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The synthesis and crystal structure of 1,2,3-tri(phenylphosphano)[3]ferrocenophane

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Abstract

1,2,3-Tri(phenylphosphano)[3]ferrocenophane has been prepared by the reaction of 1,1′-dibromoferrocene with LiP(Ph)–P(Ph)–P(Ph)Li, and its crystal structure determined by X-ray diffraction methods. The P–P bond lengths are 2.231(3) and 2.229(3) Å and the P–P–P bond angle is 93.5(2)°. The cyclopentadienyl rings are inclined at an angle of 3.43° to each other and the pseudo six-membered ring, C(1)C(6)FeP(1)P(2)P(3), is in a chair conformation.

1. Introduction

A large number of [*n*]-ferrocenophanes are known, the majority of which involve organic bridging units. [3]Ferrocenophanes containing trichalcogen bridges have been prepared and several have been structurally characterized by X-ray diffraction studies [1–4]. As part of our continuing studies of [3]ferrocenophanes in which the bridge unit is composed of inorganic atoms we now report the synthesis of 1,2,3-tri(phenylphosphano)[3]ferrocenophane, which involves a chain of three PhP groups linking the two cyclopentadienyl rings. The crystal structure of the compound is also reported, and comparisons are drawn with other compounds containing the –P–P–P– structural unit.

2. Experimental details

2.1. General

All preparations were carried out by standard Schlenk techniques [5]. All solvents were freshly distilled, dried and degassed before use and all reactions were performed under purified nitrogen.

Dichlorophenylphosphane was purchased from Aldrich Chemical Company and 1,1′-dibromoferrocene was prepared from 1,1′-dilithioferrocene and 1,2-dibromotetrafluoroethane by a published procedure [6].

Elemental analysis was performed by Butterworth Laboratories Ltd., Teddington, Middlesex, UK. ^1H and ^{31}P NMR spectra were recorded on a Brüker AM250 FT spectrometer operating at 250.13 MHz and 101.26 MHz, respectively. The spectra were recorded as $CDCl_3$ solutions with the ^1H chemical shifts quoted relative to Me_4Si and the ^{31}P chemical shifts relative to H_3PO_4. Mass spectra were recorded on a Kratos Profile HV3 instrument.

2.2. *1,2,3-Tri(phenylphosphano)[3]ferrocenophane*

A solution of dichlorophenylphosphane (5.3 g, 0.03 mol) in tetrahydrofuran (50 ml) was added dropwise to a stirred suspension of lithium pieces (0.7 g, 0.1 mol) in tetrahydrofuran (50 ml) at 0°C. After 2 h, the deep-red solution was filtered and the solvent removed under reduced pressure. Hexane (200 ml) was added, the suspension cooled to −78°C, and 1,1′-dibromoferrocene (5 g, 0.015 mol) in hexane (15 ml) added dropwise. The solution was allowed to warm to room temperature and stirring was continued for 3 days, during which a heavy yellow precipitate formed. The supernatant liquid was removed by decantation, the precipitate was broken up and then boiled in toluene (100 ml) until the red colour disappeared. The toluene was removed under reduced pressure and the residual solid

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was washed with hot petroleum spirit (50 ml). The yellow solid was dried under a vacuum and crystallized from hot dichloromethane to give yellow needles (0.52 g, 7%, m.p. 240–242°C dec.) Anal. Found: C, 65.38; H, 4.65. $C_{28}H_{23}FeP_3$ calc.: C, 66.14; H, 4.53%. ^{1}H NMR ($CDCl_3$): δ 7.5–7.0 (15H, m); 4.87 (2H, m); 4.70 (2H, m); 4.54 (2H, m); 4.38 (2H, m). ^{31}P NMR ($CDCl_3$): δ −16.13 (1P); −22.46 (2P, $J = 124$ Hz).

2.3. X-ray structure determination

Crystal data for $C_{28}H_{23}FeP_3$: $M = 508.259$, orthorhombic, space group $P2_12_12_1$, $a = 5.875(2)$, $b = 12.756(4)$, $c = 31.467(12)$ Å, $U = 2358.18$ Å^3, $Z = 4$, $D_c = 1.432$ g cm^{-3}, $F(000) = 1048$, $\lambda = 0.71069$ Å, μ (Mo Kα) = 8.528 cm^{-1}.

2.4. Data collection and processing

Data were collected using a FAST TV area detector diffractometer situated at the window of a rotating anode generator operating at 50 kV, 55 mA with a molybdenum anode as described previously [7]. Somewhat more than one hemisphere of data were recorded; 11,433 reflections were measured, giving 5722 unique and 4730 observed with $F_o > 3\sigma(F_o)$.

2.5. Solution and refinement of structure

The structure was solved by standard Patterson methods. Full matrix least squares were performed with non-hydrogen atoms assigned anisotropic thermal parameters. Phenyl carbon atoms were refined as forming a regular hexagon with C–C = 1.395 Å and angle C–C–C = 120°. All hydrogen atoms were positioned on their parent atoms with C–H = 0.96 Å. The final residuals R and R_w were 0.038 and 0.044, respectively, for the 258 variables. The computer programs used are given in ref. 8. A full table of bond lengths and angles, a table of least mean square planes, and lists of thermal parameters and structure factors are available from the authors.

