Correspondence to:

Associate Professor W. Henderson,

Department of Chemistry,

University of Waikato,

Private Bag 3105,

Hamilton,

New Zealand

e-mail: w.henderson@waikato.ac.nz

FAX: 0064-7-838-4219

"User-friendly" primary phosphines and an arsine: synthesis and characterization of new air-stable ligands incorporating the ferrocenyl group

William Henderson* and Steven R. Alley

Department of Chemistry, University of Waikato, Private Bag 3105, Hamilton, New Zealand.

Synopsis

The new ferrocene-derived primary phosphines $FcCH_2CH_2PH_2$, 1,1'-Fc'$(CH_2PH_2)_2$ and 1,2-Fc"$(CH_2PH_2)_2$ together with the arsine $FcCH_2CH_2AsH_2$ have been synthesised and characterized; $FcCH_2CH_2EH_2$ are completely air stable while 1,2-Fc"$(CH_2PH_2)_2$ is air-stable for at least several months. The crystal structure of the arsine is also described.

Abstract

Reaction of $FcCH_2CH_2P(O)(OH)_2$ or $FcCH_2P(O)(OH)(OEt)$ [Fc = Fe(η^5-C_5H_4)(η^5-C_5H_5)] with excess CH_2N_2 followed by reduction with $Me_3SiCl/LiAlH_4$ gives the air-stable primary phosphines $FcCH_2CH_2PH_2$ and the previously reported analogue $FcCH_2PH_2$ in high yields. Reduction of 1,1’-Fc’[$CH_2P(O)(OEt)_2$] [Fc’ = Fe(η^5-C_5H_4)$_2$] and 1,2-Fc”[$CH_2P(O)(OEt)_2$] [Fc” = Fe(η^5-C_5H_5)(η^5-C_5H_3)] similarly gives the new primary phosphines 1,1’-Fc’(CH_2PH_2)$_2$ and 1,2-Fc”(CH_2PH_2)$_2$ respectively. The arsine $FcCH_2CH_2AsH_2$, which is also air-stable, has been prepared by reduction of the arsonic acid $FcCH_2CH_2As(O)(OH)_2$ using Zn/HCl. An X-ray structure has been carried out on the arsine, which is only the second structure determination of a free primary arsine. The molybdenum carbonyl complex [1,2-Fc”(CH_2PH_2)$_2$Mo(CO)$_4$] was prepared by reaction of the phosphine with [Mo(CO)$_4$(pip)$_2$] (pip = piperidine), and characterized by a preliminary X-ray structure determination. However the same reaction of 1,1’-Fc’(CH_2PH_2)$_2$ with [Mo(CO)$_4$(pip)$_2$] gave [1,1’-Fc’(CH_2PH_2)$_2$Mo(CO)$_4$] and the dimer [1,1’-Fc’(CH_2PH_2)$_2$Mo(CO)$_4$]$_2$, characterized by electrospray mass spectrometry. 1,1’-Fc’[CH_2PH_2Mo(CO)$_5$]$_2$ and 1,2-Fc”[CH_2PH_2Mo(CO)$_5$]$_2$ were likewise prepared from the phosphines and excess [Mo(CO)$_5$(thf)].

1. Introduction

Primary phosphines and arsines, REH_2 (E = P, As), particularly those containing lower alkyl groups, are typically highly air-sensitive, and often pyrophoric, with high toxicity and noxious odours, making them unpleasant and difficult materials to handle. Clearly, there is a desire for compounds of this type with “user-friendly” characteristics, as recently noted by Katti *et al*.[**1**] Nevertheless, primary phosphines and arsines have a very rich chemistry, promoted by the reactivity of the E-H bond.[**2**,**3**] In recent years, there have been a number of reports on the synthesis and use of air-stable primary phosphines. The use of bulky substituents in the mesityl-type phosphines **1** has been perhaps the most general route for stabilizing primary phosphines,[**4**,**5**] though these are exclusively aryl phosphines. In the area of alkylphosphines Katti and co-workers have recently described a number of remarkably air-stable primary alkylphosphines which contain amide, carboxylate and thiol functional groups; the common feature of the air-stable derivatives is an amide linkage four bonds away from the PH_2 group.[**1**,**3**,**6**] Other air-stable alkyl derivatives include the dibenzobarrellene phosphine **2**,[**7**] together with a range of cationic derivatives of the general type $[R_3NCH_2CH_2PH_2]^+$.[**8**] During our studies into the chemistry of the hydroxymethylphosphine $FcCH_2P(CH_2OH)_2$ **3a** [Fc = $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$] we discovered that formaldehyde could be eliminated under certain circumstances, giving the primary alkyl phosphine $FcCH_2PH_2$ **3b**, which is completely air-stable in the solid and solution states.[**9**] We subsequently wished to ascertain the generality of this stabilisation by the synthesis of related ferrocene-derived primary phosphines and arsines, and the results are presented in this paper.

