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Ferrocenyl hydroxymethylphosphines $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[\eta^5\text{-C}_5\text{H}_4\text{P}(\text{CH}_2\text{OH})_2]$ and $1,1'\text{-}[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{CH}_2\text{OH})_2\}_2]$ and their chalcogenide derivatives

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Abstract

The ferrocenyl hydroxymethylphosphines $\text{FcP}(\text{CH}_2\text{OH})_2$ [$\text{Fc} = (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)$] and $1,1'\text{-Fc}'[\text{P}(\text{CH}_2\text{OH})_2]_2$ [$\text{Fc}' = \text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2$] were prepared by reactions of the corresponding primary phosphines FcPH_2 and $1,1'\text{-Fc}'(\text{PH}_2)_2$ with excess aqueous formaldehyde. The crystal structure of $\text{FcP}(\text{CH}_2\text{OH})_2$ was determined and compared with the known ferrocenyl hydroxymethylphosphine $\text{FcCH}_2\text{P}(\text{CH}_2\text{OH})_2$. The chalcogenide derivatives $\text{FcP}(\text{E})(\text{CH}_2\text{OH})_2$ and $1,1'\text{-Fc}'[\text{P}(\text{E})(\text{CH}_2\text{OH})_2]_2$ ($\text{E} = \text{O}, \text{S}, \text{Se}$) were prepared and fully characterised. Crystal structure determinations on $\text{FcP}(\text{O})(\text{CH}_2\text{OH})_2$ and $\text{FcP}(\text{S})(\text{CH}_2\text{OH})_2$ were performed, and the hydrogen-bonding patterns are compared with related compounds. The sulfide shows no hydrogen-bonding involving the phosphine sulfide group, in contrast to other reported ferrocenyl hydroxymethylphosphine sulfides. The platinum complex *cis*- $[\text{PtCl}_2\{\text{FcP}(\text{CH}_2\text{OH})_2\}_2]$ was prepared by reaction of 2 mol equivalents of $\text{FcP}(\text{CH}_2\text{OH})_2$ with $[\text{PtCl}_2(1,5\text{-cyclo-octadiene})]$, and was characterised by ^{31}P -NMR spectroscopy and negative ion electrospray mass spectrometry, which gave a strong $[\text{M} + \text{Cl}]^-$ ion. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ferrocene compounds; Hydroxymethylphosphines; Hydrogen-bonding; Platinum complexes; Crystal structures

1. Introduction

Hydroxymethylphosphines, containing $\text{P}-\text{CH}_2\text{OH}$ groups, are attractive ligands in transition metal chemistry. The hydroxyl groups help to confer water-solubility, and the reactivity of these hydroxyl groups towards amines [1] and unsaturated compounds such as alkenes [2] allows simple modification of the ligand to provide a diverse range of derivatives. Accordingly, there has been renewed interest in the coordination chemistry of hydroxymethylphosphines, particularly for catalytic and bio-medical applications [3].

Several years ago, we reported the synthesis of the ferrocene-based hydroxymethylphosphine FcCH_2P -

$(\text{CH}_2\text{OH})_2$, starting from $\text{P}(\text{CH}_2\text{OH})_3$ and $\text{FcCH}_2\text{NMe}_3^+\text{I}^-$ [4]. This air-stable, crystalline compound was found to be a useful precursor to a range of new ferrocene-based phosphines, including the primary phosphine FcCH_2PH_2 , which is air-stable [5]. Since then, other related ferrocene-derived hydroxymethyl phosphines and their derivatives have been reported [6–8]; in all of these compounds there is a CH_2 or CHMe spacer between the ferrocenyl group and the phosphine. In this paper we report the synthesis of new ferrocenyl hydroxymethylphosphines where the phosphine group is bonded directly to the cyclopentadienyl ring. The syntheses of oxide, sulfide and selenide derivatives are also described, together with a study of hydrogen-bonding patterns in the solid-state structures of a selection of these compounds. Part of this work has been published as a preliminary communication [9].

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2. Results and discussion

2.1. Synthesis of hydroxymethylphosphines

The addition of a P–H bond to formaldehyde is a standard method for the preparation of a hydroxymethylphosphorus compound [3,10,11]. The reactions of the primary phosphines FcPH_2 [$\text{Fc} = (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)$] and $1,1'\text{-Fc}'(\text{PH}_2)_2$ [$\text{Fc}' = \text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2$] with excess aqueous formaldehyde solution gave the corresponding hydroxymethylphosphines $\text{FcP}(\text{CH}_2\text{OH})_2$ (**1**) and $1,1'\text{-Fc}'[\text{P}(\text{CH}_2\text{OH})_2]_2$ (**2**) in high yields. The use of excess formaldehyde led to the initial formation of several products, presumed to contain $\text{P}-(\text{CH}_2\text{O})_n\text{-H}$ adducts ($n > 1$), which are known to form from hydroxymethylphosphines in the presence of excess formaldehyde [10]. Exposure of the crude reaction mixtures to dynamic vacuum (ca. 1 mmHg) gave the desired hydroxymethylphosphines as the sole product. Hydroxymethylphosphine **1** was isolated as a crystalline brown solid that was soluble in polar organic solvents and indefinitely stable in air. Phosphine **2** was isolated as a brown oil, and oxidation–decomposition occurred on exposure to air. Satisfactory microanalytical data could not be obtained for **2**.

Phosphine **1** gave $[2\text{M} + \text{Ag}]^+$ ions (m/z 663/665) when analysed by electrospray (ES) mass spectrometry at a cone voltage of 20 V in the presence of added AgNO_3 . At 40 V, the $[\text{M} + \text{Ag}]^+$ ion was seen (at m/z 385/387) and at 100 V, $[\text{M}]^+$ (m/z 278) was observed. The use of Ag^+ ions in the analysis of phosphine and arsine ligands provides a ready means of ionization, by the in situ formation of cationic silver–phosphine complexes [12,13]. Similarly, phosphine **2** gave ES mass spectra dominated by $[2\text{M} + \text{Ag}]^+$ (m/z 847/849) and $[\text{M} + \text{Ag}]^+$ (m/z 477/479) ions at low (20 V) and high (60 V) cone voltages, respectively.

The $^1\text{H-NMR}$ spectrum of **1** revealed that the hydroxymethyl CH_2 protons were in unique environments, with a geminal $^2J(\text{HH})$ coupling constant of 13 Hz. This was not observed in the $^1\text{H-NMR}$ spectra of the related compounds $\text{FcCH}_2\text{P}(\text{CH}_2\text{OH})_2$ and $\text{FcCH}_2\text{P}(\text{S})(\text{CH}_2\text{OH})_2$ [4], which suggests that the proximity of the bulky ferrocenyl group is restricting rotation about the P– CH_2 and/or CH_2 –O bonds. Alternatively, it is possible that conjugation of the phosphorus lone pair with the attached ferrocenyl ring in compounds without CH_2 spacers is responsible for the inequivalence of the CH_2OH protons. The CH_2 protons of **2** appeared as a multiplet.

