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# Extending the range of stabilised, primary and secondary phosphanes containing ferrocenyl or ruthenocenyl groups

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ABSTRACT

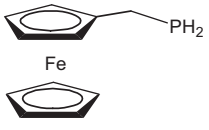
Alkylation reactions of $FcCH_2P(CH_2OH)_2$ [Fc = ($\eta^5$-$C_5H_5$)Fe($\eta^5$-$C_5H_4$)] with MeI or *p*-$BrCH_2C_6H_4NO_2$, or of $CyP(CH_2OH)_2$ with $[FcCH_2NMe_3^+]I^-$ gave hydroxymethylphosphanes $FcCH_2PR(CH_2OH)$ (R = Me, Cy or *p*-$O_2NCH_2C_6H_4$) which were converted to the new secondary phosphanes $FcCH_2PHR$ on treatment with $Na_2S_2O_5$. A series of longer-chain ferrocenylalkyl primary phosphanes $Fc(CH_2)_nPH_2$ was also prepared by reactions of the bromoalkylferrocenes $Fc(CH_2)_nBr$ ($n$ = 4, 6 or 11) with $P(CH_2OH)_3$ to give intermediate hydroxymethylphosphanes $Fc(CH_2)_nP(CH_2OH)_2$, followed by reaction with $Na_2S_2O_5$. $Fc(CH_2)_6PH_2$ was converted into its crystalline $BH_3$ adduct, which was structurally characterised. The synthesis of the new ruthenocene (Rc)-derived primary phosphane $RcCH_2PH_2$, the first example of a ruthenocene-derived primary phosphane, is also reported.



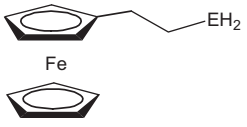
## 1. Introduction

Primary phosphanes $RPH_2$ are valuable chemical precursors, which are normally air-sensitive, are typically highly toxic, and have noxious odours. In recent years, there has been interest in the development of some remarkably air-stable primary phosphines, primarily to increase the ease of handling of these substances; [1–3] key developments in this field up to 2005 have been reviewed by Brynda [4]. One of the principal strategies that has been used for stabilising many reactive main group hydride species is a simple steric approach [5,6]. Although frequently successful, this approach runs the inherent risk that stabilisation will occur at the expense of compromising the chemistry of the phosphane group, which would be undesirable. Primary phosphanes and arsanes stabilised by non-steric means are relatively rare in the literature, but good examples of non-sterically protected, air-stable primary phosphanes are $(H_2PCH_2)_2CHCH_2NHPh$ and $(H_2PCH_2)_2CHC(O)NHPh$ [7].

We have previously reported that the ferrocenyl (Fc) group incorporated *via* a $(CH_2)_n$ spacer ($n$ = 1 or 2) stabilises primary phosphanes and an arsane in a series of crystalline compounds including $FcCH_2PH_2$ **1** [8] and $FcCH_2CH_2EH_2$ (**2**, E = P; **3**, E = As) [9] with excellent air stability (>2 years for **1**). An improved synthesis of **1** was subsequently reported [10]. In contrast, it is known that $FcPH_2$ (with no $CH_2$ groups) is rather air-sensitive, [9,11] suggesting that the alkyl spacer may be a crucial factor in affording stability. Such phosphanes, in particular $FcCH_2PH_2$ (due to its ease of synthesis from readily available precursors), have subsequently attracted interest as precursors for further derivatisation or as ligands in their own right [12–27]. Bidentate ferrocene-derived ligands containing $-CH_2PH_2$ and other donor ligand groups have also been studied [28]. Furthermore, a recent theoretical study by Higham and co-workers [29] has proposed the electronic basis for the ferrocene-imparted stabilisation, which suggests it could be quite widely applicable.




