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(Ferrocenylmethyl)phosphine, an air-stable primary phosphine

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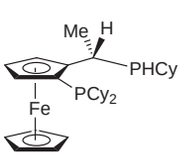
Removal of formaldehyde from the readily prepared ferrocenyl (R) hydroxymethylphosphine $RCH_2P(CH_2OH)_2$ with one mole equivalent of $Na_2S_2O_5$ gave the completely air-stable primary phosphine RCH_2PH_2 as a crystalline, sublimable solid. With $[Mo(CO)_6]$ both mono-, $[Mo(CO)_5(RCH_2PH_2)]$, and di-substituted, $[Mo(CO)_4(RCH_2PH_2)_2]$, products are readily formed, and both were characterised by structure determinations. Reaction with $[\{RuCl_2(p\text{-cym})\}_2]$ (*p*-cym = *p*-cymene) resulted in bridge splitting to give the complex $[RuCl_2(p\text{-cym})(RCH_2PH_2)]$. With $[Ru_3(CO)_{12}]$, RCH_2PH_2 reacted in analogous fashion to other primary phosphines, with two isolated products $[Ru_3(\mu\text{-H})_2(CO)_9(\mu_3\text{-PCH}_2R)]$ and $[Ru_4(CO)_{11}(\mu_4\text{-PCH}_2R)_2]$ containing cluster capping RCH_2P phosphinidine ligands, the former characterised by a structure determination. Thus, the phosphine appears to show typical co-ordinative properties of a primary phosphine, but has the added advantage of being air-stable.

Introduction

Primary and secondary phosphines (RPH_2 and R_2PH respectively) are generally reactive species, with a great deal of chemistry accessible through manipulation of the P–H bond. Examples of the many such reactions include reaction of P–H species with unsaturated compounds, acid halides, halogens, alkali metals and Lewis acids such as borane, as well as hydrolysis of the P–C bond in some instances.[1] Owing to the reactive character of primary and secondary phosphines, preparation of such phosphines with ferrocenyl $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)]$ groups incorporated into the molecule would provide a useful means for the further formation of other ferrocene-containing compounds, through reaction of the phosphine with a suitable functional group on a target molecule. As an example, the secondary phosphine R_2PH (R = ferrocenyl) has been prepared,[2] and used to produce a ferrocene-derivatised analogue of the well known chiral ligand 2,3-dihydroxy-1,4-bis(diphenylphosphino)-2,3-dihydroxy-2,3-*O*-isopropylidene-butane (DIOP).[3] The only other ferrocene-derived primary and secondary phosphines of which we are aware are 1,1′-diphosphinoferrocene, $[Fe(\eta^5\text{-}C_5H_4PH_2)_2]$,[4] and the chiral ferrocenylphosphine **1**.[5] In this paper we describe the synthesis of the primary ferrocenyl phosphine RCH_2PH_2 **2**, starting from the easily prepared $RCH_2P(CH_2OH)_2$ **3** (R = ferrocenyl).[6] The primary phosphine **2** is remarkable in that it is completely air-stable in the solid state, suggesting that it will have significant practical utility. Brief details of this work have appeared in a preliminary communication.[7]



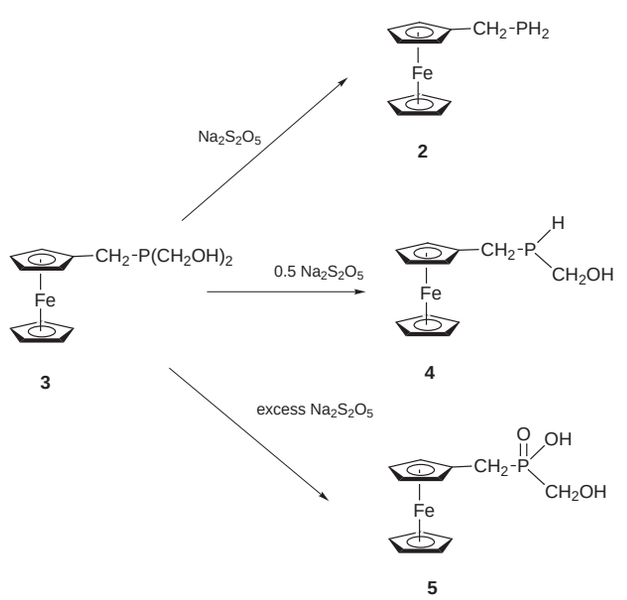
1

Results and discussion

Synthesis of RCH_2PH_2 2

The research described in this paper was prompted by a serendipitous observation, whereby it was noted that if the ferrocenyl hydroxymethylphosphine **3** was refluxed in ethanol or isobutyl alcohol, rather than methanol, unidentified side products of the reaction were observed with downfield shifts in the ^{31}P NMR spectrum at δ −130 and −54. These showed large splittings (*ca.* 200 Hz) into a triplet and doublet respectively when the spectrum was non-decoupled. These NMR signals clearly indicated that formation of stable primary and secondary phosphines was taking place under these conditions, and so rational syntheses were attempted.

The primary phosphine RCH_2PH_2 **2** [^{31}P NMR δ −129.1, t, ^1J(PH) 194 Hz] was prepared by refluxing a solution of the hydroxymethylphosphine **3** with one equivalent of $Na_2S_2O_5$ in a two-phase water/light petroleum (bp 60–80 °C) mixture (Scheme 1), giving an orange crystalline solid which could be



Scheme 1 Syntheses based on the reaction of the hydroxymethylphosphine **3** with $Na_2S_2O_5$.

purified by sublimation to give orange crystals. The compound has a very slight odour characteristic of primary phosphines. The synthesis of **2** involves the removal of formaldehyde from

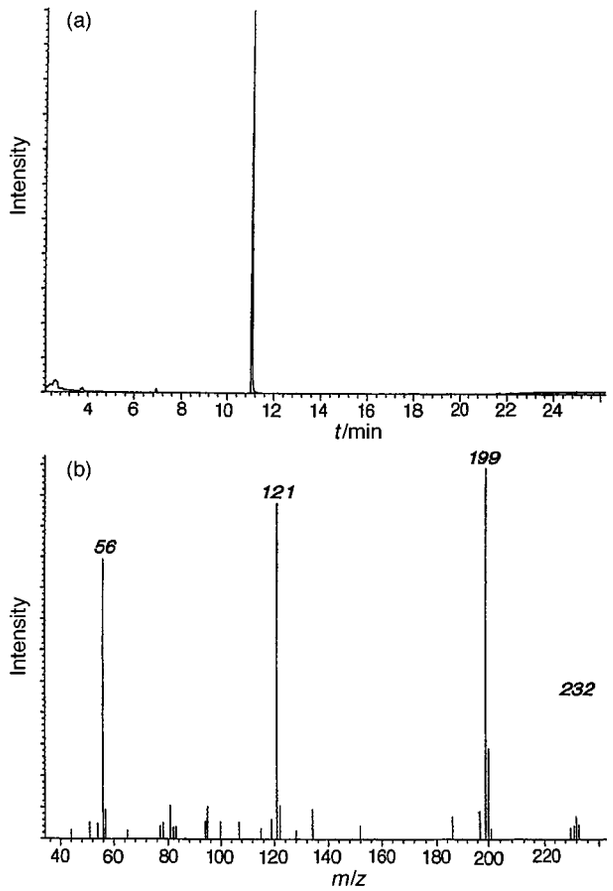
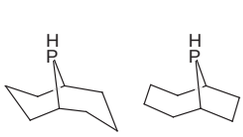


Fig. 1 (a) The GC trace of the primary phosphine RCH_2PH_2 **2** after 79 d of air-storage, showing only one chromatographic peak due to the product. (b) The EI mass spectrum of the peak with *m*/*z* assignments 232 [M^+], 199 [RCH_2^+], 121 [$FeCp^+$] and 56 [Fe^+].