2.2. Synthesis of chalcogenide derivatives

In order to provide stable, crystalline derivatives of the hydroxymethylphosphines **1** and **2** for additional characterisation data, the oxide, sulfide and selenide

derivatives were synthesised. The phosphine oxide $\text{FcP}(\text{O})(\text{CH}_2\text{OH})_2$ (**3**) was prepared from the parent hydroxymethylphosphine by reaction with an equimolar amount of hydrogen peroxide. The reaction proceeded smoothly at room temperature and was conveniently monitored by $^{31}\text{P-NMR}$ spectroscopy. The oxide **3** is an air-stable yellow crystalline solid, soluble in methanol, DMSO and water. The syntheses of the analogous sulfide **4** and selenide **5** derivatives were accomplished using powdered sulfur or selenium, and ultrasound. Ultrasound is an accepted technique in many areas of synthetic chemistry, particularly for reactions involving suspended solids [14]. In this case the reactions of $\text{FcP}(\text{CH}_2\text{OH})_2$ with S_8 or Se in THF were complete in a short period of time. The sulfide $\text{FcP}(\text{S})(\text{CH}_2\text{OH})_2$ and selenide $\text{FcP}(\text{Se})(\text{CH}_2\text{OH})_2$ were orange crystalline compounds; both are soluble in polar organic solvents and have clearly defined melting points.

In the same manner, the corresponding dioxide **6**, disulfide **7** and diselenide **8** derivatives of **2** were synthesised. The compounds are stable in air in the solid state, but prone to decomposition in solution. All three derivatives are soluble in water, methanol and DMSO, while the sulfide and selenide are also soluble in acetone. Satisfactory microanalytical data were obtained for these derivatives.

The $^{31}\text{P-NMR}$ spectra of the chalcogenide derivatives **3–8** show the expected shift compared with the phosphine itself, with the selenides **5** and **8** showing additional $^1J(\text{PSe})$ coupling (701 and 713 Hz, respectively), which compare well with other phosphine selenides, e.g. $\text{Ph}_2\text{P}(\text{Se})(\text{CH}_2\text{OH})$ (717 Hz) [13]. The $^1\text{H-NMR}$ spectra of the sulfide and selenide derivatives **4**, **5**, **7** and **8** revealed the non-equivalence of the CH_2 protons, as was observed for **1**. These gave an AB coupling pattern characteristic of geminal CH_2 protons with $^2J(\text{HH})$ around 13 Hz.

The ES mass spectra of **3–5** are dominated by peaks due to the respective $[\text{M} + \text{H}]^+$ ions. In addition, peaks due to $[2\text{M} + \text{H}]^+$, $[\text{M} + \text{Na}]^+$ and $[2\text{M} + \text{Na}]^+$ were often observed. At higher cone voltages peaks corresponding to loss of CH_2O were observed. Under ES conditions, **6–8** formed $[\text{M} + \text{X}]^+$ adducts with a range of cations. For example, the spectrum of the dioxide **6** in methanol at a cone voltage of 20 V was dominated by the $[\text{M} + \text{Na}]^+$ ion (m/z 425) but also present were $[\text{M} + \text{H}]^+$ (m/z 403), $[\text{M} + \text{Li}]^+$ (m/z 409), $[\text{M} + \text{K}]^+$ (m/z 441) and $[\text{M} + \text{Na} - \text{CH}_2\text{O}]^+$ (m/z 395), formed from adventitious metal ions in the system. To simplify the ES spectra of **6–8**, Na^+ ions (as dilute aqueous NaCl) were deliberately added; at low cone voltages the spectra simplify to two peaks due to $[\text{M} + \text{Na}]^+$ and $[2\text{M} + \text{Na}]^+$, though small peaks due to $[\text{M} + \text{Li}]^+$ and $[\text{M} + \text{K}]^+$ remained. Increasing the cone voltage led to loss of formaldehyde, giving the ions $[\text{M} + \text{Na} - n\text{CH}_2\text{O}]^+$ ($n = 1\text{–}4$). ES spectra of $1,1'\text{-Fc}'[\text{P}(\text{S})(\text{CH}_2\text{OH})_2]_2$ (**7**) at cone

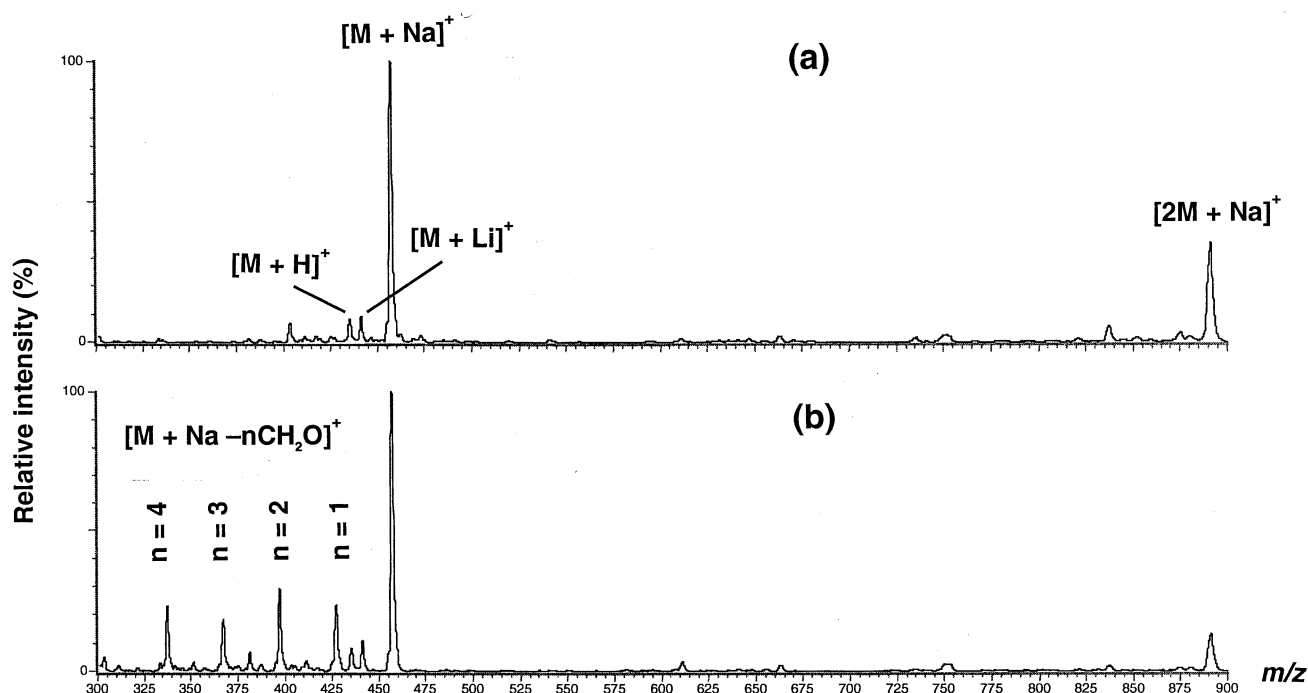


Fig. 1. ESMS (methanol solvent, NaCl added) of 1,1'-Fc[P(S)(CH₂OH)₂]₂ (7) at cone voltages of (a) 20 V (b) 60 V.

voltages of 20 and 60 V are shown in Fig. 1, where the loss of CH₂O at the higher cone voltage is clearly shown.

