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Synthesis and reactivity of the ferrocene-derived phosphine $[Fe(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4CH_2P(CH_2OH)_2\}]$

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The air-stable compound $[Fe(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4CH_2P(CH_2OH)_2\}]$ **1** has been prepared by the reaction of $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4CH_2NMe_3)]I$ with an excess of $P(CH_2OH)_3$. Compound **1** has been used to produce a range of other new compounds, thus demonstrating its versatility as a starting material; the phosphine oxide $[Fe(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4CH_2P(O)(CH_2OH)_2\}]$ **2**, phosphine sulfide $[Fe(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4CH_2P(S)(CH_2OH)_2\}]$ **3**, and other derivatives $[Fe(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4CH_2P(CH_2CH_2CN)_2\}]$ **4**, $[Fe(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4CH_2P(CH_2NEt_2)_2\}]$ **5**, $[Fe(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4CH_2P(O)(CH_2NEt_2)_2\}]$ **6**, $[Fe(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4CH_2P(Me)(CH_2OH)_2\}]I$ **7** and $[Fe(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4CH_2P(Me)CH_2OH\}]$ **8**. Crystal structure determinations for **1**, **3** and **7** are reported and the hydrogen bonding of each structure described.

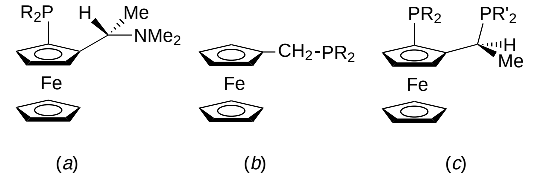
There has been a large amount of information published concerning the chemistry of phosphine ligands containing ferrocenyl moieties. This is exemplified by the enormous number of transition-metal complexes described for the chelating ligand 1,1′-bis(diphenylphosphino)ferrocene (dppf).[1] Reports of related ligands containing phosphine moieties linked directly by a P–C bond to the cyclopentadienyl ring of ferrocene [ferrocenylphosphines, Scheme 1(*a*)] are common,[2] especially since the recent rise in interest in ferrocenyl ligands displaying planar chirality.[3] However, examples of ferrocenylphosphines containing a carbon spacer between the cyclopentadienyl ring and P atom [(ferrocenylmethyl)phosphines, Scheme 1(*b*)] are less frequent; their synthesis was pioneered in the early 1960s,[4] but even 1,1′-bis(diphenylphosphinomethyl)ferrocene has only been synthesized very recently.[5] The great majority of known compounds of this type are the result of recent intense interest in chiral ferrocene ligands as auxiliaries for asymmetric synthesis and catalysis.[6] Some ferrocene compounds containing both ferrocenyl and ferrocenylmethyl fragments as substituents of the same phosphine are also known[7] [Scheme 1(*c*)].

This paper presents some detailed findings concerning $[Fe(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4CH_2P(CH_2OH)_2\}]$ **1**, a new (ferrocenylmethyl)phosphine. Some of these results have been reported in a preliminary communication,[8] and the use of **1** to prepare a novel ferrocene-containing primary phosphine has also been described elsewhere.[9] Compound **1** can be conveniently prepared in good yield from the readily available precursors $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4CH_2NMe_3)]I$ and $[P(CH_2OH)_4]Cl$, and is both crystalline and air-stable. This route to (ferrocenylmethyl)phosphines is of general applicability and could be used to prepare a wide variety of new compounds in this class, because of the potential for further reaction of the CH_2OH groups on the phosphorus. Literature methods already exist for the transformation of (hydroxymethyl)phosphine fragments into a variety of other functional groups; in general such groups react as disguised and easily manipulated P–H bonds. This report describes the synthesis of **1**, and demonstrates its use in the preparation of new types of phosphine–ferrocene compounds.

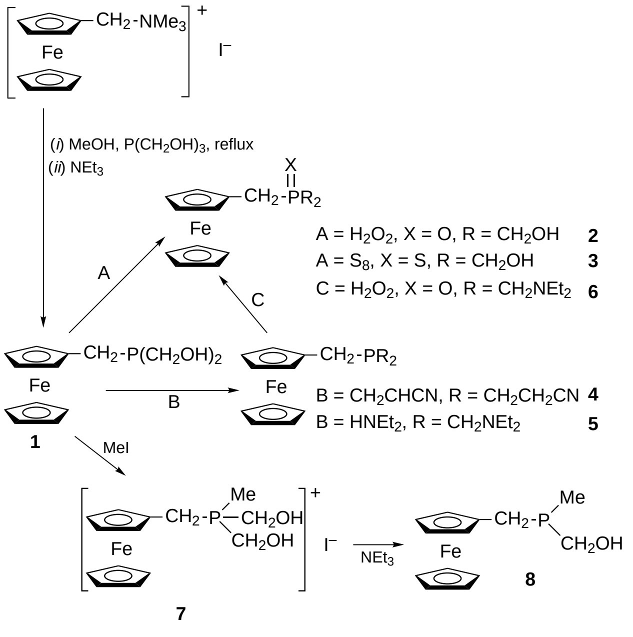
Results and Discussion

Syntheses

The various syntheses carried out in this work are summarised graphically in Scheme 2. Products were characterised by elemental analysis, Fourier-transform IR, electrospray mass spectrometry (ESMS), NMR spectroscopy and by X-ray analysis for compounds **1**, **3** and **7**. The ^{31}P NMR chemical shifts for each compound are quoted in this section; all were within the range expected for the class of compound concerned. The ESMS data and crystal structures are discussed in the following sections.



Scheme 1 Representative ferrocene–phosphine compounds: (*a*) phosphine directly linked to cyclopentadienyl ring; (*b*) carbon spacer between phosphorus and cyclopentadienyl ring; (*c*) both types of ferrocene–phosphine link are exemplified



Scheme 2 The reactions described in this paper, showing reagents used and products obtained

Refluxing a methanol solution of the well known compound $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4CH_2NMe_3)]I$[10] with an excess of $P(CH_2OH)_3$ {prepared *in situ* from $[P(CH_2OH)_4]Cl$ and KOH[11]} under an inert atmosphere leads to a substitution reaction, and presumably initial formation of the phosphonium salt $[Fe(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4CH_2P(CH_2OH)_3\}]Cl$, which will be largely converted into **1** by NMe_3 produced as a by-product of the reaction. An excess of NEt_3 is nevertheless added to ensure full dehydroxymethylation to the phosphine and, after removal of the methanol, extraction into diethyl ether yields the desired product **1** [^{31}P NMR ($CDCl_3$): δ −19.3] in good yield. Production of **1** by the direct reaction of ferrocene with $P(CH_2OH)_3$ in refluxing methanol was attempted but was unsuccessful.