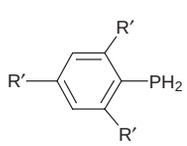
the hydroxymethylphosphine **3**, using the abstracting agent $Na_2S_2O_5$. The reverse reaction, insertion of formaldehyde into a P–H bond, is the most usual route for the synthesis of any hydroxymethylphosphine,[8] either directly, or through formation of a hydroxymethylphosphonium salt which is then treated with base. The addition of formaldehyde is a reversible process, as is apparent from the fact that attempted distillation of $P(CH_2OH)_3$ yields PH_3.[9] However, the removal of formaldehyde from a hydroxymethylphosphine to form a secondary or primary phosphine has not often been utilised synthetically. The reversible nature of this reaction was reported very recently for the separation of the [4.2.1] and [3.3.1] isomers of the secondary phosphine 'phobane' **I**, *via* reaction of intermediate hydroxymethylphosphonium salts with $Na_2S_2O_5$, a formaldehyde abstractor.[10] Another example is the recently described formation of $[RuCl_2\{P(CH_2OH)_3\}_2[\{P(CH_2OH)_2H\}_2]$ from reaction of $P(CH_2OH)_3$ with either $RuCl_3 \cdot xH_2O$ or $[RuCl_2(PPh_3)_3]$.[11]



I

It was soon realised that phosphine **2** was remarkably air-stable. In this connection it is noteworthy that the yield obtained from carrying out the synthesis in air was not significantly lower than that obtained under nitrogen. Generally, primary phosphines will oxidise very readily in the presence of oxygen, and a number of primary phosphines are pyrophoric.[12] Obviously, an air-stable primary phosphine provides great advantages over an air-sensitive one; the susceptibility of primary and secondary phosphines to oxidation has led to the widespread use of borane adducts as protecting groups for these phosphines during various syntheses or purifications.[13] The stability of **2** was tested by elemental analysis on a sample stored in an unsealed vial at room temperature after one and two months, with exemplary results. This was supported by GC-MS analysis of **2** 79 d after sublimation (Fig. 1), showing the product to be pure. After 48 d in air no oxidation products could be detected by ^{31}P NMR. Our experience has been that samples of **2** have remained stable in air for about 2 y with no sign of degradation, suggesting complete air-stability. While no rigorous examination has been carried out into the solution stability, this also appears to be good.

Very few other reports have been made concerning air-stable primary phosphines. Of these, the most frequently used is 2,4,6-tri-*tert*-butylphenylphosphine ('supermesitylphosphine', or Mes^*PH_2) **II**, first reported in 1982,[14] and later described as 'quite stable in air'.[15] In the solid state it will oxidise in a matter of months, but is air-stable to the extent that it can be recrystallised in air from hot Pr^iOH. No doubt the relative air-stability of supermesitylphosphine has encouraged its use in general chemical applications in preference to other primary phosphines, and studies using this compound and closely related derivatives are not uncommon.[16] Although not so air-stable, mesitylphosphine **III** is also a frequently used phosphine.[17,18] As far as we are aware, few examples of air-stable primary phosphines have been described but include a series of eleven cationic compounds with the general formula $[R'_2R''N(CH_2)_mPH_2]I$.[19a] No details were reported other than that the compounds were air-stable in the solid-state, and that $[Me_3N(CH_2)_2PH_2]I$ oxidised very slowly in aqueous solution exposed to air. The phosphine $S(CH_2SCH_2CH_2PH_2)_2$ has also very recently been reported and is completely air-stable.[19b]



II R′ = Bu^t
III R′ = Me

Proposing a mechanism for air-stability in supermesitylphosphine is straightforward; steric congestion would seem to be the obvious cause. Again, it might be postulated that the positively charged nature of compounds of the type $[R'_2R''N(CH_2)_mPH_2]I$ mitigates against attack by electrophilic oxygen. However, the air-stability of **2** is less readily explained. It is certainly not due to steric factors, as the ferrocenylmethyl fragment is not sterically bulky. In addition, the crystal structure determination of **2**, described later, shows the phosphine function to point away from the ferrocenyl group, ruling out the possibility of any type of stabilising interaction with the iron.

Positive-ion electrospray mass spectrometry (ESMS) of compound **2** gave an $[M]^+$ peak, resulting from oxidation of the ferrocene moiety to the ferrocenium analogue in the metal capillary of the instrument; such behaviour has been observed previously for neutral ferrocene derivatives.[20]

Crystal structure of RCH_2PH_2 2

Crystallographic confirmation of the structure of compound **2** was considered important in establishing beyond all doubt that this air-stable compound was indeed a primary phosphine. Crystals of **2** were obtained upon sublimation of the compound. The structure is shown in Fig. 2. The gross morphology is similar to that of $RCH_2P(CH_2OH)_2$ **3** reported previously,[6] with the phosphorus atom pointing away from the ferrocene fragment and the cyclopentadienyl rings in an eclipsed conformation. No notable intermolecular interactions were observed. The P–C bond length of 1.850(3) Å can be compared

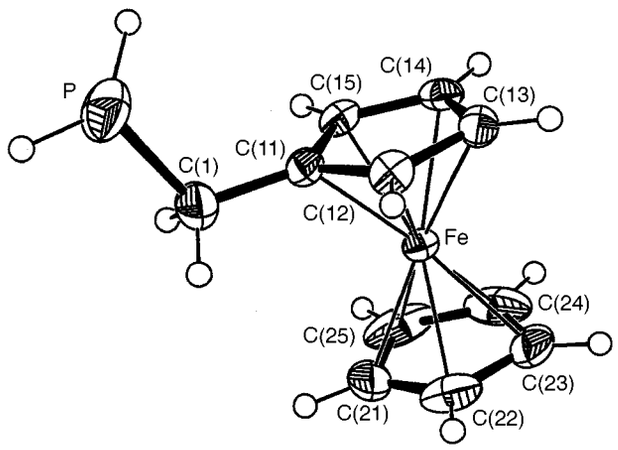
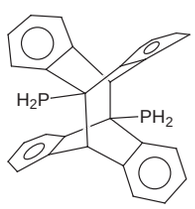


Fig. 2 An ORTEP[21] diagram for RCH_2PH_2 **2**. Selected bond lengths (Å) and angles (°): C(11)–C(1) 1.492(4), C(1)–P 1.850(3), Fe–C range = 2.022(3)–2.042(2), average = 2.035 Å; C(11)–C(1)–P 113.7°.

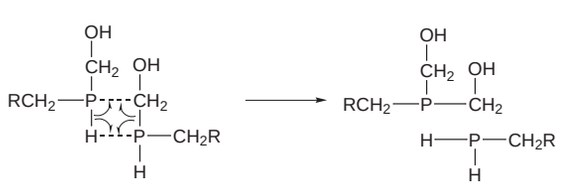
with data from other sources. The bond length is identical within experimental uncertainty to those both calculated (1.8574 Å)[22] and measured by electron diffraction (1.858 ± 0.003 Å)[23] for $MePH_2$. A search of the CSD[24] revealed only two other crystal structures reported for unco-ordinated primary phosphines, these being mesitylphosphine **6**[18] and a (9-anthracenyl)-phosphine dimer **IV**.[25] The crystal structure of the previously mentioned compound $[Me_3N(CH_2)_2PH_2]I$ has also been determined.[19] The C–P bond lengths for these three compounds are 1.807 (5), 1.864(5) and 1.89(3) Å respectively, so the same parameter for **2** lies within the values for these previously reported structures.



IV

Synthesis and characterisation of the secondary phosphine $RCH_2P(H)CH_2OH$ 4 and the phosphinic acid $RCH_2P(O)(CH_2OH)OH$ 5

The secondary phosphine **4** [^{31}P NMR δ −51.4, ^1J(PH) 204 Hz] has also been prepared by a method analogous to that used to make **2**; compound **3** was treated with a little over 0.5 mole equivalent of $Na_2S_2O_5$ in a two-phase system in air, Scheme 1. However, diethyl ether was used for the organic layer, since **4** is not soluble in light petroleum. The compound appears to be stable with respect to air oxidation, but is unstable towards disproportionation. In the solid state a two-week period is enough for **4** to be almost completely converted into a 1 : 1 mixture of **2** and **3**. The reasons why **2** and **3** should be energetically favoured over **4** are unclear. However, it is not difficult to draw a feasible concerted mechanism by which disproportionation might take place, Scheme 2. A concerted mechanism seems preferable to one involving the release of free formaldehyde as



Scheme 2 A concerted mechanism for the disproportionation of compound **4** to **2** and **3**.

this would presumably fail to lead to a 1 : 1 ratio of products, with a greater level of **2** being expected instead.