2.3. X-ray structure determinations

The crystal structure of **1** was carried out in order to provide a comparison with FcCH₂P(CH₂OH)₂, which has been structurally characterised previously [4]. Of particular interest in such compounds are the hydrogen-bonded networks formed. Selected bond lengths and angles are given in Table 1, while the molecular structure is shown in Fig. 2. The hydrogen-bonding network is very similar to that of FcCH₂P(CH₂OH)₂; each hydrox-

yl group acts as a hydrogen bond donor and acceptor. The molecules are arranged into one-dimensional chains, crosslinked by hydrogen bonds, running parallel to the *b*-axis. The hydrogen-bonded network structure is shown in Fig. 3. There are two distinct hydrogen bonds, H(4)··O(1) (1.95 Å) which link two chains together, and H(3)··O(2) (2.00 Å) which link together adjacent molecules in the same chain. Each molecule is involved in hydrogen-bonding interactions with four others. Similar hydrogen bond lengths (1.96 and 1.94 Å) were reported for hydrogen bonds in FcCH₂P(CH₂OH)₂ [4]. The two types of hydrogen bond lead to the formation of ten-membered rings between three adjacent molecules.

Table 1
Selected bond lengths (Å) and angles (°) for FcP(CH₂OH)₂ (**1**)

<i>Bond lengths</i>			
Cp Fe–C average	2.046(2)	C(1)–O(1)	1.425(2)
Range	2.035–2.052	C(2)–O(2)	1.423(2)
Cp C–C average	1.423(3)	O(1)–H(3)	0.6796
Range	1.417–1.435	O(2)–H(4)	0.7158
C(11)–P(1)	1.809(2)	H(3)··O(2) ^y	2.0061
P(1)–C(1)	1.849(2)	H(4)··O(1) ^y	1.9526
P(1)–C(2)	1.850(2)		
<i>Bond angles</i>			
C(11)–C(15) range	106.88(15)–108.41(17)	C(21)–C(25) range	107.82(18)–108.16(17)
C(12)–C(11)–P(1)	122.22(13)	P(1)–C(1)–O(1)	110.82(13)
C(15)–C(11)–P(1)	130.85(14)	C(1)–O(1)–H(3)	113.11
C(11)–P(1)–C(1)	99.18(8)	C(2)–O(2)–H(4)	106.00
C(11)–P(1)–C(2)	103.07(9)	O(1)–H(3)··O(2) ^y	162.10
P(1)–C(2)–O(2)	115.83(13)	O(2)–H(4)··O(1) ^y	179.16

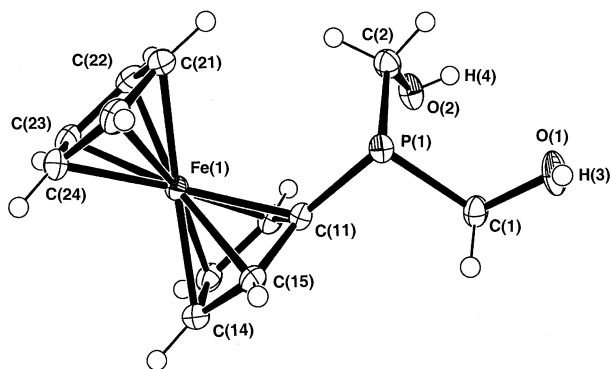


Fig. 2. Molecular structure of $\text{FcP}(\text{CH}_2\text{OH})_2$ (1) with thermal ellipsoids at the 50% probability level, and hydrogen atoms depicted as small circles.

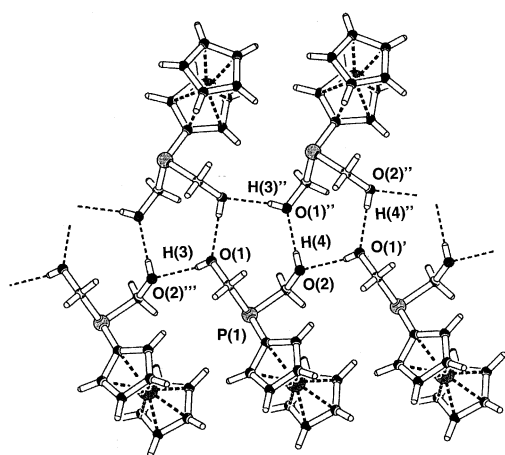


Fig. 3. Hydrogen-bonding in the structure of $\text{FcP}(\text{CH}_2\text{OH})_2$ (1).

The structures of $\text{FcP}(\text{O})(\text{CH}_2\text{OH})_2$ (3) and $\text{FcP}(\text{S})(\text{CH}_2\text{OH})_2$ (4) were also determined for comparative purposes. The molecular structure of 3 is shown in Fig. 4, with Fig. 5 showing the hydrogen-bonding network. Fig. 6 shows the molecular structure of 4, while Fig. 7 shows the hydrogen-bonding network.

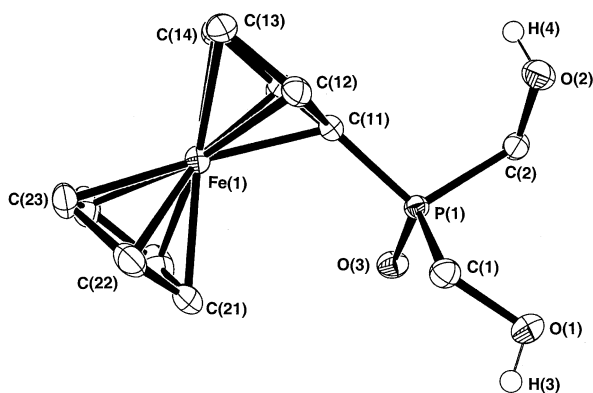


Fig. 4. Molecular structure of $\text{FcP}(\text{O})(\text{CH}_2\text{OH})_2$ (3) with thermal ellipsoids at the 50% probability level; all hydrogens (except those involved in hydrogen-bonding) are omitted.

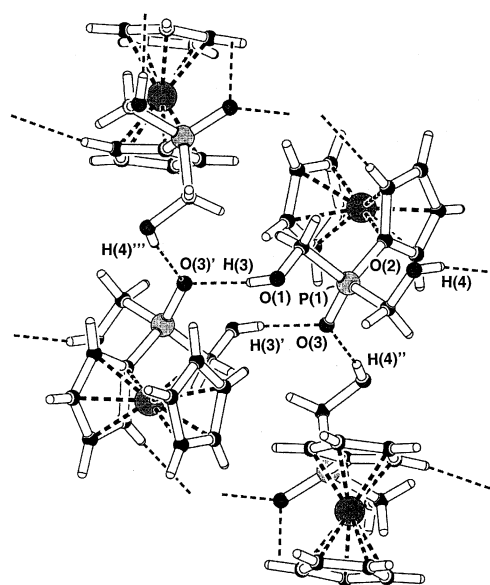


Fig. 5. Hydrogen-bonding in the structure of $\text{FcP}(\text{O})(\text{CH}_2\text{OH})_2$ (3).

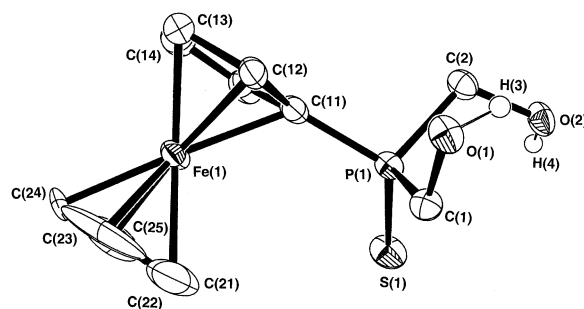


Fig. 6. Molecular structure of $\text{FcP}(\text{S})(\text{CH}_2\text{OH})_2$ (4) with thermal ellipsoids at the 50% probability level; all hydrogens (except those involved in hydrogen-bonding) are omitted.

Selected bond lengths and angles for 3 and 4 are given in Tables 2 and 3, respectively.

