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Structure of an Acetylcarbonylcyclopentadienyliron Complex with a Phosphine Ligand. I. (η-MeC$_5$H$_4$)Fe(CO)(COMe)(PPh$_2$Et)

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Abstract. The structure of acetyl(carbonyl)(ethyldiphenylphosphine)(η-methylcyclopentadienyl)iron, [(η-MeC$_5$H$_4$)Fe(CO)(COMe)(PPh$_2$Et)], [Fe(C$_6$H$_7$)(C$_2$H$_3$O)(C$_{14}$H$_{15}$P)(CO)], is reported. $M_r = 420{\cdot}25$, orthorhombic, $Pna2_1$, $a = 16{\cdot}094\,(5)$, $b = 12{\cdot}515\,(5)$, $c = 10{\cdot}459\,(4)$ Å, $V = 2106{\cdot}6\,(13)$ Å^3, $Z = 4$, $D_m = 1{\cdot}33$, $D_x = 1{\cdot}325$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 8{\cdot}07$ cm^{-1}, $F(000) = 880$, $T = 293$ K, $R(F) = 0{\cdot}061$, $wR = 0{\cdot}047$ for 1840 reflections with $F > 3\sigma(F)$. The structure shows that the geometry around Fe is pseudooctahedral. There is no ring slippage of the methylcyclopentadienyl ring. The Fe—P bond distance is 2·200 (2) Å, supporting the assumption that ethyldiphenylphosphine is a pure σ-donor ligand. The torsion angle O2—C2—Fe—(CO) (C2 = acetyl carbon) is 43° (*anti*), substantially different from the theoretically calculated value of 0°.

Introduction. The separation of σ and π effects in the bonding of phosphorus ligands to transition metals has been the subject of a considerable number of inorganic and organometallic studies involving IR, ^{13}C NMR, UV, electrochemistry and X-rays (Rahman, Liu, Prock & Giering, 1987). We have recently proposed a model of transition metal—phosphorus bonding in complexes containing various phosphine ligands, based on correlation between their redox properties and their carbonyl stretching frequencies (Rahman, Liu, Eriks, Prock & Giering, 1989). According to this model the patterns of correlation show that complexes with metal—phosphorus single bonds and complexes with metal—phosphorus multiple bonds form distinct groups. A crucial test of this model is the length of the metal—phosphorus bond. The present structure is the first of a systematic study of complexes of types [(η-MeC$_5$H$_4$)Fe(CO)(COMe)L] and [(η-C$_5$H$_5$)Fe(CO)(COMe)L] (L = phosphorus ligand) in which the Fe—P bond distance is of particular interest.

Experimental. The complex was prepared by refluxing [(η-MeC$_5$H$_4$)Fe(CO)$_2$Me] and excess ligand, PPh$_2$Et, in acetronitrile solution under nitrogen (Green & Westlake, 1971). Dark orange crystals of the title compound were obtained by slow crystallization from the acetonitrile solution. Their density was determined by flotation in mixtures of benzene and carbon tetrachloride. A parallelepiped-shaped crystal was mounted on a glass fiber with epoxy cement and placed on a Syntex $P2_1$ automated diffractometer, equipped with an Mo tube and Nb filter. Lattice parameters were calculated from 15 reflections in a 2θ range of 10·5–25·7°. Details for data collection are given in Table 1. Intensities were

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Table 1. *Data collection parameters*

Crystal size (mm)	0·28 × 0·30 × 0·46
Scan method	$\omega/2\theta$
Scan range (°)	2·0–2·3
Scan rate (° min^{-1})	2·02–29·30
2θ range (°)	4·0–55·0
Reflections collected (h,k,l)	0→19, 0→16, −14→14
$R_{\rm int}$	0·066
Number of reflections measured	5402
Number of unique reflections with $F > 3\sigma$	1840
Number of parameters refined	244
Standard reflections (hkl)	100; 136; 463
Decay of standards	None
Max./min. transmission	0·8199/0·7496
$R(F)$	0·061
wR	0·047
Goodness of fit	1·556
$\Delta\rho_{\rm min}$ (e Å^{-3})	−0·55
$\Delta\rho_{\rm max}$ (e Å^{-3})	0·7
Max. shift/e.s.d.	0·01