2. Results and discussion

2.1 Synthesis and characterization of primary phosphines

The air-stable primary ferrocene phosphine $FcCH_2PH_2$ **3b** was originally synthesised by reaction of $FcCH_2P(CH_2OH)_2$ with the formaldehyde-abstracting reagent $Na_2S_2O_5$.[**9**] We wished to employ a more general route involving reduction of phosphonate esters, with the expectation that the method could also be employed to prepare a range of related primary phosphines and arsines derived from ferrocene. The reducing agent of choice was a mixture of $LiAlH_4$ and Me_3SiCl, which has been found to be a highly effective reducing mixture in primary phosphine synthesis.[**10**] The phosphonic acid monoester $FcCH_2P(O)(OEt)OH$ was a prime candidate for reduction, because it can be synthesised in good yield starting from readily accessible $FcCH_2OH$ and $Na[P(O)(OEt)_2]$.[**11**] However, reduction of $FcCH_2P(O)(OEt)OH$ with $LiAlH_4/Me_3SiCl$ gave a very low yield of **3b**, presumably due to the formation of insoluble lithium salts which are more difficult to reduce. Subsequently, methylation of $FcCH_2P(O)(OEt)OH$ with excess diazomethane gave the mixed ester $FcCH_2P(O)(OMe)(OEt)$, which was not isolated, but reduced in high yield (>90%) to **3b** using $LiAlH_4/Me_3SiCl$. In a similar fashion, methylation of the known phosphonic acid $FcCH_2CH_2P(O)(OH)_2$ [**11**] with excess CH_2N_2, followed by $LiAlH_4/Me_3SiCl$ reduction gave the primary ethylphosphine $FcCH_2CH_2PH_2$ **4** in 82% yield. This phosphine was initially isolated as an oil which sublimed under vacuum at 40 °C to give a dark orange crystalline solid, similar to **3b**. Similarly formed from the corresponding ethyl phosphonate esters 1,1'-Fc'$[CH_2P(O)(OEt)_2]_2$ [Fc' = Fe(η^5-$C_5H_4)_2$] (which has been prepared previously) [**11**] and 1,2-Fc"$[CH_2P(O)(OEt)_2]_2$ [Fc" = Fe(η^5-C_5H_5)(η^5-C_5H_3)] were the bis-primary phosphines **5** and **6** respectively, isolated as yellow oils; phosphine **6** sublimes under vacuum as a dark orange oil. The 1,2-phosphonate isomer has not been prepared previously, and was prepared by reaction of 1,2-Fc"$(CH_2Cl)_2$ with excess $P(OEt)_3$. The phosphines **4** - **6** are soluble in petroleum spirits and possess a mild odour typical of primary phosphines.

The phosphines give the expected ^{31}P NMR signals [δ ^{31}P: -135.8 (**4**), -132.0 (**5**), and –127.6 (**6**)] appearing as triplets in their ^{1}H-coupled spectra, with $^1J(PH)$ in the range 195-198 Hz. Other primary phosphines give very similar values, e.g. $H_2PCH_2CH_2PH_2$ (193 Hz) [**12**] and **3b** (194 Hz).[**9**] The electrospray (ES) mass spectra of phosphines **4** – **6** are dominated by the $[M]^+$ ion, as also observed for a number of other ferrocene compounds by this technique, though peaks due to $[M + H]^+$ may also be observed. Spectra were typically recorded with added $AgNO_3$ which generates silver complexes *in situ*, giving $[M + Ag]^+$ ions, as has been observed for other ferrocenyl phosphines.[**13**] The IR spectra showed bands characteristic of νP-H stretches, at 2294, 2290 and 2265 cm^{-1} for **4**, **5**, and **6** respectively.

Phosphine **4** appears to be completely air-stable (a solid sample exposed to air for 2 years showed no decomposition) while **6** is stable in air for at least several months, and **5** appears to be stable for several weeks. Longer exposure of **5** leads to some degradation, monitored by ^{31}P NMR spectroscopy; residual phosphine is amenable to repurification by silica flash column chromatography using petroleum spirits as the eluting solvent. To provide a comparison, samples of the known primary ferrocene-phosphines $FcPH_2$ [**14**] and 1,1’-Fc’$(PH_2)_2$ [**15**] were synthesised by $LiAlH_4/Me_3SiCl$ reduction of $FcP(O)(OEt)_2$ and 1,1’-Fc’$[P(O)(OEt)_2]_2$ respectively, and their air-sensitivity ascertained by allowing samples to stand in air for several days. As far as we are aware, the air-sensitivity of these phosphines has not been explicitly discussed in the literature, though they have been used as starting reagents for the synthesis of other phosphines, typically using inert atmosphere techniques. 1,1’-Fc’$(PH_2)_2$ was the most rapidly oxidized in air, with a sample left for 3 days showing complete consumption of the original phosphine, and formation of a mixture of primary phosphine oxide [$RP(O)H_2$] and phosphinic acid [RP(O)(OH)H] groups. Air exposure of solutions of 1,1’-Fc’$(PH_2)_2$ in organic solvents led to immediate formation of a yellow precipitate, demonstrating the highly air-sensitive nature of this phosphine, in marked contrast to **5**. $FcPH_2$ was less reactive towards air, but was also oxidized by air over a period of several days. After 5 days exposure to air, the ^{31}P NMR spectrum showed a mixture of the primary phosphine oxide and phosphinic acid with very little residual phosphine present. These observations suggest that the presence of the alkyl spacer is a key factor in providing air stability in the ferrocenyl-phosphine system. Further studies are necessary to determine the effect of even longer alkyl spacers on phosphine stability.

