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Crystal Structure and Molecular Configuration of $Fe_2(CO)_6[C(CHO)P(Ph_2C_6H_4)]$, a Species with an Ortho-Dimetalated Phenyl Ring

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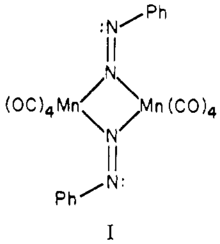
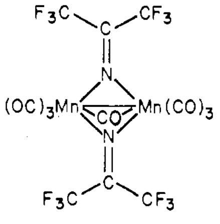
The dinuclear complex $Fe_2(CO)_6[C(CHO)P(Ph_2C_6H_4)]$, prepared previously from the reaction of $Fe_3(CO)_{12}$ and $(Me_3Sn)_2C{=}PPh_3$, has been characterized unambiguously by means of a complete three-dimensional X-ray diffraction study. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^5; No. 14] with $a = 18.886$ (6) Å, $b = 15.898$ (4) Å, $c = 17.699$ (5) Å, $\beta = 115.04$ (2)°, $V = 4814$ (2) Å^3, ρ(obsd) = 1.61 (1) g cm^{-3}, and ρ(calcd) = 1.61 g cm^{-3} for $Z = 8$ and mol wt 582.07. Diffraction data were collected on a Syntex $P2_1$ automated four-circle diffractometer using a coupled θ–2θ scan and Mo Kα radiation. The structure was solved using the multiple tangent formula method of structure solution and was refined via difference-Fourier and least-squares refinement techniques. All atoms (including all hydrogen atoms) were located, the final discrepancy indices being $R_F = 5.0\%$ and $R_{wF} = 4.4\%$ for those 4070 reflections with $I \geq \sigma(I)$ and $4.5° \leq 2\theta \leq 40°$. There are two crystallographically independent molecules within the asymmetric unit; these are chemically equivalent save for small variations in bond lengths for the bridging atoms and slight differences in the orientation of the phenyl rings about their P–C axes. The molecule contains a central $(OC)_3Fe{-}Fe(CO)_3$ unit [Fe–Fe = 2.471 (1) Å for molecule 1 and 2.466 (1) Å for molecule 2] around which is wrapped a $>C(CHO)PPh_2C_6H_4<$ moiety, acting as a doubly bridging ligand. This ligand bonds to the iron atoms through the aldehyde-bearing carbon atom (previously the "ylide" carbon) and through a dehydrogenated carbon atom of a phenyl ring which has undergone ortho dimetalation. The $Fe{-}C(C_6H_4){-}Fe$ bridges are unsymmetrical [Fe–C = 2.001 (6) and 2.159 (5) Å in molecule 1 and 1.986 (6) and 2.185 (6) Å in molecule 2]; in contrast to this, the Fe–C("ylide")–Fe bridges are fairly symmetric, with bond lengths of 2.037 (6) and 2.047 (6) Å in molecule 1 and 2.036 (6) and 2.052 (6) Å in molecule 2. The complex organophosphorus ligand, $>C(CHO)PPh_2C_6H_4<$, may, to a first approximation, be regarded as a zwitterionic species in which a formal positive charge is associated with the phosphorus atom (i.e., this is a phosphonium cation) and a negative charge is delocalized around the five non-iron-bonded carbon atoms of the C_6H_4 fragment. This latter ring thus resembles a Meisenheimer intermediate, as found in nucleophilic aromatic substitution reactions.

Introduction

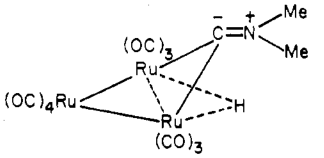
The fission reactions of a variety of organo (group 4B) derivatives of the general formula R_3MX (M = Si, Ge, Sn; X = amine,[1] sulfide,[2] allyl[3]) with polynuclear transition-metal carbonyls (or carbonyl halides) have led to a number of unusual and sometimes unexpected products.[4] In particular, reactions of this type have allowed the introduction of various organonitrogen ligands as bridging ligands in metal–carbonyl complexes. We have previously reported the crystal structures of the species $Mn_2(CO)_8[\mu\text{-}N{=}NPh]_2$[5] (I), $Mn_2(CO)_7[\mu\text{-}N{=}C(CF_3)_2]_2$[6] (II), and $(\mu\text{-}H)Ru_3(CO)_{10}[\mu\text{-}C^-{=}N^+Me_2]$[7] (III), which were prepared in this fashion.



I



II



III

Recently, Abel and Mucklejohn[8] have extended these investigations to the reactions of organophosphorus derivatives of group 4B elements with transition-metal carbonyls. Reaction of the organotin ylide $(Me_3Sn)_2C{=}PPh_3$ with $Fe_3(CO)_{12}$ yields a species of net composition "$Fe_2(CO)_7CPPh_3$", which was initially believed to contain a simple bridging ylide ligand, i.e., $\mu\text{-}C{=}PPh_3$.

However, a single-crystal X-ray diffraction study of this species (vide infra) shows it to have the structure $Fe_2(CO)_6[C(CHO)P(Ph_2C_6H_4)]$. Its formation is represented by eq 1.

$$(Me_3Sn)_2C{=}PPh_3 + Fe_3(CO)_{12} \rightarrow Fe_2(CO)_6[C(CHO)P(Ph_2C_6H_4)] + CO + (Me_3Sn)_2Fe(CO)_4 \quad (1)$$

A preliminary account of this work has appeared previously.[9]

Experimental Section

Orange-brown crystals of the complex were provided by Professor E. W. Abel of the University of Exeter, Exeter, England. The crystal used in the diffraction experiment was irregular in shape, approximating a plate of dimensions 0.4 mm × 0.3 mm × 0.1 mm. The crystal was jammed into a 0.3-mm Lindemann capillary which was subsequently flushed with argon, flame-sealed, and fixed into an aluminum pin on a eucentric goniometer head with beeswax. The goniometer head was fixed to the goniostat, and the crystal was centered in the X-ray beam of a Syntex $P2_1$ four-circle diffractometer under the control of a Data General Nova 1200 computer with 24K of 16-bit work memory and a Diablo disk unit of 1.2 million 16-bit words. (This "in-house" computing system was also used in the subsequent crystallographic structure solution.) The relative orientation and unit cell parameters of the crystal were determined, and the X-ray data were collected by methods described previously.[10] The crystal was found to possess monoclinic symmetry. Inspection of the collected data revealed the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$, consistent with the centrosymmetric space group $P2_1/c$. Specifics for data collection are given in Table I.

Solution and Refinement of Structure

All calculations were performed using the Syntex XTL Structure Determination System, including the aforementioned computing hardware and a locally modified version of the XTL conversational crystallographic program package.[11] Analytical forms of the scattering factors for neutral iron, phosphorus, oxygen, carbon, and hydrogen atoms were taken from those compiled by Cromer and Waber;[12a] real

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Table I. Experimental Data for X-ray Diffraction Study of $Fe_2(CO)_6[C(CHO)P(C_6H_5)_2(C_6H_4)]$

(A) Crystal Data[a]

crystal system: monoclinic
space group: $P2_1/c$ [C_{2h}^5; No. 14]
$a = 18.886$ (6) Å
$b = 15.898$ (4) Å
$c = 17.699$ (5) Å
$\beta = 115.04$ (2)°
$V = 4814$ (2) Å^3
$T = 24.4$ (5) °C
$Z = 8$
mol wt 582.07
ρ(obsd)[b] = 1.613 (5) g cm^{-3}
ρ(calcd) = 1.606 g cm^{-3}