**1**




**2**, E = P
**3**, E = As

The ferrocenylmethyl group has been used to impart stability to a range of other phosphanes, including the trialkylphosphanes $(FcCH_2)_3P$ [10,30] and $FcCH_2P^tBu_2$ [31]. However, to date, there have been relatively few secondary ferrocenylalkylphosphanes reported; these include $(FcCH_2)_2PH$ [10,14,18,13]. We wished to investigate the extent of this ferrocene-based stabilisation by synthesis of a series of new derivatives. In this contribution we describe some new secondary phosphane analogues $FcCH_2PHR$, together with syntheses of analogues containing a longer alkyl

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spacer between the ferrocene and phosphane $Fc(CH_2)_nPH_2$ ($n$ = 4, 6, 11), and the corresponding ruthenocene (Rc)-derived primary phosphane $RcCH_2PH_2$.

## 2. Results and discussion

### 2.1. Secondary phosphanes

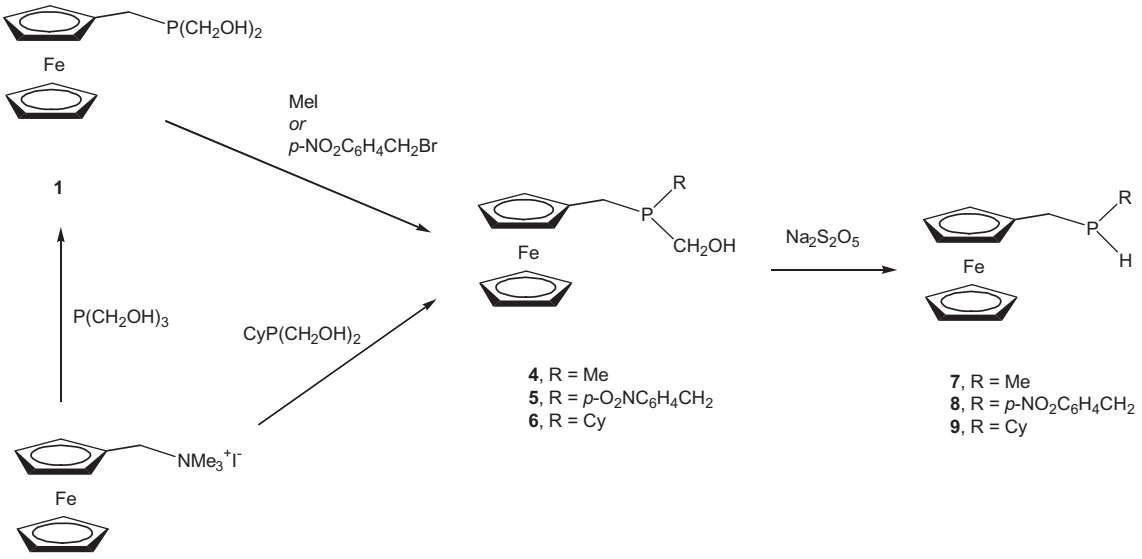
Synthesis of a series of new secondary phosphanes used the facile conversion of a P–$CH_2OH$ group into a P–H group by removal of formaldehyde, HCHO, as summarised in Scheme 1. The known hydroxymethylphosphane $FcCH_2P(CH_2OH)_2$ was readily alkylated with MeI or $p$-$BrCH_2C_6H_4NO_2$ followed by treatment with base to give the intermediate hydroxymethylphosphanes **4** and **5** respectively, while alkylation of $CyP(CH_2OH)_2$ with $[FcCH_2NMe_3]I$ correspondingly gave $FcCH_2PCy(CH_2OH)$ **6**. This route was chosen for the cyclohexyl compound, because of the poorer alkylating properties of cyclohexyl halides, and also the commercial availability of $CyPH_2$, which is readily converted into $[CyP(CH_2OH)_3]Cl$. Treatment of the reaction mixtures with $Et_3N$ ensured conversion to the hydroxymethylphosphanes, which were obtained as red-orange oils that were used directly in the preparation of the secondary phosphanes.

The hydroxymethylphosphanes **4**, **5** and **6** were treated with $Na_2S_2O_5$ in a two phase water/petroleum spirits system at reflux for 3 h under a nitrogen atmosphere, following conditions that have been previously used to convert hydroxymethylphosphanes into primary or secondary phosphanes [8,10]. After separating and washing the organic phase with water, evaporation of the organic phase yielded the desired secondary phosphanes **7**, **8**, and **9** (Scheme 1) as orange-red oils in moderate to good yields. The distinctive phosphane odour was noted from all three secondary phosphanes. The crude products were purified by preparative TLC, giving pure secondary phosphanes which solidified at −18 °C and were characterised by IR and NMR spectroscopies, ESI MS and microelemental analysis.