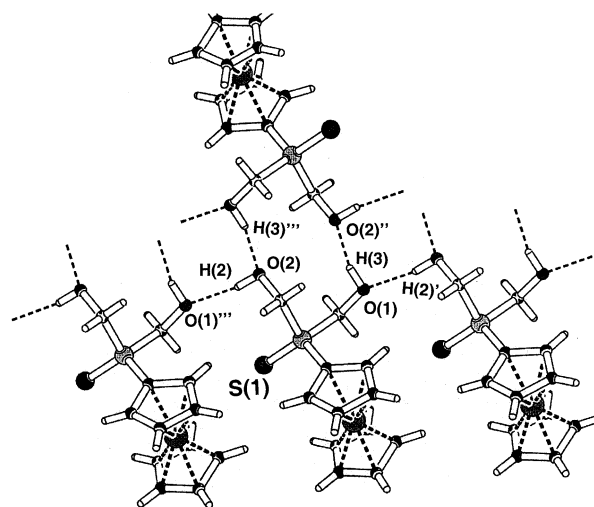


Fig. 7. Hydrogen-bonding in the structure of $\text{FcP}(\text{S})(\text{CH}_2\text{OH})_2$ (4).

Table 2
Selected bond lengths (Å) and angles (°) for $\text{FcP}(\text{O})(\text{CH}_2\text{OH})_2$ (**3**)

<i>Bond lengths</i>			
Cp. Fe–C range	2.032–2.061	P(1)–C(2)	1.820(2)
		C(1)–O(1)	1.421(2)
Cp. C–C range	1.418–1.440	C(2)–O(2)	1.418(2)
		O(1)–H(3)	0.7722
C(11)–P(1)	1.781(2)	O(2)–H(4)	0.7785
P(1)–O(3)	1.510(1)	H(3)···O(1)′	1.9134
P(1)–C(1)	1.821(2)	H(4)···O(2)′	1.9490
<i>Bond angles</i>			
C(11)–C(15) range	107.51–108.65		
C(21)–C(25) range	107.76–108.25		
C(15)–C(11)–P(1)	123.98(11)	P(1)–C(1)–O(1)	108.63(10)
C(12)–C(11)–P(1)	128.35(11)	P(1)–C(2)–O(2)	111.49(11)
C(11)–P(1)–O(3)	113.56(7)	C(1)–O(1)–H(3)	105.80
C(11)–P(1)–C(1)	107.02(7)	C(2)–O(2)–H(4)	107.15
		O(1)–H(3)···O(3)′	173.58
		O(2)–H(2)···O(2)′	167.86

The structure of **3** contains a two-dimensional hydrogen-bonding network inclined at an angle of ca. 30° to the *bc* plane. The hydrogen bonds within this network are exclusively between hydroxyl H atoms and the O atom of the PO group. Each molecule of **3** has hydrogen-bonding interactions with three adjacent molecules and to one of these, both donor and acceptor hydrogen bonds are formed. As a result, two distinct hydrogen bonds are formed, though they are very similar in length and angle about the shared hydrogen.

The structure of the sulfide **4** shows significant disorder in the unsubstituted cyclopentadienyl ring, which can be clearly seen in the thermal ellipsoids in Fig. 6. The P–S bond distance [1.955(1) Å] is comparable to that in $\text{FcCH}_2\text{P}(\text{S})(\text{CH}_2\text{OH})_2$ [1.955(8) and 1.9164(8) Å for two independent molecules] [4]. The hydrogen-bonding in **4** is reminiscent of that observed in the structure of $\text{FcP}(\text{CH}_2\text{OH})_2$ (Fig. 3). Hydrogen bonds

are formed between hydroxyl groups only; the sulfur atom is not involved in any hydrogen-bonding. This results in chains consisting of alternating eight- and 12-membered rings. This is in marked contrast to the hydrogen-bonding pattern adopted by related ferrocenyl hydroxymethylphosphine sulfides $\text{FcCH}_2\text{P}(\text{S})(\text{CH}_2\text{OH})_2$ [4] and $\text{FcCH}(\text{CH}_3)\text{P}(\text{S})(\text{CH}_2\text{OH})_2$ [6]. In each of these compounds both O–H···H bonds and O–H···S bonds are present. The hydrogen-bonding in $\text{FcCH}_2\text{P}(\text{S})(\text{CH}_2\text{OH})_2$ is composed of short chains of O–H···O bonds terminated at sulfur by O–H···S bonds. Interestingly, these compounds also possess bifurcated hydrogen bonds, though in the case of $\text{FcCH}_2\text{P}(\text{S})(\text{CH}_2\text{OH})_2$ it is a O–H hydrogen donating to two other oxygen acceptors, while in the case of $\text{FcCH}(\text{CH}_3)\text{P}(\text{S})(\text{CH}_2\text{OH})_2$ there are two O–H hydrogens donating to a sulfur atom.

The lack of O–H···S bonds in the structure of **4** is anomalous when compared with those in $\text{FcCH}_2\text{P}(\text{S})(\text{CH}_2\text{OH})_2$ and $\text{FcCH}(\text{CH}_3)\text{P}(\text{S})(\text{CH}_2\text{OH})_2$, and other (non-ferrocenyl) hydroxymethylphosphine sulfides such as $\text{Me}_2\text{P}(\text{S})\text{C}(\text{OH})\text{R}^1\text{R}^2$ [$\text{R}^1/\text{R}^2 = \text{Me}/\text{Me}$, $-(\text{CH}_2)_5-$, $\text{Me}/\text{C}(\text{O})\text{Me}$, $\text{Ph}/\text{C}(\text{O})\text{Ph}$, H/COOH], [15] $\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{OH}$ [16] and $\text{PhP}(\text{S})(\text{H})\text{C}(\text{OH})\text{Me}_2$ [17] which have been structurally characterised. It may be that removing the CH_2 spacer has increased the effective steric bulk of the ferrocenyl group, forcing hydrogen-bonding between the more distant hydroxyl groups. The poorer hydrogen bond accepting properties of a phosphine sulfide compared with a phosphine oxide are also undoubtedly important.

The P–C bonds in the oxide **3** and sulfide **4** are shorter than their counterparts in the parent phosphine **1**, reflecting the smaller size of pentavalent cf. trivalent phosphorus. Thus the P(1)–C(11) bond distances (to the cyclopentadienyl ring) are 1.781(2) and 1.783(3) Å in **3** and **4**, respectively, but 1.809(2) Å in **1**. Similarly, the

Table 3
Selected bond lengths (Å) and angles (°) for $\text{FcP}(\text{S})(\text{CH}_2\text{OH})_2$ (**4**)

<i>Bond lengths</i>			
Cp Fe–C average	2.032	P(1)–C(2)	1.835(3)
Range	1.995(4)–2.052(3)	P(1)–S(1)	1.955(1)
Cp(1) C–C average	1.423	C(1)–O(1)	1.415(3)
Range	1.412–1.439	C(2)–O(2)	1.421(3)
Cp(2) C–C average	1.356	O(1)–H(3)	0.9140
Range	1.246–1.509	O(2)–O(4)	0.8776
C(11)–P(1)	1.783(3)	H(3)···O(2)′	1.8183
P(1)–C(1)	1.835(3)	H(4)···O(1)′	1.9396
<i>Bond angles</i>			
Cp C(11)–C(15) range	107.3(3)–108.7(3)	Cp C(22)–C(25) range	101.9(4)–112.8(6)
C(12)–C(11)–P(1)	127.5(2)	P(1)–C(2)–O(2)	110.63(19)
C(15)–C(11)–P(1)	125.2(2)	C(1)–O(1)–H(3)	108.56
C(11)–P(1)–C(1)	108.01(13)	C(2)–O(2)–H(4)	104.89
C(11)–P(1)–C(2)	102.69(13)	O(1)–H(3)···O(2)′	164.72
C(11)–P(1)–S(1)	116.87(10)	O(2)–H(4)···O(1)′	153.33
P(1)–C(1)–O(1)	114.26(19)		

average P–CH₂ distances are 1.821(2) and 1.835(3) Å in **3** and **4**, respectively, but 1.850 Å in **1**.