(B) Intensity Data

radiation: Mo Kα ($\bar{\lambda}$ 0.710 73 Å)
monochromator: highly oriented graphite
reflections measd: $+h, +k, \pm l$
max 2θ measd: 40°
min 2θ measd: 4.5°
scan type: coupled θ(crystal)-2θ(counter)
scan speed: variable, 4.0–8.0°/min
scan range: symmetrical, from $[2\theta(K\alpha_1) - 0.9]°$ to $[2\theta(K\alpha_2) + 0.9]°$
bgd measurement: stationary crystal/stationary counter at beginning and end of scan, each for half of the time taken for the scan
standard reflections: 3, measd every 47 reflections; percent variances from the mean: 2.12% for 004, 2.36% for 040, and 2.49% for 400
data set information: 4696 reflections collected, of which 216 were systematic absences and 312 were standard reflections; the remaining data with $F > \sigma(F)$ were averaged,[c] making 4070 symmetry-independent reflections

(C) Data Treatment Parameters:

"ignorance factor": $p = 0.015$
absorption coeff[d]: $\mu = 1.319$ mm^{-1}

[a] Unit cell parameters were determined by a least-squares fit of the setting angles of the unresolved Mo K$\bar{\alpha}$ peaks of 15 high-angle reflections ($2\theta = 25.9$–$32.1°$). [b] Measured by neutral buoyancy of crystals in BaI_2/H_2O solution. [c] The agreement between those symmetry-equivalent reflections which were averaged was $R(I) = 2.0\%$. [d] Eight reflections at various 2θ values were measured at 10° intervals of ψ (the azimuthal angle, corresponding to rotation of the crystal about its diffraction vector for that reflection) from $\psi = 0°$ to $\psi = 350°$. The reflections and their 2θ values and ratio of maximum to minimum intensities, respectively, are as follows: 400 (9.51°, 1.280), 700 (16.68°, 1.281), $90\bar{2}$ (19.87°, 1.256), $92\bar{1}$ (21.17°, 1.286), $31\bar{1}$ (6.96°, 1.277), $63\bar{3}$ (15.13, 1.288), $130\bar{12}$ (33.38°, 1.244), and $40\bar{2}$ (8.68°, 1.256). These reflections were used to correct the intensity data empirically for absorption; for details of the absorption correction, see M. R. Churchill and F. J. Hollander, *Inorg. Chem.*, 16, 2493 (1977).

and imaginary components of anomalous dispersion were applied for all nonhydrogen atoms.[12b]

The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where the weights (w) are given by $[\sigma^2(F) + (pF)^2]^{-1}$; the value of p, the "ignorance factor", is given in Table I. Discrepancy indices are given by

$$R_F = \left[\frac{\sum||F_o| - |F_c||}{\sum|F_o|}\right] \times 100\ (\%)$$

$$R_{wF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2}\right]^{1/2} \times 100\ (\%)$$

The "goodness-of-fit" (GOF) is defined by

$$\mathrm{GOF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{n - v}\right]^{1/2}$$

where n is the number of observations and v is the number of variables in the least-squares refinement.

Normalized structure factor amplitudes, $|E(hkl)|$, were calculated from values of $|F_o(hkl)|$ with the expression

$$|E(hkl)| = |F_o(hkl)|[\epsilon\sum_j f^2\{j, \theta(hkl)\}]^{-1/2}$$

Table II. Statistical Distribution of Normalized Structure Factor Amplitudes

function	obsd	theor[a] centric	theor[a] acentric
$\langle\|E\|\rangle$	0.840	0.798	0.886
$\langle\|E\|^2\rangle$	1.000[b]	1.000	1.000
$\langle\|E^2 - 1\|\rangle$	0.888	0.968	0.736
$\|E\| > 1.0$, %	32.83	31.73	36.79
$\|E\| > 2.0$, %	3.46	4.55	1.89
$\|E\| > 3.0$, %	0.09	0.27	0.01

[a] I. L. Karle, K. S. Dragonette, and S. A. Brenner, *Acta Crystallogr.*, 19, 713 (1965). [b] Fixed by an adjustable scale factor.

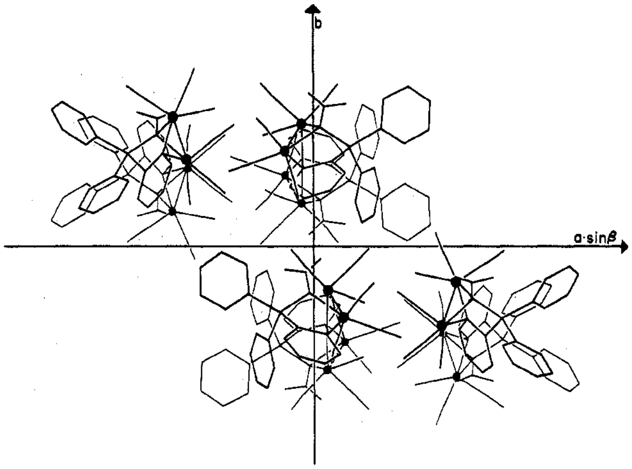


Figure 1. Packing of $Fe_2(CO)_6[C(CHO)P(Ph_2C_6H_4)]$ molecules in the unit cell, as viewed down c.

where j ranges over all atoms in the unit cell, $f\{j, \theta(hkl)\}$ is the scattering factor for atom j at the Bragg angle $\theta(hkl)$, and ϵ is a correction coefficient for the effects of the space group's symmetry.[13] The statistical distribution of $|E|$'s is listed in Table II; reasonable agreement is seen between the oberved values and the theoretical centric case. The E values were used as input to MULTAN, the multiple tangent formula method of structure solution, by Germain, Main, and Woolfson.[14]

The 412 reflections with $|E| > 1.60$ were input to MULTAN and were found to give 6977 Σ_2 relationships with "triple-product" ($|E_h E_{h'} E_{h-h'}|$) values greater than 4.50. The starting set of phases consisted of seven reflections—020 ($|E| = 1.98$), whose phase angle ($\theta = 180°$) was determined as 100% probable from a Σ_1 interaction; the reflections 021 ($|E| = 2.43$, eeo parity), $89\bar{3}$ ($|E| = 2.91$, eoo parity), and 13, 5, $\bar{3}$ ($|E| = 3.38$, ooo parity), which were used to fix the unit cell origin and were assigned phase angles of 0°; and three other reflections, 044 ($|E| = 3.06$), $13\bar{4}$ ($|E| = 3.06$), and 561 ($|E| = 2.78$), which were assigned phase angles of 0 or 180°, thereby generating eight possible tangent formula solutions. The solution with the largest "absolute figure of merit" (1.523), smallest residual (15.23), and largest "combined figure of merit" (3.00) was that for which $\phi(044) = 180°$, $\phi(13\bar{4}) = 0°$, and $\phi(561) = 0°$. This solution was used to phase an "E map", which showed eight large peaks, corresponding to two independent Fe_2CP groups in the asymmetric unit.

Refinement of positional and isotropic thermal parameters for the two independent Fe_2CP groups led to $R_F = 37.2\%$. A series of difference-Fourier syntheses, each successive one being phased by a greater number of atoms, led to the location of all remaining nonhydrogen atoms in the crystallographic asymmetric unit. Full-matrix least-squares refinement of positional and isotropic thermal parameters for these atoms converged with $R_F = 7.7\%$, $R_{wF} = 9.1\%$, and GOF = 2.12.

