$FcCH_2P(CH_2OH)_2$: a new, reactive yet air-stable ferrocene-derived phosphine [Fc = (η-C_5H_5)FeC_5H_4]

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Reaction of $FcCH_2NMe_3{}^+I^-$ with an excess of $P(CH_2OH)_3$ gives the air-stable ferrocenylphosphine $FcCH_2P(CH_2OH)_2$, characterised by an X-ray structure determination; reactivity towards reagents such as MeI, acrylonitrile and amines allows the synthesis of a range of new ferrocene-phosphine derivatives.

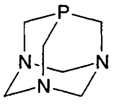
The chemistry of phosphine ligands containing the ferrocenyl group has attracted much interest over a period of many years, and there is an extensive literature on the topic.[1] Such phosphines are of interest for their coordination chemistry, including their applications to asymmetric catalysis.[2] In contrast to the large number of ferrocene-derived phosphines, and their metal complexes, which have the phosphorus directly bonded to a cyclopentadienyl ring, ligands where there is a carbon spacer between these two functionalities are somewhat rarer,[3] though chiral versions are attracting interest for their catalytic activity.[4] We are interested in developing the chemistry of hydroxymethylphosphines which also contain the ferrocenyl group. Hydroxymethylphosphines contain chemically reactive PCH_2OH groups,[5] allowing further derivatisation of the phosphine ligand. Examples include the synthesis [from $P(CH_2OH)_3$] of ligands such as $P(CH_2CH_2CN)_3$[6] and the water-soluble phosphatriazaadamantane, PTA **1**,[7] both of which have attracted recent attention. In addition, hydroxymethylphosphines themselves have been the subjects of a number of recent studies, for both their water-solubility and reactivity.[8] Here we report the first example of a ferrocene-derived hydroxymethylphosphine ligand, together with some derivatives.

Reaction of the readily available ferrocenylmethyl ammonium salt $FcCH_2NMe_3{}^+I^-$[9] with an excess of $P(CH_2OH)_3$† in refluxing methanol followed by treatment with an excess of triethylamine, and extraction with diethyl ether gave orange crystals of $FcCH_2P(CH_2OH)_2$ **2**, as shown in Scheme 1. Recrystallisation from dichloromethane–methanol–light petroleum (bp 40–60 °C) gave the product in 66% overall yield. The compound is air-stable, both in the solid state and in solution; other hydroxymethylphosphines are typically air-sensitive to some extent.

The formulation of **2** was confirmed by elemental analysis, NMR spectroscopy and electrospray mass spectrometry,‡ together with an X-ray structure determination.§ The molecular structure is shown in Fig. 1, together with selected bond lengths and angles. The structure determination of **2** is the first of a free hydroxymethylphosphine. The molecule forms a hydrogen-bonded array, propagated along the 2_1 screw axis, parallel to the *a*-axis of the unit cell; the resulting ten-membered rings are formed by hydrogen bonding between three molecules of **2**.

Treatment of **2** with hydrogen peroxide or elemental sulfur afforded the phosphine oxide (δ_P 45.8, $CDCl_3$) and sulfide (δ_P 47.6, $CDCl_3$) derivatives $FcCH_2P(X)(CH_2OH)_2$ (X = O, S) respectively. Representative metal complexes of **2**, *cis*-$[PtCl_2(\mathbf{2})_2]$ and $[AuCl(\mathbf{2})]$ were readily prepared by reaction of a dichloromethane solution of **2** with $[PtCl_2(cod)]$ (cod = cycloocta-1,5-diene) and $[AuCl(CNBu^t)]$ respectively. The ^{31}P NMR spectrum of the platinum complex showed the expected single resonance, with ^{195}Pt satellites [$^1J(PtP)$ 3427 Hz].

The unique reactivity of hydroxymethylphosphines facilitates the ready synthesis of other functionalised phosphines derived from **2**. Thus, reaction of **2** with an excess of MeI yields the phosphonium salt $FcCH_2P(Me)(CH_2OH)_2{}^+I^-$ **3**, characterised by an X-ray structure determination and electrospray mass spectrometry (*m*/*z* 307, M^+). Subsequent treatment of **3** with an excess of triethylamine generates the mono(hydroxymethyl)phosphine $FcCH_2P(Me)CH_2OH$ (δ_P −33.1, $CDCl_3$). Reaction of **2** with an excess of acrylonitrile affords $FcCH_2P(CH_2CH_2CN)_2$ (δ_P −22.1, $CDCl_3$), while reaction with an excess of diethylamine proceeds rapidly *via* a Mannich-type condensation reaction,[5] giving $FcCH_2P(CH_2NEt_2)_2$, characterised as the phosphine oxide (δ_P 45.0, $CDCl_3$). This reactivity towards amine groups can be exploited to immobilise the phosphine **2** on amine-containing supports, such as 3-aminopropylsilica. The phosphine **2** thus represents a convenient new reagent for the incorporation of ferrocene groups into amine-containing materials.