Preliminary structural investigations indicated that the selenide FcP(Se)(CH₂OH)₂ (**5**) is isostructural to the sulfide. This was also observed for the related series Ph₂P(E)(CH₂OH) (E = S, Se).^[16] Unit cell parameters for **5** are given in the Section 3.

2.4. Metal complexes of FcP(CH₂OH)₂ and 1,1'-Fc'[P(CH₂OH)₂]₂

Gold, ruthenium, platinum and palladium complexes of FcCH₂P(CH₂OH)₂ were reported soon after the original synthesis of FcCH₂P(CH₂OH)₂ [18]. Since that time no further studies on the coordination chemistry of ferrocenyl hydroxymethylphosphines have been published. It was, therefore, of interest to prepare some metal complexes of **1** and **2**; platinum was chosen as the metal for study.

The complex [PtCl₂(cod)] (cod = 1,5-cyclo-octadiene) was reacted with two equivalents of **1** to give the complex *cis*-[PtCl₂{FcP(CH₂OH)₂]₂ (**9**) in good yield. This complex was an air-stable orange powder, soluble in polar solvents such as methanol, DMSO and water. Characterisation of **9** was achieved by NMR, ES mass spectrometry and elemental analysis. Thus, the ³¹P {¹H}-NMR spectrum shows a single resonance at δ 5.8 showing coupling to platinum [¹J(PtP) 3514 Hz], characteristic for phosphine ligands *trans* to chloride [19]. The ES mass spectra of **9** were of some interest, since metal chloride complexes typically give an [M–Cl]⁺ ion (sometimes solvated) in positive ion ES spectra [20]. However, **9** gave only a very weak [M–Cl]⁺ ion (*m/z* 787). Surprisingly the negative ion ES spectrum was dominated by an intense peak at *m/z* 857, assigned as [M+Cl][–]; the chloride ion is presumably associated with the Pt complex via hydrogen bonding to the OH groups.

The reaction of 1,1'-Fc'[P(CH₂OH)₂]₂ with one equivalent of [PtCl₂(cod)] gave **10** as the principal product. The complex was sparingly soluble in water and methanol, but is soluble in DMSO in which decomposition occurred. The complex gave a strong [M+Cl][–] ion (*m/z* 671) in the negative ion ES spectrum, with a weak peak at *m/z* 1307 assigned as [2M+Cl][–]. Purification of this complex by recrystallisation was not successful.

2.5. Conclusions

Using the standard addition of formaldehyde to a P–H bond, we have synthesised two new ferrocenyl hydroxymethylphosphines, FcP(CH₂OH)₂ and 1,1'-Fc'[P(CH₂OH)₂]₂. Oxide, sulfide and selenide derivatives have been synthesised to provide further characterization data, and a study of the solid-state structures of

FcP(E)(CH₂OH)₂ (E = O, S, Se) reveals a different hydrogen-bonding pattern in the sulfide compared with the related FcCH₂P(S)(CH₂OH)₂. These compounds appear to be less stable than analogues containing a CH₂ spacer between the cyclopentadienyl ring and the phosphorus atom. The phosphine 1,1'-Fc'[P(CH₂OH)₂]₂ can be considered to be a water-soluble analogue of the well-known dpfp ligand, 1,1'-Fc'(PPh₂)₂ [21], and as such, possesses considerable potential as a ligand in coordination chemistry. The synthesis and characterization of other coordination complexes of this ligand, and their catalytic activities are subjects worthy of further investigation.

3. Experimental

3.1. General experimental procedures

³¹P {¹H}, ¹H and ¹³C {¹H}-NMR spectra were recorded on a Bruker AC300P instrument at 121.51, 300.133 or 75.47 MHz, respectively, with chemical shifts relative to external 85% H₃PO₄ (³¹P) or external SiMe₄ (¹H, ¹³C). Unambiguous assignment of OH signals in ¹H-NMR spectra was achieved by addition of D₂O. The atom numbering scheme for the Fc and 1,1'-Fc' groups is as reported previously [22]. Non-equivalent CH₂OH protons are noted as Ha/Hb. Melting points were recorded on a Reichert Jung hotstage apparatus and are uncorrected. IR spectra were recorded as KBr disks, with the exception of **2** which was recorded as a film between KBr windows. Sonication reactions were carried out using a NEY ULTRASONIK 104X ultrasound bath; flasks were placed in zones of maximum cavitation, identified by the use of aluminium foil.

ES mass spectra of phosphines and chalcogenide derivatives thereof were recorded in positive-ion mode on a VG Platform II instrument, in methanol solvent (unless otherwise stated); further details of the instrumentation have been given previously [22]. Isotope patterns were calculated using the ISOTOPE program [23]. Silver ions (ca. 2 drops of 0.1 mol l^{–1} AgNO₃) were added to the phosphines to aid ionization by the formation of silver complexes *in situ* [12,13]. Sodium ions (ca. 2 drops of 0.1 mol l^{–1} aqueous NaCl) were added to **6–8** before analysis. The platinum complexes **9** and **10** were analysed in MeCN–H₂O solution (1:1 v/v) using negative ion mode.

3.2. Materials

Formaldehyde (40% w/v) (BDH), selenium powder (Unilab), and powdered sulfur (BDH) were used as supplied. Hydrogen peroxide (Andrew Chemicals) was standardised by titration with standardised KMnO₄ prior to use. The complex [PtCl₂(cod)] was synthesised

by the literature procedure [24]. The primary phosphines FcPH_2 and $1,1'\text{-Fc'-(PH}_2)_2$ were prepared as described previously [25].

3.3. Synthesis of $\text{FcP}(\text{CH}_2\text{OH})_2$ (**1**)

Aqueous formaldehyde (0.25 ml, 40% w/v) was added to a solution of FcPH_2 (0.26 g, 1.2 mmol) in THF (5 ml) under nitrogen, and the solution stirred for 18 h. The volatiles were removed under vacuum, and the crude product held under vacuum for ca. 72 h to remove excess formaldehyde, giving an orange microcrystalline solid (0.33 g, 96%). M.p. 100–106 °C. Found: C, 51.8; H, 5.5%. $\text{C}_{12}\text{H}_{15}\text{FeO}_2\text{P}$ requires C, 51.8; H, 5.4%. ^{31}P $\{^1\text{H}\}$ -NMR (CDCl_3), δ -24.7 (s). ^{13}C $\{^1\text{H}\}$ -NMR (CDCl_3), δ 62.90 [d, $^1\text{J}(\text{PC})$ 17, PCH_2OH], 69.08 (s, C4), 70.24 [d, $^3\text{J}(\text{PC})$ 3.8, C3], 73.22 [d, $^2\text{J}(\text{PC})$ 14, C2], C1 not observed. ^1H -NMR (CDCl_3), δ 2.56 (2H, br s, OH), 4.24 (5H, s, C_5H_5), 4.30 [2H, dd, $^2\text{J}(\text{HH})$ 13, $^3\text{J}(\text{HH})$ 5, Ha/Hb], 4.40 (2H, s, C_5H_4), 4.45 [2H, br d, $^2\text{J}(\text{HH})$ 13, Ha/Hb], 4.50 (2H, s, C_5H_4). ESMS (cone voltage 100 V, with added AgNO_3), $[\text{M}]^+$ (m/z 279, 100%), $[\text{M}+\text{Ag}]^+$ (m/z 385/387, 49%), $[2\text{M}+\text{Ag}]^+$ (m/z 663/665, 95%). IR (cm^{-1}) 3261(br, s), 3096(m), 2889(m), 1161(m), 1106(m), 1021(m), 999(m), 867(m), 834(m), 805(m), 686(w), 499(w), 486(m), 453(m).