The phosphine oxide $[Fe(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4CH_2P(O)(CH_2OH)_2\}]$ **2** [^{31}P NMR ($CDCl_3$): δ 45.8] and sulfide $[Fe(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4CH_2P(S)(CH_2OH)_2\}]$ **3** [^{31}P NMR ($CDCl_3$): δ 44.0] were prepared by reaction of compound **1** with H_2O_2 or elemental sulfur respectively. Elemental analysis of **2** proved to be non-reproducible and inaccurate, although the product appeared pure according to NMR spectroscopy. This difficulty with elemental analysis has been attributed to the inclusion of water into the crystal lattice of the product through strong hydrogen bonding. Although drying under vacuum did not remove this water, water was evolved during melting point determination. Thermogravimetric analysis showed a large endothermic peak at 99.3 °C, confirming the presence of water in the lattice.

The (cyanoethyl)phosphine $[Fe(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4CH_2P(CH_2CH_2CN)_2\}]$ **4** [^{31}P NMR ($CDCl_3$): δ −22.1] was prepared by reaction of compound **1** with acrylonitrile. It is a ferrocene-modified analogue of tris(2-cyanoethyl)phosphine, first prepared in 1959[12] and since subjected to a number of studies of its co-ordination chemistry.[13] This is largely due to interest in the relative affinities of the soft phosphorus and harder nitrogen donor atoms toward various metals. Similarly **4** is a multidentate ligand with the potential for a variety of bonding modes. The reaction of **1** with suitable activated alkenes other than acrylonitrile should prove just as straightforward and could be used to produce (ferrocenylmethyl)phosphines with a great variety of different functional groups [equation (1)]. The

$$[Fe(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4CH_2P(CH_2OH)_2\}] + CR^1{}_2 = CHR^2 \longrightarrow [Fe(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4CH_2P(CR^1{}_2CH_2R^2)_2\}] \quad (1)$$

successful reaction of (hydroxymethyl)phosphine groups with, for instance, acrylamide and acrylic acid, has been reported previously.[11]

Another well established reaction of (hydroxymethyl)phosphines is Mannich-type condensation with amines. This has been used to prepare compounds $[Fe(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4CH_2P(CH_2NEt_2)_2\}]$ **5** and $[Fe(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4CH_2P(O)(CH_2NEt_2)_2\}]$ **6**. The phosphine **5** [^{31}P NMR ($CDCl_3$): δ −48.3], prepared by reaction of **1** with diethylamine under nitrogen, was mildly air-sensitive and was only partially characterised. Of greater interest to us was the air-stable phosphine oxide **6**, prepared by controlled oxidation of **5** with H_2O_2. The preparation of **6** [^{31}P NMR ($CDCl_3$): δ 45.0] demonstrates that reaction of **1** with multifunctional amines could be used to produce ferrocene-containing polymers, which can be made air-stable by oxidation of the phosphine centre. Similarly the reaction of polyether amines with $P(CH_2OH)_3$ followed by phosphine oxidation has previously been used successfully for the preparation of polymers which proved to be excellent supports for enzyme immobilisation.[14] Synthesis of ferrocene-containing polymers by a wide variety of different methods has attracted considerable attention in the literature due to their potential for use as electrode coatings and non-linear optical (NLO) materials.[15] The ease with which **1** can be incorporated into solid amine-containing supports has been qualitatively assessed by reaction with aminopropyl silica. Aminopropyl silica immersed in a solution of **1** and then rinsed remained permanently yellow, while similar treatment with **2** or **3** led to much less marked staining, as would be expected since hydroxymethyl functionalities of phosphorus(v) compounds such as **2** and **3** are inactivated towards this Mannich-type reaction with amine groups.

The production of racemic $[Fe(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4CH_2P(Me)(CH_2OH)\}]$ **8** [^{31}P NMR ($CDCl_3$): δ −33.1] through initially alkylating compound **1** with methyl iodide to give the phosphonium salt $[Fe(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4CH_2P(Me)(CH_2OH)_2\}]I$ **7** [^{31}P NMR ($CDCl_3$): δ 26.2], followed by treatment with triethylamine, represents another potentially useful synthetic route for the substitution of hydroxymethyl groups in **1** by other functionalities [equations (2) and (3); X = I, Br or Cl]. Similar

$$[Fe(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4CH_2P(CH_2OH)_2\}] + RX \longrightarrow [Fe(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4CH_2PR(CH_2OH)_2\}]^+ \quad (2)$$

$$[Fe(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4CH_2PR(CH_2OH)_2\}]^+ + NEt_3 \longrightarrow [Fe(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4CH_2PR(CH_2OH)\}] \quad (3)$$

reactions with other (hydroxymethyl)phosphines have been reported previously.[11,16,17]

ESMS Analysis

It is only recently that use has been made of ESMS in order to investigate ferrocene derivatives. While the first investigation[18] of this kind demonstrated that ferrocene and its derivatives are oxidised by ESMS to the molecular cation rather than undergoing protonation, further experience has shown that certain compounds can exhibit protonation during ESMS.[19] The relative levels of the M^+ and $[M + H]^+$ signals observed can fluctuate from sample to sample, and the oxidisability and basicity of the particular compound being investigated influence which of the two signals is dominant. In the present study the neutral ferrocene derivatives **1**–**4** and **8** were characterised by ESMS and in each of these cases the M^+ ion dominated over $[M + H]^+$ formation. However, for the compounds **5** and **6** the $[M + H]^+$ species was observed in preference to M^+. This is presumably because of the presence of basic amine functionalities in these two compounds, allowing the protonated species to be more easily formed than is the case with the other neutral ferrocene derivatives investigated. In the case of **6** the phosphine oxide group may also act as a good H^+ acceptor.

Greater sensitivity in the ESMS detection of the unco-ordinated phosphines **1**, **4** and **5** was achieved using a previously published method[20] whereby $AgNO_3$ is added to samples. In spectra of samples treated in this way the M^+ or $[M + H]^+$ ion is still visible but is typically dominated by strong $[M + Ag]^+$ and $[2M + Ag]^+$ ion signals. Curiously, this method did not appear to be so effective in the case of compound **8**. It was thought that addition of Na^+ to samples of the phosphine oxide **2** and sulfide **3** in the form of NaCl might act in a similar fashion to the Ag^+ by forming charged complexes *in situ* and thus increasing sensitivity of detection for these compounds. However, while the $[M + Na]^+$ signals were visible in the ESMS spectra, the M^+ signals were easily the most significant.

Owing to its ionic nature compound **7** gave an easily detectable $[M - I]^+$ signal.