Refinement was continued using anisotropic thermal parameters for all iron, phosphorus, and oxygen atoms and for the "ylide" carbon atoms of the two independent molecules; the discrepancy indices were thereby reduced to $R_F = 6.2\%$ and $R_{wF} = 7.1\%$. A difference-Fourier synthesis now revealed the positions of all 30 hydrogen atoms, with peak heights ranging from 0.65 e Å^{-3} down to 0.31 e Å^{-3}. Hydrogen

Table III. Positional and Isotropic Thermal Parameters[a,b]

atom	x	y	z	B_{iso}, Å^2	atom	x	y	z	B_{iso}, Å^2
		(A) Molecule 1					(B) Molecule 2		
Fe(11)	0.10709 (5)	−0.10654 (5)	0.25879 (5)		Fe(21)	0.41815 (5)	−0.21309 (6)	0.11911 (5)	
Fe(12)	0.14598 (5)	−0.24140 (5)	0.33468 (5)		Fe(22)	0.46560 (5)	−0.12914 (5)	0.24831 (5)	
P(1)	−0.01959 (9)	−0.21822 (10)	0.27563 (9)		P(2)	0.59673 (9)	−0.19884 (10)	0.23127 (10)	
C(1)	0.0631 (3)	−0.1586 (4)	0.3351 (3)		C(2)	0.5157 (3)	−0.1398 (3)	0.1661 (3)	
C(10)	0.0639 (4)	−0.1104 (4)	0.4049 (4)	3.36 (13)	C(20)	0.5260 (4)	−0.0762 (4)	0.1126 (4)	3.77 (14)
O(10)	0.0069 (2)	−0.0929 (3)	0.4174 (2)		O(20)	0.5837 (2)	−0.0700 (3)	0.0985 (3)	
C(11)	0.1441 (4)	−0.0183 (4)	0.3272 (4)	3.26 (13)	C(21)	0.3722 (4)	−0.1485 (4)	0.0280 (4)	4.14 (15)
O(11)	0.1665 (2)	0.0389 (3)	0.3699 (3)		O(21)	0.3401 (3)	−0.1107 (3)	−0.0316 (3)	
C(12)	0.0277 (4)	−0.0508 (4)	0.1817 (4)	3.13 (13)	C(22)	0.4425 (4)	−0.2962 (4)	0.0653 (4)	3.81 (14)
O(12)	−0.0217 (2)	−0.0141 (3)	0.1310 (3)		O(22)	0.4559 (3)	−0.3482 (3)	0.0296 (3)	
C(13)	0.1771 (4)	−0.0915 (4)	0.2165 (4)	3.79 (14)	C(23)	0.3247 (4)	−0.2500 (4)	0.1061 (4)	3.74 (14)
O(13)	0.2221 (3)	−0.0819 (3)	0.1896 (3)		O(23)	0.2645 (3)	−0.2725 (3)	0.0989 (3)	
C(14)	0.1477 (4)	−0.3194 (4)	0.4091 (4)	3.71 (14)	C(24)	0.5297 (4)	−0.0585 (5)	0.3255 (4)	4.58 (16)
O(14)	0.1552 (3)	−0.3680 (3)	0.4589 (3)		O(24)	0.5654 (3)	−0.0098 (4)	0.3748 (4)	
C(15)	0.2215 (4)	−0.1754 (4)	0.3990 (4)	3.67 (14)	C(25)	0.3965 (4)	−0.0583 (4)	0.1811 (4)	3.79 (14)
O(15)	0.2727 (2)	−0.1349 (3)	0.4457 (3)		O(25)	0.3520 (3)	−0.0076 (3)	0.1411 (3)	
C(16)	0.2119 (4)	−0.3012 (4)	0.3064 (4)	3.72 (14)	C(26)	0.4078 (4)	−0.1494 (4)	0.3047 (4)	3.80 (14)
O(16)	0.2543 (3)	−0.3388 (3)	0.2889 (3)		O(26)	0.3688 (3)	−0.1630 (3)	0.3375 (3)	
C(101)	−0.1042 (3)	−0.1664 (4)	0.1988 (3)	2.59 (12)	C(201)	0.6288 (3)	−0.2817 (4)	0.1835 (3)	2.61 (12)
C(102)	−0.1396 (4)	−0.1015 (4)	0.2222 (4)	3.84 (14)	C(202)	0.6625 (4)	−0.2629 (4)	0.1298 (4)	4.17 (14)
C(103)	−0.2044 (4)	−0.0604 (4)	0.1620 (4)	4.70 (15)	C(203)	0.6790 (4)	−0.3270 (4)	0.0855 (4)	4.63 (15)
C(104)	−0.2325 (4)	−0.0829 (4)	0.0810 (4)	4.81 (16)	C(204)	0.6621 (4)	−0.4088 (4)	0.0954 (4)	4.57 (15)
C(105)	−0.1998 (4)	−0.1464 (4)	0.0562 (4)	4.49 (15)	C(205)	0.6318 (4)	−0.4280 (4)	0.1500 (4)	4.96 (16)
C(106)	−0.1341 (4)	−0.1892 (4)	0.1154 (4)	3.67 (13)	C(206)	0.6146 (4)	−0.3652 (4)	0.1948 (4)	4.35 (15)
C(107)	−0.0570 (3)	−0.2872 (4)	0.3313 (3)	2.64 (12)	C(207)	0.6838 (3)	−0.1437 (4)	0.2994 (4)	3.16 (13)
C(108)	−0.1277 (3)	−0.3277 (4)	0.2870 (3)	3.21 (13)	C(208)	0.7479 (4)	−0.1895 (4)	0.3512 (4)	3.76 (14)
C(109)	−0.1569 (4)	−0.3830 (4)	0.3278 (4)	3.96 (14)	C(209)	0.8155 (4)	−0.1486 (4)	0.4062 (4)	4.52 (15)
C(110)	−0.1165 (4)	−0.3960 (4)	0.4115 (4)	4.49 (15)	C(210)	0.8185 (4)	−0.0634 (5)	0.4092 (4)	4.69 (15)
C(111)	−0.0479 (4)	−0.3554 (4)	0.4564 (4)	4.22 (15)	C(211)	0.7565 (4)	−0.0168 (4)	0.3579 (4)	5.14 (16)
C(112)	−0.0176 (3)	−0.2998 (4)	0.4166 (4)	3.37 (13)	C(212)	0.6884 (4)	−0.0559 (4)	0.3021 (4)	4.00 (14)
C(113)	0.0291 (3)	−0.2737 (4)	0.2236 (3)	2.50 (12)	C(213)	0.5467 (3)	−0.2449 (4)	0.2868 (3)	2.99 (12)
C(114)	0.0090 (4)	−0.3559 (4)	0.1887 (4)	3.80 (14)	C(214)	0.5850 (4)	−0.2773 (4)	0.3699 (4)	4.12 (14)
C(115)	0.0356 (4)	−0.3834 (4)	0.1324 (4)	4.18 (14)	C(215)	0.5445 (4)	−0.3309 (4)	0.3980 (4)	4.51 (15)
C(116)	0.0807 (4)	−0.3306 (4)	0.1088 (4)	3.87 (14)	C(216)	0.4683 (4)	−0.3545 (4)	0.3463 (4)	4.35 (15)
C(117)	0.1022 (3)	−0.2523 (4)	0.1418 (3)	3.33 (13)	C(217)	0.4314 (4)	−0.3245 (4)	0.2668 (4)	3.82 (14)
C(118)	0.0781 (3)	−0.2189 (4)	0.2032 (3)	2.58 (12)	C(218)	0.4674 (3)	−0.2652 (4)	0.2315 (3)	3.08 (12)
H(10)	0.1132	−0.0907	0.4445	4.35	H(20)	0.4849	−0.0368	0.0868	4.74
H(102)	−0.1200	−0.0851	0.2791	4.84	H(202)	0.6745	−0.2061	0.1229	5.15
H(103)	−0.2288	−0.0160	0.1782	5.70	H(203)	0.7020	−0.3136	0.0486	5.64
H(104)	−0.2761	−0.0537	0.0408	5.80	H(204)	0.6715	−0.4520	0.0636	5.56
H(105)	−0.2209	−0.1623	−0.0009	5.48	H(205)	0.6223	−0.4853	0.1582	5.96
H(106)	−0.1105	−0.2334	0.0981	4.66	H(206)	0.5930	−0.3798	0.2328	5.35
H(108)	−0.1562	−0.3174	0.2290	4.20	H(208)	0.7460	−0.2492	0.3496	4.74
H(109)	−0.2048	−0.4118	0.2974	4.96	H(209)	0.8596	−0.1807	0.4416	5.53
H(110)	−0.1366	−0.4341	0.4390	5.49	H(210)	0.8644	−0.0361	0.4476	5.68
H(111)	−0.0207	−0.3650	0.5147	5.22	H(211)	0.7595	0.0429	0.3601	6.13
H(112)	0.0299	−0.2706	0.4478	4.36	H(212)	0.6452	−0.0230	0.2661	4.98
H(114)	−0.0228	−0.3916	0.2050	4.79	H(214)	0.6375	−0.2620	0.4049	5.12
H(115)	0.0231	−0.4385	0.1096	5.17	H(215)	0.5686	−0.3522	0.4533	5.52
H(116)	0.0972	−0.3495	0.0679	4.87	H(216)	0.4413	−0.3922	0.3666	5.35
H(117)	0.1340	−0.2187	0.1240	4.32	H(217)	0.3798	−0.3433	0.2330	4.82

