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(4-*tert*-Butylphenyl)phospha[1]ferrocenophane

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Key indicators

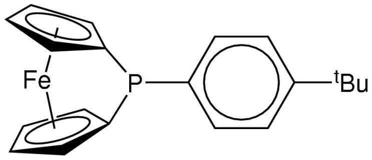
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.008 Å
R factor = 0.063
wR factor = 0.165
Data-to-parameter ratio = 14.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title structure, [Fe(η-C_5H_4)$_2$P{*p*-C_6H_5-C(CH_3)$_3$}] or [Fe($C_{20}H_{21}$P)], the cyclopentadienyl (Cp) rings of the ferrocenophane are tilted towards the bridging P atom, with a tilt angle of 26.9 (3)°. Weak intermolecular C—H$\cdots\pi$(Cp-ring) interactions link molecules into sheets parallel to the *bc* plane.

Comment

Ring-strained ferrocenophanes are useful precursors to polyferrocenyl materials which possess numerous properties of interest in materials science (Kulbaba & Manners, 2001; Nguyen *et al.*, 1999). In particular, polyferrocenylphosphines are able to act as ligands for transition metal compounds (Fellman *et al.*, 1983; Cao *et al.*, 2001) and possess high refractive indices (Paquet *et al.*, 2004*a*,*b*). As part of our exploration of these materials, we synthesized the title compound, (I), as a monomer for the corresponding polyferrocenylphosphine.



(I)

The structure of (I) is shown in Fig. 1 and selected bond lengths and angles are given in Table 1. The cyclopentadienyl (Cp) rings of the ferrocenophane are tilted towards the bridging P atom. The angle formed between the least-squares planes of the Cp rings bonded to Fe is 26.9 (3)° and the P atom is displaced by 1.008 (4) and 0.974 (8) Å from the least-squares planes of the Cp rings defined by C1–C5 and C6–C10, respectively. The Fe—C distances in the tilted phospha[1]-ferrocenophane moiety range from 1.984 (5) Å for Fe1—C6 to 2.089 (6) Å for Fe1—C8 and the angle *Cg*1$\cdots$Fe$\cdots$*Cg*2 is 159.8 (2)° (where *Cg*1 and *Cg*2 are the centroids of the rings defined by C1–C5 and C6–C10, respectively). The C6—P1—C1 angle is strained, with a value of 90.6 (2)°. A search of the November 2004 release of the Cambridge Structural Database (Allen, 2002) revealed only five previous structure determinations of phosphorus(III)-bridged [1]ferrocenophanes (where the Cp rings are unsubstituted). In each of these structures, the tilt angle is similar to that in the title compound. The values of the tilt angles for these compounds with general formula Fe[(η-C_5H_4)(η-C_5H_4)]P—*X*, are 27.9° for *X* = diisopropylamino (Herberhold *et al.*, 1999), 27.1 and 26.9° for *X* = *tert*-butyl and phenyl, respectively (Butler *et al.*, 1983),

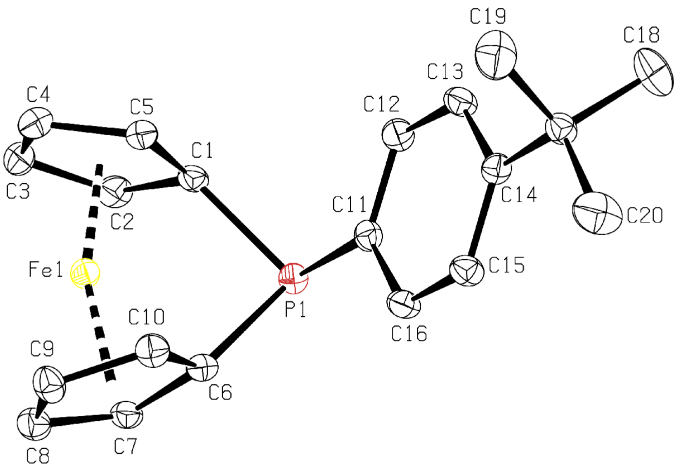


Figure 1
View of (I), with ellipsoids drawn at the 30% probability level. H atoms are not shown.

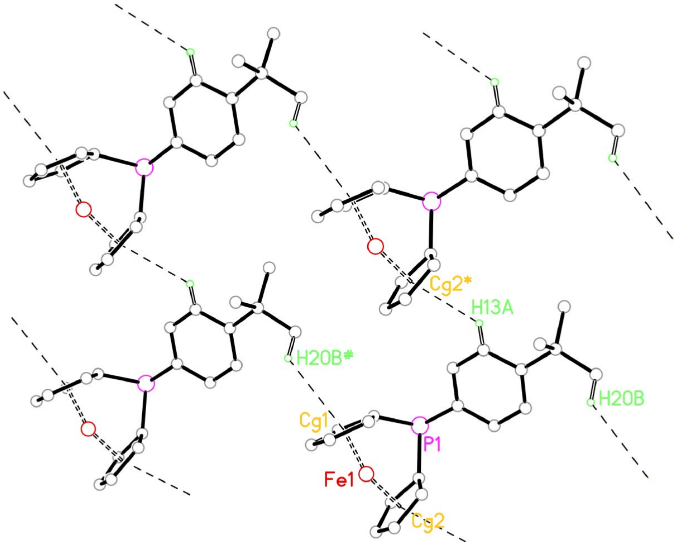


Figure 2
Packing diagram for (I), showing weak C—H$\cdots\pi$(Cp-ring) interactions as single dashed lines. *Cg*1 and *Cg*2 are the centroids of the Cp rings C1–C5 and C6–C10, respectively. [Symmetry codes: (*) $x + 1, y, z$; (#) $x, y + 1, z$.]