2.2 Synthesis and characterization of the primary arsine $FcCH_2CH_2AsH_2$

Having synthesised a number of air-stable primary phosphines, we wished to synthesise a corresponding primary arsine, to see if the ferrocene-based stabilization was extended to arsines. One of the classical methods for the synthesis of primary arsines involves the reduction of an arsonic acid.[**16**] $FcCH_2CH_2As(O)(OH)_2$ is readily available [from $FcCH_2CH_2Br$ and sodium arsenite].[**11**] Reduction of this with Zn/HCl in a two-phase water-petroleum spirits system gave the primary arsine **7** as a crystalline orange solid. The arsine, like the corresponding phosphine **4**, appears to be air-stable, though a detailed study was not carried out. The compound is soluble in petroleum spirits and other organic solvents (except lower alcohols and DMSO), has the expected unpleasant but mild odour, and sublimes under vacuum to give single crystals suitable for an X-ray diffraction study. To the best of our knowledge, there has only been one previous structure determination of a free primary arsine, that of **1** (R = ^{i}Pr) [**4**], though the silyl-arsine 2,4,6-$^{i}Pr_3C_6H_2Si(^{t}Bu)(AsH_2)_2$ has also been characterized.[**17**] Only a few transition metal complexes of primary arsines have also been structurally characterized, e.g. $[PhAsH_2\text{-}Cr(CO)_5]$.[**18**] We are unaware of any reports of ferrocene-derived primary arsines in the literature. This contrasts with the much larger number of tertiary ferrocenyl arsines such as those containing $AsMe_2$ groups.[**19**]

The molecular structure of **7** is shown in Figure 1, together with the atom numbering scheme. Selected bond lengths and angles are given in Table 1. The structure confirms the compound as a primary arsine. The CH_2CH_2 group is slightly disordered, and extends away from the ferrocenyl moiety, with major [95%; C(1) and C(2)] and minor [5%; C(111) and C(112)] components of the disorder modelled. The $CH_2CH_2AsH_2$ substituent is approximately coplanar with the cyclopentadienyl ring to which it is attached, with torsion angles C(11)-C(1)-C(2)-As 177.19° and C(11)-C(111)-C(112)-As 175.91°. The As-C bond distance, 1.966(6) Å, is highly comparable to that of the R= ^{i}Pr derivative of **1**, 1.968(3) Å.[**4**] Single crystals of the corresponding phosphine

4 were also obtained by sublimation of the compound under vacuum, and a preliminary X-ray structure determination showed the compound to be isomorphous and hence isostructural to **7**. A full structure determination was therefore not continued.

2.3 Molybdenum carbonyl complexes of ferrocene-derived primary phosphines

Molybdenum carbonyl complexes of the phosphines **5** and **6** were prepared in the expectation that crystalline complexes would be formed, providing additional characterization of the phosphines themselves, which were isolated as oils. A wide range of molybdenum carbonyl complexes of phosphines are known, for example primary phosphines readily react with $L_2M(CO)_4$ [M = Cr, Mo, W; L_2 = norbornadiene or L = piperidine (pip)] to give complexes $(RPH_2)_2M(CO)_4$[**20**] and reactions between RPH_2 (R = 1-adamantyl) and $M(CO)_6$ (M = Cr, Mo, W) giving $[Mo(CO)_5(RPH_2)]$ have also been described.[**21**] Ferrocenyl phosphine derivatives of $Mo(CO)_5$ [**9**] and $M(CO)_4$ (M = Cr, Mo, W) have been previously reported.[**9**,**22**]

The reaction of 1,2-Fc”$(CH_2PH_2)_2$ **6** with $[Mo(CO)_4(pip)_2]$ in refluxing dichloromethane gave the expected complex **8** as the sole product, a yellow crystalline solid which gave satisfactory microanalytical data. Coordination of the phosphine resulted in a shift of the ^{31}P NMR signal from *ca.* δ –128 in the free phosphine to *ca.* δ –79 in the complex. Crystals of **8** were obtained from dichloromethane-petroleum spirits, and to fully characterize the complex, an X-ray structure determination was carried out. However, the crystal was weakly diffracting, and coupled with ambiguities in space group assignment and likely disorder, an adequate refinement was not obtained, so discussion of bond parameters was clearly not justified. However, the overall structure of the complex (Figure 2) is clear, and confirms the formulation as a chelate complex formed by the bidentate bis(primary) phosphine, with the seven-membered ring adopting a boat conformation. The negative-ion electrospray mass spectrum of **8** in methanol with added NaOMe gave a very strong $[M - H]^-$ ion as the base peak, due to deprotonation of one of the PH hydrogens. We have used this ionization technique previously in ES characterization of molybdenum carbonyl complexes of $FcCH_2PH_2$ [**9**]; the alternative addition of OMe^- to a coordinated CO ligand [**23**] was not observed for this complex.

The reaction of 1,1'-$Fc'(CH_2PH_2)_2$ **5** with $[Mo(CO)_4(pip)_2]$ in refluxing dichloromethane yielded two compounds. The major product was the expected chelate complex **9a**, isolated as a yellow crystalline solid using silica thin layer chromatography, and fully characterized. The negative ion ES mass spectrum at a cone voltage of 10 V showed both $[M - H]^-$ (*m/z* 487) and $[M - H - CO]^-$ ions; increasing the cone voltage to 60V results in the sequential loss of up all 4 CO ligands. The minor product **9b**, also isolated by chromatography, was identified by ESMS as the dimeric species [1,1'-$Fc'(CH_2PH_2)_2Mo(CO)_4]_2$. Thus, the ES spectrum of **9b** in methanol with added NaOMe gave a single ion due to [**9b** – H]$^-$ at *m/z* 971, with no evidence of the monomeric species. The formation of **9b** could be minimized (but not eliminated) by carrying out the reaction in dilute solution. The ES spectrum of the reaction mixture showed both **9a** and **9b**, but no evidence for larger oligomers.