[a] Esd's, shown in parentheses, have been right adjusted to the last digit of the preceding number. These are derived from the inverse of the final least-squares matrix. [b] Hydrogen atoms were fixed in calculated positions and were assigned isotropic thermal parameters of 1.0 + that of their attached carbon (see text).

atoms were now included in the model in idealized positions (d(C–H) = 0.95 Å[15] with appropriate sp^2 geometry). Continued refinement led to final convergence with R_F = 5.0%, R_{wF} = 4.4%, and GOF = 1.627 for the 4070 reflections with $I \geq \sigma(I)$ and $2\theta \leq 40°$ (Mo Kα radiation). The largest shift during the final cycle of refinement was 5% of the associated esd. A final difference-Fourier synthesis had, as its largest feature, a peak of height 0.55 e Å^{-3} at (0.852, −0.388, 0.378); the analysis is thus both correct and complete. The final n:v ratio was 4070:399 or 10.2:1. There was no evidence for secondary extinction; the worst disagreement between $|F_o|$ and $|F_c|$ was $5.9\sigma(|F_o|)$ for the $65\bar{5}$ reflection.

The average value of $\sum w(|F_o| - |F_c|)^2$ showed no significant variations as a function of $|F_o|$, $(\sin\theta)/\lambda$, identity or parity of Miller indices, or sequence number. The weighting scheme is therefore satisfactory.

Final positional and thermal parameters are collected in Tables III and IV.

Results and Discussion

Figure 1 shows the arrangement of molecules within the crystal, as viewed down c. There are two independent molecules of $Fe_2(CO)_6[C(CHO)P(Ph_2C_6H_4)]$ within the unit cell; these are referred to (below) as molecule 1 and molecule 2. The scheme used for labeling atoms (see Figure 2) is such that the first numerical integer indicates the molecule number; the system is otherwise identical from one molecule to the other. Stereoscopic views of the two molecules appear in Figure 3. It will be noticed that there are slight differences in the rotational orientations of phenyl groups about their P–C axes from molecule 1 to molecule 2. This difference assures us that there are truly two independent molecules in the crystallographic asymmetric unit and that we have not accidently chosen a subgroup of the true space group.

Interatomic distances and angles are collected in Tables V and VI; least-squares planes are listed in Table VII.

The complex consists of a central $(OC)_3Fe$–$Fe(CO)_3$ unit around which is wrapped a $>C(CHO)PPh_2C_6H_4<$ moiety, acting as a doubly bridging ligand. This complex organo-

Table IV. Anisotropic Thermal Parameters[a,b]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\langle U\rangle$[c]
				(A) Molecule 1			
Fe(11)	2.76 (4)	2.54 (4)	3.15 (4)	0.02 (4)	1.31 (3)	0.30 (3)	0.174, 0.186, 0.204
Fe(12)	2.68 (4)	2.83 (4)	2.67 (4)	0.24 (4)	0.77 (3)	0.34 (3)	0.168, 0.195, 0.205
P(1)	2.59 (7)	2.48 (8)	2.47 (7)	−0.06 (6)	0.99 (6)	0.12 (6)	0.172, 0.178, 0.187
C(1)	2.8 (3)	2.6 (3)	1.9 (3)	−0.5 (2)	0.9 (2)	0.0 (2)	0.16, 0.16, 0.21
O(10)	5.0 (2)	4.0 (2)	3.9 (2)	0.2 (2)	2.4 (2)	−0.3 (2)	0.20, 0.23, 0.25
O(11)	4.7 (2)	3.8 (2)	5.0 (2)	−1.2 (2)	1.4 (2)	−0.6 (2)	0.19, 0.26, 0.28
O(12)	4.2 (2)	4.4 (2)	5.0 (2)	0.1 (2)	0.9 (2)	1.3 (3)	0.20, 0.24, 0.30
O(13)	6.2 (3)	5.0 (3)	9.4 (3)	0.3 (2)	5.8 (3)	0.7 (2)	0.20, 0.25, 0.36
O(14)	6.1 (3)	5.9 (3)	5.8 (3)	0.6 (2)	2.1 (2)	3.4 (2)	0.18, 0.28, 0.35
O(15)	3.9 (2)	4.4 (3)	5.2 (2)	−0.3 (2)	−0.2 (2)	0.2 (2)	0.19, 0.24, 0.33
O(16)	5.3 (3)	7.0 (3)	5.1 (2)	2.3 (2)	2.3 (2)	0.2 (2)	0.21, 0.25, 0.33
				(B) Molecule 2			
Fe(21)	2.81 (4)	3.25 (5)	3.25 (4)	−0.10 (4)	1.06 (3)	−0.11 (4)	0.187, 0.203, 0.211
Fe(22)	3.18 (4)	2.75 (5)	3.46 (4)	0.22 (4)	1.41 (4)	−0.21 (4)	0.179, 0.203, 0.213
P(2)	2.78 (8)	2.54 (8)	3.40 (8)	−0.05 (7)	1.20 (6)	−0.01 (6)	0.179, 0.188, 0.211
C(2)	3.4 (3)	2.0 (3)	3.3 (3)	0.1 (2)	1.6 (2)	0.3 (2)	0.16, 0.20, 0.21
O(20)	4.8 (2)	4.6 (3)	6.0 (3)	−0.0 (2)	3.0 (2)	1.0 (2)	0.21, 0.25, 0.29
O(21)	6.5 (3)	6.3 (3)	4.6 (3)	−0.5 (2)	0.1 (2)	1.4 (2)	0.21, 0.27, 0.36
O(22)	5.5 (3)	6.9 (3)	5.6 (3)	1.0 (2)	1.4 (2)	−2.8 (2)	0.20, 0.25, 0.37
O(23)	4.0 (2)	8.4 (4)	5.9 (3)	−1.4 (2)	2.3 (2)	−0.1 (2)	0.20, 0.27, 0.33
O(24)	6.4 (3)	8.6 (4)	9.2 (4)	−1.8 (3)	2.7 (3)	−5.8 (3)	0.20, 0.29, 0.44
O(25)	5.7 (3)	5.2 (3)	5.6 (3)	2.4 (2)	2.3 (2)	1.5 (2)	0.19, 0.27, 0.32
O(26)	7.9 (3)	6.0 (3)	7.5 (3)	0.8 (3)	5.6 (3)	0.8 (2)	0.21, 0.27, 0.35

[a] See footnote *a* of Table III. [b] These have units of Å² and they enter the equation for the calculated structure factor in the form $\exp[-0.25(a^{*2}h^2B_{11} + b^{*2}k^2B_{22} + c^{*2}l^2B_{33} + 2a^*b^*hkB_{12} + 2a^*c^*hlB_{13} + 2b^*c^*klB_{23})]$. [c] These values are the root-mean-square amplitudes of vibration (in Å) of the atom along the three principal axes (minor, median, and major, respectively) of its vibrational ellipsoid. For relative orientations, see the figures.