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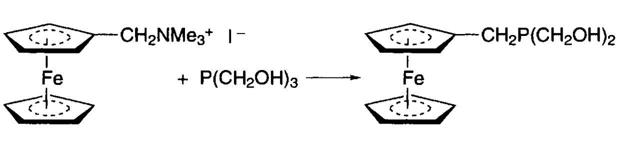

Scheme 1

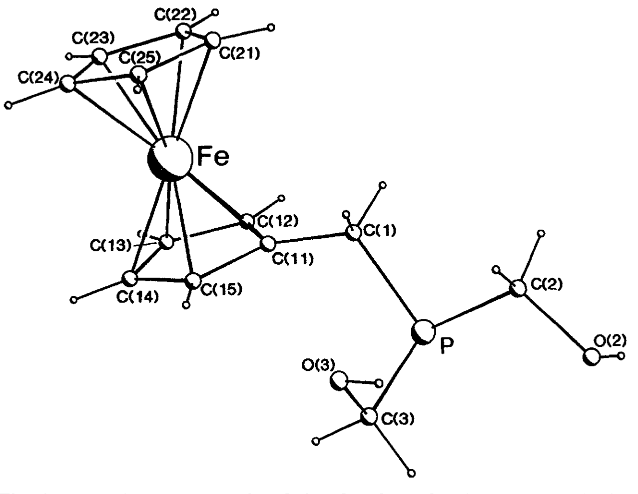

Fig. 1 Molecular structure of $FcCH_2P(CH_2OH)_2$ **2**, with atom numbering scheme. Selected bond lengths (Å) and angles (°) C(1)–C(11) 1.489(6), P–C(1) 1.858(4), P–C(2) 1.862(4), P–C(3) 1.851(4), C(2)–O(2) 1.429(5), C(3)–O(3) 1.423(5), Fe–C 2.034(4)–2.047(5), average 2.040(4), C(11)–C(1)–P 114.6(3), C(1)–P–C(2) 95.0(2), C(1)–P–C(3) 101.3(2), C(2)–P–C(3) 99.5(2), P–C(2)–O(2) 111.9(3), P–C(3)–O(3) 116.2(3).

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Footnotes

† $P(CH_2OH)_3$ was prepared by the reaction of methanolic $P(CH_2OH)_4Cl$ (obtained as Retardol C from Albright & Wilson Ltd., UK, as an 80% m/m aqueous solution) with 1 mol equiv. of KOH under a nitrogen atmosphere.

‡ Anal. Found: C, 52.9; H, 6.0. $C_{13}H_{17}FeO_2P$ requires C, 53.5; H, 5.9%. Mp 104–106 °C. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ −19.3. Electrospray mass spectrometric analysis with added $AgNO_3$[10] at a cone voltage of 60 V showed the following ions (*m*/*z*); $[2M + Ag]^+$ (690.8), $[M + Ag]^+$ (398.9), $[M]^+$ (292.1) and $[FcCH_2]^+$ (199.0). The observation of the ferrocenium ion may be as a result of oxidation by silver ions, or alternatively by electrochemical oxidation in the electrospray capillary.[11]

§ Accurate cell parameters and intensity data were recorded on a Nicolet R3 diffractometer, using a crystal of dimensions 0.70 × 0.45 × 0.25 mm, at −115 °C. *Crystal data*: $M_r = 292.10$; orthorhombic, space group $P2_12_12_1$, $a = 6.299(2)$, $b = 11.561(2)$, $c = 17.519(2)$ Å, $U = 1275.8(4)$ Å^3, $D_c = 1.521$ g cm^{-3} ($Z = 4$), $F(000) = 608$, μ(Mo-Kα) = 1.29 mm^{-1}, $\lambda = 0.71073$ Å. A total of 1421 reflections were collected using ω-scans in the range $4 < 2\theta < 50°$. Of these 1401 were unique ($R_{\text{merge}} = 0.0140$ after the data were corrected for absorption based on a series of psi-scans). The structure was solved by direct methods and developed routinely. Full-matrix least-squares refinement was based on F^2, with all non-hydrogen atoms anisotropic and with ring and CH_2 hydrogen atoms included in calculated positions with isotropic temperature factors 1.2 times that of the U_{iso} of the atom to which they are bonded. The hydroxy hydrogen atoms were located in a penultimate electron density map and were refined with fixed isotropic temperature factors. The refinement converged at $R_1 = 0.0297$ [for 1242 reflections with $I > 2\sigma(I)$] and $wR_2 = 0.0667$ (all data) $\{w = [\sigma^2(F_o^2) + (0.0593P)^2]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3)\}$; final GOF = 0.957. The final difference map showed no peak > + 0.385 e Å^{-3} and no hole < −0.294 e Å^{-3}. A Flack x parameter of 0.04(3) showed the refinement had been carried out with the correct polarity. Programs used were SHELXS-86[12] and SHELXL-93.[13] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/101.

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