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Acta Cryst. (1993). C**49**, 680–682

Diphenylphosphinoferrocene

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(*Received* 9 *March* 1992; *accepted* 5 *October* 1992)

Abstact. (η^5-Cyclopentadienyl)[1-(diphenylphosphino)-η^5-cyclopentadienyl]iron, $[Fe(C_5H_5)(C_{17}H_{14}P)]$, $M_r = 370.21$, triclinic, $P\bar{1}$, $a = 8.344$ (1), $b = 9.387$ (1), $c = 12.527$ (2) Å, $\alpha = 97.27$ (1), $\beta = 101.18$ (1), $\gamma = 110.79$ (1)°, $V = 879.2$ (2) Å^3, $Z = 2$, $D_x = 1.398$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.94$ mm^{-1}, $F(000) = 384$, $T = 298$ K, $R = 0.031$ for 2606 observed reflections. The title compound shows an eclipsed geometry for the ferrocenyl rings, with a rotation of 6.6 (1)° from an exact eclipsed conformation. The cyclopentadienyl rings are essentially parallel, the dihedral angle between them being 1.4°. Both phenyl rings are approximately orthogonal to the cyclopentadienyl rings.

Introduction. As part of our studies on unsymmetric ferrocenyl diphosphines, we have synthesized diphenylphosphinoferrocene and determined its X-ray crystal structure in order to compare it with other ferrocenyl mono- and diphosphines.

Experimental. $(C_5H_5)Fe(C_5H_4PPh_2)$ was obtained by the transmetalation of $(C_5H_4SnBu_3)Fe(C_5H_4PPh_2)$ (Wright, 1990) with 1 equiv. of ^{n}BuLi followed by treatment with water. Crystals suitable for X-ray crystallographic studies were obtained by slow evaporation of a dichloromethane solution at 298 K. A prismatic crystal with dimensions 0.41 × 0.39 × 0.48 mm was used. Cell constants were derived from least-squares refinement of 25 reflections in the range $15 \leq 2\theta \leq 32.62°$. Intensity data were collected at 298 K using the $\theta/2\theta$ scan mode on a Nonius CAD-4 diffractometer equipped with graphite-monochromated Mo $K\alpha$ radiation, with scan width $(0.60 + 0.35\tan\theta)°$ and scan speed 1–8° min^{-1}. A total of 3315 reflections were measured with $2 \leq 2\theta \leq 50°$ ($-9 \leq h \leq 8$, $0 \leq k \leq 11$, $-14 \leq l \leq 14$) which were averaged to 2606 unique reflections with $R_{\rm int} = 0.015$. Three standard reflections ($20\bar{5}$, $10\bar{5}$, $21\bar{4}$) were measured every 7200 s and only small (< 1.5%) random variations were observed. Lorentz and polarization corrections were applied. An empirical absorption correction based on a series of ψ scans was applied to the data: $T_{\rm min} = 0.927$, $T_{\rm max} = 0.999$.

The structure was solved by direct methods and refined by full-matrix least-squares routines, initially with isotropic and finally with anisotropic thermal parameters for non-H atoms. All H atoms were located in a difference Fourier synthesis and fixed in the final cycles of refinement. $\sum w(|F_o| - |F_c|)^2$ was minimized, where $w = 1/[\sigma^2(F_o) + (0.01|F_o|)^2]$. Final $R = 0.031$, $wR = 0.038$, $R_{\rm all} = 0.039$ and $S = 1.84$ were obtained using 217 variables and 2606 observed reflections [$I_o > 2.5\sigma(I_o)$]. The largest Δ/σ was 0.001;

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0108-2701/93/040680-03$06.00

Table 1. *Final fractional coordinates and equivalent isotropic thermal parameters* (Å^2)

B_{eq} is the mean of the principal axes of the thermal ellipsoid.

	x	y	z	B_{eq}
Fe	0.10597 (4)	0.66310 (4)	0.33692 (3)	3.307 (2)
P	−0.13993 (9)	0.89087 (8)	0.30374 (5)	3.87 (3)
C(1)	−0.0920 (3)	0.7229 (3)	0.2585 (2)	3.52 (1)
C(2)	0.0146 (3)	0.7050 (3)	0.1853 (2)	3.74 (1)
C(3)	0.0097 (4)	0.5512 (3)	0.1726 (2)	4.38 (1)
C(4)	−0.1006 (4)	0.4718 (3)	0.2370 (2)	4.58 (1)
C(5)	−0.1636 (3)	0.5755 (3)	0.2901 (2)	3.94 (1)
C(6)	0.3561 (4)	0.8281 (3)	0.4065 (2)	4.80 (1)
C(7)	0.2485 (4)	0.8273 (3)	0.4810 (2)	4.25 (1)
C(8)	0.1870 (4)	0.6757 (3)	0.5040 (2)	4.23 (1)
C(9)	0.2555 (4)	0.5840 (3)	0.4439 (2)	4.89 (2)
C(10)	0.3607 (4)	0.6794 (4)	0.3834 (2)	5.16 (2)
C(11)	−0.3390 (3)	0.8556 (3)	0.1933 (2)	3.63 (1)
C(12)	−0.4154 (4)	0.9649 (3)	0.1966 (2)	4.14 (1)
C(13)	−0.5696 (4)	0.9415 (3)	0.1183 (3)	4.79 (2)
C(14)	−0.6509 (4)	0.8071 (4)	0.0364 (4)	4.86 (2)
C(15)	−0.5783 (4)	0.6982 (4)	0.0324 (2)	5.37 (2)
C(16)	−0.4232 (4)	0.7213 (3)	0.1100 (2)	4.92 (2)
C(17)	0.0309 (3)	1.0457 (3)	0.2633 (2)	3.77 (1)
C(18)	0.0120 (4)	1.0799 (3)	0.1576 (2)	4.20 (1)
C(19)	0.1473 (4)	1.1982 (3)	0.1331 (2)	4.91 (2)
C(20)	0.3038 (4)	1.2812 (3)	0.2126 (3)	5.55 (2)
C(21)	0.3251 (4)	1.2491 (3)	0.3172 (3)	5.95 (2)
C(22)	0.1888 (4)	1.1339 (3)	0.3431 (2)	5.15 (2)