3. Results and discussion

The title compound was prepared in 7% yield as air-stable needle-like yellow crystals from the reaction of 1,1′-dibromoferrocene with LiP(Ph)–P(Ph)–P(Ph)Li, generated *in situ* [9] from the reaction of lithium pieces with dichlorophenylphosphane. In the mass spectrometer the compound shows a molecular ion, with the stepwise loss of PhP groups and $(M - 185)^+$ as the most abundant ion.

TABLE 1. Fractional atomic coordinates ($\times 10^4$) for $C_{28}H_{23}P_3Fe$

	x	y	z
Fe(1)	2546(1)	79(1)	2378(1)
C(1)	3994(6)	1377(3)	2111(1)
C(2)	5250(7)	1048(3)	2482(1)
C(3)	3773(8)	1073(3)	2836(1)
C(4)	1623(7)	1404(3)	2696(1)
C(5)	1715(6)	1584(3)	2248(1)
C(6)	2493(7)	−1090(2)	1935(1)
C(7)	220(6)	−795(3)	2056(1)
C(8)	−1(7)	−963(3)	2502(1)
C(9)	2109(7)	−1354(3)	2653(1)
C(10)	3631(6)	−1433(3)	2311(1)
P(1)	2693(2)	532(1)	1215(1)
C(11)	3100(5)	1276(3)	402(1)
C(12)	4116(5)	1447(3)	8(1)
C(13)	6236(5)	1008(3)	−82(1)
C(14)	7340(5)	397(3)	222(1)
C(15)	6324(5)	226(3)	617(1)
C(16)	4204(5)	666(3)	707(1)
P(2)	5319(2)	1386(1)	1591(1)
C(21)	2792(5)	3299(2)	1478(1)
C(22)	2565(5)	4319(2)	1324(1)
C(23)	4296(5)	4762(2)	1080(1)
C(24)	6255(5)	4185(2)	990(1)
C(25)	6483(5)	3165(2)	1144(1)
C(26)	4751(5)	2722(2)	1388(1)
P(3)	3919(2)	−1042(1)	1424(1)
C(31)	3014(5)	−2139(2)	685(1)
C(32)	1855(5)	−2831(2)	418(1)
C(33)	−186(5)	−3282(2)	551(1)
C(34)	−1070(5)	−3042(2)	951(1)
C(35)	89(5)	−2350(2)	1218(1)
C(36)	2131(5)	−1899(2)	1085(1)

The ^{1}H NMR spectrum for the cyclopentadienyl protons consists of four multiplets, consistent with an ABCD pattern, as would be expected from the low symmetry associated with the $(PhP)_3$ bridge. The ^{31}P NMR spectrum shows an AB_2 pattern with δ_A −16.13, δ_B −22.46 and $J_{AB} = 124$ Hz. These chemical shifts compare with the value δ −17.1 reported [10] for $[Fe(C_5H_4PPh_2)_2]$, but the coupling constant is much smaller than values of approximately 250 Hz reported for other compounds containing a P_3 chain [9,11]. For further characterization of this new bridged ferrocene, an X-ray crystal structure was obtained.

Atomic parameters for the crystal structure are given in Table 1 and a view of the molecule illustrating the numbering scheme is shown in Fig. 1.

Bond distances and selected bond angles are listed in Tables 2 and 3, respectively.

The P–P bond lengths (2.231(3) and 2.229(3) Å) compare with those of 1,2,3 triphenyl-1,2,3-triphosphaindan, $[Ph_3P_3C_6H_4]$ (2.209(3) Å) [12], $[((CF_3)P)_4]$ (2.213(5) Å) [13], $[((CF_3)P)_5]$ (2.223(7) Å), [14], $[(PhP)_5]$ (2.217(6)Å) [15], and $[(PhP)_6]$ (2.237(3) Å) [16], but are considerably longer than is typical for diphosphanes (2.004(6)–2.034(2) Å) [17].

The P–P–P bond angle (93.5 (2)°) is smaller than the angle in $[Ph_3P_3C_6H_3]$ (97.3(1)°), the ranges of

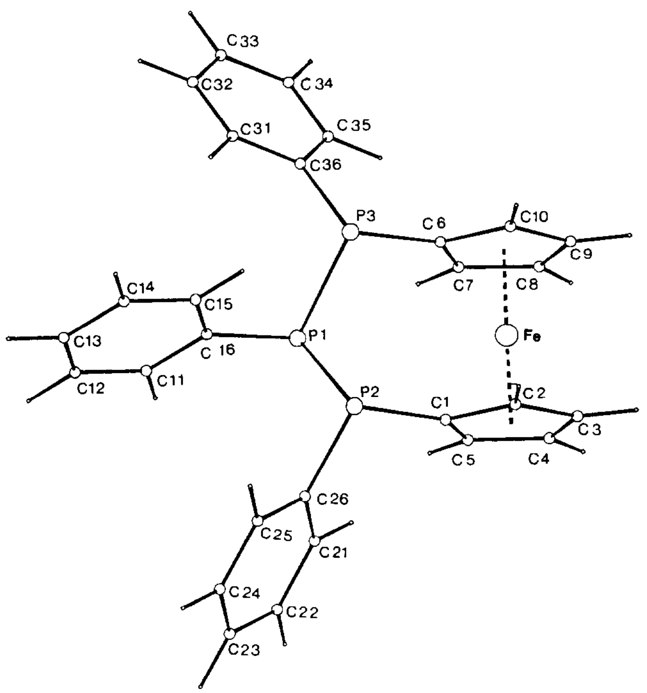

Fig. 1. A view of the X-ray crystal structure of $C_{28}H_{23}FeP_3$ showing the numbering scheme adopted.