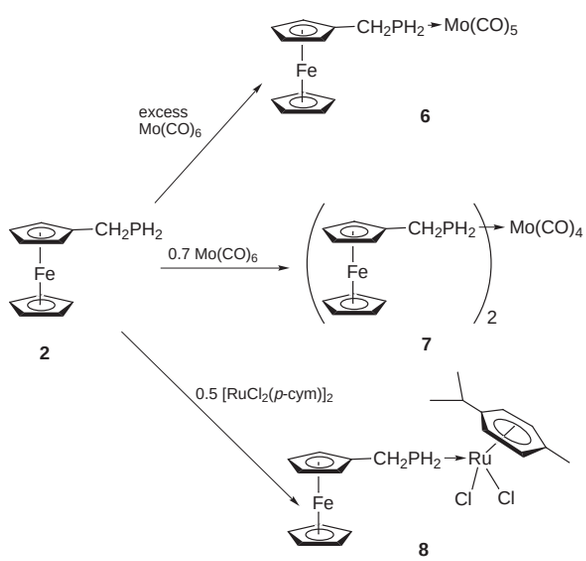
Other methods have been briefly investigated to prepare compound **2** from **3**; a sample of **3** was heated under vacuum to 120 °C, leading to the sublimation of a mixture of products. The major product was in fact unchanged **3**, but **2** and **4** were also present as the next most abundant materials. Heating **3** in solution at temperatures >80 °C also leads to formaldehyde loss with consequent formation of **2** and **4**.

It was found that treating compound **3** with a large excess of $Na_2S_2O_5$ in a two-phase system of water and light petroleum (bp 60–80 °C) did not lead to synthesis of the primary phosphine **2**, as might be expected. Instead, the phosphinic acid **5** (Scheme 1) [^{31}P NMR (D_2O) δ 37.4] was produced as the major product, with most of the colour in the two-phase reaction system present in the aqueous layer. This compound proved difficult to isolate, for several reasons. The aqueous layer from which **5** was isolated contained various sodium salts used in the reaction; it could be present in the reaction mixture as its conjugate base; the solubility properties of the acid and its conjugate base in various solvents were not as distinct as might be hoped, and the free acid was rather soluble in both water and in organic solvents. Nevertheless, **5** can be isolated as a crude preparation in moderate yield, or as a pure compound in very low yield. It is interesting that it is produced from this reaction, since $Na_2S_2O_5$ is usually considered a reducing rather than an oxidising agent, and in this regard it is noteworthy that **5** is still formed when the reaction is carried out in the absence of oxygen.

The secondary phosphine **4** gave an $[M]^+$ ion in the positive-ion electrospray mass spectrum, whereas the phosphinic acid **5** gave a peak corresponding to $[M - H]^-$, as expected for an organophosphorus acid.[26]

Molybdenum carbonyl complexes of RCH_2PH_2 2

Several complexes of compound **2** have been prepared, in order to show that despite its air-stability it still displays normal co-ordinative behaviour; the compounds prepared are shown in Scheme 3. The molybdenum(0) complex $[Mo(CO)_5(RCH_2PH_2)]$ **6** [^{31}P NMR δ −63.2, t, ^1J(PH) 315 Hz] was prepared by the standard technique of UV irradiating a thf solution of $[Mo(CO)_6]$ under nitrogen in the presence of **2**. Irradiation leads to replacement of a carbonyl with a labile thf molecule, which is in turn displaced by the phosphine. When the reaction was carried out using equimolar amounts of the two reagents considerable amounts of the di- and tri-substituted complexes



Scheme 3 Syntheses of metal complexes of RCH_2PH_2 **2**.

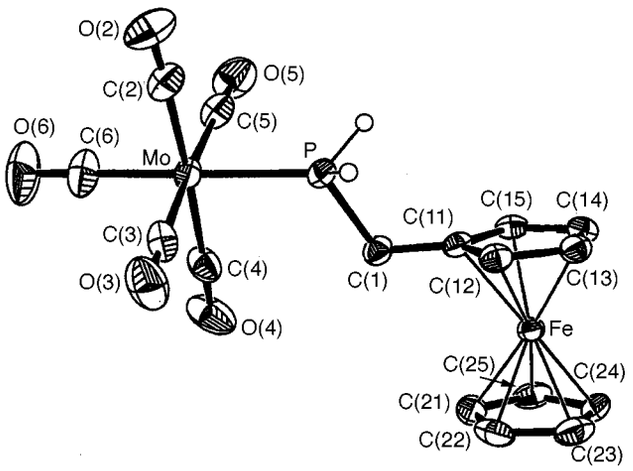


Fig. 3 An ORTEP diagram for $[Mo(CO)_5(RCH_2PH_2)]$ **6**. All hydrogen atoms are omitted for clarity, except for the PH hydrogens, shown in calculated positions.

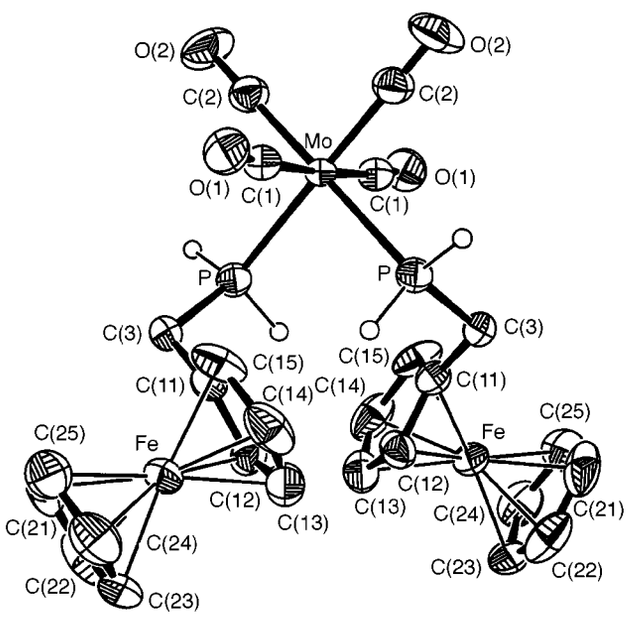


Fig. 4 An ORTEP diagram for *cis*-$[Mo(CO)_4(RCH_2PH_2)_2]$ **7**. All hydrogen atoms have been omitted for clarity, except for PH hydrogens, shown in calculated positions.

were also produced as side-products. The use of $[Mo(CO)_6]$ in large excess minimises these impurities, and unlike the two starting materials **6** does not appear to be volatile. If stored in the solid state at −30 °C it is moderately stable, but in solution or in the solid state at room temperature it is susceptible to degradation on exposure to air.

The disubstituted product $[Mo(CO)_4(FcCH_2PH_2)_2]$ **7** [^{31}P NMR δ −55.9, t, ^1J(PH) 308 Hz] was produced in low yield by heating a decalin solution of $[Mo(CO)_6]$ and **2** to 100 °C for 15 h. The product crystallised out of the cooled and evaporating solution, and while it did appear to be more air-stable than **6** crystals did darken over a period of weeks.