3.4. Synthesis of $1,1'\text{-Fc'}[P(\text{CH}_2\text{OH})_2]_2$ (**2**)

Following the method for **1**, 40% formaldehyde (0.41 ml) was added to a solution of $1,1'\text{-Fc'-(PH}_2)_2$ (0.24 g, 0.97 mol) in THF (5 ml) under nitrogen, and the mixture stirred for 24 h. Workup gave 0.348 g (98%) of **2** as a viscous orange–brown oil. ^{31}P $\{^1\text{H}\}$ -NMR (d^6 -DMSO), δ -31.0 (s). ^1H -NMR (d^6 -DMSO), δ 4.02 (8H, m, CH_2), 4.34 (4H, br s, C_5H_4), 4.39 [4H, d, $^3\text{J}(\text{PH})$ 1.7, C_5H_4], 4.89 (3.6H, br s, OH). ESMS (cone voltage 60 V with added AgNO_3), $[\text{M}+\text{Ag}]^+$ (m/z 477/479, 100%). IR (cm^{-1}) 3412(br, s), 2905(br, s), 1191(m), 1159(m), 1019(br, m), 871(m), 831(m).

3.5. Synthesis of $\text{FcP}(\text{O})(\text{CH}_2\text{OH})_2$ (**3**)

Aqueous hydrogen peroxide (0.05 ml, 3.16 mol l^{-1}) was added to a solution of **1** (0.047 g, 0.17 mmol) in methanol (2 ml). After 15 min ^{31}P -NMR revealed the reaction to be complete. The solvent was removed under reduced pressure to give 0.048 g (97%) of **3** as a yellow powder. M.p. crystals bubble at 159–170 °C, melting at 171–176 °C. Found: C, 49.0; H, 5.3. $\text{C}_{12}\text{H}_{15}\text{FeO}_3\text{P}$ requires C, 49.0; H, 5.1%. ^{31}P $\{^1\text{H}\}$ -NMR (d^6 -DMSO): δ 38.2 (s). ^{13}C $\{^1\text{H}\}$ -NMR (d^6 -DMSO): δ 59.52 [d, $^1\text{J}(\text{PC})$ 84, PCH_2OH], 70.88 (s, C4), 72.61 [d, $^3\text{J}(\text{PC})$ 9.6, C3], 72.75 [d, $^2\text{J}(\text{PC})$ 11.4, C2], C1 not observed. ^1H -NMR (d^6 -DMSO): δ 3.97 (4H, br s, PCH_2OH), 4.39 (5H, s, H4), 4.54 (4H, br s, H2/H3), 5.39 (2H, br s,

PCH_2OH). ESMS: (cone voltage 20 V) $[\text{M}+\text{H}]^+$ (m/z 295, 100%). IR (cm^{-1}): 3289(br, s), 3096(m), 2921(m), 1206(m), 1185(m), 1122(s, $\nu\text{P}=\text{O}$), 1038(s), 915(m), 878(m), 834(m), 763(m), 692(w), 622(w), 506(w), 458(s).

3.6. Synthesis of $\text{FcP}(\text{S})(\text{CH}_2\text{OH})_2$ (**4**)

A mixture of **1** (0.043 g, 0.15 mmol) and powdered sulfur (0.005 g, 0.15 mmol) in THF (5 ml) was sonicated for 30 min. The solvent was then removed under reduced pressure to give 0.047 g (99%) of **4** as an orange oil that crystallised upon standing. M.p. 122–126 °C. Found: C, 46.3; H, 4.9%. $\text{C}_{12}\text{H}_{15}\text{FeO}_2\text{PS}$ requires C, 46.5; H, 4.9%. ^{31}P $\{^1\text{H}\}$ -NMR (CDCl_3): δ 47.6 (s). ^{13}C $\{^1\text{H}\}$ -NMR (CDCl_3): δ 61.04 [d, $^1\text{J}(\text{PC})$ 59, PCH_2OH], 70.03 (s, C4), 71.55 [d, $^2\text{J}(\text{PC})$ 12, C2], 72.13 [d, $^3\text{J}(\text{PC})$ 9, C3]. ^1H -NMR (CDCl_3): δ 2.76 [2H, dd, $^3\text{J}(\text{HH})$ 6, $^3\text{J}(\text{PH})$ 6, CH_2OH], 4.05 [2H, ddd, $^2\text{J}(\text{HH})$ 13, $^3\text{J}(\text{HH})$ 4.2, $^2\text{J}(\text{PH})$ 1.6, Ha/Hb], 4.15 [2H, ddd, $^2\text{J}(\text{HH})$ 13, $^3\text{J}(\text{HH})$ 6.3, $^2\text{J}(\text{PH})$ 1.6, Ha/Hb], 4.36 (5H, s, H4), 4.52 [2H, dt, $^3\text{J}(\text{HH})$ 3.6, $^4\text{J}(\text{PH})$ 1.7, H3], 4.56 [2H, dt, $^3\text{J}(\text{HH})$ 3.5, $^3\text{J}(\text{PH})$ 1.7, H2]. ESMS: (cone voltage 20 V) $[\text{M}+\text{H}]^+$ (m/z 311, 100%). IR (cm^{-1}): 3285(br, s), 3104(w), 2893(m), 1416(m), 1178(s), 1107(m), 1039(s), 881(w), 831(m), 766(m), 712(m), 618(m), 485(m), 465(m).

3.7. Synthesis of $\text{FcP}(\text{Se})(\text{CH}_2\text{OH})_2$ (**5**)

A mixture of **1** (0.10 g, 0.4 mmol) and selenium powder (0.3 g, 4 mmol) in THF (5 ml) was sonicated for 30 min and the excess selenium removed by filtration. The solvent was removed under reduced pressure to give 0.13 g (95%) of **5** as an orange oil that crystallised upon standing. M.p. 116–118 °C. Found: C, 40.8; H, 4.5%. $\text{C}_{12}\text{H}_{15}\text{FeO}_2\text{PSe}$ requires C, 40.4; H, 4.2%. ^{31}P $\{^1\text{H}\}$ -NMR (CDCl_3): δ 39.1 [s+d, $^1\text{J}(\text{PSe})$ 701]. ^{13}C $\{^1\text{H}\}$ -NMR (CDCl_3): δ 60.92 [d, $^1\text{J}(\text{PC})$ 51, PCH_2OH], 70.14 (s, C4), 72.16 [d, $^3\text{J}(\text{PC})$ 9, C3], 72.28 [d, $^2\text{J}(\text{PC})$ 8.5, C2], C1 not observed. ^1H -NMR (CDCl_3): δ 3.1 (2H, br s, CH_2OH), 4.08 [2H, d, $^2\text{J}(\text{HH})$ 12, Ha/Hb], 4.20 [2H, d, $^2\text{J}(\text{HH})$ 12, Ha/Hb], 4.36 (5H, s, H4), 4.53 (2H, br s, H2), 4.60 (2H, br s, H3). ESMS: (cone voltage 20 V) $[\text{M}+\text{H}]^+$ (m/z 358, 100%). IR (cm^{-1}): 3297(br, s), 3105(w), 2885(m), 1411(m), 1175(s), 1108(m), 1042(s), 880(w), 827(m), 806(m), 758(m), 537(w), 482(m).