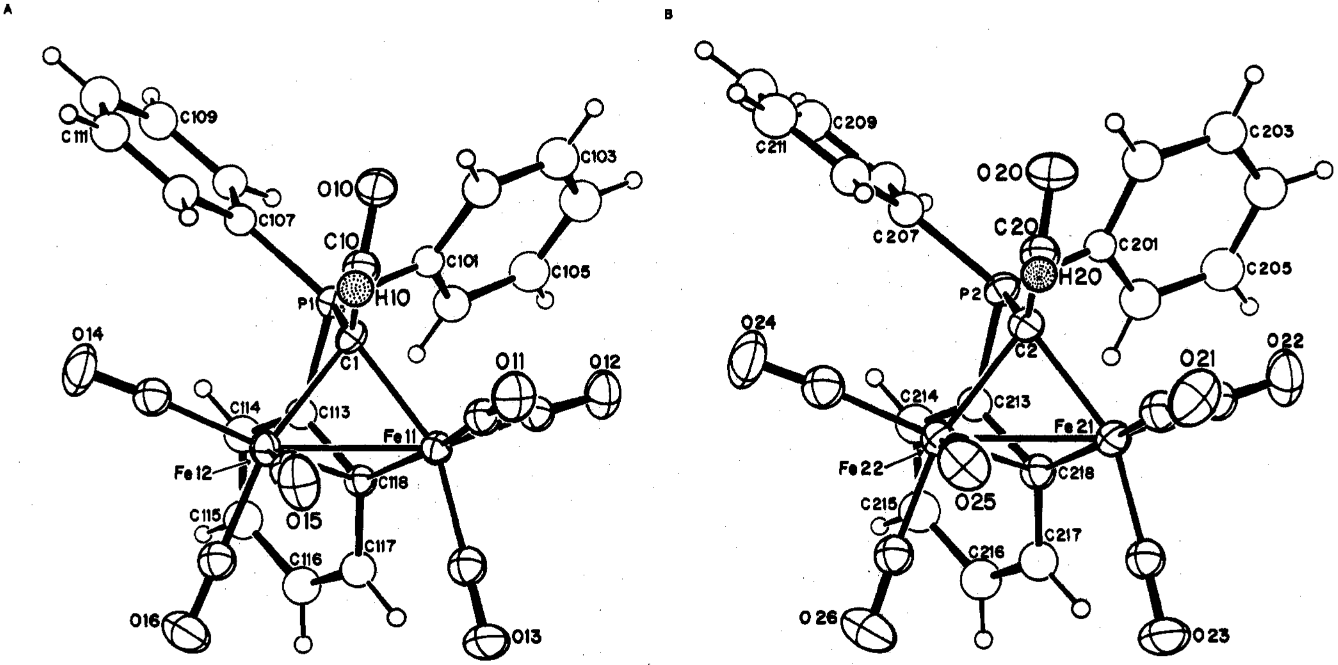
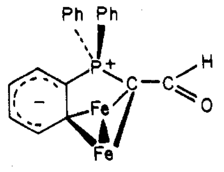


Figure 2. Numbering of atoms in the $Fe_2(CO)_6[C(CHO)P(Ph_2C_6H_4)]$ molecules: (A) molecule 1; (B) molecule 2. Note that the geometry depicted for molecule 2 is that related by inversion to that defined by the list of atomic coordinates; this transformation facilitates direct comparison of the molecules in the same basic enantiomeric form. [ORTEP-II drawings; 30% probability ellipsoids for all atoms except hydrogen atoms.]

phosphorus fragment was formed from the original ylide (>C═PPh$_3$) by a type of hydroformylation reaction in which an aldehydic function has been added to the ylide carbon; this aldehyde group is clearly derived from a carbonyl ligand of the parent $Fe_3(CO)_{12}$ molecule and a hydrogen atom transferred from one of the ortho carbon atoms in one phenyl ring of the PPh_3 system. The dehydrogenated ortho carbon atom has undergone dimetalation and now bridges the two iron atoms.

Individual molecules of $Fe_2(CO)_6[C(CHO)P(Ph_2C_6H_4)]$ are chiral; the crystal, however, consists of an ordered racemic mixture of each of the enantiomeric forms by virtue of crystallographic inversion centers and *c* glide planes.

In valence bond terms, the complex organophosphorus ligand is perhaps best thought of occurring as structure IV,



IV

Table V. Interatomic Bond Distances (Å) and Esd's[a]

molecule 1		molecule 2	
A. Iron–Iron and Iron–Bridging Carbon Distances			
Fe(11)–Fe(12)	2.471 (1)	Fe(21)–Fe(22)	2.466 (1)
	mean: 2.468 ± 0.004 Å[b]		
Fe(11)–C(1)	2.037 (6)	Fe(21)–C(2)	2.036 (6)
Fe(12)–C(1)	2.047 (6)	Fe(22)–C(2)	2.052 (6)
	mean: 2.043 ± 0.008 Å[b]		
Fe(11)–C(118)	2.001 (6)	Fe(21)–C(218)	1.986 (6)
Fe(12)–C(118)	2.159 (5)	Fe(22)–C(218)	2.185 (6)
	mean: 2.083 ± 0.104 Å[b]		
B. Iron–Carbonyl Distances			
Fe(11)–C(11)	1.791 (6)	Fe(21)–C(21)	1.780 (8)
Fe(11)–C(12)	1.778 (7)	Fe(21)–C(22)	1.799 (7)
Fe(11)–C(13)	1.790 (8)	Fe(21)–C(23)	1.795 (7)
Fe(12)–C(14)	1.800 (7)	Fe(22)–C(24)	1.787 (7)
Fe(12)–C(15)	1.749 (7)	Fe(22)–C(25)	1.753 (7)
Fe(12)–C(16)	1.798 (7)	Fe(22)–C(26)	1.793 (7)
	mean: 1.784 ± 0.017 Å[b]		
C. Phosphorus–Carbon Distances			
P(1)–C(1)	1.748 (6)	P(2)–C(2)	1.749 (6)
	mean: 1.748 ± 0.001 Å[b]		
P(1)–C(101)	1.800 (6)	P(2)–C(201)	1.803 (6)
P(1)–C(107)	1.806 (6)	P(2)–C(207)	1.802 (6)
P(1)–C(113)	1.785 (6)	P(2)–C(213)	1.784 (6)
	mean: 1.797 ± 0.010 Å[b]		
D. Carbon–Oxygen Distances			
C(10)–O(10)	1.218 (9)	C(20)–O(20)	1.220 (9)
	mean: 1.219 ± 0.001 Å[b]		
C(11)–O(11)	1.144 (8)	C(21)–O(21)	1.141 (8)
C(12)–O(12)	1.144 (8)	C(22)–O(22)	1.133 (9)
C(13)–O(13)	1.147 (9)	C(23)–O(23)	1.147 (10)
C(14)–O(14)	1.134 (8)	C(24)–O(24)	1.147 (9)
C(15)–O(15)	1.165 (8)	C(25)–O(25)	1.163 (8)
C(16)–O(16)	1.143 (9)	C(26)–O(26)	1.135 (9)
	mean: 1.145 ± 0.010 Å[b]		
E. Carbon–Carbon Distances			
a. sp^2 Carbon–sp^3 Carbon			
C(1)–C(10)	1.448 (8)	C(2)–C(20)	1.453 (9)
C(113)–C(118)	1.424 (8)	C(213)–C(218)	1.437 (9)
C(117)–C(118)	1.446 (8)	C(217)–C(218)	1.448 (9)
	mean: 1.443 ± 0.011 Å[b]		
b. sp^2 Carbon–sp^2 Carbon			
C(101)–C(102)	1.384 (9)	C(201)–C(202)	1.382 (9)
C(102)–C(103)	1.400 (10)	C(202)–C(203)	1.398 (10)
C(103)–C(104)	1.348 (9)	C(203)–C(204)	1.369 (10)
C(104)–C(105)	1.350 (10)	C(204)–C(205)	1.350 (10)
C(105)–C(106)	1.415 (9)	C(205)–C(206)	1.397 (10)
C(106)–C(101)	1.387 (8)	C(206)–C(201)	1.387 (9)
C(107)–C(108)	1.388 (9)	C(207)–C(208)	1.378 (9)
C(108)–C(109)	1.392 (9)	C(208)–C(209)	1.395 (10)
C(109)–C(110)	1.365 (9)	C(209)–C(210)	1.356 (10)
C(110)–C(111)	1.363 (10)	C(210)–C(211)	1.359 (10)
C(111)–C(112)	1.395 (9)	C(211)–C(212)	1.393 (10)
C(112)–C(107)	1.387 (8)	C(212)–C(207)	1.397 (9)
C(113)–C(114)	1.427 (8)	C(213)–C(214)	1.432 (8)
C(114)–C(115)	1.364 (9)	C(214)–C(215)	1.373 (10)
C(115)–C(116)	1.381 (10)	C(215)–C(216)	1.390 (10)
C(116)–C(117)	1.362 (9)	C(216)–C(217)	1.365 (9)
	mean: 1.382 ± 0.021 Å[b]		