The PH stretches of **7**, **8** and **9** appeared in the range 2268–2278 $cm^{-1}$, as a medium to strong band, consistent with values of *ca.* 2280 ± 10 $cm^{-1}$ typically observed for this class of compound [32]. Compounds **8** and **9** were characterised by positive-ion ESI MS in MeOH, giving the $[M]^+$ parent ion at the expected $m/z$ value. The observation of an $[M]^+$ ion for ferrocenyl compounds in ESI MS analysis is common, [33] and arises from electrochemical oxidation in the electrospray capillary [34]. Phosphane **9** was also analysed by an alternative technique previously used to aid ionisation of phosphanes [35,36] and arsanes [37], by *in situ* formation of cationic silver(I)-phosphane adducts upon addition of a small quantity of $AgNO_3$. Applying this methodology for **9**, the corresponding silver adducts $[M+Ag]^+$ and $[2M+Ag]^+$ were easily observed with much higher intensity than that of $[M]^+$ observed in the absence of added $Ag^+$. Confirmation of the silver adduct ions was readily achieved by comparison of experimental and calculated isotope patterns, which are highly distinctive from the presence of $^{107}Ag$ and $^{109}Ag$ isotopes.

The $^{31}P$ NMR resonances for **7**, **8** and **9** appeared at $\delta$ −73.5, −49.1 and −41.1 ppm respectively, as a doublet with a $^1J_{PH}$ coupling constant in the expected range (192–199 Hz). The $^{31}P$ NMR signal for **7** was the furthest upfield (by *ca.* 30 ppm), consistent with the methyl group being the most electron-donating and hence the most shielding of the three organic substituents on phosphorus. The PH proton signals of **7**, **8** and **9** appeared in the $^1H$ NMR spectra at *ca.* $\delta$ 3.3 ppm as a doublet of multiplets with $^1J_{PH}$ and $^3J_{HH}$ coupling constants of ∼196 and ∼6 Hz, respectively; these resonances are shifted further downfield (by ∼0.4 ppm) compared to $FcCH_2PH_2$ **1** ($\delta$ 2.9 ppm) [8].

Overalkylated by-products (Scheme 2) were also isolated from the syntheses of **8** and **9**. Compound **10** was obtained as a yellow solid in poor yield (3%) from the synthesis of **9**, precipitating out upon re-extraction of the crude product with diethyl ether or a mixture of diethyl ether and petroleum spirits; the compound was characterised by NMR spectroscopy and ESI MS. The $^{31}P$ NMR spectrum showed a singlet at $\delta$ −7.6 ppm, shifted by 34 ppm further downfield compared to the corresponding secondary phosphane **9**. In the $^1H$ NMR spectrum, the $CH_2$ proton signal appeared as a singlet at $\delta$ 2.5 ppm, while the cyclohexyl protons gave unresolved multiplets at $\delta$ 1.2–1.8. The integration of the signals agreed with the number of protons in the expected environments ($CH_2$:$C_6H_{11}$:Fc = 4:11:18). [Scheme 3 shows the atom numbering scheme for the secondary phosphanes]. The positive-ion ESI mass spectrum with added $AgNO_3$ gave silver adducts $[M+Ag]^+$ ($m/z$ 620), and $[2M+Ag]^+$ ($m/z$ 1132). The compound appeared to be unstable in $CDCl_3$ solution, decomposing after 2 weeks at room temperature in a capped NMR tube in air; the $^{31}P$ NMR signal disappeared and the solution turned from yellow to dark brown. Crude **9** was also found to contain a trace amount of $CyPH_2$ by $^{31}P$ NMR spectroscopy (a triplet at $\delta$ −110.2 with a

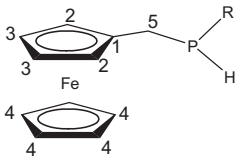



**Scheme 1.** Synthesis of the ferrocenyl-substituted secondary phosphanes $FcCH_2PHR$ **7**, **8** and **9** (R = Me, Cy or $p$-$O_2NCH_2C_6H_4$).