Table 2. *Positional and thermal parameters of atoms in* (η-MeC$_5$H$_4$)(CO)Fe(COMe)(PPh$_2$Et)

	x	y	z	$U_{\rm eq}$(Å^2 × 10^3)*
Fe	0·0492 (1)	0·1576 (1)	0·0000	42·7 (4)
P	0·0490 (1)	0·3170 (1)	0·0886 (2)	40 (1)
C1	0·0097 (5)	0·2007 (6)	−0·1402 (8)	56 (3)
C2	−0·0582 (6)	0·1248 (6)	0·0711 (8)	65 (3)
C3	−0·1209 (6)	0·0658 (8)	−0·0078 (16)	119 (5)
C4	0·1591 (5)	0·0893 (7)	−0·0790 (9)	57 (3)
C5	0·0961 (8)	0·0091 (8)	−0·0599 (11)	69 (4)
C6	0·0789 (7)	0·0034 (8)	0·0709 (11)	71 (4)
C7	0·1266 (6)	0·0823 (7)	0·1325 (8)	59 (3)
C8	0·1762 (5)	0·1331 (6)	0·0409 (8)	52 (3)
C9	0·1999 (6)	0·1134 (7)	−0·2024 (10)	88 (4)
C10	0·1078 (4)	0·4214 (4)	0·0063 (9)	41 (2)
C11	0·1449 (5)	0·4013 (6)	−0·1117 (7)	47 (3)
C12	0·1881 (5)	0·4819 (7)	−0·1743 (8)	60 (3)
C13	0·1942 (5)	0·5824 (6)	−0·1222 (8)	58 (3)
C14	0·1579 (5)	0·6021 (5)	−0·0068 (11)	62 (3)
C15	0·1144 (5)	0·5255 (6)	0·0581 (8)	58 (3)
C16	0·0943 (5)	0·3207 (5)	0·2500 (6)	46 (3)
C17	0·0460 (6)	0·2895 (7)	0·3527 (7)	72 (3)
C18	0·0804 (9)	0·2844 (8)	0·4746 (10)	89 (5)
C19	0·1612 (9)	0·3108 (6)	0·4907 (11)	91 (4)
C20	0·2111 (6)	0·3388 (6)	0·3923 (10)	75 (4)
C21	0·1778 (5)	0·3437 (6)	0·2692 (7)	55 (3)
C22	−0·0508 (5)	0·3856 (6)	0·1104 (9)	60 (3)
C23	−0·0960 (5)	0·4070 (6)	−0·0128 (14)	81 (4)
O1	−0·0164 (4)	0·2259 (5)	−0·2408 (6)	85 (3)
O2	−0·0836 (4)	0·1438 (5)	0·1779 (6)	82 (3)

$^*U_{\rm eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

Table 3. *Bond distances* (Å) *and selected angles* (°) *in* (η-MeC$_5$H$_4$)(CO)Fe(COMe)(PPh$_2$Et)

Fe—P	2·200 (2)	C5—C6	1·397 (11)
Fe—C1	1·687 (9)	C6—C7	1·406 (14)
Fe—C2	1·925 (10)	C7—C8	1·400 (10)
Fe—C4	2·130 (8)	C10—C11	1·394 (11)
Fe—C5	2·101 (9)	C10—C15	1·416 (9)
Fe—C6	2·122 (10)	C11—C12	1·389 (10)
Fe—C7	2·088 (8)	C12—C13	1·374 (10)
Fe—C8	2·110 (8)	C13—C14	1·363 (13)
P—C10	1·829 (7)	C14—C15	1·367 (11)
P—C16	1·840 (7)	C16—C17	1·383 (10)
P—C22	1·835 (8)	C16—C21	1·389 (10)
C1—O1	1·177 (9)	C17—C18	1·392 (13)
C2—O2	1·213 (10)	C18—C19	1·353 (14)
C2—C3	1·499 (14)	C19—C20	1·352 (15)
C4—C8	1·396 (11)	C20—C21	1·396 (11)
C4—C5	1·440 (14)	C22—C23	1·504 (15)
C4—C9	1·479 (12)		
C1—Fe—C2	93·7 (4)	C10—P—C22	100·2 (3)
C1—Fe—P	94·3 (3)	C16—P—C22	102·8 (4)
C2—Fe—P	91·6 (3)	Fe—C1—O1	176·6 (8)
Fe—P—C10	116·7 (3)	O2—C2—C3	112·1 (9)
Fe—P—C16	114·1 (2)	Fe—C2—O2	128·0 (7)
Fe—P—C22	118·6 (3)	Fe—C2—C3	119·8 (8)
C10—P—C16	102·0 (4)	P—C22—C23	113·6 (6)

Cyclopentadienyl ring C—C—C
Range: 106·7–108·9; av: 108·0°
Phenyl rings C—C—C
Range: 118·2–122·7; av: 120·0°