3.8. Synthesis of $1,1'\text{-Fc'}[P(\text{O})(\text{CH}_2\text{OH})_2]_2$ (**6**)

Aqueous hydrogen peroxide (0.22 ml of a 3.16 mol l^{-1} solution, 1.1 mmol) was added to a solution of **2** (0.13 g, 0.55 mmol) in methanol (4 ml) and the solution stirred for 10 min, at which time ^{31}P -NMR showed the reaction to be complete. The solvent was removed under reduced pressure to give 0.14 g (98%) of **6** as a brown oil. Found: C, 41.9; H, 5.5. $\text{C}_{14}\text{H}_{20}\text{FeO}_6\text{P}_2$ requires C, 41.8;

H, 5.0%. ^{31}P $\{^1\text{H}\}$ -NMR (d^6 -DMSO): δ 39.2 (s). ^{13}C $\{^1\text{H}\}$ -NMR (d^6 -DMSO): δ 59.23 [d, $^1J(\text{PC})$ 84, PCH_2OH], 72.25 [d, $^1J(\text{PC})$ 96, C1], 73.90 [d, $^3J(\text{PC})$ 8.5, C3], 74.12 [d, $^2J(\text{PC})$ 10.4, C2]. ^1H -NMR (d^6 -DMSO): δ 3.99 (8H, br s, PCH_2OH), 4.71 (8H, br s, H2/H3), 5.65 (3.7H, br s, PCH_2OH). ESMS: (cone voltage 20 V, Na^+ added) $[\text{M}+\text{H}-4\text{CH}_2\text{O}]^+$ (m/z 305, 13%), $[\text{M}+\text{H}-3\text{CH}_2\text{O}]^+$ (m/z 335, 14%), $[\text{M}+\text{H}-2\text{CH}_2\text{O}]^+$ (m/z 365, 11%), $[\text{M}+\text{H}-\text{CH}_2\text{O}]^+$ (m/z 395, 13%), $[\text{M}+\text{H}]^+$ (m/z 403, 6%), $[\text{M}+\text{Li}]^+$ (m/z 409, 6%), $[\text{M}+\text{Na}]^+$ (m/z 425, 100%), $[\text{2M}+\text{Na}]^+$ (m/z 827, 67%).

3.9. Synthesis of 1,1'-Fc'[P(S)(CH₂OH)₂]₂ (7)

Elemental sulfur (0.02 g, 0.63 mmol) was added to a solution of **2** (0.06 g, 0.15 mmol) in methanol (5 ml) under a nitrogen atmosphere and the mixture sonicated for 15 min. The solution was filtered to remove excess sulfur and the solvent removed under reduced pressure to give 0.056 g (83%) of **7** as a pure (by ^{31}P -NMR) orange oil. Diffusion of diethyl ether vapour into an acetone solution of the crude product gave 5 mg (7%) of crystalline **7**. The low crystalline yield is attributed to decomposition of **7** in solution. M.p. 138–143 °C. Found: C, 38.8; H, 4.7%. $\text{C}_{14}\text{H}_{20}\text{FeO}_4\text{P}_2\text{S}_2$ requires C, 38.7; H, 4.6%. ^{31}P $\{^1\text{H}\}$ -NMR (d^6 -DMSO): δ 43.8 (s). ^{13}C $\{^1\text{H}\}$ -NMR (d^6 -DMSO): δ 62.65 [d, $^1J(\text{PC})$ 65, PCH_2OH], 73.58 [d, $^1J(\text{PC})$ 78, C1], 74.80 [d, $^3J(\text{PC})$ 10, C3], 74.92 [d, $^2J(\text{PC})$ 9, C2]. ^1H -NMR (d^6 -DMSO): 4.05 [4H, dd, $^2J(\text{HH})$ 13.4, $^3J(\text{HH})$ 5.9, Ha/Hb], 4.12 [4H, dd, $^2J(\text{HH})$ 13.4, $^3J(\text{HH})$ 4.2, Ha/Hb], 4.72 (4H, m, H3), 4.76 (4H, m, H2), 5.69 (4H, br m, PCH_2OH). ESMS: (cone voltage 20 V, Na^+ added) $[\text{M}+\text{H}]^+$ (m/z 435, 9%), $[\text{M}+\text{Li}]^+$ (m/z 441, 10%), $[\text{M}+\text{Na}]^+$ (m/z 457, 100%), $[\text{2M}+\text{H}]^+$ (m/z 891, 36%).

3.10. Synthesis of 1,1'-Fc'[P(Se)(CH₂OH)₂]₂ (8)

Powdered selenium (0.15 g, 2 mmol, excess) was added to a solution of **2** (0.24 g, 0.64 mmol) in methanol (5 ml). The solution was placed under a dinitrogen atmosphere and sonicated for 5 min. The solution was then filtered to remove excess selenium and the solvent removed to give 0.16 g (48%) of **8** as an orange brown oil. Evaporation to dryness of a methanol– CH_2Cl_2 solution gave 0.032 g (10%) of **8** as bright red crystals. M.p. 147–149 °C. Found: C, 32.5; H, 4.2%. $\text{C}_{14}\text{H}_{20}\text{FeO}_4\text{P}_2\text{Se}_2$ requires C, 31.8; H, 3.8%. ^{31}P $\{^1\text{H}\}$ -NMR (d^6 -DMSO): δ 33.2 [s+d, $^1J(\text{PSe})$ 713]. ^{13}C $\{^1\text{H}\}$ -NMR (d^6 -DMSO): δ 62.64 [d, $^1J(\text{PC})$ 57, PCH_2OH], 72.14 [d, $^1J(\text{PC})$ 70, C1], 75.33 [d, $^3J(\text{PC})$ 6.4, C3], 75.45 [d, $^2J(\text{PC})$ 7.7, C2]. ^1H -NMR (d^6 -DMSO): δ 4.14 [4H, dd, $^2J(\text{HH})$ 13.1, $^3J(\text{HH})$ 5.8, Ha/Hb], 4.23 (4H, dd, $^2J(\text{HH})$ 13.1, $^3J(\text{HH})$ 6.6, Ha/Hb], 4.76 (4H, br s, H3), 4.82 (4H, br s, H2), 5.79 [4H, dt, $^3J(\text{HH}) = ^3J(\text{PH})$ 6,

CH_2OH]. ESMS: (cone voltage 20 V, Na^+ added) $[\text{M}+\text{H}]^+$ (m/z 529, 29%), $[\text{M}+\text{Na}]^+$ (m/z 551, 100%), $[\text{2M}+\text{Na}]^+$ (m/z 1079, 33%). IR (cm^{-1}): 3428(br s), 3300(br, s), 3108(w), 3897(m), 1184(s), 1040(s), 866(w), 817(m), 761(m), 614(w), 540(w), 497(m), 471(m), 434(w).