Examples of such mono- and di-substituted molybdenum(0) carbonyl phosphine complexes are not uncommon,[27] and indeed these compounds are also not the first mononuclear molybdenum carbonyl phosphinoferrocene compounds synthesized, with $[Mo(CO)_5(PR_3)]$ (R = ferrocenyl) being one early example of a previously reported compound of this type.[28]

The structures for compounds **6** and **7** are of course closely related. We are aware of only two other structures reported with the general formula $Mo(CO)_{6-m}(RPH_2)_m$, these being *fac*-$[Mo(CO)_3\{H_2PC(Me)=CH_2\}_3]$[29] and *cis*-$[Mo(CO)_4\{Bu^nN[(CH_2)_2PH_2]_2\}]$.[30] The paucity of known structures is surprising in view

Table 1 Selected bond lengths (Å) and angles (°) for $[Mo(CO)_5(RCH_2PH_2)]$ **6**, with estimated standard deviations (e.s.d.s) in parentheses

P–Mo	2.5056(10)	P–H(2A)	1.250
C(1)–P	1.836(3)	P–H(2B)	1.257
C(11)–C(1)	1.494(4)	C(2)–O(2)	1.148(5)
Mo–C(2)	2.048(4)	C(3)–O(3)	1.143(5)
Mo–C(3)	2.019(4)	C(4)–O(4)	1.137(5)
Mo–C(4)	2.043(4)	C(5)–O(5)	1.140(6)
Mo–C(5)	2.063(4)	C(6)–O(6)	1.148(5)
Mo–C(6)	2.007(4)		
Cp rings range	1.403(6)–1.432(5)	average	1.417(5)
Mo–P–C(1)	118.84(11)	P–Mo–C(2)	91.39(12)
C(11)–C(1)–P	114.3(2)	P–Mo–C(3)	90.44(12)
C(1)–P–H(2A)	94.53	P–Mo–C(4)	90.09(13)
C(1)–P–H(2B)	98.05	P–Mo–C(5)	86.36(12)
Mo–P–H(2A)	123.69	P–Mo–C(6)	178.0(2)
Mo–P–H(2B)	123.51	C(6)–Mo–C(2)	89.3(2)
C(3)–Mo–C(5)	176.8(2)	C(6)–Mo–C(3)	91.5(2)
C(2)–Mo–C(4)	176.2(3)	C(6)–Mo–C(4)	89.4(2)
		C(6)–Mo–C(5)	91.7(2)

Table 2 Selected bond lengths (Å) and angles (°) for $[Mo(CO)_4(RCH_2PH_2)_2]$ **7**, with e.s.d.s in parentheses

P(1)–Mo(1)	2.518(2)	Mo(1)–C(1)	2.047(8)
P(1)–C(3)	1.843(7)	Mo(1)–C(2)	1.984(8)
C(3)–C(11)	1.508(10)	C(1)–O(1)	1.138(9)
		C(2)–O(2)	1.156(9)
Cp rings range	1.36(2)–1.433(11)	average	1.401(13)
C(11)–C(3)–P(1)	111.3(5)	P(1)–Mo(1)–C(1)	91.8(2)
C(3)–P(1)–Mo(1)	122.0(3)	P(1)–Mo(1)–C(2)	179.1(2)
Mo(1)–C(1)–O(1)	175.0(7)	P(1)–Mo(1)–P(1)*	89.37(9)
Mo(1)–C(2)–O(2)	177.9(7)	P(1)–Mo(1)–C(1)*	90.6(2)
C(1)–Mo(1)–C(1)*	176.6(4)	P(1)–Mo(1)–C(2)*	90.4(2)
C(2)–Mo(1)–C(2)*	89.8(5)		

* Denotes atom related by symmetry operation.

of the large number of molybdenum carbonyl phosphine derivatives which are known, including complexes containing primary phosphines with other ligands. It is noted that the former compound is a trisubstituted compound, unlike **6** or **7**; no monosubstituted compound analogous to **6** has been reported. The structures of **6** and **7** are shown in Figs. 3 and 4 respectively, and selected bond lengths and angles are given in Tables 1 and 2.

Compound **6** adopts the expected arrangement whereby steric interactions in the molecule are minimised by *anti* conformation of the ferrocenyl and $Mo(CO)_5$ groups about the C(1)–P bond [torsion angle C(11)–C(1)–P–Mo 179.49(20)°]. The C(1)–P–Mo–C(2) torsion angle is also around 180°. Together, these factors mean there is an approximate mirror plane through the molecule in the plane C(11)–P–Mo. The replacement of a carbonyl group with the ligand **2**, which is not such a good π acceptor, results in a marginal shortening of the Mo–C(6) bond. The geometry about the Mo is almost perfectly octahedral.

The phosphine ligands in compound **7** adopt a *cis* configuration, with the molecule lying on a crystallographic twofold rotation axis. The ferrocene units are not oriented away from each other, but instead lie quite close together. Unlike **6**, the orientation about the C–P bond is not *anti*, but is instead reasonably acute [torsion angle Mo(1)–P(1)–C(3)–C(11) −65.17(59)°]. While the geometry around the molybdenum is octahedral, it is clear that the carbonyls C(1)–O(1) are bent away from the ferrocene groups. The P–H hydrogens could not be located in the difference map, and were instead included in the refinement in calculated positions.

The P–Mo bond lengths for compounds **6** and **7** are similar, and are essentially the same as the average P–Mo distance for

the compounds $[Mo(CO)_3\{H_2PCMe{=}CH_2\}_3]$ and *cis*-$[Mo(CO)_4\{Bu^nN[(CH_2)_2PH_2]_2\}]$ described earlier [P–Mo 2.501(1) and 2.510, 2.515 Å respectively]. These distances lie within the normal range for molybdenum(0) phosphine complexes.[31]

The complexes **6** and **7** have been analysed by negative-ion electrospray mass spectrometry (ESMS) in methanol solvent, in the presence of a small amount of sodium methoxide which acts as an ionisation agent. This ionisation method has been used previously for metal carbonyl complexes,[20,32] with nucleophilic addition of methoxide at a carbonyl ligand occurring to give a negatively charged derivative, $[M + OMe]^-$. However, if metal–hydride species were present, the methoxide may effect proton abstraction giving a $[M - H]^-$ ion. Such deprotonated ions are also observed for both **6** and **7**, with the abstracted proton undoubtedly being one of the relatively acidic P–H protons. For **6**, at a cone voltage of 20 V, a small peak is also seen due to $[M - H - CO]^-$; loss of CO ligands is a normal phenomenon seen with the ESMS technique, and the degree to which ligands are lost can be tuned by adjusting the cone voltage. For **7**, a large peak was also observed due to the species $[Mo(CpCH_2PH_2)(RCH_2PH_2)(CO)]^-$ at *m/z* 467, *i.e.* $[M - 3CO - FeCp]^-$, possibly due to fragmentation of the parent ion.

Synthesis of ruthenium(II) *p*-cymene complex 8

The *p*-cymene complex $[RuCl_2(\eta^6\text{-}C_{10}H_{14})(RCH_2PH_2)]$ **8** [^{31}P NMR δ −27.7, t, ^1J(PH) 359 Hz] was synthesized through the bridge-splitting reaction of $[\{RuCl_2(\eta^6\text{-}C_{10}H_{14})\}_2]$. This gave a complex which was quite air-stable, in accord with normal co-ordinative behaviour for a primary phosphine.[33]

Reaction of RCH_2PH_2 2 with $[Ru_3(CO)_{12}]$

One very notable aspect of primary and secondary phosphine chemistry is their predisposition towards breakage of the weak P–H bond and formation of complexed phosphide or phosphinidine fragments upon reaction with metal centres.[34] These formally anionic ligands can co-ordinate to a single metal centre, or form bridging and capping ligands in multinuclear species. The reaction of a primary phosphine such as **2** with metal carbonyl clusters should prove an effective way of producing clusters with capping or bridging phosphinidine- or phosphide-ferrocene moieties. The reactions of primary (and secondary[35]) phosphines with metal carbonyl clusters have in fact been rather extensively investigated and many products characterised.[36,37]

The reaction of compound **2** with $[Ru_3(CO)_{12}]$ was carried out in refluxing cyclohexane and led to the formation of at least seven products, judging by the number of bands which could be successfully separated by preparative TLC on silica gel. Only two major products were isolated however, and these were unambiguously characterised as $[Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}PCH_2R)]$ **9** [^{31}P NMR δ 76.9] and $[Ru_4(CO)_{11}(\mu_4\text{-}PCH_2R)_2]$ **10** [^{31}P NMR δ 193.0]. A comparison of the IR data in the carbonyl region for **9** and **10** with data for related compounds is given in Table 3, showing the close relationship between the observed bands of the related compounds $[Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}PPh)]$[36,39,40] and $[Ru_4(CO)_{11}(\mu_4\text{-}PPh)_2]$.[40,41] Microanalytical data were satisfactory, and the ESMS data, which also support this assignment, are discussed later. Both compounds **9** and **10** appeared pure by ^{31}P NMR. Their synthesis, following a literature procedure for $[Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}PPh)]$,[36] illustrates the normal behaviour of primary phosphine **2**.