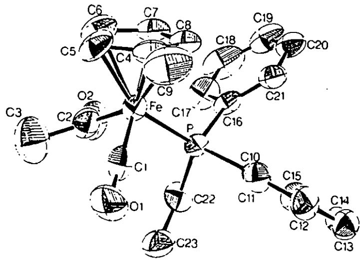

Fig. 1. Geometry of the complex and numbering of the atoms. The thermal ellipsoids are scaled to the 50% probability level.

corrected for Lorentz–polarization and absorption effects. The positions of the Fe and P atoms were determined from a Patterson map. Since the z axis in space group $Pna2_1$ is a polar axis, the z coordinate of the iron was arbitrarily assigned as 0·00. All non-H atoms were located from a successive least-squares refinement and difference electron density calculations. They were refined first with isotropic and later with anisotropic thermal parameters, to values of the residuals $R = 0{\cdot}073$ and $wR = 0{\cdot}065$, where $w = [\sigma(F_o)]^{-2}$ and $\sigma(F_o)$ is obtained from counting statistics. At this point H atoms were included in the calculations. Some of these were observable in difference electron density maps, others were placed in calculated positions with C—H distances of 1·00 Å. In the final calculations the positions of the H atoms were not refined, and they were given an isotropic thermal parameter $U = 1{\cdot}3$ times the U value of the atom to which they are attached. The final values of the residuals were $R = 0{\cdot}061$ and $wR = 0{\cdot}047$. The function minimized was $\sum w(|F_o| - |F_c|)^2$. Final atomic coordinates for the non-H atoms are shown in Table 2.* Atomic scattering

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, least-squares planes and dihedral angles and Fig. 2 showing the torsion angle around C2—Fe have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51973 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Comparison of molecular bond lengths* (Å) *with literature results*

Complex	Fe—P	Fe—C(≡O)	Fe—C(=O)	Fe—Cp*	Fe—Cp†	Ref.
[(η-MeC$_5$H$_4$)Fe(CO)-(COMe)PPh$_2$Et]	2·200 (2)	1·687 (9)	1·925 (10)	2·110	1·738	(*a*)
[(η-C$_5$H$_5$)Fe(CO)-(COMe){Ph$_2$PNH-CH(Me)(Ph)}]	2·188 (2)	1·749 (7)	1·976 (6)	2·131	1·756	(*b*)
[(η-C$_5$H$_5$)Fe(CO)-(COOC$_{10}$H$_{19}$)PPh$_3$]	2·214 (2)	1·670 (6)	1·825 (6)	2·113	1·743	(*c*)
[(η-1-CH$_3$-3-PhC$_5$H$_3$)-Fe(CO)(COMe)PPh$_3$]	2·216 (3)	1·700 (14)	1·964 (12)	2·136	1·758	(*d*)
(*RS*)-*E*-[(η-C$_5$H$_5$)Fe(CO)-(COCH=CHMe)PPh$_3$]	2·195 (1)	1·738 (3)	1·958 (3)	2·115	1·745	(*e*)
(*Z*)-[(η-C$_5$H$_5$)Fe(CO)-(COMe=CHMe)PPh$_3$]	2·205 (1)	1·729 (5)	1·974 (5)	2·096	1·729	(*f*)
[(η-C$_5$H$_5$)Fe(CO)-{COCH(Me)Et}PPh$_3$]	2·193 (1)	1·733 (3)	1·964 (3)	2·121	1·752	(*g*)
(*R*)-[(η-C$_5$H$_5$)Fe(CO)-(PPh$_3$)COCH$_2$CH$_2$O] [(*R*)-menthyl)]	2·191 (8)	1·73 (3)	1·98 (3)	2·11	1·74	(*h*)
[(η-C$_5$H$_5$)Fe(CO)-{η^1-(*Z*)-C(O)C(Me)-=C(Ph)Me}P(OPh)$_3$]	2·110 (1)	1·740 (3)	1·966 (3)	2·101	1·737	(*i*)
[(η-C$_5$H$_5$)Fe(CO)-{η^1-(*E*)-C(O)C(Me)-=C(Me)SPh}P(OPh)$_3$]						
A form	2·106 (1)	1·748 (6)	1·968 (5)	2·102	1·740	
B form	2·110 (1)	1·724 (6)	1·957 (6)	2·094	1·767	(*i*)

References: (*a*) this paper; (*b*) Korp & Bernal (1981); (*c*) Reisner, Bernal, Brunner & Muschiol (1978); (*d*) Attig, Teller, Wu, Bau & Wojcicki (1979); (*e*) Davies, Dorder-Hedgecock, Sutton & Walker (1986); (*f*) Baird, Davies, Jones, Prout & Warner (1984); (*g*) Baird, Bandy, Davies & Prout (1983); (*h*) Davies, Dorder-Hedgecock, Sutton, Walker, Bourne, Jones & Prout (1986); (*i*) Reger, Mintz & Lebioda (1986).