The results reported here are basically in agreement with a previous study of the behaviour of ferrocenyl- and ferrocenylmethyl-phosphines under ESMS conditions.[21]

Crystal structures

Structure elucidation by X-ray diffraction was performed for compounds **1**, **3** and **7**. Selected bond lengths and angles and structure diagrams are give in Tables 1, 2 and 3 and Figs. 1, 2 and 3 respectively. In each case the cyclopentadienyl rings

Table 1 Selected bond lengths (Å) and angles (°) for compound **1**

Fe–C av[a]	2.040(4)	P–C(1)	1.858(4)
range	2.034(4)–2.047(5)	P–C(2)	1.862(4)
C–C av[a]	1.414(6)	O(3)–C(3)	1.423(5)
range	1.399(7)–1.424(6)	O(2)–C(2)	1.429(5)
C(1)–C(11)	1.489(6)	O(2)–H(2)	0.74(5)
P–C(3)	1.851(4)	O(3)–H(3)	0.73(5)
C–C–C av[b]	108.0(4)	C(11)–C(1)–P	114.6(3)
range	107.2(4)–108.6(4)	O(2)–C(2)–P	111.9(3)
C–C–C av[c]	108.0(4)	O(3)–C(3)–P	116.2(3)
range	107.6(5)–108.7(4)	C(15)–C(11)–C(1)	125.0(4)
C(3)–P–C(1)	101.3(2)	C(12)–C(11)–C(1)	127.7(4)
C(3)–P–C(2)	99.5(2)	H(2)–O(2)–C(2)	113(4)
C(1)–P–C(2)	95.0(2)	H(3)–O(3)–C(3)	110(4)

[a] In cyclopentadienyl rings. [b] In substituted cyclopentadienyl ring. [c] In unsubstituted cyclopentadienyl ring.

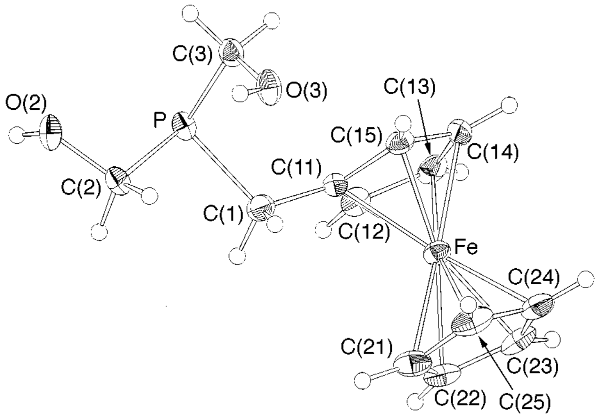


Fig. 1 A ZORTEP[22] diagram depicting the crystal structure of compound **1**. Thermal ellipsoids are drawn at the 40% probability level

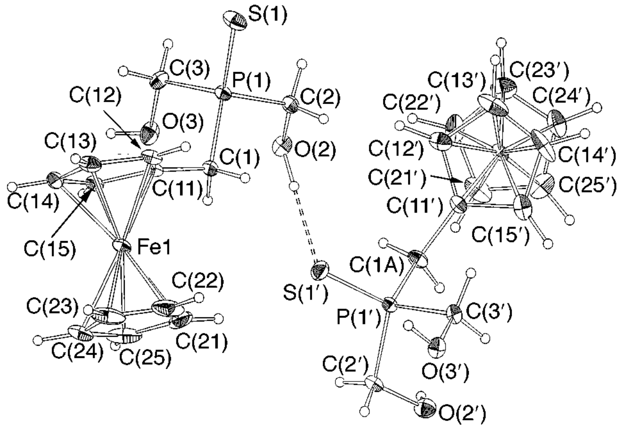


Fig. 2 A ZORTEP diagram depicting the crystal structure of both independent molecules for compound **3**, with the O–H···S hydrogen bond between them. Thermal ellipsoids are drawn at the 30% probability level

adopted an eclipsed conformation, with the phosphorus atom directed away from the ferrocene unit. Intramolecular bond distances and angles for all three compounds are within normal ranges.

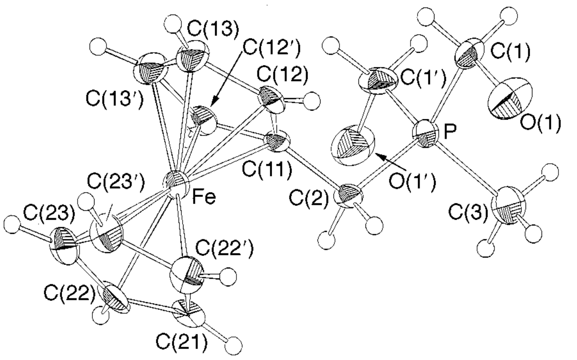


Fig. 3 A ZORTEP diagram depicting the crystal structure of the phosphonium cation of compound **7**. Thermal ellipsoids are drawn at the 40% probability level. The molecule lies on a crystallographic mirror plane incorporating the C(2), C(3), C(11), C(21), P(1) and Fe(1) atoms [also I(1), not shown]

Structures of (hydroxymethyl)phosphines should be of interest for their hydrogen bonding, and indeed the three compounds investigated show a variety of hydrogen-bonded structural motifs. In **1** hydrogen bonding leads to an elegant array of ten-membered rings of the type O(2)–C(2)–P–C(3)–O(3)–H···O(2)–H···O(3)–H between three neighbouring molecules (Fig. 4). This hydrogen-bonding system propagates up the 2_1 screw axis parallel to the *a* axis. The distance between hydrogen-bonded oxygens is 2.675 Å for O(2)–H···O(3) links and 2.662 Å for O(3)–H···O(2). The H···O distances are 1.962 and 1.942 Å respectively, while hydrogen-bond angles are respectively 167.0 and 164.9°.

Compound **3** crystallises with two independent molecules in the unit cell, and with a hydrogen-bonding array that consists of short discrete networks of O–H···O bonds which terminate at sulfur with an O–H···S hydrogen bond. The hydrogen-bonding array is diagrammatically presented in Fig. 5 and relevant distances and angles are given in Table 4. Phosphine oxides are good hydrogen-bond acceptors[24] and many crystal structures have been reported which shown strong intra-[25] and inter-molecular[26] hydrogen bonding of the phosphine oxide functionality. In contrast, relatively few crystal structures have been reported where there is potential to study the hydrogen-bonding behaviour of phosphine sulfides. Although it would be expected that the phosphine sulfide functionality is a weaker hydrogen-bond receptor than the oxide, the observed O···S distances of 3.1 and 3.3 Å in the structure of **3** suggest a reasonably intense hydrogen-bonding interaction.

The quality of crystallographic data obtained for compound **7** is appreciably lower than for the other two structure determinations, and the hydroxyl hydrogens could not be reliably located. However, the probable hydrogen-bonding pattern in this system can be deduced. The shortest oxygen–oxygen distances in the crystal are 4.267 Å, which precludes any appreciable hydrogen-bonding interactions between oxygens, in contrast with the situation for the other two structures. Instead the crystal packing is characterised by a pattern of I^-···H–O(1)–C(1)–P–C(1′)–O(1′)–H···I^-···H–O(1) hydrogen-bonding interactions (Fig. 6) between the cations and anions. The O···I distance is 3.386 Å and the C(1)–O(1)···I angle is 105.5°.