**10**, R = Cy
**11**, R = *p*-$O_2NC_6H_4CH_2$

**12**, R = *p*-$O_2NC_6H_4CH_2$

**Scheme 2.** Overalkylated byproducts **10**, **11** and **12**.




**Scheme 3.** Atom labelling used in NMR assignments of ferrocenyl secondary phosphanes; hydrogen atoms are numbered according to the carbon to which they are bonded.

$^1J_{PH}$ coupling constant of 194 Hz, consistent with the literature chemical shift of −110.1 ppm) [38].

Compounds **11** and **12** were isolated from the synthesis of **8** by chromatography of the crude product on a TLC plate, eluting with a 1:1 mixture of dichloromethane and petroleum spirits. Compound **11** was obtained as a red oil in very low yield (0.8 %) from the fraction at $R_f$ 0.33, and **12** as a red solid in moderate yield (24%) from the fraction at $R_f$ 0.66 after removal of the solvents under reduced pressure. Compound **11** was only partially characterised by $^{31}P$ (singlet at $\delta$ −12.3 ppm), $^1H$ and $^{13}C$ NMR spectroscopies as it was obtained only in very low yield. Compound **12** was characterised by ESI MS, microelemental analysis, $^{31}P$, $^1H$ and $^{13}C$ NMR and IR spectroscopies. Positive-ion ESI MS of **12** in MeOH with added $AgNO_3$ showed the molecular ion, $[M]^+$ (*m/z* observed. 502.074; calcd. 502.073) and the corresponding silver adduct, $[M+Ag]^+$ (*m/z* observed 608.978; calcd. 608.979). The IR spectrum of **12** showed N–O stretches at 1513 and 1343 $cm^{-1}$ as very strong bands, very similar to **8**.

The oxidative stability of the phosphanes was qualitatively investigated by $^{31}P$ NMR monitoring of $CDCl_3$ solutions (prepared in air) in a capped NMR tube at room temperature. Secondary phosphanes are generally readily oxidised in air to form the corresponding oxides, $R_2P(O)H$, which are also relatively unstable and can be further oxidised to give the stable phosphinic acid, $R_2P(O)OH$. The least stable secondary phosphane was $FcCH_2PH(CH_2C_6H_4NO_2)$ **8**, which was completely oxidised in little over 2 weeks. By contrast, the cyclohexylphosphane **9** showed reasonable air stability under the given conditions and the $^{31}P$ NMR signal was observed for more than 4 months. The methylphosphane **7** appeared to show intermediate stability, being fully oxidised in around 6 weeks.

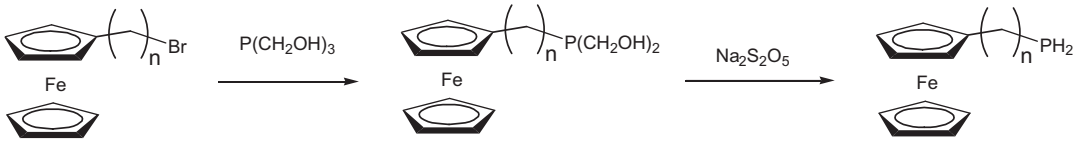
### 2.2. Long chain ferrocenylalkylphosphanes $Fc(CH_2)_nPH_2$

To date, the longest alkylene spacer which has been incorporated into a ferrocene-substituted primary phosphane is the $CH_2CH_2$ group in $FcCH_2CH_2PH_2$ **2** [9]. We wished to explore the synthesis of compounds with longer chain spacers and accordingly a series of new ferrocenylalkyl primary phosphanes were prepared by extensions of the reported literature methods [8,39] with minor modifications where needed; Scheme 4 summarises the syntheses.