maximum and minimum residual electron densities in the final difference Fourier map were 0.290 and −0.230 e Å^{-3}, respectively. The final atomic parameters are given in Table 1. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (Ibers & Hamilton, 1974). Computations were carried out on a MicroVAX 3600 with the *NRCC* package (Gabe, Lee & Le Page, 1985). Selected bond distances and angles are given in Table 2. An *ORTEP*II (Johnson, 1976) plot of the molecule is given in Fig. 1.*

Discussion. The Fe—C distances are in the range found in ferrocene and its derivatives (Haaland, 1979; Bruce, 1982). The average distances are 2.043 (3) Å to the unsubstituted cyclopentadienyl (Cp) ring and 2.042 (24) Å to the substituted Cp ring. The C—C bonds of the substituted Cp ring are in the range 1.415 (4)–1.440 (4) Å, averaging 1.423 (4) Å. An interesting feature is the comparative shortness of the C—C bonds in the free Cp ring [1.405 (5)–1.421 (5) Å]. These values are in common with those found in related monosubstituted ferrocenes (Roberts, Silver, Yamin, Drew & Eberhardt, 1988; McEwen, Sullivan & Day, 1983; Houlton, Roberts, Silver & Drew, 1990).

Table 2. *Selected bond distances* (Å) *and angles* (°)

Fe—C(1)	2.044 (2)	Fe—C(2)	2.045 (2)
Fe—C(3)	2.049 (2)	Fe—C(4)	2.039 (2)
Fe—C(5)	2.033 (3)	Fe—C(6)	2.042 (3)
Fe—C(7)	2.052 (2)	Fe—C(8)	2.046 (2)
Fe—C(9)	2.041 (3)	Fe—C(10)	2.036 (3)
P—C(1)	1.810 (3)	P—C(11)	1.840 (3)
P—C(17)	1.843 (3)	C(1)—C(2)	1.429 (4)
C(1)—C(5)	1.440 (3)	C(2)—C(3)	1.417 (4)
C(3)—C(4)	1.416 (4)	C(4)—C(5)	1.415 (4)
C(6)—C(7)	1.414 (4)	C(6)—C(10)	1.405 (5)
C(7)—C(8)	1.420 (4)	C(8)—C(9)	1.409 (4)
C(9)—C(10)	1.421 (5)		

C(1)—C(2)—C(3)	108.9 (2)	C(2)—C(1)—C(5)	106.6 (2)
C(2)—C(3)—C(4)	107.8 (2)	C(3)—C(4)—C(5)	108.6 (2)
C(1)—C(5)—C(4)	108.2 (2)	C(7)—C(6)—C(10)	108.5 (2)
C(6)—C(7)—C(8)	107.3 (2)	C(7)—C(8)—C(9)	108.5 (2)
C(8)—C(9)—C(10)	107.5 (2)	C(6)—C(10)—C(9)	108.1 (3)
P—C(1)—C(2)	129.2 (3)	P—C(1)—C(5)	124.2 (2)
P—C(11)—C(12)	118.4 (2)	P—C(11)—C(16)	123.6 (2)
P—C(17)—C(18)	124.3 (2)	P—C(17)—C(22)	118.0 (2)
C(1)—P—C(11)	100.7 (1)	C(1)—P—C(17)	101.1 (1)
C(11)—P—C(17)	101.4 (1)	Fe—C(1)—P	127.5 (1)

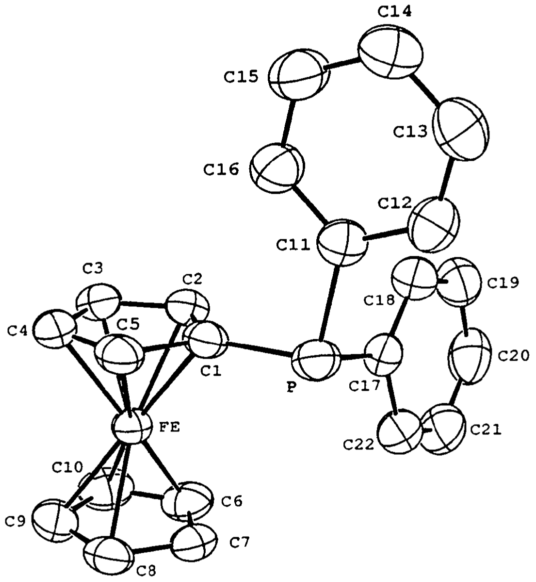

Fig. 1. *ORTEP*II (Johnson, 1976) plot of a diphenylphosphinoferrocene.