Conclusion

Compound **1** is readily prepared and handled, and is a versatile precursor for synthesis of different (ferrocenylmethyl)phosphines. It has been demonstrated that a number of such products are accessible through simple reactions of the hydroxymethyl groups, utilising known reaction routes for (hydroxymethyl)phosphines. These compounds show a variety of hydrogen-bonding modes in the solid state.

We are currently developing other reactions of compound **1**, preparations of other (ferrocenylmethyl)phosphines by reaction of $[Fe(\eta-C_5H_5)(\eta-C_5H_4CH_2NMe_3)]I$ with functionalised (hydroxymethyl)phosphines, preparation of chiral (ferrocenylmethyl)phosphines, and are investigating the electrochemistry of these compounds. Co-ordination chemistry of **1** has also been investigated and will be reported elsewhere.

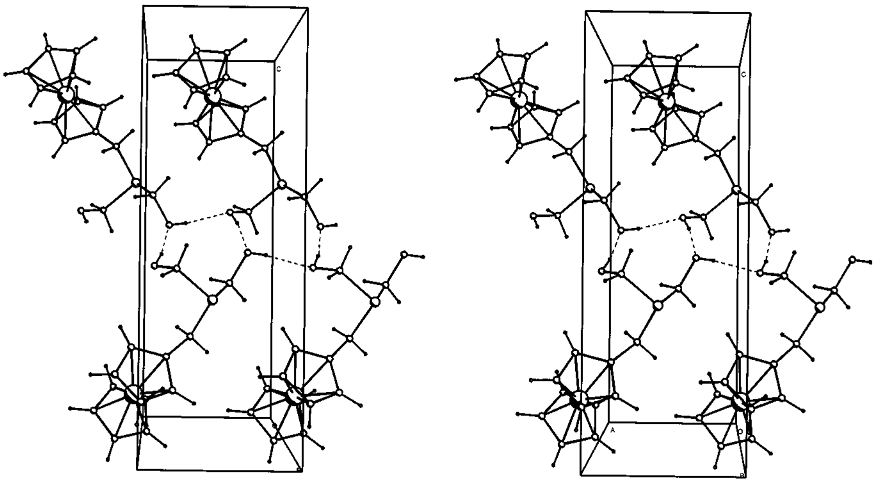


Fig. 4 A PLUTO[23] stereodiagram depicting the hydrogen-bonding array for compound **1**

Table 2 Selected bond lengths (Å) and angles (°) for compound **3**. Atoms belonging to molecule 2 are elsewhere denoted by primes

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
Fe–C average	2.035(2)	2.031(2)	P(1)–C(2)	1.836(2)	1.829(2)
range	2.018(3)–2.045(2)	2.019(2)–2.042(3)	P(1)–S(1)	1.9556(8)	1.9164(8)
C–C average[a]	1.404(4)	1.408(4)	C(1)–C(11)	1.496(3)	1.501(3)
range	1.347(5)–1.427(6)	1.390(4)–1.424(3)	C(2)–O(2)	1.413(3)	1.407(3)
P(1)–C(1)	1.817(2)	1.823(2)	C(3)–O(3)	1.415(3)	1.423(3)
P(1)–C(3)	1.821(2)	1.825(2)			
C–C–C average[b]	108.0(2)	108.0(2)	C(3)–P(1)–S(1)	111.66(8)	109.99(8)
range	107.4(2)–108.5(2)	107.2(2)–108.9(2)	C(2)–P(1)–S(1)	110.48(8)	111.78(8)
C–C–C average[c]	108.0(3)	108.0(2)	C(11)–C(1)–P(1)	113.4(2)	116.1(2)
range	105.8(3)–109.6(3)	107.7(2)–108.2(2)	O(2)–C(2)–P(1)	114.3(2)	111.45(14)
C(1)–P(1)–C(3)	106.0(1)	106.1(1)	O(3)–C(3)–P(1)	111.1(2)	110.79(14)
C(1)–P(1)–C(2)	105.2(1)	104.6(1)	C(12)–C(11)–C(1)	126.6(2)	126.4(2)
C(3)–P(1)–C(2)	106.4(1)	105.8(1)	C(15)–C(11)–C(1)	126.0(2)	125.8(2)
C(1)–P(1)–S(1)	116.43(8)	117.74(8)			

[a] In cyclopentadienyl rings. [b] In substituted cyclopentadienyl ring. [c] In unsubstituted cyclopentadienyl ring.

Table 3 Selected bond lengths (Å) and angles (°) for compound **7**

Fe–C average[a]	2.034(15)	P–C(2)	1.79(2)
range	1.99(2)–2.06(1)	P–C(3)	1.81(2)
C(11)–C(13) average	1.42(2)	P–C(1)	1.82(2)
range	1.36(3)–1.43(2)	C(1)–O(1)	1.38(2)
C(21)–C(23) average	1.42(2)	C(2)–C(11)	1.51(3)
range	1.38(3)–1.44(2)		
C–C–C average[b]	108(1)	C(3)–P–C(1)	109.1(6)
range	107(2)–109(1)	C(1)–P–C(1′)	110.5(9)
C–C–C average[c]	108(2)	O(1)–C(1)–P	107.0(9)
range	103(2)–113(2)	C(11)–C(2)–P	113(1)
C(2)–P–C(3)	109.0(9)	C(12)–C(11)–C(2)	126.4(8)
C(2)–P–C(1)	109.6(6)		

[a] In cyclopentadienyl rings. [b] In substituted cyclopentadienyl ring. [c] In unsubstituted cyclopentadienyl ring.

Experimental

General

The compound [Fe(η-C_5H_5)(η-$C_5H_4CH_2NMe_3$)]I[10] and aminopropyl silica[27] were prepared *via* literature methods; [$P(CH_2OH)_4$]Cl was obtained as Retardol C from Albright & Wilson Ltd., Oldbury, UK, as an 80% w/w aqueous solution and used as supplied. Solvents used were LR grade or better. Light petroleum was of b.p. 60–80 °C. Elemental analyses were performed by the Microanalytical Laboratory, Chemistry Department, University of Otago, Dunedin, New Zealand. The Fourier-transform IR spectra were obtained using a Bio-Rad FTS40 spectrometer. Samples were run as KBr discs unless otherwise stated. The ESMS spectra were recorded in positive-ion mode on a VG Platform II instrument with MeCN–water (1 : 1 v/v) as the mobile phase. Small quantities of $AgNO_3$ or NaCl were added as appropriate to aid ion formation. Skimmer cone voltages were varied in order to maximise spectrum quality, and identification of ions was aided by comparison of observed and calculated isotope distribution patterns.[28] The NMR spectra were obtained using a Bruker AC300 spectrometer, with $SiMe_4$ as an external standard, in $CDCl_3$ solution unless otherwise stated, operating at 75.47 MHz for ^{13}C, 300.13 MHz for ^{1}H, and 121.51 MHz for ^{31}P. Two-dimensional NMR experiments were used to unambiguously assign signals for compounds **1** and **4**. Other spectra were fully assigned by comparison with these compounds. The atom numbering system used in the crystal structures of **1** and **3** is used for assignments. Melting points were determined using a Reichert Thermopan melting-point microscope and are uncorrected. Thermogravimetric analysis of **2** was carried out using a Perkin-Elmer DSC6 calorimeter, with the sample heated from 50 to 160 °C at 15 °C min^{-1}.