Reaction of the bromoalkylferrocenes $Fc(CH_2)_nBr$ ($n$ = 4, 6 and 11) with excess $P(CH_2OH)_3$ [generated *in situ* from $P(CH_2OH)_4Cl$ with KOH], in refluxing methanol followed by workup with added $NEt_3$ gave the hydroxymethylphosphanes $Fc(CH_2)_nP(CH_2OH)_2$ ($n$ = 4 **13**, 6 **14** or 11 **15**) as red oils in good yields. Attempted crystallisation of the crude phosphanes **13** and **14** [methanol/dichloromethane/petroleum spirits] was not successful, and the compounds were used in the conversion to the primary phosphanes without further purification. However, recrystallisation of $Fc(CH_2)_{11}P(CH_2OH)_2$ **15** from the same solvent mixture gave a yellow solid which gave satisfactory microanalytical data. The $^{31}P$ NMR signals for **13**, **14** and **15** appeared as singlets at ∼$\delta$ −22 ppm, shifted further downfield by $\delta$ 3 ppm compared to $FcCH_2P(CH_2OH)_2$ [36]. This is consistent with the extended length of the alkylene spacer, which effectively isolates the deshielding ferrocene group from the phosphorus. ESI MS analysis of **13**, **14** and **15** in MeOH with added $AgNO_3$ gave $[M+Ag]^+$ and/or $[2M+Ag]^+$ ions; in the absence of $AgNO_3$, the molecular ions $[M]^+$ were observed.

The hydroxymethylphosphanes **13**, **14** and **15** were treated with $Na_2S_2O_5$ in a two-phase water-petroleum spirits mixture in air or under an $N_2$ atmosphere for 3 h, Scheme 4. After work-up, removal of the solvent from the organic phase gave the desired primary phosphanes **16**, **17** and **18** as yellow-red oils in moderate to good yields (**16** 35%; **17** 83%; **18** 28%) with distinctive phosphane odours. The crude products were purified by chromatography (preparative TLC), eluting with petroleum spirits or a mixture of petroleum spirits/diethyl ether or petroleum spirits/dichloromethane. The desired bands were collected and extracted with dichloromethane; evaporation gave the products as yellow-red oils.

The primary phosphanes **16**, **17** and **18** were characterised by $^{31}P$, $^1H$ and $^{13}C$ NMR and IR spectroscopies, and by ESI and GC mass spectrometries. Phosphanes **17** and **18** could not be completely purified by chromatography on a preparative TLC plate or by recrystallisation, and gave unsatisfactory microanalytical data; the characterisation of these compounds is therefore based on spectroscopic data. However, phosphane **16** could be purified by microdistillation [$10^{-6}$ torr, 65 °C, 12 h] and was obtained as an oil which was analytically pure. The $\nu$P–H stretches in the IR spectra of $Fc(CH_2)_nPH_2$ (**16**, **17** and **18**) were observed at 2289, 2283 and 2290 $cm^{-1}$, respectively, as a medium to strong intensity band, consistent with literature values for other related compounds $Fc(CH_2)_nPH_2$ ($n$ = 1 **1**; 2285s $cm^{-1}$ or $n$ = 2 **2**; 2294 m $cm^{-1}$). ESI MS showed the molecular ions $[M]^+$ in positive-ion mode at a




**13**, n = 4
**14**, n = 6
**15**, n = 11

**16**, n = 4
**17**, n = 6
**18**, n = 11

**Scheme 4.** Synthesis of longer-chain ferrocene-substituted primary phosphanes.

capillary exit voltage of 150 V, while EI MS also showed a strong molecular ion, together with the usual fragment ions $[FcCH_2]^+$, $[CpFe]^+$ and $[Fe]^+$.

The $^{31}P$ NMR resonances for **16**, **17** and **18** appeared as a triplet at ~$\delta$ −136 ppm with a $^1J_{PH}$ coupling constant of ~194 Hz. The signals are shifted upfield by ~7 ppm compared to $FcCH_2PH_2$ **1** [8] (*cf.* $\delta$ −129.1 ppm), but are the same as that for $FcCH_2CH_2PH_2$ **2** [9] (*cf.* $\delta$ −135.8 ppm), suggesting that the deshielding effect of ferrocene becomes negligible beyond two σ-bonds. The $^1J_{PH}$ coupling constant was consistent with that for **1** and **2**. The phosphane protons of **16**, **17** and **18** appeared in the $^1H$ NMR spectra at $\delta$ 2.7 ppm, the same as that for **2** [9] but shifted slightly upfield by $\delta$ 0.2 ppm compared to **1**, due to the lack of a deshielding effect from the ferrocene group. The $^1J_{PH}$ and $^3J_{HH}$ coupling constants of 194–195 and 7 Hz, respectively, also agree with the literature values for **1** and **2** [8,9].

