2.709 (2) Å, is markedly longer than that (2.523 (1) Å) in $\text{Fe}_2(\text{CO})_9$.¹² This may be due in part to the steric requirements of the diphosphine ligand. The P to P separation is 3.00 (4) Å, but this ligand is probably not the source of any strict constraint on the metal-to-metal distance just because of its flexibility, as already discussed. It is probable that the Fe-Fe distance is longer because bridging CO groups tend to pull metal atoms together and one such group has considerably less effect than three. The present Fe-Fe distance is similar to that in the (tetramethylcyclooctatetraene) $\text{Fe}_2(\text{CO})_5$ molecule, *viz.*, 2.724 (4) Å which also has a single bridging CO group.¹⁵ In cases where there is no bridging CO group, the distances can get very much longer still, depending upon the nature of the ligands. Examples are $\text{C}_8\text{H}_{12}\text{Fe}_2(\text{CO})_6$, 2.764 (3) Å,¹⁶ (azulene) $\text{Fe}_2(\text{CO})_5$, 2.782 (1) Å,¹⁷ and $\text{C}_7\text{H}_8\text{Fe}_2(\text{CO})_6$, 2.866 (1) Å.¹⁸

The mean Fe-CO(terminal) distance (1.79 ± 0.02 Å) is shorter than that (1.835 (3)) in $\text{Fe}_2(\text{CO})_9$. This may be in part the result of replacing two CO ligands by phosphine ligands which are better donors but poorer acceptors, thus enhancing the Fe-C π bonding to the remaining CO groups. However, the drastic structural change may also play a role in altering the Fe-CO(terminal) distance. The mean Fe-CO(bridge) distance,

2.00 ± 0.02 Å, is not significantly different from that in $\text{Fe}_2(\text{CO})_9$, 2.016 (3) Å, although the angle at the bridging carbon atom, 85.6 (5)°, is much larger than that in $\text{Fe}_2(\text{CO})_9$, 77.6 (1)°, because of the longer Fe-Fe distance.

The mean Fe-P distance here, 2.253 (3) Å, is significantly longer than that in $[(\text{Ph}_2\text{P})_2\text{CH}_2]\text{Fe}(\text{CO})_3$,¹⁴ *viz.*, 2.209 (3) Å, where the ligand behaves as a chelate. No simple explanation for this is apparent to us; indeed because the four-membered ring in the latter compound should be strained, one might have expected the opposite relationship. The mean Fe-P distance in the present case is, however, quite similar to those in the isomeric $\text{Fe}_3(\text{CO})_{11}(\text{PPh}_3)$ molecules,¹⁹ *viz.*, 2.24 (1) and 2.25 (1) Å. All of these Fe-P distances, however, are considerably longer than the Fe-P(OPh)₃ distance²⁰ in $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3\text{P}(\text{OPh})_3$ (2.126 (3) Å) as would be expected because of the superior π -acceptor ability of the phosphite ligand. The difference, 0.07–0.12 Å, is entirely comparable to that in the pair of compounds $\text{Cr}(\text{CO})_5\text{PPh}_3$ and $\text{Cr}(\text{CO})_5\text{P}(\text{OPh})_3$, *viz.*, 0.11 Å.²¹

The Molecule in Solution. The structural and dynamical properties of the molecule in solution, as revealed by the ir and nmr spectra (Figure 3), are of exceptional interest. First, it is virtually certain from the ir spectrum that the structure observed in the crystal is preserved in its essentials in solution. This structure, even if it assumes full mirror symmetry, should have six infrared-active terminal CO stretches and one infrared-active bridging CO stretch. This is precisely what is observed. This proves that the symmetry is not higher and that there is no sensible alternative to the conclusion that the structure observed in the crystal is retained as the only significantly populated structure in solution.

The carbon-13 nmr spectrum shows that the molecule is a fluxional one in the sense that carbonyl ligands are scrambled rapidly on the nmr time scale at room temperature. The molecule has four different structural positions for CO ligands, if the idealized mirror symmetry is assumed in making the count. The fact

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that only one signal, with a chemical shift typical of terminal CO ligands,^{6,7,22} is observed²³ indicates that bridge and terminal CO groups are interchanging with each other and that every CO ligand has ready access to each of the four types of structural site. In addition, the 1-2-1 triplet structure shows that all CO ligands spend equal time on each iron atom.²⁴ Thus, the major conclusion is that all seven CO groups are rapidly scrambled over all seven sites at 25°.

The mechanism by which this scrambling occurs is not yet established. The slow exchange limit appears, on the basis of exploratory low temperature measurements, to be well below -100°; thus far difficulties both with solvents and with instrumentation have prevented us from obtaining the data which might permit the assignment of a mechanism.

The most straightforward mechanism would be based upon the now well-established^{3-5,7,25,26} principle that in binuclear species concerted, pairwise opening and closing of bridges is an allowed, facile process. Thus, the singly bridged structure could rearrange to a triply bridged one and then return to a singly bridged

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(23) The possibility that a signal due to the bridging CO group has been missed (in which case scrambling of only the terminal CO ligands among themselves would be indicated) seems remote since (1) the presence of the shiftless relaxation reagent¹¹ should assure essentially equal T_1 's for bridging and terminal CO ligands and (2) in the fast exchange limit a triplet one-sixth the intensity of the observed triplet should have been easily seen.

(24) The possibility that the diphosphine ligand is rapidly interchanging its P-Fe linkages in a manner which does not lead to loss of P-C coupling would also account for the triplet structure but does not seem plausible.

(25) F. A. Cotton, *Bull. Soc. Chim. Fr.*, (1) 2587 (1973).

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one in which the originally bridging CO group is now in a terminal position and one of the previously terminal CO groups which swung into a bridging position remains there. There are several ways to choose the pair of terminal CO groups that are to occupy bridging positions in the unstable, triply bridged intermediate, but in any case several repetitions of the process will completely scramble all of the CO groups.

The main drawback of this mechanism is that the proposed intermediate must be quite strained, as discussed above in explaining why the singly bridged structure is stable. There is simply no way to estimate whether the strain would be so great as to rule out the mechanism just described. If this mechanism is indeed untenable, more elaborate, two-part processes would have to be considered. However, it would be premature to indulge in speculative discussions of these until all possibilities for obtaining further experimental data in or near the slow exchange limit have been explored.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-4422.