The $Mo(CO)_5$ derivatives of phosphines **5** and **6** have also been synthesised from $[Mo(CO)_6]$, *via* the labile intermediate complex $[Mo(CO)_5(thf)]$ (thf = tetrahydrofuran).[**24**] Thus, reaction of **5** with a large excess of $[Mo(CO)_5(thf)]$ gave the complex 1,1'-Fc'[$CH_2PH_2Mo(CO)_5$]$_2$ **10** as the sole product. Again, the reaction can be conveniently monitored by ^{31}P NMR spectroscopy, with a shift from δ –132 for the free ligand to δ –62.5 on complex formation. The complex was purified by silica thin layer chromatography, and was isolated as a yellow crystalline solid. The negative-ion ES spectrum of **10** in methanol with added NaOMe gave solely the $[M - H]^-$ ion at a cone voltage of 5 V and, as the cone voltage is increased, there is stepwise loss of all 10 CO ligands, as shown in Figure 3. The reaction of 1,2-Fc"(CH_2PH_2)$_2$ with [$Mo(CO)_5$(thf)] gave the analogous complex 1,2-Fc"[$CH_2PH_2Mo(CO)_5$]$_2$ **11** as the principal product. The electrospray mass spectrum in methanol with added NaOMe showed $[M - H]^-$ and $[M + OMe]^-$ ions. Complexes **10** and **11** both give triplets in their proton-coupled ^{31}P NMR spectra, with ^{1}J(PH) *ca.* 320 Hz, consistent with the presence of coordinated PH_2 groups.

The molybdenum carbonyl derivatives of phosphines **5** and **6** are easily prepared and handled, and provide additional evidence for the identity of the phosphines themselves, in the form of satisfactory microanalytical and spectroscopic data. The complexes are yellow crystalline solids which turn green upon prolonged exposure (several months) to air. The $Mo(CO)_4$ derivatives decompose on heating, whereas the $Mo(CO)_5$ derivatives have clearly defined melting points. Apart from complex **8**, the yields of the Mo complexes were relatively poor, presumably due to decomposition and losses on purification.

Conclusions

We have shown that the incorporation of -CH_2- or –CH_2CH_2- spacer groups in ferrocene-derived primary phosphines and an arsine dramatically increases their air stability compared with phosphines such as 1,1'-Fc'$(PH_2)_2$, where the PH_2 groups are bonded directly to the cyclopentadienyl rings. The resulting compounds, which are easily handled, and in some cases crystalline and sublimable, can be considered to be "user-friendly" primary phosphine ligands, complementary to $FcCH_2PH_2$ prepared earlier by us, and to the range of other stable primary phosphines reported by other workers. The anticipated reactivity of the P-H (and As-H) bonds in these materials, coupled with the long-standing interest in the versatile and flexible coordination chemistry of ligands such as dppf [1,1'-Fc'$(PPh_2)_2$] [**25**] and recently synthesised analogues such as 1,1'-Fc'$(CH_2PPh_2)_2$ [**26**] suggests that the phosphines reported herein could be valuable precursors for the synthesis of new ferrocene-based phosphine ligands. While the factors providing air stability in the ferrocenyl primary phosphine/arsine system are not currently understood, the synthesis of related compounds may provide insights, and studies in this area are planned.

3. Experimental

3.1 General experimental procedures

General experimental techniques and instrumentation were as described in a recent publication.[**11**] Elemental microanalyses were carried out by the Campbell Microanalytical Laboratory, University of Otago, New Zealand. All reactions were carried out under a nitrogen atmosphere unless otherwise stated, using solvents which were dried and distilled prior to use. Petroleum spirits refers to the fraction of boiling point range 40-60 °C. IR spectra of primary phosphines and their Mo complexes were recorded as dichloromethane solutions. NMR spectra were recorded in $CDCl_3$ solution unless otherwise stated. Numbering of monosubstituted and 1,1'-disubstituted ferrocenyl compounds was as used previously.[**11**] For the 1,2-disubstituted compounds the numbering scheme used is shown in Scheme 1.

Gc-ms data were acquired using a Hewlett-Packard 5890 series 1 gas chromatograph coupled to a Hewlett Packard 5970 series mass selective detector operating at 70 eV. Samples were introduced as dichloromethane solutions and were eluted using a 50-280 °C temperature ramp, at 10 °C min^{-1} with a 3 min. solvent delay and an HP1 column containing crosslinked methylsilicone gum.

Electrospray mass spectra were recorded as described before,[**11**] using methanol as the solvent and mobile phase. A small quantity of aqueous $AgNO_3$ (0.1 M, *ca.* 1 mmol per mL of sample solution) was added to the primary phosphines to generate charged silver complexes *in situ*.[**13**] Small quantities of NaOMe in methanol were added to the Mo carbonyl complexes to promote ionization by deprotonation.[**23**] Ion assignment was assisted by comparison of observed and calculated isotope distribution patterns, the latter obtained using the ISOTOPE program.[**27**]

The following compounds were used as supplied from commercial sources: $Mo(CO)_6$ (Pressure Chemical Co.), triethylphosphite (BDH), $LiAlH_4$ (Aldrich), zinc powder (Prolabo) and Me_3SiCl (Aldrich). Other chemicals used were at least of reagent grade. The compounds $FcCH_2CH_2P(O)(OH)_2$ [**11**], $FcCH_2CH_2As(O)(OH)_2$ [**11**],

$FcCH_2P(O)(OEt)(OH)$ [**11**], $FcP(O)(OEt)_2$ [**11**], 1,1'-Fc'$[P(O)(OEt)_2]_2$ [**11**], 1,1'-Fc'$[CH_2P(O)(OEt)_2]_2$ [**11**], $[Mo(CO)_4(pip)_2]$ [**28**] and 1,2-Fc''$(CH_2OH)_2$ [**29**] were prepared by the literature procedures, and diazomethane was prepared from nitrosomethylurea and KOH following the literature procedure.[**30**] $[Mo(CO)_5(thf)]$ was generated *in situ* by modification of the literature method.[**24**] This involved irradiating a solution of $Mo(CO)_6$ in thf using a Lighting Technology MBF 400W lamp, placed 10 cm from the reaction vessel (Pyrex Schlenk flask).