[a] See footnote *a* of Table III. [b] The errors associated with the mean values were calculated from $\sigma = [\Sigma_n(\bar{x} - x_i)^2/(N-1)]^{1/2}$, where $\bar{x}$ is the mean, x_i is the value of the *i*th observation, and *N* is the number of observations taken.

Table VI. Intramolecular Angles (deg) and Esd's[a]

molecule 1		molecule 2	
A. Iron–Iron–Carbon Angles			
Fe(12)–Fe(11)–C(1)	52.97 (16)	Fe(22)–Fe(21)–C(2)	53.19 (17)
Fe(11)–Fe(12)–C(1)	52.59 (16)	Fe(21)–Fe(22)–C(2)	52.62 (17)
	mean: 52.83 ± 0.30°[b]		
Fe(12)–Fe(11)–C(118)	56.58 (16)	Fe(22)–Fe(21)–C(218)	57.60 (18)
Fe(11)–Fe(12)–C(118)	50.67 (15)	Fe(21)–Fe(22)–C(218)	50.10 (16)
	mean: 53.74 ± 3.90°[b]		
Fe(12)–Fe(11)–C(11)	111.77 (22)	Fe(22)–Fe(21)–C(21)	111.77 (24)
Fe(12)–Fe(11)–C(12)	144.06 (22)	Fe(22)–Fe(21)–C(22)	144.55 (23)
Fe(12)–Fe(11)–C(13)	103.95 (22)	Fe(22)–Fe(21)–C(23)	104.45 (23)
Fe(11)–Fe(12)–C(14)	154.81 (22)	Fe(21)–Fe(22)–C(24)	155.82 (25)
Fe(11)–Fe(12)–C(15)	78.82 (23)	Fe(21)–Fe(22)–C(25)	81.06 (23)
Fe(11)–Fe(12)–C(16)	112.90 (22)	Fe(21)–Fe(22)–C(26)	110.56 (22)
B. Carbon–Iron–Carbon Angles			
C(1)–Fe(11)–C(118)	81.94 (23)	C(2)–Fe(21)–C(218)	82.56 (24)
C(1)–Fe(12)–C(118)	77.96 (22)	C(2)–Fe(22)–C(218)	77.48 (23)
C(1)–Fe(11)–C(11)	91.24 (27)	C(2)–Fe(21)–C(21)	92.82 (29)
C(1)–Fe(11)–C(12)	105.28 (27)	C(2)–Fe(21)–C(22)	104.25 (28)
C(1)–Fe(11)–C(13)	155.83 (27)	C(2)–Fe(21)–C(23)	156.59 (28)
C(1)–Fe(12)–C(14)	102.52 (27)	C(2)–Fe(22)–C(24)	103.21 (30)
C(1)–Fe(12)–C(15)	91.48 (28)	C(2)–Fe(22)–C(25)	90.39 (29)
C(1)–Fe(12)–C(16)	164.06 (27)	C(2)–Fe(22)–C(26)	162.26 (28)
C(11)–Fe(11)–C(12)	95.14 (30)	C(21)–Fe(21)–C(22)	94.57 (32)
C(11)–Fe(11)–C(13)	91.83 (31)	C(21)–Fe(21)–C(23)	89.80 (32)
C(12)–Fe(11)–C(13)	98.31 (31)	C(22)–Fe(21)–C(23)	98.71 (32)
C(14)–Fe(12)–C(15)	100.37 (32)	C(24)–Fe(22)–C(25)	100.61 (34)
C(14)–Fe(12)–C(16)	92.27 (31)	C(24)–Fe(22)–C(26)	93.54 (33)
C(15)–Fe(12)–C(16)	91.67 (32)	C(25)–Fe(22)–C(26)	92.26 (32)
	mean: 94.92 ± 3.70°[b]		

Table VI (*Continued*)