27.0 (6)° for X = Cl (Honeyman *et al.*, 1995) and 27.4° for X = menthyl (Brunner *et al.*, 2000). Where the s.u. values are not given, they are unavailable.

In the crystal structure of (I), weak intermolecular C—H$\cdots\pi$(Cp-ring) interactions link molecules into sheets parallel to the *bc* plane (see Table 2 and Fig. 2). These sheets are organized face-to-face so that the P atoms from inversion-related molecules [P1$\cdots$P1$^{\rm iii}$; symmetry code: (iii) $1 - x, 1 - y, 1 - z$] are 3.251 (3) Å apart (see Fig. 3). This distance is shorter than the sum of the van der Waals radii of 3.6 Å (Bondi, 1964), but longer than the distance of 3.15 Å (no s.u. available) found in the related structure Fe[(η-C_5H_4)(η-C_5H_4)]P-menthyl (Butler *et al.*, 1983). We conclude that the close proximity of the P atoms is a result of crystal-packing forces.

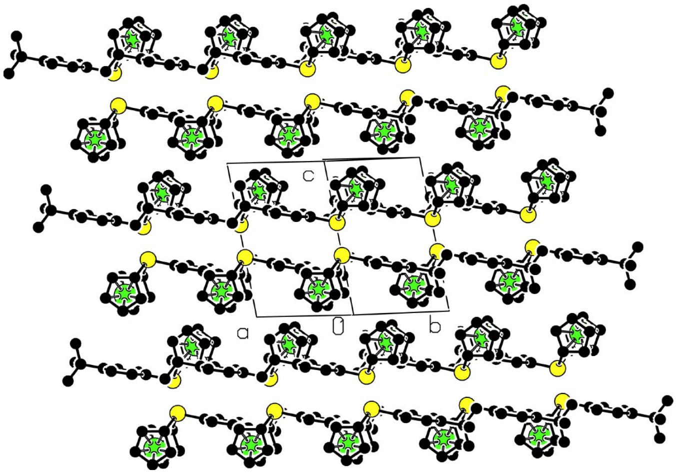


Figure 3
View of the packing in (I), showing the close proximity of P atoms in the crystal structure. Colour codes; green Fe, yellow P and black C.

Experimental

Compound (I) was prepared *via* the method reported by Paquet *et al.* (2004*b*). Deep-red crystals of (I) were obtained by slow concentration of a benzene solution at room temperature under an N_2 atmosphere.

Crystal data

[Fe($C_{20}H_{21}P$)]
M_r = 348.19
Triclinic, $P\overline{1}$
a = 8.0529 (3) Å
b = 10.1125 (4) Å
c = 10.3508 (4) Å
α = 88.706 (2)°
β = 77.492 (2)°
γ = 89.568 (2)°
V = 822.70 (6) Å^3

Z = 2
D_x = 1.406 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 7882 reflections
θ = 2.6–27.5°
μ = 1.01 mm^{-1}
T = 150 (1) K
Block, deep red
0.30 × 0.24 × 0.23 mm

Data collection

Nonius KappaCCD diffractometer
φ scans and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing 1995)
$T_{\min}$ = 0.755, $T_{\max}$ = 0.789
7882 measured reflections
2877 independent reflections

2445 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.061
$\theta_{\max}$ = 25.0°
$h = -9 \rightarrow 9$
$k = -12 \rightarrow 11$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.165
S = 1.12
2877 reflections
200 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + 3.5656P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.84 e Å^{-3}
$\Delta\rho_{\min}$ = −0.47 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.022 (5)

Table 1
Selected geometric parameters (Å, °).

P1—C11	1.820 (5)	P1—C1	1.860 (5)
P1—C6	1.844 (5)		
C11—P1—C6	102.5 (2)	C6—P1—C1	90.6 (2)
C11—P1—C1	101.9 (2)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C13—H13$A\cdots Cg2^{i}$	0.95	2.93	3.659 (6)	135
C20—H20$B\cdots Cg1^{ii}$	0.98	3.09	3.693 (8)	121

Symmetry codes: (i) $1 + x, y, z$; (ii) $x, y - 1, z$. $Cg1$ and $Cg2$ are the centroids of the Cp rings C1–C5 and C6–C10, respectively

All H atoms were placed in calculated positions, with C—H distances of 1.00 (Cp), 0.95 (phenyl) and 0.98 Å (methyl), and were included in the refinement in riding-model approximation, with $U_{\rm iso} = 1.2U_{\rm eq}$ ($1.5U_{\rm eq}$ for methyl) of the carrier atom.

Data collection: *COLLECT* (Nonius, 2002); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL/PC*; molecular graphics: *SHELXTL/PC* and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL/PC*.

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