Syntheses

[Fe(η-C_5H_5){η-$C_5H_4CH_2P(CH_2OH)_2$}] 1. A solution of

Table 4 Hydrogen-bond lengths (Å) and angles (°) for the hydrogen-bonding array in compound **3**. The bifurcated nature of the hydrogen bonding of O(2′)–H to O(2) and O(3) means these bonds are longer than is the case for the O(3)–H · · · O(3′) hydrogen bond

	Hydrogen–acceptor distance (Å)	Oxygen–acceptor distance (Å)	O–H–acceptor angle (°)
O(2′)–H · · · O(2)	2.29	3.06	143
O(2′)–H · · · O(3)	2.28	2.99	136
O(3)–H · · · O(3′)	1.84	2.74	159
O(2)–H · · · S′	2.23	3.14	163
O(3′)–H · · · S	2.56	3.33	143

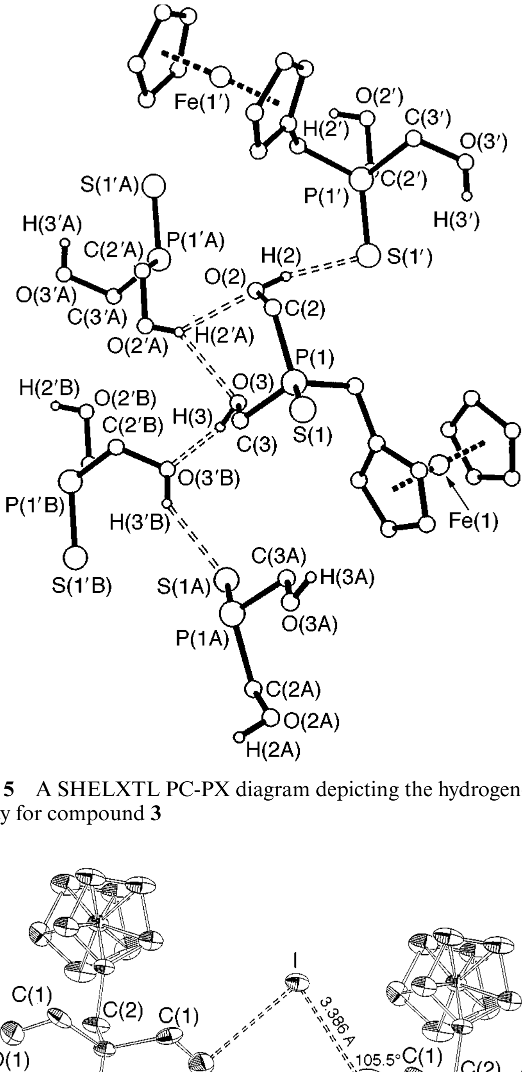


Fig. 5 A SHELXTL PC-PX diagram depicting the hydrogen-bonding array for compound **3**

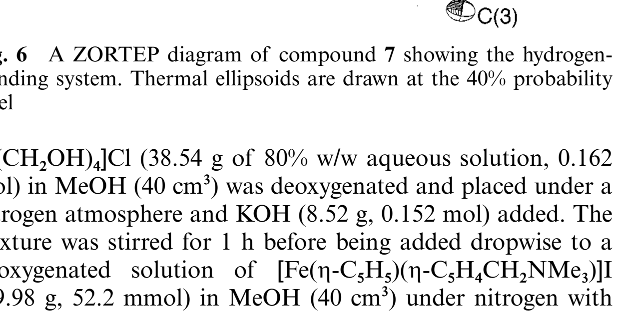


Fig. 6 A ZORTEP diagram of compound **7** showing the hydrogen-bonding system. Thermal ellipsoids are drawn at the 40% probability level

[P(CH$_2$OH)$_4$]Cl (38.54 g of 80% w/w aqueous solution, 0.162 mol) in MeOH (40 cm^3) was deoxygenated and placed under a nitrogen atmosphere and KOH (8.52 g, 0.152 mol) added. The mixture was stirred for 1 h before being added dropwise to a deoxygenated solution of [Fe(η-C$_5$H$_5$)(η-C$_5$H$_4$CH$_2$NMe$_3$)]I (19.98 g, 52.2 mmol) in MeOH (40 cm^3) under nitrogen with stirring. The reaction mixture was refluxed under nitrogen for 20 h, and the solvent was then removed under vacuum until large amounts of precipitate were observed. Water (30 cm^3), diethyl ether (85 cm^3) and NEt$_3$ (35 cm^3) were added and the solution stirred for 1 h. The aqueous layer was removed and re-extracted with Et$_2$O (30 cm^3), and both ether extracts were combined and washed with water (3 × 20 cm^3), then filtered. Removal of the ether under reduced pressure yielded the crude product as a microcrystalline orange solid (14.33 g, 94% yield). Recrystallisation of the product by addition of light petroleum to a warm CH$_2$Cl–MeOH solution followed by cooling to *ca.* −30 °C gave yellow-orange crystals (10.69 g, 70% yield), m.p. 104–106 °C (Found: C, 53.5; H, 6.2; N, 0.0. C$_{13}$H$_{17}$FeO$_2$P requires C, 53.5; H, 5.9; N, 0.0%). IR (cm^{-1}): 3371s, 3289s, 1463w, 1434m, 1412m, 1269w, 1232w, 1185w, 1104m, 1038w, 1003s, 922w, 885w, 854m, 827m, 807m, 754w, 657w, 572w, 500m and 483m. ESMS (with added AgNO$_3$, cone voltage = +60 V): *m*/*z* 691, [2*M* + Ag]$^+$; 399, [*M* + Ag]$^+$; 292, [*M*]$^+$; and 199, [Fe(C$_5$H$_5$)(C$_5$H$_4$CH$_2$)]$^+$. ^{31}P-{^{1}H} NMR: δ −19.3. ^{1}H NMR: δ 2.59 (OH, br s), 2.96 (C$_5$H$_4$C*H*$_2$P, s, 2 H), 4.04–4.10 and 4.25–4.33 (PCH$_2$O, m, 4 H), 4.09 [C(13)H and C(14)H, t, *J* = 1.8, 2 H], 4.14 [C(21)–C(25), s, 5 H] and 4.18 [C(12) and C(15), t, *J* = 1.8 Hz, 2 H]. ^{13}C-{^{1}H} NMR: δ 18.66 [C$_5$H$_4$*C*H$_2$P, d, *J* = 11.2], 61.72 [PCH$_2$O, d, *J* = 22.6 Hz], 67.73 [C(13) and C(14), s], 68.80 [C(12) and C(15), s], 68.89 [C(21)–C(25), s] and 84.22 [C(11), s].