angles found for $[((CF_3)P)_5]$ (94.6–107.5 ± 0.4°) and for $[(PhP)_5]$ (94.05(17)–107.24(19), mean 100.01 (54)°), but is considerably greater than in $[((CF_3)P)_4]$ (84.7°). Differences in the C–C–P exocyclic angles at the cyclopentadienyl rings, (120.9(4) and 132.4(3)°) at C(1) and (121.9(4) and 131.0(3)°) at C(6) are observed. This is a structural feature which has been found in other [3]-metallocenophanes [18]. An asymmetry of C–C–P angles is also present at C(16), C(26) and C(36). This systematic difference in the two C–C–P angles from a tervalent phosphorus atom to a phenyl group has also been noted in $[Ph_3P_3C_6H_4]$ and in the phosphobenzenes [12,15,16].

TABLE 2. Bond distances (Å) [a] for $C_{28}H_{23}FeP_3$

Fe–C(1)	2.043(5)	Fe–C(6)	2.042(5)
Fe–C(2)	2.039(6)	Fe–C(7)	2.033(6)
Fe–C(3)	2.051(6)	Fe–C(8)	2.039(6)
Fe–C(4)	2.039(6)	Fe–C(9)	2.039(5)
Fe–C(5)	2.023(5)	Fe–C(10)	2.042(5)
C(1)–C(2)	1.445(6)	C(6)–C(7)	1.440(6)
C(2)–C(3)	1.412(6)	C(7)–C(8)	1.424(6)
C(3)–C(4)	1.403(7)	C(8)–C(9)	1.419(6)
C(4)–C(5)	1.429(6)	C(9)–C(10)	1.405(7)
C(5)–C(1)	1.432(6)	C(10)–C(6)	1.427(6)
C(1)–P(2)	1.810(6)	C(6)–P(3)	1.814(6)
P(2)–P(1)	2.229(3)	P(3)–P(1)	2.231(3)
P(1)–C(16)	1.836(5)		
P(2)–C(26)	1.850(5)		
P(3)–C(36)	1.854(5)		

[a] E.s.d.s, given in parentheses, are applicable to the least significant digits.

TABLE 3. Selected bond angles (°) [a] for $C_{28}H_{23}FeP_3$

P(2)–P(1)–P(3)	93.5(2)		
C(1)–P(2)–P(1)	100.3(2)	C(1)–P(2)–C(26)	103.9(2)
C(6)–P(3)–P(1)	98.2(2)	C(6)–P(3)–C(36)	103.2(2)
C(7)–C(6)–P(3)	131.0(3)	C(10)–C(6)–P(3)	121.9(4)
C(5)–C(1)–P(2)	132.4(3)		
P(2)–C(1)–C(2)	120.9(4)		
C(1)–P(2)–C(26)	103.9(2)	C(6)–P(3)–C(36)	103.2(2)
P(1)–P(2)–C(26)	98.2(2)	P(1)–P(3)–C(36)	100.3(2)
P(2)–P(1)–C(16)	94.7(2)	P(3)–P(1)–C(16)	100.6(2)
P(1)–C(16)–C(15)	124.8(2)		
P(1)–C(16)–C(11)	115.2(2)		
P(2)–C(26)–C(25)	115.6(2)		
P(2)–C(26)–C(21)	124.3(2)		
P(3)–C(36)–C(35)	123.9(2)		
P(3)–C(36)–C(31)	116.0(2)		

[a] E.s.d.s, given in parentheses, are applicable to the least significant digits.

The cyclopentadienyl rings are not precisely parallel, the angle between the normals to the ring planes being 3.43°, a value comparable in magnitude to that found for trichalcogen bridged [3]ferrocenophanes [1,2,4]. Atoms P(2) and P(3) are displaced from the cyclopentadienyl rings to which they are attached by 0.066 and 0.047 Å, respectively. These displacements are towards the iron atom, and result in a non-bonded P(2)–P(3) separation of 3.247 Å.

In 1,2,3-triphenyl-1,2,3-triphosphaindan [12] and in $[Pt\{(CF_3)P(CF_3)P(CF_3)PC(CF_3)=C(CF_3)\}(PPh_3)_2]$ [11], the polyphosphane heterocyclic rings are approximately planar, but in the present compound the pseudo six-membered ring, FeC(1)C(6)P(2)P(1)P(3) is in a chair conformation with the phenyl group on P(1) in the sterically less hindered *exo* position.

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