The longer-chain primary phosphanes were found to have significant stability towards air, such that the compounds could easily be handled and stored in air for moderate periods (weeks) without significant oxidation occurring. However, investigation of the air-stability of $CDCl_3$ solutions of the phosphanes by $^{31}P$ NMR spectroscopy showed that over a period of several months, oxidation with loss of the characteristic $RPH_2$ signal occurred. The longest-chain primary phosphane $Fc(CH_2)_{11}PH_2$ **18** was fully oxidised after ~3 months and was the least air stable of the series, while $Fc(CH_2)_4PH_2$ **16** and $Fc(CH_2)_6PH_2$ **17** were stable for around 4 months.

Borane adducts of phosphanes are often formed in order to stabilise, and to furnish more highly crystalline derivatives. The chemistry of phosphane-boranes has been recently reviewed [40]. Glueck et al. [10] have reported that the ferrocenyl primary phosphane $FcCH_2PH_2$ **1** forms a crystalline borane adduct on reaction with $BH_3(SMe_2)$. Since it was not possible to grow a single crystal of any of the primary phosphanes prepared in this study, $Fc(CH_2)_6PH_2$ **17** was derivatised by reaction with $BH_3(SMe_2)$ to give the borane adduct $Fc(CH_2)_6PH_2(BH_3)$ **19** (Scheme 5) in order to obtain X-ray crystallographic structural data on an adduct. Reaction of **17** with $BH_3(SMe_2)$ in dry hexane at −64 °C under an $N_2$ atmosphere followed by workup gave $Fc(CH_2)_6PH_2(BH_3)$ **19** in moderate yield (26%) as orange needles, which were analytically pure. The P–H and B–H stretches were observed as overlapping strong broad bands at around 2398 $cm^{-1}$. The increase in the P–H stretching frequency from 2280 to 2398 $cm^{-1}$ upon the addition of $BH_3$ is consistent with that observed for $FcCH_2PH_2(BH_3)$ [10]. Positive-ion ESI MS analysis at a capillary exit voltage of 100 V showed the $[M]^+$ ion (*m/z* observed 316.119; calcd. 316.120 for $C_{16}H_{26}BFeP$) together with the sodium and potassium adducts, $[M+Na]^+$ (*m/z* observed 339.109; calcd. 339.111 for $C_{16}H_{26}BFeNaP$) and $[M+K]^+$ (*m/z* observed 355.058; calcd. 355.084 for $C_{16}H_{26}BFeKP$), respectively. The presence of Fe and B provide a unique isotopic signature for the ions, with good agreement observed between experimental and calculated isotope patterns.

The proton-coupled $^{31}P$ NMR spectrum of **19** showed a broad triplet at $\delta$ −52.3 ppm with a $^1J_{PH}$ coupling constant of 362 Hz, Fig. 1. The broadening comes from coupling to boron, consistent with the description in the literature for $FcCH_2PH_2(BH_3)$ [10]. The $^1H$ NMR spectrum showed the phosphane protons at $\delta$ 4.5 ppm as a doublet of sextets with $^1J_{PH}$ and $^3J_{HH}$ coupling constants of 360 and 1 Hz, respectively. The borane proton signal was observed at $\delta$ 1.4 ppm as an unresolved multiplet. In the $^{13}C$ NMR spectrum, the $^1J_{PC}$ coupling constant for the $PCH_2$ carbon (35.4 Hz) was consistent with that for $FcCH_2PH_2{\cdot}BH_3$ [10]. Resonances were assigned according to 2D NMR data but definitive assignments could not be made for the methylene proton signals of the alkyl chain due to overlap. The adduct was stable in air at ambient temperature; neither decomposition nor oxidation of the compound was noted upon handling or storing for at least 1 week in air at room temperature.