molecule 1		molecule 2	
	C. Angles about Bridging Carbons		
Fe(11)-C(1)-Fe(12)	74.4 (2)	Fe(21)-C(2)-Fe(22)	74.2 (2)
Fe(11)-C(1)-P(1)	109.4 (3)	Fe(21)-C(2)-P(2)	110.5 (3)
Fe(12)-C(1)-P(1)	98.0 (3)	Fe(22)-C(2)-P(2)	96.5 (3)
Fe(11)-C(1)-C(10)	119.4 (4)	Fe(21)-C(2)-C(20)	118.6 (4)
Fe(12)-C(1)-C(10)	127.7 (4)	Fe(22)-C(2)-C(20)	129.3 (4)
P(1)-C(1)-C(10)	119.0 (4)	P(2)-C(2)-C(20)	118.9 (4)
Fe(11)-C(118)-Fe(12)	72.8 (2)	Fe(21)-C(218)-Fe(22)	72.3 (2)
	mean: 72.6 ± 0.4°[b]		
	D. Angles about Phosphorus		
C(1)-P(1)-C(101)	119.2 (3)	C(2)-P(2)-C(201)	117.1 (3)
C(1)-P(1)-C(107)	117.2 (3)	C(2)-P(2)-C(207)	118.4 (3)
C(1)-P(1)-C(113)	93.1 (3)	C(2)-P(2)-C(213)	93.7 (3)
C(101)-P(1)-C(107)	105.2 (3)	C(201)-P(2)-C(207)	106.1 (3)
C(101)-P(1)-C(113)	108.8 (3)	C(201)-P(2)-C(213)	108.6 (3)
C(107)-P(1)-C(113)	112.8 (3)	C(207)-P(2)-C(213)	112.2 (3)
	E. Angles about Carbonyl Carbons		
C(1)-C(10)-O(10)	125.8 (6)	C(2)-C(20)-O(20)	124.5 (6)
	mean: 125.2 ± 0.9°[b]		
Fe(11)-C(11)-O(11)	178.7 (6)	Fe(21)-C(21)-O(21)	176.3 (6)
Fe(11)-C(12)-O(12)	177.7 (6)	Fe(21)-C(22)-O(22)	178.1 (6)
Fe(11)-C(13)-O(13)	179.8 (6)	Fe(21)-C(23)-O(23)	178.6 (6)
Fe(12)-C(14)-O(14)	174.4 (6)	Fe(22)-C(24)-O(24)	174.4 (7)
Fe(12)-C(15)-O(15)	175.9 (6)	Fe(22)-C(25)-O(25)	175.4 (6)
Fe(12)-C(16)-O(16)	179.4 (6)	Fe(22)-C(26)-O(26)	177.2 (6)
	mean: 177.2 ± 1.9°[b]		
	F. Angles within the Dimetalated Ring		
C(113)-C(118)-C(117)	114.3 (5)	C(213)-C(218)-C(217)	113.4 (5)
	mean: 113.8 ± 0.6°[b]		
C(118)-C(113)-C(114)	122.2 (5)	C(218)-C(213)-C(214)	123.2 (6)
C(113)-C(114)-C(115)	119.8 (6)	C(213)-C(214)-C(215)	118.5 (6)
C(114)-C(115)-C(116)	119.5 (6)	C(214)-C(215)-C(216)	120.6 (6)
C(115)-C(116)-C(117)	122.4 (6)	C(215)-C(216)-C(217)	121.3 (6)
C(116)-C(117)-C(118)	121.7 (6)	C(216)-C(217)-C(218)	122.9 (6)
	mean: 121.2 ± 1.6°[b]		
	G. Angles within Phenyl Rings		
C(106)-C(101)-C(102)	118.8 (6)	C(206)-C(201)-C(202)	118.7 (6)
C(101)-C(102)-C(103)	119.9 (6)	C(201)-C(202)-C(203)	120.3 (6)
C(102)-C(103)-C(104)	120.6 (7)	C(202)-C(203)-C(204)	120.2 (6)
C(103)-C(104)-C(105)	121.0 (7)	C(203)-C(204)-C(205)	119.9 (7)
C(104)-C(105)-C(106)	119.9 (6)	C(204)-C(205)-C(206)	121.1 (7)
C(105)-C(106)-C(101)	119.8 (6)	C(205)-C(206)-C(201)	119.8 (6)
C(112)-C(107)-C(108)	119.5 (6)	C(212)-C(207)-C(208)	118.7 (6)
C(107)-C(108)-C(109)	119.9 (6)	C(207)-C(208)-C(209)	120.4 (6)
C(108)-C(109)-C(110)	119.7 (6)	C(208)-C(209)-C(210)	120.2 (7)
C(109)-C(110)-C(111)	121.2 (6)	C(209)-C(210)-C(211)	120.6 (7)
C(110)-C(111)-C(112)	119.9 (6)	C(210)-C(211)-C(212)	120.4 (7)
C(111)-C(112)-C(107)	119.6 (6)	C(211)-C(212)-C(207)	119.7 (6)
	mean: 120.0 ± 0.7°[b]		

[a] See footnote *a* of Table III. [b] See footnote *b* Table V.

with the phosphorus atom being the center for a phosphonium cation. Relevant distances in molecule 1 are P(1)–C(101) = 1.800 (6) Å, P(1)–C(107) = 1.806 (6) Å, P(1)–C(113) = 1.785 (6) Å, and P(1)–C(1) = 1.748 (6) Å; for molecule 2, the analogous distances are P(2)–C(201) = 1.803 (6) Å, P(2)–C(207) = 1.802 (6) Å, P(2)–C(213) = 1.784 (6) Å, and P(2)–C(2) = 1.749 (6) Å. Angles about the phosphorus atom (See Table VI, section D) show significant deviations from the idealized tetrahedral value of 109.47°, with ranges of 93.1 (3)–119.2 (3)° for angles at P(1) and 93.7 (3)–118.4 (3)° for angles at P(2). In each case the smallest angle is the C("ylide")–P–C(C_6H_4) bond angle; this angle is, of course, reduced due to the chelation of the iron atoms by the aldehyde-bearing carbon and the dehydrogenated carbon of the C_6H_4 ring.

The formal positive charge on the phosphonium ion is counterbalanced by a formal negative charge delocalized over the five sp^2-hybridized carbon atoms of the C_6H_4 ring. Conjugation about the six-membered ring is broken by dimetalation of the ortho position (specifically, of C(118) in molecule 1 and C(218) in molecule 2); this ring thus approximates a Meisenheimer complex found in nucleophilic aromatic substitution reactions (cf. structure VI in the sequence V → VI → VII).

V VI VII

In keeping with this view, the C_6H_4 systems each deviate only slightly from planarity. In molecule 1, C(118) lies −0.031 (6) Å from the planar system (root-mean-square deviation 0.008 Å) defined by atoms C(113)–C(117); in molecule 2, C(218) lies −0.037 (6) Å from the planar system (root-

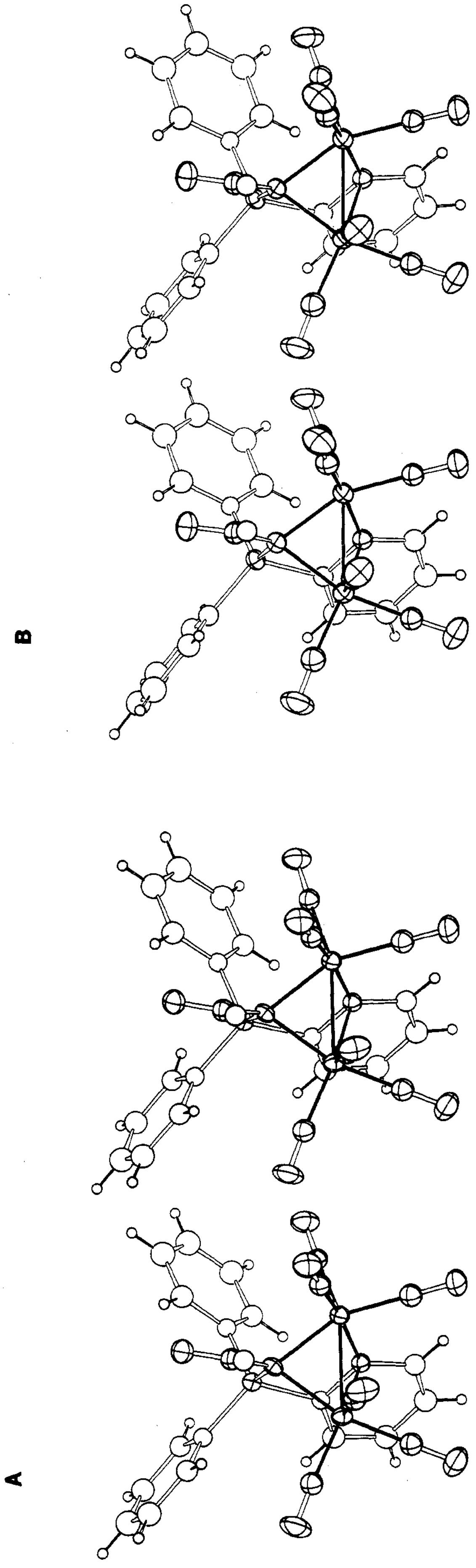


Figure 3. Stereoscopic diagrams of the $Fe_2(CO)_6[C(CHO)P(Ph_2C_6H_4)]$ molecules: (A) molecule 1; (B) molecule 2 (inverted as in Figure 2B). [ORTEP-II drawings; 30% probability ellipsoids.]