The crystal structure of compound **9** was carried out; the compound crystallised in the $P\bar{1}$ space group with two independent molecules in the asymmetric unit. The structure of one of the molecules is shown in Fig. 5, and selected bond lengths and angles for both molecules in Table 4. The major difference between the two molecules concerns the position of the two bridging hydrogens, which of course can also be viewed as a difference in orientation of the ferrocenyl group about the capping phosphorus–carbon bond; other atoms also show minor shifts in relative position. In many respects, details of the structure are similar to those for the structure of $[Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}PPh)]$, in which the three crystallographically independent molecules differed only in orientation of the phenyl ring above the triangle of Ru atoms.[39] Bond lengths for compound **9** are very similar to those reported for $[Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}PPh)]$ and another previously reported analogous structure, $[Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}PC_6H_4OCH_3)]$.[38] The unbridged Ru–Ru bond [Ru(1)–Ru(2) 2.838, Ru(2′)–Ru(3′) 2.839 Å] is shorter than those Ru–Ru bonds supported by a bridging hydrogen [Ru(1)–Ru(3) 2.931, Ru(2)–Ru(3) 2.927, Ru(1′)–Ru(2′) 2.946, Ru(1′)–Ru(3′) 2.938 Å]. This confirms the

Table 3 Comparison of carbonyl IR data for compounds **9** and **10** with those of analogous compounds previously reported

Compound	$\tilde{\nu}$(CO)/cm^{-1}
9	2105m, 2072s, 2046s, 2028m, 2014s, 1998s, 1984m
$[Ru_3H_2(CO)_9(PPh)]$[40]	2105m, 2073s, 2045s, 2030m, 2018s, 1998s, 1985m
10	2077w, 2037s, 2015s, 1979m, 1829w
$[Ru_4(CO)_{11}(PPh)_2]$[40]	2075m, 2035s, 2018s, 1980s, 1838m

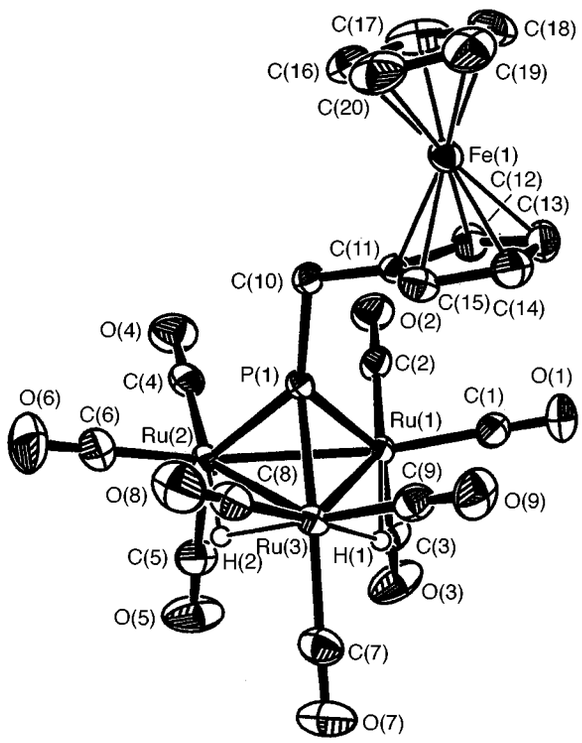


Fig. 5 An ORTEP diagram of one of the independent molecules (molecule 1) of $[Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}PCH_2R)]$ **9**. Cyclopentadienyl and CH_2 hydrogen atoms have been omitted for clarity.

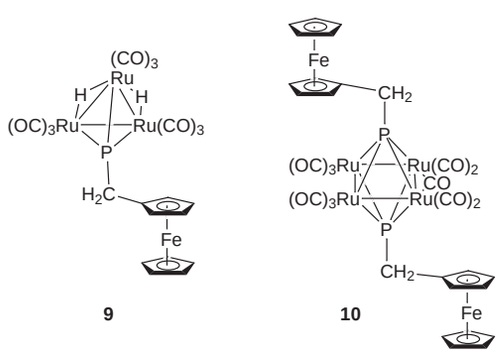


Table 4 Selected bond lengths (Å) and angles (°) for the two independent molecules of $[Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}PCH_2R]$ **9**, with e.s.d.s in parentheses

Molecule 1		Molecule 2	
Ru(1)–Ru(2)	2.8379(5)	Ru(1′)–Ru(2′)	2.9463(6)
Ru(1)–Ru(3)	2.9311(5)	Ru(1′)–Ru(3′)	2.9377(5)
Ru(2)–Ru(3)	2.9267(5)	Ru(2′)–Ru(3′)	2.8386(5)
Ru(1)–P(1)	2.2828(9)	Ru(1′)–P(1′)	2.3168(8)
Ru(2)–P(1)	2.2930(8)	Ru(2′)–P(1′)	2.2840(8)
Ru(3)–P(1)	2.3153(9)	Ru(3′)–P(1′)	2.2778(8)
Ru(1)–H(1)	1.838	Ru(1′)–H(3)	1.766
Ru(3)–H(1)	1.755	Ru(2′)–H(3)	1.734
Ru(2)–H(2)	1.711	Ru(1′)–H(4)	1.795
Ru(3)–H(2)	1.785	Ru(3′)–H(4)	1.727
av. Fe–C for substituted Cp ring	2.038(3)	av. Fe′–C′ for substituted Cp ring	2.045(3)
av. Fe–C for unsubstituted Cp ring	2.031(4)	av. Fe′–C′ for unsubstituted Cp ring	2.038(3)
Ru(1)–Ru(2)–Ru(3)	61.100(11)	Ru(1′)–Ru(2′)–Ru(3′)	61.004(9)
Ru(2)–Ru(1)–Ru(3)	60.944(9)	Ru(2′)–Ru(1′)–Ru(3′)	57.688
Ru(1)–Ru(3)–Ru(2)	57.957(11)	Ru(1′)–Ru(3′)–Ru(2′)	61.380
Ru(1)–P(1)–Ru(3)	79.20(3)	Ru(1′)–P(1′)–Ru(3′)	79.48(3)
Ru(1)–P(1)–Ru(2)	76.66(3)	Ru(1′)–P(1′)–Ru(2′)	79.64(3)
Ru(2)–P(1)–Ru(3)	78.85(3)	Ru(2′)–P(1′)–Ru(3′)	76.96(3)
Ru(1)–Ru(3)–P(1)	49.91(2)	Ru(1′)–Ru(3′)–P(1′)	50.84(2)
Ru(1)–Ru(2)–P(1)	51.51(2)	Ru(1′)–Ru(2′)–P(1′)	50.67(2)
Ru(2)–Ru(1)–P(1)	51.83(2)	Ru(2′)–Ru(1′)–P(1′)	49.69(2)
Ru(2)–Ru(3)–P(1)	50.24(2)	Ru(2′)–Ru(3′)–P(1′)	51.62(2)
Ru(3)–Ru(1)–P(1)	50.89(2)	Ru(3′)–Ru(1′)–P(1′)	49.67(2)
Ru(3)–Ru(2)–P(1)	50.91(2)	Ru(3′)–Ru(2′)–P(1′)	51.42(2)
Ru(1)–P(1)–C(10)	132.06(11)	Ru(1′)–P(1′)–C(10′)	127.30(11)
Ru(2)–P(1)–C(10)	138.82(10)	Ru(2′)–P(1′)–C(10′)	138.32(11)
Ru(3)–P(1)–C(10)	128.64(11)	Ru(3′)–P(1′)–C(10′)	132.97(11)
P(1)–C(10)–C(11)	109.5(2)	P(1′)–C(10′)–C(11′)	110.8(2)
Ru(1)–H(1)–Ru(3)	109.3	Ru(1′)–H(3′)–Ru(2′)	114.6
Ru(2)–H(2)–Ru(3)	113.6	Ru(1′)–H(4′)–Ru(3′)	113.0
Ru(1)–Ru(2)–C(4)	94.74(11)	Ru(1′)–Ru(2′)–C(4′)	103.29(12)
Ru(1)–Ru(3)–C(9)	97.91(10)	Ru(1′)–Ru(3′)–C(9′)	99.53(12)
Ru(2)–Ru(1)–C(2)	95.05(10)	Ru(2′)–Ru(1′)–C(2′)	95.06(11)
Ru(2)–Ru(3)–C(8)	97.01(11)	Ru(2′)–Ru(3′)–C(8′)	95.20(12)
Ru(3)–Ru(1)–C(1)	100.18(10)	Ru(3′)–Ru(1′)–C(1′)	95.69(11)
Ru(3)–Ru(2)–C(6)	103.96(12)	Ru(3′)–Ru(2′)–C(6′)	96.12(12)