[Fe(η-C$_5$H$_5$){η-C$_5$H$_4$CH$_2$P(O)(CH$_2$OH)$_2$}] 2. Aqueous hydrogen peroxide (10 cm^3, 0.234% w/w, 0.688 mmol) was added to a solution of compound **1** (0.200 g, 0.685 mmol) in MeOH (20 cm^3). The resulting solution was stirred in air for 7 min before the solvent was partly removed under vacuum (temperature maintained at *ca.* 15 °C), causing the product **2** to precipitate. This was filtered off and washed with water, then dried under vacuum yielding the crude product as a yellow powder (0.157 g, 72%). Yellow crystals were obtained by recrystallisation using the same method as for **1** (0.120 g, 55%), m.p. 126–135 °C (Found: C, 48.6; H, 5.9. C$_{13}$H$_{17}$FeO$_3$P·0.67H$_2$O requires C, 48.8; H, 5.8%). IR (cm^{-1}): 3310s, 3272s, 3137s, 2897m, 1690w (br), 1464w, 1426m, 1409m, 1241w, 1206m, 1144s, 1128s, 1104m, 1090m, 1038s, 1022m, 999m, 923w, 891w, 859m, 833m, 812m, 791m, 731m, 701m, 661w, 501m, 486m and 456m. ESMS (with added NaCl, cone voltage = +40 V): *m*/*z* 639, [2*M* + Na]$^+$; 331, [*M* + Na]$^+$; and 308, [*M*]$^+$. ^{31}P-{^{1}H} NMR: δ 45.8. ^{1}H NMR [(CD$_3$)$_2$SO]: δ 2.95 [C$_5$H$_4$C*H*$_2$P, d, *J* = 12.0, 2 H], 3.72 [PCH$_2$O, d, *J* = 3.4, 4 H], 4.18 [C(13)H and C(14)H, t, *J* = 1.5 Hz, 2 H], 4.23 [C(21)–C(25), s, 5 H] and 4.29 [C(12)H and C(15)H, s, 2 H]. ^{13}C-{^{1}H} NMR: δ 25.81 [C$_5$H$_4$*C*H$_2$P, d, *J* = 55.5], 55.30 [PCH$_2$O, d, *J* = 80.2 Hz], 68.49 [C(13) and C(14), s], 69.06 [C(21)–C(25), s] and 69.26 [C(12) and C(15), s]; C(11) not observed.

[Fe(η-C$_5$H$_5$){η-C$_5$H$_4$CH$_2$P(S)(CH$_2$OH)$_2$}] 3. Elemental sulfur (0.043 g, 1.35 mmol) and compound **1** (0.202 g, 0.693 mmol) were dissolved in toluene (20 cm^3) with a small amount of MeOH present to effect full solubilisation. The solution was refluxed in air for 3 h and most of the solvent removed under vacuum. The solution was cooled to *ca.* −30 °C and crystals formed. These were collected by vacuum filtration and washed with toluene before drying under vacuum to yield the crude product as a yellow powder (0.188 g, 84%). Dark orange crystals were obtained by recrystallisation using the same method as for **1** (0.162 g, 72%), m.p. 115–118 °C (Found: C, 48.0; H, 5.3. C$_{13}$H$_{17}$FeO$_2$PS requires C, 48.2; H, 5.3%). IR (cm^{-1}): 3407s, 3326s, 3264s, 1389w, 1361w, 1164w, 1105m, 1041s, 1027s, 999w, 881w, 850w, 826m, 802m, 753w, 690w, 627m, 610w, 573w, 555w, 500m, 483m and 436w. ESMS (with added NaCl, cone voltage = +40 V): *m*/*z* 671, [2*M* + Na]$^+$; 347, [*M* + Na]$^+$; and 324, [*M*]$^+$. ^{31}P-{^{1}H} NMR: δ 44.0. ^{1}H NMR: δ 3.23 [$C_5H_4C\mathit{H}_2P$, d, *J* = 12.6, 2 H], 3.87–3.91 (PCH_2O, m, 4 H), 4.15 [C(21)H–C(25)H, s, 5 H], 4.18 [C(13)H and C(14)H, t, *J* = 1.5 Hz, 2 H] and 4.24 [C(12)H and C(15)H, s, 2 H]. ^{13}C-{^{1}H} NMR: δ 30.11 [$C_5H_4\mathit{C}H_2P$, d, *J* = 41.8], 58.62 (PCH_2O, d, *J* = 53.8 Hz), 68.87 [C(13) and C(14)], 69.10 [C(12) and C(15)] and 69.18 [C(21)–C(25)]; C(11) not observed.

[Fe(η-C_5H_5){η-$C_5H_4CH_2P(CH_2CH_2CN)_2$}] 4. Compound **1** (0.400 g, 1.37 mmol) was dissolved in MeOH (20 cm^3) and acrylonitrile (0.20 cm^3, 3.04 mmol) added. The solution was stoppered and stirred in air for 90 min, after which time solvent was removed under vacuum. A crystallisation from $CHCl_3$–ether was used to precipitate an impurity, with the supernatant decanted off and the solvent removed to yield the product as an orange oil, which hardened to a semi-crystalline solid when cooled to 0 °C overnight (0.428 g, 92%). A sample for elemental analysis was obtained by twice washing a portion of the solid with ether prior to analysis. The product proved too amorphous to be suitable for melting point determination (Found: C, 59.6; H, 5.7; N, 8.2. $C_{17}H_{19}FeN_2P$ requires C, 60.4; H, 5.7; N, 8.3%). IR (cm^{-1}): 3334s, 2248w, 1651s, 1560s, 1481s, 1423s, 1393w, 1347w, 1327s, 1276w, 1104m, 1038m, 1023m, 1001m, 924w, 819s, 679m, 589s, 498s and 484s. ESMS (with added $AgNO_3$, cone voltage = +60 V): *m*/*z* 783, [2*M* + Ag]$^+$; 445, [*M* + Ag]$^+$; 338, [*M*]$^+$; and 199, [Fe(C_5H_5)($C_5H_4CH_2$)]$^+$. ^{31}P-{^{1}H} NMR: δ −22.1. ^{1}H NMR: δ 1.57–1.78 (CH_2CN, m, 4 H), 2.31 [$PC\mathit{H}_2CH_2$, t of d, ^{2}*J*(PH) = 10.0, ^{3}*J*(H) = 7.9, 4 H], 2.69 ($C_5H_4C\mathit{H}_2P$, d, *J* = 3.9), 4.05 [C(12)H and C(15)H, t, *J* = 1.7, 2 H], 4.11 [C(13)H and C(14)H, t, *J* = 1.4 Hz, 2 H] and 4.12 [C(21)H–C(25)H, s, 5 H]. ^{13}C-{^{1}H} NMR: δ 14.48 ($P\mathit{C}H_2CH_2$, d, *J* = 23.4), 22.29 ($\mathit{C}H_2CN$, d, *J* = 17.3), 27.72 ($C_5H_4\mathit{C}H_2P$, d, *J* = 16.7), 68.09 [C(13) and C(14)], 68.58 [C(12) and C(15)], 68.96 [C(21)–C(25)], 81.87 [C(11), d, *J* = 5.5] and 119.30 (CN, d, *J* = 11.7 Hz).