Table VII. Least-Squares Planes (and Esd's)[a] and Dihedral Angles

atom[b]	dev,[c] Å	atom[b]	dev,[c] Å
(A) Molecule 1			
Plane 1a: $-0.4024X - 0.4753Y - 0.7824Z = -2.4757$			
Fe(11)*	0.000	P(1)	1.646 (2)
Fe(12)*	0.000	C(10)	−1.035 (6)
C(1)*	0.000	O(10)	−0.854 (4)
Plane 1b: $0.9901X - 0.0029Y - 0.1403Z = -0.4941$			
Fe(11)*	0.000	C(118)*	0.000
Fe(12)*	0.000		
Plane 1c: $-0.5573X + 0.3715Y - 0.7425Z = -3.6550$			
C(113)*	0.003 (6)	C(116)*	0.012 (6)
C(114)*	−0.001 (6)	C(117)*	−0.007 (6)
C(115)*	−0.008 (7)	C(118)	−0.031 (6)
Plane 1d: $0.7400X + 0.6568Y - 0.1449Z = -4.7586$			
C(101)*	0.001 (6)	C(104)*	0.006 (8)
C(102)*	−0.000 (7)	C(105)*	−0.005 (7)
C(103)*	−0.004 (7)	C(106)*	0.001 (7)
Plane 1e: $0.6308X - 0.7559Y - 0.1752Z = 0.2637$			
C(107)*	0.013 (6)	C(110)*	0.006 (7)
C(108)*	−0.010 (6)	C(111)*	−0.001 (7)
C(109)*	0.001 (7)	C(112)*	−0.009 (6)
(B) Molecule 2			
Plane 2a: $-0.3501X + 0.7819Y - 0.5157Z = -6.0865$			
Fe(21)*	0.000	P(2)	−1.637 (2)
Fe(22)*	0.000	C(20)	1.025 (6)
C(2)*	0.000	O(20)	0.801 (4)
Plane 2b: $0.9971X + 0.0750Y - 0.0139Z = 6.7039$			
Fe(21)*	0.000	C(218)*	0.000
Fe(22)*	0.000		
Plane 2c: $0.5350X - 0.7762Y - 0.3338Z = 5.8641$			
C(213)*	−0.003 (6)	C(216)*	0.000 (7)
C(214)*	0.006 (7)	C(217)*	0.002 (6)
C(215)*	−0.005 (7)	C(218)	−0.037 (6)
Plane 2d: $-0.6646X + 0.0928Y - 0.7414Z = -9.5893$			
C(201)*	0.013 (6)	C(204)*	0.017 (7)
C(202)*	−0.011 (7)	C(205)*	−0.009 (7)
C(203)*	−0.006 (7)	C(206)*	−0.010 (7)
Plane 2e: $0.7157X - 0.0027Y - 0.6984Z = 4.2971$			
C(207)*	−0.007 (6)	C(210)*	−0.008 (7)
C(208)*	0.003 (7)	C(211)*	0.002 (8)
C(209)*	0.005 (7)	C(212)*	0.006 (7)

Dihedral Angles

plane	to plane	angle, deg	plane	to plane	angle, deg
1a	1b	106.70	2a	2b	106.45
1a	1c	51.51	2a	2c	51.53
1b	1c	116.62	2b	2c	118.67
1c	1d	93.48	2c	2d	79.62
1c	1e	120.16	2c	2e	128.17
1d	1e	90.25	2d	2e	92.41

[a] Equations of planes are expressed in orthonormal (Å) coordinates (X, Y, Z) which are related to the fractional coordinates (x, y, z) by the transformation

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} a & 0 & c\cos\beta \\ 0 & b & 0 \\ 0 & 0 & c\sin\beta \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

[b] Those atoms marked by an asterisk were given unit weight in the corresponding plane; those unmarked were given zero weight.

[c] See footnote a of Table III.

mean-square deviation 0.004 Å) defined by atoms C(213)–C(217). A consideration of angles within the C_6H_4 system shows the internal angle at the dimetalated carbon atom to be reduced toward the regular tetrahedral value. Thus C(113)–C(118)–C(117) = 114.3 (5)° and C(213)–C(218)–C(217) = 113.4 (5)°. Other angles within this carbocyclic system average 121.2 ± 1.6° (see Table VI, section F). Carbon–carbon bond lengths involving the dimetalated carbon atoms are C(113)–C(118) = 1.424 (8) Å and C(118)–C(117) = 1.446 (8) Å for molecule 1 and C(213)–C(218) = 1.437 (9) Å and C(218)–C(217) = 1.448 (9) Å for molecule 2.

The iron–$C(C_6H_4)$–iron bridges are each unsymmetrical; for molecule 1, Fe(11)–C(118) = 2.001 (6) Å and Fe(12)–C(118) = 2.159 (5) Å, with the angle Fe(11)–C(118)–Fe(12) being 72.8 (2)°, and for molecule 2, Fe(21)–C(218) = 1.986 (6) Å, Fe(22)–C(218) = 2.185 (6) Å, and Fe(21)–C(218)–Fe(22) = 72.3 (2)°. However, the iron–C("ylide")–iron bridges are rather more regular; in molecule 1, Fe(11)–C(1) = 2.037 (6) Å, Fe(12)–C(1) = 2.047 (6) Å, with Fe(11)–C(1)–Fe(12) = 74.4 (2)°, and in molecule 2, Fe(21)–C(2) = 2.036 (6) Å, Fe(22)–C(2) = 2.052 (6) Å, and Fe(21)–C(2)–Fe(22) = 74.2 (2)°.

As can clearly be seen in the stereodiagrams (Figure 3a and b), the $(OC)_3Fe$–$Fe(CO)_3$ backbone of each molecule takes up an irregular conformation, rather close to eclipsed, but with obvious perturbations. The two independent iron–iron bond lengths Fe(11)–Fe(12) = 2.471 (1) Å and Fe(21)–Fe(22) = 2.466 (1) Å, differ by 0.005 Å or approximately 3.5σ. This is reasonable, in view of the different iron–(bridging atom) distances from one molecule to another.

The present complex is known to be diamagnetic and (in common with most iron–carbonyl complexes) is expected to obey the EAN (effective atomic number) rule. Conventional electron counting, however, leads to only 17 electrons per iron atom. Our initial thought was that (despite the reasonable appearance of eq 1) there might be hydride ligands bridging the iron atoms. Detailed difference-Fourier maps, based on data with successively sharp cutoffs as a function of $(\sin\theta)/\lambda$, revealed no such features. We are forced to conclude, then, that obtention of the appropriate noble gas configuration is brought about by some other method. The two obvious possibilities are as follows: (i) that there is an iron–iron double bond or (ii) that the bridging dimetalated phenyl group acts, in some way, as a four-electron donor to the Fe–Fe system. We see no way of distinguishing uniquely between these possibilities.

The aldehyde groups on the "ylide" carbon atoms do not lie strictly perpendicular to their appropriate iron–iron vectors but are bent slightly to the right (cf. Figure 3a and b), presumably to counterbalance the contrary displacement of the phosphorus atoms, the precise positions of which are strongly influenced by the asymmetry in the Fe(11)–C(118)–Fe(12) and Fe(21)–C(218)–Fe(22) systems. These aldehyde groups have the expected planar geometry; appropriate interatomic parameters include C(1)–C(10) = 1.448 (8) Å, C(10)–O(10) = 1.218 (9) Å, and C(1)–C(10)–O(10) = 125.8 (6)° (molecule 1) and C(2)–C(20) = 1.453 (9) Å, C(20)–O(20) = 1.220 (9) Å, and C(2)–C(20)–O(20) = 124.5 (6)° (molecule 2).

All other features of the molecular geometry (i.e., carbonyl and phenyl parameters) are normal (see Tables V–VII).

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Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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