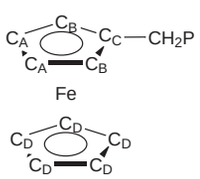
position of the bridging hydrogens which were in any case located as the four highest residual electron density peaks after inclusion of all other atoms. The distance from P to the Ru at the apex of the two bridging hydrogens [P(1)–Ru(3) 2.315, P(1′)–Ru(1′) 2.317 Å] is greater than the other P–Ru distances [P(1)–Ru(2) 2.293, P(1)–Ru(1) 2.283, P(1′)–Ru(2′) 2.284, P(1′)–Ru(3′) 2.278 Å]. The average Ru–H distance is 1.764 Å and the average Ru–H–Ru bond angle is 112.6°. In both independent molecules the ferrocene unit is situated such that it lies above an Ru–Ru bond bridged by hydrogen. Steric interactions with carbonyl groups may be the factor that makes this a preferable conformation to one where the ferrocenyl group lies over the unbridged Ru–Ru bond, since the equatorial carbonyl groups flanking a H-bridged Ru–Ru bond are splayed wider than is the case for unsupported Ru–Ru bonds [*e.g.* bond angles: Ru(3)–Ru(2)–C(6) 104.0, Ru(1)–Ru(2)–C(4) 94.7°]. In both molecules the ferrocene cyclopentadienyl rings adopt an eclipsed conformation.

Compound **9** shows two peaks in the negative-ion ESMS spectrum with added NaOMe, the larger corresponding to $[M + OMe]^-$ (*m*/*z* 819) and the smaller to $[M - H]^-$ (*m*/*z* 788). The first is presumably produced by methoxide addition, and the second by removal of a cluster hydride.[20,32] Compound **10** also shows two peaks in the ESMS spectrum with methoxide added, the first corresponding to methoxide addition, $[M + OMe]^-$ (*m*/*z* 1203) and the second due to subsequent loss of a CO ligand, $[M + OMe - CO]^-$ (*m*/*z* 1175). As expected, no deprotonated ion was observed for this cluster.

In summary, the simplicity of synthesis of the primary phosphine **2**, together with its ease of handling, make it ideal for studying the reactivity of a primary phosphine. This reactivity appears, based on the limited number of studies carried out to date, to be characteristic of other primary phosphines.

Experimental

For general synthetic and analytical details, see ref. 6. Light petroleum refers to the fraction of bp 60–80 °C. The IR spectra of carbonyl compounds were run only over the carbonyl stretch region in a light petroleum solution, unless stated otherwise. Electrospray mass spectra of carbonyl compounds were recorded in negative-ion mode in methanol solvent, with the addition of a small amount of NaOMe to aid ion formation.[20,32] The NMR spectra were recorded in $CDCl_3$ solution, unless otherwise stated. Where integration of ^{31}P NMR spectra was required (*e.g.* in the analysis of the disproportionation of the secondary phosphine **4**), the acquisition delay was increased from 2 to 3 s, and spectra were run in non-decoupled mode. Two-dimensional NMR experiments helped in the unambiguous assignment of spectra for compound **2**. Scheme 4 depicts the labelling scheme used in assignment of ferrocenyl NMR signals. The GC-MC analysis was carried out using a HP 5890 Series 1 gas chromatograph coupled to a HP 3970 Series Mass Selective Detector. The column was a HP1 column containing cross-linked methylsilicone gum, 24 m × 0.2 mm × 0.33 μm film thickness. A HP 7673A Autosampler was used to inject a solution of **2**, and the temperature was increased from 80 to 280 °C at a rate of 8 °C min^{-1}, with 1.5 min hold time.



Scheme 4 Atom labelling used in NMR assignments of the cyclopentadienyl rings.

The compounds $[Ru_3(CO)_{12}]$ (Strem) and $[Mo(CO)_6]$ (Alfa) were used as supplied. The starting hydroxymethylphosphine $RCH_2P(CH_2OH)_2$ **3**[6] and the complex $[\{RuCl_2(p\text{-cym})\}_2]$[42] (*p*-cym = *p*-cymene) were prepared by the literature methods. Other chemicals used were of at least LR grade.

Syntheses

RCH_2PH_2 2. The compound $RCH_2P(CH_2OH)_2$ **3** (4.003 g, 13.70 mmol) and $Na_2S_2O_5$ (2.605 g, 13.70 mmol) were added to a two-phase solvent system consisting of distilled water (60 ml) and light petroleum (60 ml). The mixture was stirred and refluxed in air for 3 h. After cooling, the aqueous layer was removed and the organic layer washed with distilled water (3 × 20 ml). The solvent was removed under vacuum to yield the crude product as an orange crystalline solid (1.913 g, 60%). The crude product was slowly sublimed over one week (30 °C, dynamic vacuum of 0.01 mmHg) onto a water-cooled cold-finger, yielding the pure product **2** as orange crystals (1.662 g, 52%) which can be stored in air at ambient temperature, mp 44–46 °C. Thirty-three days after preparation: found C, 56.87; H, 5.75%. Sixty-one days after preparation: found C, 57.07; H, 5.52%. Calculated for $C_{11}H_{13}FeP$: C, 56.94; H, 5.65%. IR (KBr disk, cm^{-1}): 3091w, 2903w, 2285s (P–H), 1769w, 1640w, 1463m, 1409m, 1391m, 1232m, 1194w, 1103s, 1076m, 1037m, 1023s, 998m, 924m, 862m, 817s, 500s and 481s. ESMS (cone voltage 20V), *m*/*z* 232 $[M]^+$. ^{31}P-$\{^1H\}$ NMR: δ −129.1 [t, ^1J(PH) 194 Hz]. ^1H NMR: δ 2.62 (RCH_2P, s, 2 H), 2.94 [PH_2, d of t, ^1J(PH) 192, ^3J(HH) 8, 2 H], 4.08 (C_AH, t, *J* 2, 2 H), 4.12 (C_BH, t, *J* 2, 2 H) and 4.14 (C_DH, s, 5 H). ^{13}C-$\{^1H\}$ NMR: δ 14.58 [RCH_2P, d, *J*(PC) 9], 67.47 (C_A, s), 67.97 (C_B, s), 68.80 (C_D, s) and 89.15 (C_C, d, *J* 3 Hz).