3.2 Synthesis of $FcPH_2$

To a slurry of $LiAlH_4$ (0.32 g, 8.5 mmol) and Me_3SiCl (1 mL, 8.5 mmol) in thf (10 mL) was added a solution of $FcP(O)(OEt)_2$ (0.91 g, 2.8 mmol) in thf (10 mL). The reaction mixture was stirred for 12 h, and then methanol (5 mL) added carefully with stirring to destroy excess $LiAlH_4$, and the solvent removed under reduced pressure. The residue was extracted with petroleum spirits (5 x 10 mL) and the combined organic fractions filtered through celite. The solvent was then removed to give 0.5 g (87%) of $FcPH_2$ as a brown oil that crystallized on standing. ^{31}P NMR, δ –143.3 [t, $^{1}J(PH)$ 203], lit. δ ^{31}P –145.1. [**14**]

3.3 Synthesis of 1,1'-Fc'$(PH_2)_2$

A solution of 1,1'-Fc'$[P(O)(OEt)_2]_2$ (0.54 g, 1.2 mmol) in thf (5 mL) was added to a suspension of $LiAlH_4$ (0.27 g, 7 mmol) and Me_3SiCl (0.9 mL, 7 mmol) in diethyl ether.

The reaction mixture was stirred at room temp. for 12 h and methanol (5 mL) was added carefully with stirring to destroy excess $LiAlH_4$. The solvent was removed under reduced pressure and the residue extracted with petroleum spirits (5 x 10 mL). The combined organic fractions were filtered through celite and the solvent removed to give 0.24 g (82%) of 1,1'-Fc'$(PH_2)_2$ as a brown oil that crystallized on standing. ^{31}P NMR, δ –143.8. Lit. δ ^{31}P (C_6D_6) –145.5. [**15**(a)]

3.4 Synthesis of $FcCH_2PH_2$ **3b**

Excess ethereal CH_2N_2 was added to a slurry of $FcCH_2P(O)(OEt)(OH)$ (0.99 g, 3.2 mmol) in methanol (5 mL) and the mixture stirred until the solid had completely dissolved. Excess CH_2N_2 was removed by purging with nitrogen, and the solvent was removed under vacuum. The residual brown oil was dissolved in thf (5 mL) and added dropwise to a slurry of $LiAlH_4$ (0.7 g, 19.2 mmol) and Me_3SiCl (2.4 mL, 19.2 mmol) in thf (10 mL). The mixture was stirred for 12 h and methanol (5 mL) was carefully added dropwise to destroy excess $LiAlH_4$. The solvent was removed under vacuum and the residue extracted with petroleum spirits (5 x 10 mL), the combined extracts filtered through celite, and the solvent removed under vacuum to give $FcCH_2PH_2$ as a crystalline yellow-orange solid, yield 0.69 g, 92%. The sample was spectroscopically identical to a sample prepared by the literature procedure.[**9**] ^{31}P NMR ($CDCl_3$), δ –129.09 [t, ^{1}J(PH) 193 Hz].

3.5 Synthesis of $FcCH_2CH_2PH_2$ **4**

Excess ethereal CH_2N_2 was added slowly to a slurry of $FcCH_2CH_2P(O)(OH)_2$ (0.39 g, 1.34 mmol) in dichloromethane (5 mL) and stirred until the solid had completely dissolved. Nitrogen was bubbled through the solution to remove excess CH_2N_2, and then the solvent was removed under vacuum. The residue was dissolved in thf (5 mL) and added dropwise to a slurry of $LiAlH_4$ (0.25 g, 6.7 mmol) and Me_3SiCl (0.72 g, 6.7 mmol) in thf (10 mL). The resulting mixture was stirred for 12 h at room temp., methanol (5 mL) carefully added dropwise to destroy excess $LiAlH_4$, and the mixture stirred for 30 min. The solvent was removed under vacuum and the residue dissolved in petroleum spirits (20 mL). The yellow solution was filtered through celite and the solvent removed to give 0.27 g (82%) of $FcCH_2CH_2PH_2$ as a yellow powder. M.p. 53-55 °C. Found: C, 58.7; H, 6.0. $C_{12}H_{15}FeP$ requires C, 58.6; H, 6.1%. ^{31}P NMR, δ –135.8 [t, $^1J(PH)$ 195]. $^{13}C\text{-}\{^1H\}$ NMR, δ 15.50 [d, $^1J(PC)$ 8.4, PCH_2], 33.25 [d, $^2J(PC)$ 3, $PCH_2\underline{\mathbf{C}}H_2$], 67.33 (s, C3), 68.05 (s, C2), 68.57 (s, C4), 89.04 [d, $^3J(PC)$ 6, C1]. ^1H NMR, δ 2.57 [2H, dt, $^2J(PH)$ 2.5, $^3J(HH)$ 7, PCH_2], 2.74 [2H, dt, $^1J(PH)$ 194, $^3J(HH)$ 7, PH_2], 4.08-4.12 (11H, m, $C\underline{\mathbf{H}}_2CH_2PH_2$/H2/H3/H4). ESMS (cone voltage 40 V, with added $AgNO_3$), $[M]^+$ (*m/z* 246, 8%), $[M + Ag]^+$ (*m/z* 353/355, 100%). Gc-ms: $[M]^+$ (*m/z* 246), $[M - PH_2]^+$ (*m/z* 213), $[FcCH_2]^+$ (*m/z* 199), $[FeCp]^+$ (*m/z* 121), $[Fe]^+$ (*m/z* 56). IR (ν_{max}, cm^{-1}): 2294 (m, νPH).