[Fe(η-C_5H_5){η-$C_5H_4CH_2P(CH_2NEt_2)_2$}] 5 and [Fe(η-C_5H_5)-{η-$C_5H_4CH_2P(O)(CH_2NEt_2)_2$}] 6. Compound **1** (0.200 g, 0.683 mmol) was dissolved in CH_2Cl_2 (10 cm^3) and placed under nitrogen. Diethylamine (1.00 cm^3, 9.71 mmol) was added and the solution stirred for 2 h, after which time the solvent was removed under vacuum, giving **5** as a yellow oil. ESMS (with added $AgNO_3$, cone voltage = +60 V): *m*/*z* 912, [2*M* + Ag]$^+$; 403, [*M* + H]$^+$; and 199, [Fe(C_5H_5)($C_5H_4CH_2$)]$^+$. ^{31}P-{^{1}H} NMR: δ −48.3. ^{1}H NMR: δ 0.99 [$CH_2C\mathit{H}_3$, t, ^{3}*J*(HH) = 7.1, 12 H], 2.53–2.69 ($C\mathit{H}_2CH_3$ and $C_5H_4C\mathit{H}_2P$ and PCH_2N, m, 14 H), 4.03 [C(13)H and C(14)H, t, ^{3}*J*(HH) = 1.8 Hz, 2 H], 4.08–4.09 [C(12)H and C(15)H and C(21)–C(25), m, 7 H). ^{13}C-{^{1}H} NMR: δ 11.75 ($CH_2\mathit{C}H_3$), 27.00 [$C_5H_4\mathit{C}H_2$, d, ^{1}*J*(PC) = 16.3], 48.14 [$\mathit{C}H_2CH_3$, d, ^{3}*J*(PC) = 8.6], 53.66 [PCH_2N, d, ^{1}*J*(PC) = 7.4], 67.36 [C(13) and C(14)], 68.77 [C(21)–C(25)], 68.97 [C(12) and C(15)] and 84.56 [C(11), d, ^{2}*J*(PC) = 7.7 Hz].

The product was redissolved in MeOH (30 cm^3) and aqueous H_2O_2 solution added (5 cm^3, 0.469%, 0.690 mmol). The mixture was stirred for 15 min, then most of the solvent was removed under vacuum with temperature of the mixture maintained at *ca.* 15 °C. The residue was extracted with ether (20 cm^3), and the organic layer washed with water (3 × 10 cm^3) and dried under vacuum to give crude compound **6** as a pale orange solid (0.249 g, 87%). Recrystallisation from acetone–pentane cooled to *ca.* −30 °C gave an orange powder (0.154 g, 54%). More product, though less pure, can be obtained by recrystallisation of the evaporated supernatant, m.p. 102–107 °C (Found: C, 60.2; H, 8.6; N, 6.5. $C_{21}H_{35}FeN_2OP$ requires C, 60.3; H, 8.4; N, 6.7%). IR (cm^{-1}): 3095m, 2964s, 2931s, 2872m, 2810s, 1466m, 1457m, 1422w, 1386m, 1371m, 1336w, 1297w, 1252m, 1243s, 1199m, 1170s, 1141s, 1104s, 1064m, 1039w, 1019w, 998m, 976w, 926w, 860m, 816s, 784m, 597w, 490s and 434m. ESMS (cone voltage = +20 V): *m*/*z* 837, [2*M* + H]$^+$; and 419, [*M* + H]$^+$. ^{31}P-{^{1}H} NMR: δ 45.0. ^{1}H NMR: δ 0.98 [$CH_2C\mathit{H}_3$, t, ^{3}*J*(HH) = 7.1, 12 H], 2.60–2.77 ($C\mathit{H}_2CH_3$ and PCH_2N, m, 12 H), 3.02 [$C_5H_4C\mathit{H}_2P$, d, ^{2}*J*(PH) = 13.9, 2 H], 4.09 [C(13)H and C(14)H, t, ^{3}*J*(HH) = 1.8, 2 H], 4.11 [C(21)–C(25), s, 5 H] and 4,22 [C(12)H and C(15)H, t, ^{3}*J*(HH) = 1.6 Hz, 2 H]. ^{13}C-{^{1}H} NMR: δ 11.25 ($CH_2\mathit{C}H_3$), 28.93 [$C_5H_4\mathit{C}H_2P$, d, ^{1}*J*(PC) = 59.8], 48.28 [$\mathit{C}H_2CH_3$, d, ^{3}*J*(PC) = 7.2], 50.35 [PCH_2N, d, ^{1}*J*(PC) = 81.5 Hz], 67.99 [C(13) and C(14)], 68.99 [C(21)–C(25)], 69.44 [C(12) and C(15)] and 79.26 [C(11)].