$RCH_2P(H)CH_2OH$ 4. Compound **3** (0.100 g, 0.342 mmol) and $Na_2S_2O_5$ (0.037 g, 0.195 mmol) were dissolved in a two-phase system consisting of water (10 ml) and diethyl ether (10 ml). The mixture was refluxed with stirring for 3 h, at which point the organic phase was removed and washed with water (3 × 10 ml). Removal of the solvent under reduced pressure gave the product **4** as a yellow oil (0.070 g, 78%) (Found: C, 55.25; H, 5.97. Calc. for $C_{12}H_{15}FeOP$: C, 55.00; H, 5.77%). IR (KBr disk, cm^{-1}): 3927w, 3509m, 3331s(br), 3093s, 2906s, 2849m, 2284s (P–H), 1763w, 1724w, 1642w, 1466s, 1412s, 1287w, 1234m, 1192m, 1105s, 1037s, 1021s, 1003s, 947m, 925s, 820s, 709w, 639w, 594w, 496s and 421m. ESMS (cone voltage 20 V): *m*/*z* 262 $[M]^+$. ^{31}P-$\{^1H\}$ NMR: δ −51.4 [d, ^1J(PH) 204 Hz]. ^1H NMR: δ 2.78–2.82 (RCH_2P, m, 2 H), 3.06–3.82 [PH, m, ^1J(PH) 204, 1 H] and 4.06–4.15 (Cp H and PCH_2O, m, 11 H). ^{13}C-$\{^1H\}$ NMR: δ 18.48 (RCH_2P, d, *J* 11), 57.92 [PCH_2O, d, *J*(PC) 15], 67.71 (C_A, d, *J* 7), 68.31–68.46 (C_B, m), 68.89 (C_D, s), and 86.13 (C_C, d, *J* 7 Hz).

$RCH_2P(O)(OH)CH_2OH$ 5. *Method A.* Compound **3** (0.100 g, 0.344 mmol) and $Na_2S_2O_5$ (0.300 g, 1.58 mmol) were dissolved in a two-phase system of water (10 ml) and diethyl ether (10 ml), and the mixture refluxed overnight. After cooling, a small amount of NaOH was added to the reaction mixture to ensure alkalinity, which was confirmed with litmus paper. The aqueous layer was then removed and acidified with *ca.* 2 mol L^{-1} HCl, and extracted with chloroform (2 × 20 ml). Removal of the chloroform under reduced pressure gave the crude product **5** as a yellow oil (0.024 g, 24%), which proved difficult to purify by crystallisation.

Method B. Compound **3** (0.200 g, 0.683 mmol) and $Na_2S_2O_5$ (0.601 g, 3.16 mmol) were dissolved in a two-phase system of water (10 ml) and diethyl ether (10 ml), and the mixture refluxed overnight. The aqueous layer was removed and dried under reduced pressure with heating to no more than *ca.* 35 °C. The residue was purified by TLC on silica gel, with pure methanol as the eluting solvent. The product band was yellow, R_f 0.35. Recrystallisation of this product was carried out from warm MeOH–diethyl ether cooled to *ca.* −30 °C. The material thus obtained was then dissolved in water (10 ml) and a small amount of *ca.* 2 mol L^{-1} HCl added. This acid solution was then extracted with ethyl acetate (10 ml). Removal of solvent from the organic layer under reduced pressure gave **5** as a yellow crystalline solid in poor yield (0.005 g, 2%), but in purity suitable for elemental analysis, mp *ca.* 170 °C (decomp.) (Found: C, 48.6; H, 4.7. $C_{12}H_{15}FeO_3P$ requires C, 49.0; H, 4.5%). IR (KBr disk, cm^{-1}): 3380m, 1637m, 1465w, 1403w, 1208w, 1151w, 1105m, 1069s, 1040s, 977s, 921w, 881w, 817m, 784w, 466w and 419w. ESMS (negative-ion mode), cone voltage 20 V: *m*/*z* 293, $[M - H]^-$. ^{31}P-$\{^1H\}$ NMR (D_2O): δ 37.4. ^1H NMR (D_2O): δ 3.00 (RCH_2P, d, *J* 15, 2 H), 3.72 (PCH_2O, d, *J* 6, 2 H), 4.40 (C_AH, unresolved t, 2 H), 4.45 (C_DH, s, 5 H) and 4.50 (C_BH, unresolved t, 2 H). ^{13}C-$\{^1H\}$ NMR (D_2O): δ 29.94 (RCH_2P, d, *J* 86), 58.88 (PCH_2O, d, *J* 108 Hz), 68.04 (C_A, s), 69.39 (C_D, s), 69.76 (C_B, s) and 81.17 (C_C, s).

$[Mo(CO)_5(RCH_2PH_2)]$ 6. Compound **2** (0.100 g, 0.430 mmol) and $[Mo(CO)_6]$ (1.546 g, 5.857 mmol) were dissolved in dry, oxygen-free thf (20 ml) and placed under a nitrogen atmosphere. The solution was exposed to UV light and stirred for 3 h. The solvent was removed under reduced pressure, and the residue heated at 30 °C for several days under dynamic vacuum until all the excess of $[Mo(CO)_6]$ had sublimed onto a cold-finger. The product was then dissolved in dry, oxygen-free dichloromethane and filtered to remove molybdenum degradation products. Removal of the solvent under reduced pressure gave the product **6** as a yellow powder (0.191 g, 95%). Crystals suitable for an X-ray analysis were obtained by cooling a hot methanolic solution to *ca.* −30 °C, although most of the compound in solution decomposed due to exposure to oxygen, mp 123–127 °C (Found: C, 41.7; H, 2.7. $C_{16}H_{13}FeMoO_5P$ requires C, 41.1; H, 2.8%). IR (petroleum spirits, cm^{-1}): 2077w, 1989m, 1955s, 1917w. ESMS (negative-ion mode) cone voltage 20 V, *m*/*z* 469 $[M - H]^-$, 441 $[M - H - CO]^-$. ^{31}P-$\{^1H\}$ NMR: δ −63.2 [d, ^1J(PH) 315]. ^1H NMR: δ 2.92 ($FcCH_2P$, d of t, *J* 7, *J* 4, 2 H), 4.12-4.15 (Cp-H, m, 9 H), 4.36 [PH_2, d of t, ^1J(PH) 320, ^3J(HH) 7, 2 H]. ^{13}C-$\{^1H\}$ NMR: δ 23.04 ($FcCH_2P$, d, *J* 23), 68.12 (C_B, d, *J* 2), 68.31 (C_A, s), 68.99 (C_D, s), 85.02 (C_C, s), 203.94, 204.76 and 204.88 (CO, 3 × s).

$[Mo(CO)_4(RCH_2PH_2)_2]$ 7. Compound **2** (0.146 g, 0.627 mmol) and $[Mo(CO)_6]$ (0.118 g, 0.446 mmol) were dissolved in decalin (10 ml) and a small quantity of light petroleum (0.5 ml). The solution was purged and placed under a nitrogen atmosphere, before heating at 100 °C for 15 h. As the solution cooled orange crystals of compound **7** were formed, which were removed by filtration. Partial evaporation of the supernatant under nitrogen over several days furnished more crystals, giving an overall final yield of 0.0305 g (20%). The crystals proved suitable for structure elucidation and other forms of analysis, but the presence of decomposition products which were difficult to separate from the desired product made a good elemental analysis unobtainable, mp 141–145 °C (Found: C, 48.0; H, 4.1. $C_{26}H_{26}Fe_2MoO_4P_2$ requires C, 46.5; H, 3.9%). IR (KBr disk, cm^{-1}): 2074w, 2020s, 1995w, 1945s, 1913s and 1873s. ESMS (negative ion), cone voltage 20 V: *m*/*z* 672, $[M - H]^-$; 467, $[M - 3CO - FeCp]^-$. ^{31}P-$\{^1H\}$ NMR: δ −55.9 [t, ^1J(PH) 308 Hz]. ^1H NMR: δ 2.79–2.85 [RCH_2P, d of t, ^2J(PH) 3, ^3J(HH) 7, 2 H], 4.12–4.15 (Cp H, m, 9 H) and 4.16 [PH_2, d of t, ^1J(PH) 318, ^3J(HH) 7 Hz, 2 H]. ^{13}C-$\{^1H\}$ NMR: δ 23.14 (RCH_2P, s), 68.05 (C_A, s), 68.31 (C_B, s), 68.95 (C_D, s), 107.79 (C_C, s), 199.67 (CO, s) and 200.42 (CO, s).