3.6 Synthesis of 1,1'-Fc'$(CH_2PH_2)_2$ **5**

1,1'-Fc'[$CH_2P(O)(OEt)_2$]$_2$ (0.45 g) was dissolved in thf (5 mL) and added to a slurry of $LiAlH_4$ (0.18 g, 4.7 mmol) and Me_3SiCl (0.53 g, 4.7 mmol) in thf (10 mL) and the mixture stirred at room temp. for 6 h. Methanol (5 mL) was carefully added dropwise to destroy excess $LiAlH_4$, the mixture stirred for 30 min. and the volatiles removed under vacuum. The residue was dissolved in petroleum spirits (20 mL), filtered through celite and the solvent removed from the filtrate to give **5** as a yellow oil (0.16 g, 62%). ^{31}P NMR, δ –132.0 [t, $^1J(PH)$ 196]. ^{13}C-{^1H} NMR, δ 14.30 [d, $^1J(PC)$ 8.7, CH_2P], 68.29 (s, C3), 68.57 [d, $^3J(PC)$ 2.7, C2], 89.30 [d, $^2J(PC)$ 3, C1]. ^1H NMR, δ 1.54 (4H, br s, CH_2P), 2.93 [4H, dt, $^1J(PH)$ 192, $^3J(HH)$ 7, PH_2], 4.04 (8H, s, H2/H3). ESMS (cone voltage 40 V, with added $AgNO_3$) $[M]^+$ (*m/z* 278, 100%), $[M + Ag]^+$ (*m/z* 385/387, 45%). IR (cm^{-1}): 3082(m), 2922(m), 2290(s, νPH_2), 1083(m), 1039(m), 1019(w), 927(m), 859(w), 852(w), 823(w), 485(m).

3.7 Synthesis of 1,2-Fc"(CH_2PH_2)$_2$ **6**

1,2-Fc"(CH_2Cl)$_2$ was generated by a minor modification of the literature procedure [**31**] as follows: To 1,2-Fc"(CH_2OH)$_2$ (0.23g, 0.93 mmol) in thf (10 mL) under nitrogen was added pyridine (0.15 g, 1.86 mmol) and freshly distilled PCl_3 (0.25 g, 1.86 mmol). The reaction mixture was stirred for 1 h, filtered, and the filtrate evaporated to dryness to give crude 1,2-Fc"(CH_2Cl)$_2$. Triethylphosphite (3 mL) was added and the mixture refluxed for 4 h. Volatiles were removed under vacuum and the resulting brown oil purified by alumina flash column chromatography using an ethyl acetate to methanol solvent gradient. The 1,2-Fc"[$CH_2P(O)(OEt)_2$] was isolated as a viscous brown oil (0.39 g, 85%). This was dissolved in thf (5 mL) and added to a slurry of $LiAlH_4$ (0.30 g, 8 mmol) and Me_3SiCl (0.87 g, 8 mmol) in thf (10 mL) under nitrogen, and the mixture stirred for 9 h. Methanol (5 ml) was carefully added dropwise to destroy excess $LiAlH_4$, the mixture stirred for 30 min., and the volatiles removed under vacuum. The residue was dissolved in petroleum spirits (20 mL), filtered through celite, and the solvent removed giving the product **6** as a yellow crystalline solid which melted on warming to room temperature. Yield 0.18 g, 80%. ^{31}P NMR, δ –127.6 [t, $^{1}J(PH)$ 198]. $^{13}C-\{^{1}H\}$ NMR, δ 12.86 [d, $^{1}J(PC)$ 10, CH_2P], 65.64 (s, C1), 67.39 (s, C2), 69.43 (s, C4), 86.94 (s, C3). ^{1}H NMR, δ 2.62 (4H, m, CH_2P), 2.94 [4H, dt, $^{1}J(PH)$ 196, $^{3}J(HH)$ 7, PH_2], 4.00 [1H, t, $^{3}J(HH)$ 2.5, H1], 4.05 (5H, s, H4), 4.01 [2H, d, $^{3}J(HH)$ 2.5, H2]. ESMS (cone voltage 20 V, with added $AgNO_3$) $[M + Ag]^+$ (*m/z* 385/387, 100%). IR (cm^{-1}): 3097(w), 2916(m), 2285(s, νPH_2), 1105(s), 1080(m), 1034(m), 997(m), 929(w), 819(m), 485(m).

3.8 Synthesis of $FcCH_2CH_2AsH_2$ **7**

$FcCH_2CH_2As(O)(OH)_2$ (0.11 g, 0.33 mmol) was dissolved in 0.13 M aqueous NaOH (10 mL), and to this was added powdered zinc (0.21 g, 3.3 mmol) and petroleum spirits (15 mL). The mixture was placed under a nitrogen atmosphere and concentrated hydrochloric acid (10 mL) added dropwise with stirring over 10 min. The layers were separated and the aqueous phase extracted with petroleum spirits (10 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and the solvent removed to give 0.055 g (57%) of **7** as a yellow oil that crystallized on standing. M.p. 44-46 °C. Found: C, 50.3; H, 5.6. $C_{12}H_{15}AsFe$ requires 49.7; H, 5.2%. $^{13}C-\{^{1}H\}$ NMR, δ 14.02 (s, $AsCH_2$), 33.55 (s, $AsCH_2\underline{\mathbf{C}}H_2$), 67.57 (s, C2), 68.26 (s, C3), 68.84 (s, C4), 90.16 (s, C1). ^{1}H NMR, δ 1.84 (2H, m, CH_2As), 2.24 [2H, t, ^{3}J(HH) 6, AsH_2], 2.65 [2H, t, $C\underline{\mathbf{H}}_2CH_2As$, ^{3}J(HH) 7.9], 4.09 [4H, m, ^{3}J(HH) 1.5, H2/H3], 4.14 (5H, s, H4). Gc-ms $[M]^+$ (*m/z* 290), $[FcCH_2CH_2]^+$ (*m/z* 213), $[M\text{-}AsH_3]^+$ (*m/z* 212), $[CpFe]^+$ (*m/z* 121), $[Fe]^+$ (*m/z* 56).

