

An air-stable, primary alkylphosphine: FcCH_2PH_2 [Fc = $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)$]

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Sodium metabisulfite-mediated elimination of formaldehyde from the ferrocene-derived hydroxymethylphosphine $\text{FcCH}_2\text{P}(\text{CH}_2\text{OH})_2$ yields the primary phosphine FcCH_2PH_2 , which has been fully characterised, including an X-ray crystal structure; the phosphine is completely air-stable.

Phosphine ligands containing ferrocene moieties are attracting interest for their coordination chemistry,¹ with significant recent emphasis on applications of metal complexes of chiral ferrocenylphosphines in asymmetric catalysis.² In a recent communication³ we described the synthesis of the air-stable, crystalline hydroxymethylphosphine $\text{FcCH}_2\text{P}(\text{CH}_2\text{OH})_2$ **1** from readily accessible $\text{FcCH}_2\text{NMe}_3^+\text{I}^-$ and $\text{P}(\text{CH}_2\text{OH})_3$, and reasoned that this compound should be a versatile precursor for the synthesis of a wide range of other ferrocene-derived phosphines. Here we report that **1** can be used to synthesise the remarkably air-stable, crystalline primary alkylphosphine FcCH_2PH_2 **2**.

Reaction of **1** with 1 mol equiv. of aqueous sodium metabisulfite was carried out in a two-phase aqueous–light petroleum (bp 60–80 °C) mixture, at reflux. FcCH_2PH_2 **2** was isolated from the light petroleum layer in 60% yield. It is particularly noteworthy that this reaction may be carried out in air; indeed the use of an inert (dinitrogen) atmosphere provides no significant increase in yield or purity of the product. The synthesis of **2** demonstrates the use of $\text{P}(\text{CH}_2\text{OH})_3$ as a masked, easily handled PH_3 equivalent. Orange crystals of **2**, of analytical purity,[‡] and suitable for a single-crystal X-ray structure determination,[§] were obtained by sublimation of the product *in vacuo*, onto a water-cooled coldfinger.

The molecular structure, shown in Fig. 1 together with selected bond distances and angles, unambiguously confirms **2** as the primary phosphine. Examination of the Cambridge Crystallographic Database⁴ indicates that only two other X-ray structure determinations of free primary phosphines have been reported previously.⁵ The P–C bond distance of **2**, 1.850(3) Å, is identical within experimental error to the P–C bond lengths calculated (1.8574 Å)⁶ and measured by electron diffraction (1.858 ± 0.003 Å)⁷ for PH_2Me .

The ³¹P NMR spectrum (CDCl_3) of **2** shows a resonance at $\delta -129$, showing a large ¹J(PH) coupling of 194 Hz in the proton-coupled spectrum. This chemical shift is comparable with those of other primary phosphines, which give ³¹P NMR resonances in the region $\delta -110$ to -160 .⁸ The positive-ion electrospray mass spectrum (1 : 1 MeCN–H₂O) yielded the oxidised ion 2⁺, as observed for other (low-basicity) ferrocene-derived species.⁹

Primary phosphines are typically highly air-sensitive; many derivatives, particularly those containing lower alkyl groups,

are pyrophoric. Only a very small number of primary phosphines are known to us to have been reported as air-stable,¹⁰ including other sterically unhindered primary phosphines of the type $[\text{RR}'_2\text{N}(\text{CH}_2)_n\text{PH}_2]\text{I}$.¹¹ Phosphine **2** appears to be completely air-stable both in the solid and solution states. The reasons for this are not immediately obvious, but the inclusion of the redox-active ferrocenyl group may be important in kinetically stabilising the phosphine towards oxidation. The structure of **2** shows that the PH_2 group is directed away from the Fe atom so there is no intramolecular interaction which would account for its lack of susceptibility to oxidation. After exposure of solid **2** to air at room temp. for 48 days no oxidation products could be detected by ³¹P NMR.

In view of the air-stability of **2**, it was of interest to see whether it possessed typical ligand properties towards transition-metal centres. Preliminary studies suggest that the coordination chemistry of **2** is not significantly compromised by the factors that lead to its air-stability, since the *cis*-[Mo(CO)₄(**2**)₂] complex **3** can be prepared by the thermal reaction of Mo(CO)₆ with **2** in decalin at 100 °C. Complex **3**, which is also air-stable, has been characterised by NMR spectroscopy (³¹P{¹H} NMR, CDCl_3 , $\delta_{\text{P}} -63.2$), electrospray mass spectrometry (negative-ion mode in MeOH with added NaOMe; $[\text{M} - \text{H}]^-$ at m/z 673), and by a single-crystal X-ray diffraction study, full details of which will be published separately.