$[RuCl_2(\eta^6\text{-}C_{10}H_{14})(RCH_2PH_2)]$ 8. Compound **2** (0.060 g, 0.259 mmol) and $[\{RuCl_2(\eta^6\text{-}C_{10}H_{14})\}_2]$ (0.079 g, 0.130 mmol) were dissolved in dichloromethane (10 ml) and the solution purged and placed under nitrogen. The solution was refluxed

Table 5 Crystallographic data for compounds RCH_2PH_2 **2**, $[Mo(CO)_5(RCH_2PH_2)]$ **6**, $[Mo(CO)_4(RCH_2PH_2)_2]$ **7** and $[Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}PCH_2R)]$ **9**

	2	**6**	**7**	**9**
Empirical formula	$C_{11}H_{13}FeP$	$C_{16}H_{13}FeMoO_5P$	$C_{26}H_{26}Fe_2MoO_4P_2$	$C_{20}H_{13}FeO_9PRu_3$
M_r	232.04	468.02	672.05	787.33
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1$	$C2/c$	$P\bar{1}$
a/Å	13.7111(9)	7.4816(1)	20.626(3)	9.961(1)
b/Å	7.5225(5)	10.4412(1)	10.426(2)	15.506(3)
c/Å	10.5662(7)	11.5305(1)	12.324(1)	16.496(2)
α/°				83.96(1)
β/°	107.448(5)	96.780(1)	90.95(1)	88.72(1)
γ/°				80.79(1)
V/Å^3	1039.7(1)	894.43(2)	2649.9(7)	2501.0(6)
D_c (g cm^{-3})	1.482	1.738	1.685	2.091
Z	4	2	4	4
F(000)	480	464	1352	1512
μ(Mo-Kα)/mm^{-1}	1.29	1.62	1.70	2.43
T/°C	−105	−70	−105	−73
Crystal size/mm	0.52 × 0.44 × 0.24	0.28 × 0.20 × 0.08	0.38 × 0.30 × 0.014	0.70 × 0.62 × 0.56
Total reflections	3406	5604	3147	9576
Unique reflections	3032	2093	2899	8809
R_{int}	0.0279	0.0265	0.0265	0.0072
T_{min}	0.408	0.755	0.525	0.728
T_{max}	0.560	0.908	0.612	0.842
$R1$ [$I > 2\sigma(I)$]	0.0411	0.0213	0.0621	0.0220
$wR2$ (all data)	0.1235	0.0476	0.1495	0.0493
Goodness of fit	1.032	1.037	1.067	1.079
Electron density/e Å^{-3}				
maximum	0.639	0.293	1.025	0.480
minimum	−0.454	−0.403	−0.476	−0.375
Solution and refinement	SHELXS 86,[43] SHELXL 93[44]	SHELXS 86, SHELXL 93	SHELXS 86, SHELXL 93	SHELXTL-PC,[45] SHELXL 93
Flack parameter	—	0.09(2)	—	—

for 20 min, before the solvent was removed under reduced pressure to give the crude product in quantitative yield. Recrystallisation by vapour diffusion of pentane into a dichloromethane solution gave **8** as a brown powder (0.120 g, 86%) mp 187–190 °C (decomp.) (Found: C, 46.6; H, 5.1. $C_{21}H_{27}Cl_2FePRu$ requires C, 46.9; H, 5.1%). IR (KBr disk, cm^{-1}): 3445s, 3089w, 3037m, 2961s, 2921m, 2872w, 2361s, 2338m, 1652m, 1468m, 1459m, 1386m, 1240w, 1200w, 1122w, 1104m, 1071m, 1059m, 1037m, 1022m, 1000m, 924m, 887s, 848w, 820s, 800m, 736w, 668w, 498s, 482s, 448m and 422m. ^{31}P-{^{1}H} NMR: δ −27.7 [t, ^1J(PH) 359 Hz]. ^{1}H NMR: δ 1.21 [CH(CH_3)$_2$, d, J 7, 6 H], 2.16 ($C_6H_4CH_3$, s, 3 H), 2.72 [CH(CH$_3$)$_2$, h, J 7, 1 H], 3.13 (RCH_2P, d of t, J 9, J 6, 2 H), 4.14 (C_DH, s, 5 H), 4.17 (C_AH, d, J 2), 4.19 (C_BH, d, J 2), 4.81 [PH$_2$, d of t, ^1J(PH) 358, ^3J(HH) 6, 2 H], 5.20 [CH$_3$C(CH)$_2$, d, J 6, 2 H] and 5.33 [Pr^{i}C(CH)$_2$, d, J 6, 2 H]. ^{13}C-{^{1}H} NMR: δ 18.55 ($C_6H_4CH_3$, s), 18.61 (RCH$_2$P, d, J 28), 22.31 [CH(CH_3)$_2$, s], 30.91 [CH(CH$_3$)$_2$, s], 68.24 (C_A, s), 68.54 (C_B, s), 69.14 (C_D, s), 83.91 (C_C, s), 85.74 [CH$_3$C(CH)$_2$, d, J 5], 85.99 [Pr^{i}C(CH)$_2$, d, J 3 Hz], 102.69 [CH$_3$C(CH)$_2$, s] and 105.90 [(CH$_3$)$_2$CHC(CH)$_2$, s].

Reaction of RCH_2PH_2 2 with $[Ru_3(CO)_{12}]$. Compound **2** (0.050 g, 0.216 mmol) and $[Ru_3(CO)_{12}]$ (0.138 g, 0.216 mmol) were dissolved in cyclohexane (20 ml), purged, and refluxed under nitrogen for 75 min. After cooling the solvent was removed under reduced pressure. The product was applied to a silica TLC plate as a dichloromethane solution, and eluted with 15% dichloromethane in light petroleum. The second yellow band with R_f 0.51 and a series of dark, closely overlapping bands between the baseline and R_f 0.16 were both removed using methanol and dried under vacuum to give crude yields of $[Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}PCH_2R)]$ **9** (0.0263 g, 16%) and $[Ru_4(CO)_{11}(\mu_4\text{-}PCH_2R)_2]$ **10** (0.0338 g, 13%). Orange block crystals of **9** suitable for elemental analysis and structure analysis were obtained by slow evaporation of a light petroleum solution at −30 °C. Black feather-like crystals of **10** suitable for elemental analysis were obtained by recrystallisation from warm pentane–dichloromethane–diethyl ether. Compound **9** (Found: C, 30.8; H, 1.9. $C_{20}H_{13}FeO_9PRu_3$ requires C, 30.5; H, 1.7%): ^{31}P-{^{1}H} NMR δ 76.9s. Compound **10** (Found: C, 34.3; H, 1.5. $C_{33}H_{22}Fe_2O_{11}P_2Ru_4$ requires C, 33.8; H, 1.9%): ^{31}P-{^{1}H} NMR δ 193.0s.

Crystal structure determinations for compounds RCH_2PH_2 2, $[Mo(CO)_5(RCH_2PH)_2]$ 6, $[Mo(CO)_4(RCH_2PH_2)_2]$ 7 and $[Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}PCH_2R)]$ 9

Crystal data for the structures are given in Table 5; preliminary details of the structure of **2** have been published in communication form.[7] In the case of compounds **2**, **7** and **9** raw data were corrected for absorption based on a series of ψ scans. For **6** the data were corrected empirically for absorption using SADABS.[46]

All 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 and hydrogen atoms (except for P–H) included in calculated positions with isotropic thermal parameters 1.2 times that of the U_{iso} of the atom to which they are bonded. For both **2** and **6** 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. They could not be located in the case of **7**, and so were included in calculated positions.

CCDC reference number 186/1405.

See http://www.rsc.org/suppdata/dt/1999/1785/ for crystallographic files in .cif format.

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