3.9 Synthesis of [1,2-Fc"($CH_2PH_2)_2Mo(CO)_4$] **8**

Bisphosphine **6** (0.06 g, 0.23 mmol) was dissolved in dichloromethane (5 mL) under nitrogen, and a solution of $[Mo(CO)_4(pip)_2]$ (0.08 g, 0.23 mmol) in dichloromethane (5 mL) added. The solution was refluxed and monitored by ^{31}P NMR until reaction was deemed complete (*ca.* 2 h). The solution was concentrated and purified by silica flash column chromatography using 1:1 dichloromethane-petroleum spirits as the eluting solvent. The solvent was removed giving **8** as a bright yellow powder, 0.092g (82%). M.p. 133-135 °C. Found: C, 39.7; H, 3.5. $C_{16}H_{16}FeMoO_4P_2$ requires C, 39.5; H, 3.3%. ^{31}P-{^{1}H} NMR, δ –78.5 [^{1}J(PH) 312 in ^{1}H-coupled spectrum]. ESMS (cone voltage 5 V with added NaOMe), $[M – H]^-$ (*m/z* 485, 100%). IR (cm^{-1}) 2960(w), 2917(w), 2028(vs), 1926(vs), 1105(w), 1075(w), 1010(w), 931(m), 6060(w), 583(w).

3.10 Synthesis of [1,1'-Fc'($CH_2PH_2)_2Mo(CO)_4$] **9a** *and [1,1'-Fc'($CH_2PH_2)_2Mo(CO)_4]_2$* **9b**

A solution of 1,1'-Fc'$(CH_2PH_2)_2$ **5** (0.056 g, 0.2 mmol) in dichloromethane (5 mL) was added to a solution of $[Mo(CO)_4(pip)_2]$ (0.076 g, 0.2 mmol) and the solution refluxed for

2 h. The solvent was removed under vacuum and the products **9a** (0.015 g, 15%) and **9b** (0.002 g) were isolated from the residue using silica thin layer chromatography with 4:6 dichloromethane-petroleum spirits as the developing solvent.

Complex **9a**: M.p. 146-148 °C (decomp.). Found: C, 39.8; H, 3.1. $C_{16}H_{16}FeMoO_4P_2$ requires C, 39.5; H, 3.3%. ^{31}P NMR, δ –79.8 [tm, $^1J(PH)$ 308]. ^1H NMR, δ 2.89 [4H, m, CH_2P], 4.18 [4H, t, $^3J(HH)$ 1.7, H3], 4.23 [4H, t, $^3J(HH)$ 1.7, H2], 4.76 [dm, $^1J(PH)$ 311, PH_2]. ESMS (cone voltage 5 V with added NaOMe), $[M – H]^-$ (*m/z* 487, 100%), $[M – H – CO]^-$ (*m/z* 459, 98%). IR (cm^{-1}): 2984(w) 2027(s), 1909(s), 1041(w), 937(w), 609(w), 579(w).

Complex **9b**: ESMS (cone voltage 5 V with added NaOMe) $[M – H]^-$ (*m/z* 971, 100%).

3.11 Synthesis of 1,1'-Fc'$[CH_2PH_2Mo(CO)_5]_2$ **10**

$Mo(CO)_6$ (1.62 g, 6 mmol) was dissolved in thf (15 mL) under nitrogen and a solution of 1,1'-Fc'$(CH_2PH_2)_2$ **5** (0.057 g, 0.2 mmol) in thf (5 mL) added. The solution was exposed to UV light for 3 hours, the solvent removed under vacuum and excess $Mo(CO)_6$ removed by sublimation under vacuum at 45 °C over 2 days. The residue was dissolved in dichloromethane (2 mL) and purified by silica thin layer chromatography using 4:6 dichloromethane-petroleum spirits as the eluting solvent. The solvent was removed to give 0.052 g (36%) of **10** as a yellow crystalline solid. M.p. 138-142 °C. Found: C, 35.3; H, 2.1. $C_{22}H_{16}FeMo_2O_{10}P_2$ requires C, 35.2; H, 2.2%. ^{31}P NMR, δ –62.5 [t,

^{1}J(PH) 320]. ^{1}H NMR, δ 2.89 (4H, m, CH_2P), 4.14 (8H, br s, H2/H3), 4.36 [4H, dt, ^{1}J(PH) 319, ^{3}J(HH) 7, PH_2]. ESMS (cone voltage 5 V with added NaOMe,) [M – H]$^-$ (*m/z* 749, 100%). IR (cm^{-1}): 3053(w), 2990(w), 2076(s), 1941(s), 928(w), 876(w), 606(m), 582(m).