The molecular structure of $Fc(CH_2)_6PH_2(BH_3)$ **19** is shown in Fig. 2, and selected bond lengths and angles are given in Table 1. The compound appears to be structurally very similar to $FcCH_2PH_2(BH_3)$ [10] except the extended alkyl spacer was absent in the latter compound. The hexyl chain adopts the classical staggered structure, maximising the separation of the ferrocenyl and $PH_2(BH_3)$ groups. The B–H bond lengths and H–B–H bond angles of **19** [1.074(18)–1.127(18) Å and 112.2(13)–114.8(14)° respectively] are comparable to those for $FcCH_2PH_2{\cdot}BH_3$ [1.08(2)–1.10(2) Å and 111.1(15)–113.9(15)°]. The P-H bond lengths are also very comparable. The P–B bond length and B–P–H and P–B–H angles of **19** [1.9204(17) Å and 113.8(9)–115.0(8) and 102.9(10)–106.2(10)° respectively] are also essentially the same as those in $FcCH_2PH_2(BH_3)$ [1.9230(17) Å and 115.7(9)–115.8(9) and 102.6(10)–109.1(11)°] but the C–P–B bond angle of 117.18(7)° in **19** is significantly larger than that of $FcCH_2PH_2(BH_3)$ [113.01(7)°].

### 2.3. Synthesis and characterisation of the ruthenocene-derived primary phosphane $RcCH_2PH_2$

To investigate whether the stabilisation effect was unique to ferrocene or could be extended to other metallocenes, the ruthenocene compound $RcCH_2PH_2$ [Rc = ($\eta^5$-$C_5H_5$)Ru($\eta^5$-$C_5H_4$)] was prepared. No ruthenocenylmethylphosphane compounds ($\eta^5$-$C_5H_5$)Ru($\eta^5$-$C_5H_4CH_2PR_2$) derived from mono-substituted ruthenocene have been previously reported, though there have been a number of studies on the 1,3-di-substituted pincer precursors ($\eta^5$-$C_5H_5$)Ru{$\eta^5$-$C_5H_3(CH_2PR_2)_2$} (R = $^t$Bu, $^i$Pr), [41] 1,2-disubsti-

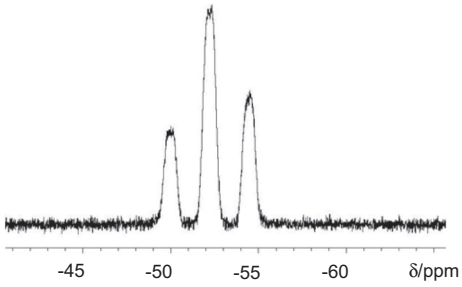
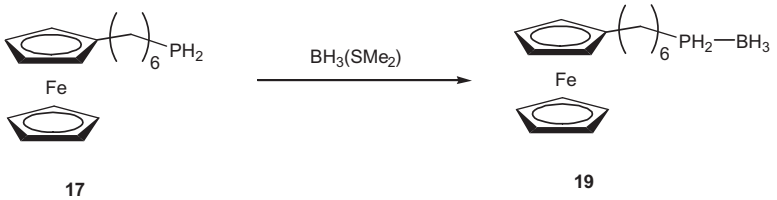