3.11. Synthesis of cis-[PtCl₂{FcP(CH₂OH)₂]₂] (9)

A solution of $[\text{PtCl}_2(\text{cod})]$ (0.03 g, 0.09 mmol) in dichloromethane (5 ml) was added to a solution of $\text{FcP}(\text{CH}_2\text{OH})_2$ **1** (0.05 g, 0.18 mmol) in dichloromethane (4 ml) at room temperature (r.t.). After 30 min. the volume was reduced to ca. 1 ml and petroleum spirits (5 ml) added. The resulting precipitate was filtered, washed liberally with petroleum spirits (30 ml) and dried under vacuum to give 0.06 g (76%) of **9** as an orange powder. M.p. 208–214 °C (dec.). Found: C, 34.7; H, 3.7%. $\text{C}_{24}\text{H}_{30}\text{Cl}_2\text{Fe}_2\text{O}_4\text{P}_2\text{Pt}$ requires C, 35.1; H, 3.7%. ^{31}P $\{^1\text{H}\}$ -NMR (d^6 -DMSO): δ 0.5 [s+d, $^1J(\text{PPt})$ 3514]. ^{13}C $\{^1\text{H}\}$ -NMR (d^6 -DMSO): δ 56.9 [d, $^1J(\text{PC})$ 53, PCH_2OH], 70.13 (s, C4), 70.73 (s, C3), 74.17 (s, C2), C1 not observed. ^1H -NMR (d^6 -DMSO): 3.32 (8H, br s, PCH_2OH), 4.38 (10H, s, H4), 4.45 (4H, s, H3), 4.61 (4H, s, H2), 5.42 (4H, br s, PCH_2OH). ESMS: ($\text{MeCN}-\text{H}_2\text{O}$, negative ion, cone voltage 20 V) $[\text{PtCl}_2\{\text{FcP}(\text{CH}_2\text{OH})_2\}_2+\text{Cl}]^-$ (m/z 857, 100%).

3.12. Reaction of 1,1'-Fc'[P(CH₂OH)₂]₂ (2) with [PtCl₂(cod)]

To a solution of **2** (0.047 g, 0.12 mmol) in methanol (5 ml) under a nitrogen atmosphere was added a solution of $[\text{PtCl}_2(\text{cod})]$ (0.048 g, 0.12 mmol) in dichloromethane (5 ml). As the addition progressed a colour change from orange to red and back to orange was observed. The mixture was stirred for 30 min. before the volume was halved and diethyl ether (20 ml) was added. The resulting precipitate was filtered under nitrogen and washed liberally with petroleum spirits before being dried under vacuum. The resulting product was a pale orange powder (0.045 g) that was shown to be nearly pure 1,1'-Fc'[P(CH₂OH)₂]₂PtCl₂ (**10**) by ^{31}P $\{^1\text{H}\}$ -NMR and ESMS. Purification by recrystallisation was unsuccessful. ^{31}P $\{^1\text{H}\}$ -NMR (d^6 -DMSO): δ 10.39 [s+d, $^1J(\text{PPt})$ 3619]. ESMS: ($\text{MeCN}-\text{H}_2\text{O}$, negative ion, cone voltage 20 V), $[\text{M}+\text{Cl}]^-$ (m/z 671, 100%), $[\text{2M}+\text{Cl}]^-$ (m/z 1307, 4%).

3.13. X-ray structure determinations for 1, 3 and 4

Single crystals of **1** were obtained by diffusion of pentane vapour into a dichloromethane–methanol (10:1 v/v) solution at –20 °C. Crystals of **3** were grown from a diethyl ether–dichloromethane–methanol (10:10:1 v/v) solution at –20 °C, and crystals of **4** were obtained by diffusion of diethyl ether vapour into dichloro-

methane-methanol (10:1) solution at r.t. Crystallographic data were collected on a Siemens SMART CCD diffractometer, corrected for absorption using SADABS [26] and are summarised in Table 4. The structures were solved by the direct methods option of SHELXL-97 [27] and developed routinely using full-matrix least-squares refinement based on F_o^2 .

For **1**, all non-hydrogen atoms were refined using anisotropic temperature factors and hydrogen atoms were found from peaks of residual electron density in the penultimate electron density map, and were refined with isotropic temperature factors. All hydrogen atoms in **3** were found by inspection of the penultimate electron density map and included in the final refinement cycle with isotropic temperature factors; all bond lengths and angles were within accepted ranges. All non-hydrogen atoms in the structure of **4** were refined using anisotropic temperature factors. Hydrogen atoms were placed in calculated positions, except for those involved in hydrogen bonding [H(3) and H(4)], which were located in the penultimate electron density map. The unsubstituted cyclopentadienyl ring is significantly disordered and contains the bulk of the residual electron density. All bond lengths and angles fell within accepted ranges except for those of the disordered cyclopentadienyl ring which were smaller than usual.

Table 4
Collection and refinement details for FcP(CH₂OH)₂ (**1**), FcP(O)(CH₂OH)₂ (**3**) and FcP(S)(CH₂OH)₂ (**4**)

	1	3	4
Empirical formula	C ₁₂ H ₁₄ FeO ₂ P	C ₁₂ H ₁₄ FeO ₃ P	C ₁₂ H ₁₄ FeO ₂ PS
Formula weight	278.06	294.06	310.12
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
<i>a</i> (Å)	12.2386(1)	12.0043(2)	6.1824(1)
<i>b</i> (Å)	6.1101(1)	9.0816(2)	12.3340(2)
<i>c</i> (Å)	16.3344(2)	12.1713(3)	16.5799(1)
β (°)	110.941(1)	115.953(1)	90.101(1)
<i>V</i> (Å ³)	1140.79(3)	1193.08(4)	1264.28(3)
<i>Z</i>	4	4	4
<i>D</i> _{calc} (g cm ⁻³)	1.619	1.637	1.629
<i>F</i> (000)	576	608	640
λ (Mo-K α) (Å)	0.7107	0.7107	0.7107
μ (Mo-K α) (mm ⁻¹)	1.44	1.39	1.47
Temperature (K)	150(2)	150(2)	150(2)
2 θ Range for data collection (°)	1.8–26.5	2–26.4	2–27
Total reflections	10314	6848	7543
Unique reflections	2357	2414	2748
<i>R</i> _{int}	0.0327	0.0163	0.0179
<i>T</i> _{min}	0.789304	0.780287	0.683877
<i>T</i> _{max}	0.972041	0.938976	0.840068
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0254	0.0209	0.0396
<i>wR</i> ₂	0.0659 ^a	0.0544 ^b	0.0975 ^c
Goodness-of-fit	1.033	1.036	1.039

^a $w = [\sigma^2(F_o)^2 + (0.0422P^2) + 0.29P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$.

^b $w = [\sigma^2(F_o)^2 + (0.0312P^2) + 0.45P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$.

^c $w = [\sigma^2(F_o)^2 + (0.0444P^2) + 2.72P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$.

3.14. Crystal data for (**5**)

Crystals of **5** suitable for single crystal X-ray analysis were grown by evaporation to dryness of a methanol–CH₂Cl₂ solution. Unit cell parameters: Monoclinic, space group $P2_1/n$, *a* 6.233(1), *b* 12.367(5), *c* 16.690(6) Å, β 90.29(2)°.

4. Supplementary information

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 171958 (**1**), 190334 (**3**) and 190335 (**4**). Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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