The method of formaldehyde abstraction from **1** can also be extended to the synthesis of the secondary phosphine $\text{FcCH}_2\text{PH}(\text{CH}_2\text{OH})$ **4**, when 0.5 mol equiv. of sodium metabisulfite is used. This phosphine is readily characterised by the doublet resonance [¹J(PH) 205 Hz] observed in the proton-coupled ³¹P NMR spectrum at $\delta -50.7$. In contrast to **2**, phosphine **4** cannot be readily sublimed under the same conditions, the lower volatility of **4** being presumably due to the presence of relatively strong hydrogen bonding involving the hydroxymethyl group. However, it is worth noting that the attempted conversion of **1** to **2** by pyrolysis (dynamic vacuum, 120 °C, <0.05 mmHg) led to sublimation of mainly unreacted **1**, together with some **2** and **4**.

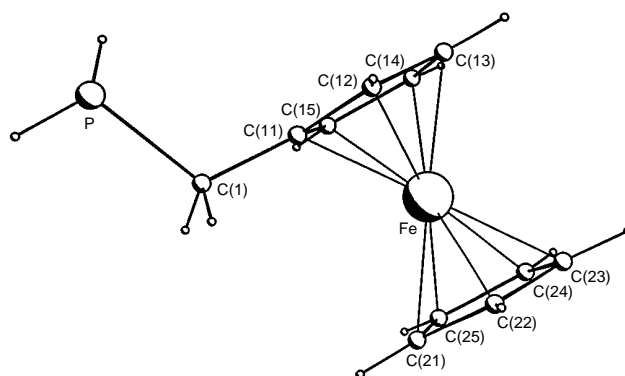
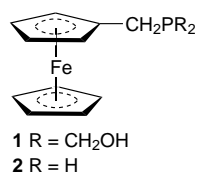


Fig. 1 Molecular structure of FcCH_2PH_2 **2**, with atom numbering scheme. Selected bond lengths (Å) and angles (°): C(11)–C(1) 1.492(4), C(1)–P 1.850(3), Fe–C 2.022(3)–2.042(2), av. 2.035 Å; C(11)–C(1)–P 113.7(2).

In summary, the simplicity of synthesis and ease of handling of **2** make it ideal for studying the reactivity of a primary phosphine. The inclusion of the ferrocene centre will permit the ready development of organophosphine derivatives having excellent redox properties.

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Footnotes

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‡ Anal. (after sixty-one days storage of sample in air). Found: C, 57.07; H, 5.52. Calc. for $\text{C}_{11}\text{H}_{13}\text{FeP}$: C, 56.94; H, 5.65%. Mp. 44–46 °C.

§ *Crystal data* for **2**: $\text{C}_{11}\text{H}_{13}\text{FeP}$, $M_r = 232.04$; monoclinic, space group $P2_1/c$, $a = 13.7111(9)$, $b = 7.5225(5)$, $c = 10.5662(7)$ Å, $\beta = 107.448(5)^\circ$, $U = 1039.7(1)$ Å³, $D_c = 1.482$ g cm⁻³ for $Z = 4$. $F(000) = 480$, $\mu(\text{Mo-K}\alpha) = 1.29$ mm⁻¹, $\lambda = 0.71073$ Å, $T = -105$ °C, crystal size = $0.52 \times 0.44 \times 0.24$ mm. A total of 3190 reflections were collected using ω scans with $4 < 2\theta < 60^\circ$. Of these 3032 were unique ($R_{\text{merge}} = 0.0279$ after absorption correction applied, based on ψ scans, $T_{\text{min,max}} = 0.403, 0.558$). 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 hydrogen atoms (except for P-H hydrogens) included in calculated positions with isotropic temperature factors 1.2 times that of the U_{iso} of the atom to which they are bonded. A penultimate electron density map showed two peaks which could be assigned to the H atoms on the P. These were included in fixed positions in the final refinement cycles. The refinement converged at $R_1 = 0.0411$ [for 2407 reflections with $(I) > 2\sigma(I)$] and $wR_2 = 0.1235$ (all data) $\{w = [\sigma^2(F_o^2) + (0.0525P)^2 + 0.81P]^{-1}$ where $P = [\max(F_o^2, 0) + 2F_c^2/3]$; final GOF = 1.032. The final difference map showed no peak greater than $+0.639$ e Å⁻³ and no hole larger than -0.454 e Å⁻³. Programs used were SHELXS-86¹² 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 182/302.

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