3.12 Synthesis of 1,2-Fc"[$CH_2PH_2Mo(CO)_5]_2$ **11**

Theis complex was prepared by a similar method to **10**, starting from $Mo(CO)_6$ (0.361 g, 1.3 mmol) and 1,2-Fc"$(CH_2PH_2)_2$ **6** (0.038 g, 0.13 mmol), except that the dichloromethane extract was treated with activated charcoal, and chromatographic separation used 4:6 diethyl ether-petroleum spirits, giving 0.025 g (24%) of **11** as a yellow powder. M.p. 119-121 °C. Found: C, 35.5; H, 2.3. $C_{22}H_{16}FeMo_2O_{10}P_2$ requires C, 35.2; H, 2.2%. ^{31}P NMR, δ –61.4 [t, ^{1}J(PH) 318]. ^{13}C-{^{1}H} NMR, δ 21.90 [d, ^{1}J(PC) 22, CH_2], 67.51 (s, C3), 68.33 (s, C2), 70.04 (s, C4), 83.64 [d, ^{2}J(PC) 5, C1], 204.6 [d, ^{2}J(PC) 9, CO], 208.4 [d, ^{2}J(PC) 24, CO]. ^{1}H NMR, δ 2.93 (4H, m, $C\underline{\mathbf{H}}_2PH_2$), 4.13 (5H, s, H4), 4.20 [1H, dd, ^{3}J(HH) 2.5, H3], 4.24 [2H, d, ^{3}J(HH) 2.5, H2], 4.40 [4H, dt, ^{1}J(PH) 319, ^{3}J(HH) 6.7, PH_2]. ESMS (cone voltage 10 V with added NaOMe), [M – H]$^-$ (*m/z* 749, 100%), [M + OMe]$^-$ (*m/z* 781, 28%). IR (cm^{-1}): 2955(w), 2925(w), 2871(w), 2349(w), 2076(s), 1948(s), 1937(s), 1919(s), 1916(s), 1106(w), 1090(w), 1038(w), 999(w), 927(w), 882(w), 606(m), 582(m).

3.13 Crystal structure determinations of $FcCH_2CH_2PH_2$ **4** and *$FcCH_2CH_2AsH_2$* **7**

Crystals were obtained by sublimation onto a water-cooled (*ca.* 15 °C) cold finger at 30 °C under vacuum (*ca.* 1 mm Hg).

Crystal data for **4***:* $C_{12}H_{15}FeP$, M = 245.1, monoclinic, space group = $P2_1/c$, a = 10.382(3), b = 7.550(2), c = 14.247(4) Å, β = 96.870(4)°, V = 1108.82(8) $Å^3$.

Crystal data for **7***:* $C_{12}H_{15}AsFe$, M = 290.01, monoclinic, space group = $P2_1/c$, a = 14.3996(1), b = 7.5871(1), c = 10.4835(1) Å, β = 97.496(1)°, V = 1135.55(2) $Å^3$, T = 293(2) K, Z = 4, F(000) = 584, ρ_{calc} = 1.696 g cm^{-3}, $\mu(Mo\text{-}K_\alpha)$ = 4.18 mm^{-1}, 10760 reflections measured, 4587 unique (R_{int} 0.0257) which were used in all calculations.

The data were collected on a Bruker AXS SMART diffractometer at 293(2) K with $1.4 < \theta < 26.6°$, and the Fe and As atoms located by Patterson methods. The remainder of the structure developed routinely using direct methods with full-matrix least-squares refinement based on F^2. Atoms C(1) and C(2) were each disordered over two positions with occupancies of 0.95 and 0.05. Hydrogen atoms were placed in calculated positions except for the As-H hydrogens, which were not located. Refinement converged to $R_F = 0.043$, $wR(F^2) = 0.1051$ (all data), where $w = [\sigma^2(F_o)^2 + (0.0514P^2 + 2.88P]^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$. The largest residual electron density peaks in the final density map did not exceed 0.614 and –1.108 e $Å^{-3}$.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC, No. xxxxxx. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ [FAX +44(1223)336-033] or e-mail deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

3.14 Crystal structure determination of [1,2-Fc''($CH_2PH_2)_2Mo(CO)_4$] **8**

Suitable crystals of the complex were grown from a dichloromethane-petroleum spirits solution at –20 °C. The crystal proved to be weakly diffracting and the data set was of poor quality. Attempts at solving the structure in space group $I4_1/a$ were partially successful, but adequate refinement could not be achieved.

Crystal data: $C_{16}H_{16}FeO_4P_2Mo$, M = 486, tetragonal, space group = $I4_1/a$, a = b = 35.0413(1), c = 6.2610(1) Å, V = 7687.84(1) Å^3.

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Table 1.

Selected bond lengths (Å) and angles (°) for $FcCH_2CH_2AsH_2$ **7**

C(1)-C(11)	1.518(7)	C(1)-C(2)	1.517(9)
C(2)-As(1)	1.966(6)	Fe-C (average)	2.039(4)
Fe-C (range)	2.032(4)-2.045(4)	Cp C-C (average)	1.404(7)
Cp C-C (range)	1.379(7)-1.428(6)		

C(12)-C(11)-C(1)	131.4(4)	C(11)-C(1)-C(2)	112.2(5)
C(1)-C(2)-As(1)	111.9(4)	C(15)-C(11)-C(1)	121.2(4)

Substituted Cp ring C-C-C range	107.2(4)-108.8(4)
Unsubstituted Cp ring C-C-C range	107.3(4)-108.7(4)

Captions for Figures

Fig. 1. Molecular structure of $FcCH_2CH_2AsH_2$ **7**, showing the atom numbering scheme. Thermal ellipsoids are at the 50% probability level.

Fig. 2. Molecular structure (Pluton diagram) of 1,2-Fc"$(CH_2PH_2)_2Mo(CO)_4$ **8** with all hydrogen atoms omitted.

Fig. 3. Negative ion ES spectra (in methanol with added sodium methoxide) of 1,1'-Fc'$[CH_2PH_2Mo(CO)_5]_2$ **10** at various cone voltages, showing the loss of all ten CO ligands with increasing cone voltage.