* Average Fe—C distance.
† Distance to ring center.

factors are from *International Tables for X-ray Crystallography* (1974). Computations were done with the *UCLA Crystallographic Program Package* (Strouse, 1978) as modified at Argonne National Laboratory.

Discussion. Table 3 gives values for the most important interatomic distances and angles. Fig. 1 shows the molecule, not including H atoms, and gives the numbering system for the atoms.

Of considerable importance is the Fe—P bond length of 2·200 (2) Å. According to the theoretical ideas we have developed (Rahman, Liu, Eriks, Prock & Giering, 1989), there should be two significantly different values for this bond length, depending on whether the phosphine ligand is a pure σ donor or a σ-donor/π-acceptor ligand. In the former case we predict the Fe—P bond length to be long, around 2·20 Å, and in the latter case we expect it to be short, around 2·10 Å or less. The present ligand, ethyldiphenylphosphine, is predicted by our correlation scheme to be a pure σ donor, and it is satisfying that the Fe—P bond length is found in the region of long values. Table 4 shows values for Fe—P bond lengths in complexes that have been reported in the literature. The first eight compounds contain ligands that we classify as pure σ donors, while the last two are σ-donor/π-acceptor ligands. The Fe—P distance values support our predictions. In addition, Table 4 also shows that large changes in the sizes of the substituted cyclopentadienyl and/or acetyl ligands do not affect the Fe—P distance significantly.

The second noteworthy result is that the Fe atom is centroid with respect to the cyclopentadiene ring. The distances Fe—C(4–8) average 2·110 (11) Å, and the deviations from the average correspond to two standard deviations in the distance values. The distance from iron to the center of the five-membered ring is 1·738 (9) Å, almost identical to those reported for all complexes in Table 4, most of which do not have a methyl group on the cyclopentadiene ring. Thus, one may conclude that the presence of the methyl group on the five-membered ring has neither electronic nor steric effects on the iron-to-ring distance. The Fe atom has pseudooctahedral coordination geometry, three coordination sites being occupied by the cyclopentadiene ring (piano-stool configuration). The angles P—Fe—C1, P—Fe—C2 and C1— Fe—C2 are each close to 90° (Table 3).

The third interesting feature of the structure concerns the torsion angle O2—C2—Fe—(CO). It can best be seen in Fig. 2,* which shows the molecule viewed directly along the C2—Fe bond. The car-

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* See deposition footnote.

bonyl group and the carboxyl oxygen, O2, are *anti*, but the torsion angle is 43°, in contrast to the value of 0°(*anti*) or 0°(*syn*) calculated theoretically using extended Huckel and *ab initio* SCF MO methods (Davies, Seeman & Williams, 1986; Bodner, Patton, Smith, Georgiou, Tam, Wong, Strouse & Gladysz, 1987). The minimum found in those calculations is not deep, however, and a significant difference of 43° may not be surprising for steric reasons.

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Structure du [Pd{(C$_6$H$_5$O)$_2$P(O)NP(S)(C$_6$H$_5$O)$_2$}$_2$]

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Abstract. Bis[(diphenoxyphosphoryl)(diphenoxythiophosphoryl)amido-*N*,*S*]palladium(II), M_r = 1099·3, monoclinic, $P2_1/c$, a = 11·827 (2), b = 12·175 (2), c = 18·830 (2) Å, β = 116·48 (5)°, V = 2427 (2) Å^3, Z = 2, D_m = 1·48, D_x = 1·50 Mg m^{-3}, graphite-monochromatized Mo $K\bar{\alpha}$ radiation, λ = 0·7107 Å, μ = 0·65 mm^{-1}, F(000) = 1120, T = 293 K. The structure was solved by the heavy-atom method and refined to R = 0·049 for 4302 independent reflexions. The Pd atom lies on a centre of symmetry and is coordinated by two N and two S atoms from two molecules of the ligand in a planar arrangement. Pd—N and Pd—S bond lengths are 2·055 and 2·342 Å, respectively, and the N—Pd—S angles are 78·53 and 101·47°, respectively.

Introduction. Les éthers des acides du phosphore sont utilisés souvent comme les extractants dans la

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