The P—C(ferrocene) distance of 1.810 (3) Å compares with 1.802 (7), 1.817 (11), 1.819 (5) and 1.813 (3) Å for the corresponding distances in [$(C_5H_5)Fe\{C_5H_3(PPh_2)(CHMeNMe_2)\}$] (Einstein & Willis, 1980), [$(C_5H_5)Fe(C_5H_4)]_2PPh$ (Houlton, Roberts, Silver & Drew, 1990), $(C_5H_4PPh_2)_2Fe$ (Casellato, Ajo, Valle, Corain, Longato & Graziani, 1988) and [$C_5H_4PPh(^iPr)]_2Fe$ (Liu & Chen, 1991), respectively. The title compound shows shorter P—C(ferrocenyl) than P—C(aromatic) distances in common with values obtained in related compounds mentioned above, probable evidence for conjugation of the substituent with the Cp ring. The C—C—C

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* Lists of structure factors, anisotropic thermal parameters, bond distances and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55697 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1023]

bond angles vary from 106.59 (21) to 108.85 (22)°, the angle at the substituted atom being the smallest at 106.59 (21)°.

The two Cp groups are planar and eclipsed; a rotation of 6.6° from an exactly eclipsed conformation with the two rings approximately parallel (dihedral angle of 1.4° between the two rings). The P atom is displaced from the attached Cp plane away from the Fe atom by -0.034 (5) Å. Both phenyl rings are approximately orthogonal to the Cp planes. The dihedral angles between plane I [defined by C(1)–C(5)] and plane III [C(11)–C(16)], plane I and plane IV [C(17)–C(22)], and plane II [C(6)–C(20)] and plane IV are 86.64 (11), 97.59 (12) and 98.97 (13)°, respectively. The dihedral angle between the two phenyl rings is 78.33 (11)°. The phenyl rings are planar with the P atom slightly displaced from planes III and IV by 0.085 (4) and -0.031 (4) Å, respectively. The structural features of the title compound can be seen as intermediate between the ferrocene structure and that of 1,1′-bis(diphenylphosphino)-ferrocene.

JAA is grateful to the National Science Council of Taiwan for a senior postdoctoral fellowship. The authors are indebted to the National Science Council for partial financial support. We also thank Mr Y. S. Wen who helped in the diffraction-data collection.

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Acta Cryst. (1993). **C49**, 682–684

Structure of the 2-Pyridylhydrazone of Ferrocenecarbaldehyde

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(*Received* 30 *March* 1992; *accepted* 13 *November* 1992)

Abstract. Ferrocenecarbaldehyde 2-pyridylhydrazone, $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^5\text{-}\mathrm{C_{11}H_{10}N_3})]$, $M_r = 305.17$, monoclinic, $P2_1/a$, $a = 9.972$ (1), $b = 8.308$ (1), $c = 17.010$ (2) Å, $\beta = 97.371$ (4)°, $V = 1397.7$ Å^3, $Z = 4$, $D_x = 1.45$ g cm^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0.71069$ Å, $\mu = 10.7$ cm^{-1}, $F(000) = 632$, $T = 293$ K, $R = 0.036$ and $wR = 0.049$ for 2283 observed reflections. The molecule exhibits an E configuration, has an N═C bond length of 1.274 (4) Å and an N—N bond length of 1.368 (4) Å. The cyclopentadienyl rings are eclipsed with Fe—C distances of 2.037 (4) to 2.051 (3) Å, mean 2.042 (4) Å. The cyclopentadienyl rings are essentially parallel. The pyridyl group is not coplanar with the cyclopentadienyl ring, but inclined at an angle of 27.5 (2)° to it.

Introduction. We have become interested in ferrocenyl derivatives that have the capacity to act as ligands (Houlton, Roberts, Silver & Drew, 1990; Houlton, Ibrahim, Dilworth & Silver, 1990; Houlton, Roberts, Silver & Parish, 1991). Such compounds have the potential to be redox-active, thus permitting the 'tuning' of the coordinated metal by oxidation of the ferrocenyl Fe atom. Oxidizable ferrocenyl ligands would allow the synthesis of potentially multifunctional drugs, *via* the known antitumour activity or iron-sandwich compounds (Köpf-Maier & Köpf, 1987; Houlton, Roberts & Silver, 1991) and the incorporation of chelated metal-containing cytotoxic groups. We report here the structure of the 2-pyridylhydrazone of ferro-

0108-2701/93/040682-03$06.00