[Fe(η-C_5H_5){η-$C_5H_4CH_2P(Me)(CH_2OH)_2$}]I 7. Compound **1** (0.302 g, 1.03 mmol) was dissolved in MeOH (10 cm^3), and MeI (1.0 cm^3, 16 mmol) was slowly added with swirling. The solution was heated to 50 °C for 15 min, then ether (120 cm^3) added to precipitate **7** as a yellow powder (0.411 g, 92%). Recrystallisation from hot MeOH gave orange crystals (0.306 g, 68%), m.p. (decomp.) *ca.* 170 °C (Found: C, 38.8; H, 4.5. $C_{14}H_{20}FeIO_2P$ requires C, 38.7; H, 4.6%). IR (cm^{-1}): 3253s, 1427m, 1404w, 1388w, 1306w, 1285w, 1200w, 1103w, 1035s, 996m, 960m, 921m, 882m, 865w, 839m, 814m, 499s and 479s. ESMS (cone voltage = +20 V): *m*/*z* 307, [*M* − I]$^+$; and 291, [*M* − I − CH_4]$^+$. ^{31}P-{^{1}H} NMR [$(CD_3)_2SO$]: δ 26.2. ^{1}H NMR [$(CD_3)_2SO$]: δ 1.67 [CH_3, d, *J* = 14.2, 3 H], 3.57 [$C_5H_4C\mathit{H}_2P$, d, *J* = 13.7 Hz, 2 H] and 4.29–4.43 (cyclopentadienyl H and PCH_2O, m, 11 H). ^{13}C-{^{1}H} NMR [$(CD_3)_2SO$]: δ 3.15 (CH_3, d, *J* = 47.9), 22.18 ($C_5H_4CH_2P$, d, *J* = 40.6), 55.54 (PCH_2O, d, *J* = 56.2 Hz), 72.53 [C(13) and C(14)], 72.94 [C(21)–C(25)], 73.24 [C(12) and C(15)] and 78.84 [C(11)].

[Fe(η-C_5H_5){η-$C_5H_4CH_2P(Me)CH_2OH$}] 8. Compound **7** (0.167 g, 0.384 mmol) was dissolved in ether (40 cm^3) and water (25 cm^3) and NEt_3 (1.0 cm^3, 14 mmol) added. The mixture was stirred for 2 h. The organic layer was then extracted and washed with water (2 × 20 cm^3) before drying under vacuum. The product **8** was obtained as a yellow oil (0.099 g, 94%). Attempts to purify it further by chromatography were unsuccessful. IR (cm^{-1}): 3361s, 3092s, 2966s, 2897s, 2814s, 1636w, 1466s, 1421s, 1351m, 1287m, 1233m, 1195w, 1152w, 1104s, 1021s, 1002s, 925s, 897s, 818s, 716w and 593w. ESMS (cone voltage = +10 V): *m*/*z* 291, [*M* + CH_3]$^+$; and 277 [*M* + H]$^+$. ^{31}P-{^{1}H} NMR: δ −33.1. ^{1}H NMR: δ 0.98 [CH_3, d, ^{2}*J*(PH) = 2.7, 3 H], 2.60–2.64 ($C_5H_4C\mathit{H}_2P$, m, 2 H), 3.81 [PCH_2O, d, ^{2}*J*(PH) = 7.7 Hz, 2 H] and 4.07–4.11 (cyclopentadienyl H, m, 9 H). ^{13}C-{^{1}H} NMR: δ 7.12 [CH_3, d, ^{1}*J*(PC) = 14.7], 26.64 [$C_5H_4\mathit{C}H_2P$, d, ^{1}*J*(PC) = 13.9], 62.27 [PCH_2O, d, ^{1}*J*(PC) = 15.1], 67.59 [C(13) and C(14)], 68.70 [C(12) and C(15)], 68.79 [C(21)–C(25)] and 84.08 [C(11), d, ^{2}*J*(PC) = 7.7 Hz].

Crystallography

Crystallographic data for compounds **1**, **3** and **7** are given in Table 5. Crystals were obtained by procedures detailed in the previous section. Raw data were corrected for absorption based on a series of ψ scans, and structures were solved by direct methods and developed routinely. Full-matrix least-squares refinement was based on F^2, with all non-hydrogen atoms anisotropic. Hydrogen atoms were included in calculated positions with isotropic thermal parameters 1.2 times that of the U_{iso} of the atom to which they are bonded, with the following exceptions: in **1** atoms H(2) and H(3) [bonded to atoms O(2) and O(3) respectively] were located in a penultimate electron-density map and refined with fixed isotropic thermal parameters; in **3** atoms H(2) and H(3) and H(2′) and H(3′) [bonded to atoms O(2), O(3), O(2′) and O(3′) respectively] were located in a penultimate electron-density map and refined in a riding model; in **7** the hydroxyl hydrogen could not

Table 5 Crystallographic data for compounds **1**, **3** and **7**

	1	**3**	**7**
Empirical formula	$C_{13}H_{17}FeO_2P$	$C_{13}H_{17}FeO_2PS$	$C_{14}H_{20}FeIO_2P$
M_r	292.10	324.15	434.02
Space group	$P2_12_12_1$	$P\bar{1}$	*Pnma*
Crystal system	Orthorhombic	Triclinic	Orthorhombic
a/Å	6.299(2)	10.765(1)	14.875(7)
b/Å	11.561(2)	11.024(2)	9.727(8)
c/Å	17.519(2)	12.791(1)	10.868(6)
α/°		67.93(1)°	
β/°		80.69(1)°	
γ/°		77.95(1)°	
U/Å^3	1275.8(4)	1369.9(3)	1572(2)
D_c/g cm^{-3}	1.521	1.572	1.833
Z	4	4	4
F(000)	608	672	856
μ(Mo-Kα)/mm^{-1}	1.29	1.360	3.019
T/°C	−115	−83(2)	−115(2)
Crystal size/mm	0.70 × 0.45 × 0.25	0.32 × 0.24 × 0.19	0.50 × 0.20 × 0.15
ω Scans/°	$2.11 < \theta < 25$	$2.54 < \theta < 25$	$2.32 < \theta < 22.49$
Total reflections	1421	5560	1275
Unique reflections	1401	4736	1095
R_{merge}	0.0140	0.0106	0.0367
T_{min}	*a*	0.675	0.3643
T_{max}	*a*	0.953	0.6467
$R1$ [$I > 2\sigma(I)$]	0.0297	0.0269	0.0704
$wR2$ (all data)	0.0667^b	0.0648^c	0.2025^d
Goodness of fit	0.957	1.048	0.979
Maximum, minimum electron density/ e Å^{-3}	0.385, −0.294	0.315, −0.389	1.678, −1.208
Flack *x* parameter	0.04(3)	—	—
Diffractometer	Nicolet R3	Siemens P4	Siemens P4
Solution and refinement programs	SHELXS 86[29], SHELXL 93[30]	SHELXTL PC,[31] SHELXL 93	SHELXS 86, SHELXL 93

[a] Absorption correction was performed but transmission factors were not recorded. [b] $w = [\sigma^2(F_o^2) + (0.0593P)^2]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$. [c] $w = [\sigma^2(F_o^2) + (0.0288P)^2 + 1.09P]^{-1}$ where $P = [\max(F_o^2, 0) + 2F_c^2]/3$. [d] $w = [\sigma^2(F_o^2) + (0.1327P)^2]^{-1}$ where $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

be located. Calculated positions for the C(3) methyl group of **7** were established such that the C(3)–P bond configuration was staggered.

Drawing programs XPMA[22] and PLUTO[23] assisted in the investigation of hydrogen bonding, and structures illustrated in this publication were drawn with ZORTEP[22] and SHELXTL PC-XP.[32]

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