**Fig. 1.** Proton-coupled $^{31}P$ NMR spectrum of $Fc(CH_2)_6PH_2(BH_3)$ **19**.




**Scheme 5.** Conversion of $Fc(CH_2)_6PH_2$ **17** to its borane adduct $Fc(CH_2)_6PH_2{\cdot}BH_3$ **19**.

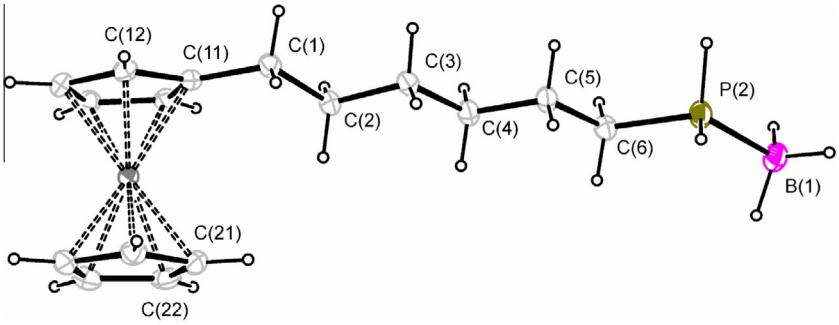



**Fig. 2.** Molecular structure of $Fc(CH_2)_6PH_2(BH_3)$ **19** showing the atom numbering scheme.

**Table 1**
Selected bond lengths (Å) and angles (°) for $Fc(CH_2)_6PH_2(BH_3)$ **19**.

| | | | |
|---|---|---|---|
| P(2)–C(6) | 1.8164(13) | P(2)–B(1) | 1.9204(17) |
| P(2)–H(4) | 1.305(19) | P(2)–H(5) | 1.29(2) |
| B(1)–H(1) | 1.074(18) | B(1)–H(2) | 1.127(18) |
| B(1)–H(3) | 1.11(2) | | |
| C(6)–P(2)–B(1) | 117.18(7) | C(6)–P(2)–H(4) | 104.0(8) |
| B(1)–P(2)–H(4) | 115.0(8) | C(6)–P(2)–H(5) | 103.0(8) |
| B(1)–P(2)–H(5) | 113.8(9) | H(4)–P(2)–H(5) | 102.0(12) |
| P(2)–B(1)–H(1) | 106.1(10) | P(2)–B(1)–H(2) | 102.9(10) |
| H(1)–B(1)–H(2) | 114.8(14) | P(2)–B(1)–H(3) | 106.2(10) |
| H(1)–B(1)–H(3) | 113.4(14) | H(2)–B(1)–H(3) | 112.2(13) |

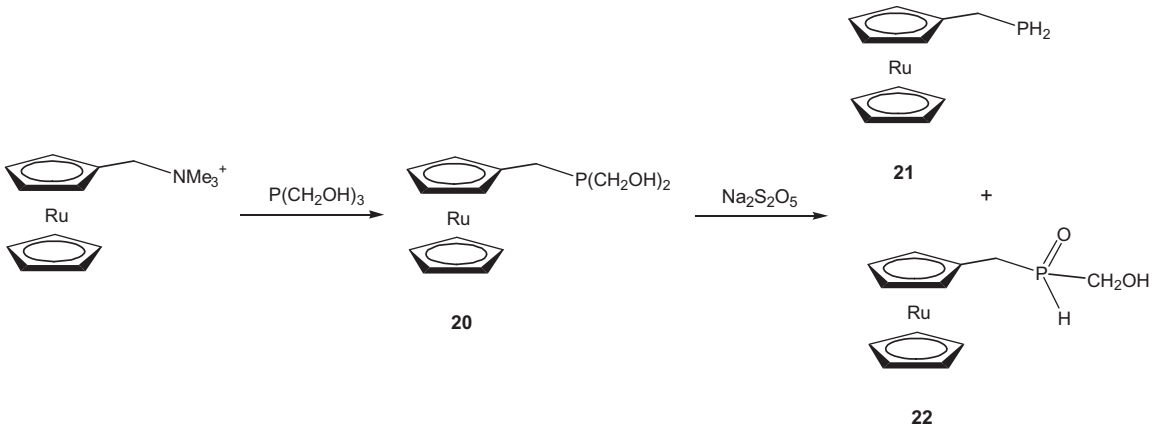
tuted compounds such as $(\eta^5\text{-}C_5Me_5)Ru\{C_5H_3(PPh_2)(CHMePCy_2)\}$ [42] and the 1,1′-disubstituted $Ru(\eta^5\text{-}C_5H_4CHMePPh_2)_2$ [43]. Several phosphonium salts such as $RcCHRPPh_3^+$ (R = H, Me) are also known [44].

Synthetic methods analogous to those used to synthesise $FcCH_2PH_2$ were used to synthesise the ruthenocenylmethyl phosphane $RcCH_2PH_2$, and are summarised in Scheme 6. Ruthenocene (RcH) was converted to $RcCH_2NMe_2$ and subsequently $[RcCH_2NMe_3]^+I^-$ using literature methods (refer Section 4). $[RcCH_2NMe_3]^+I^-$ was then refluxed with excess $P(CH_2OH)_3$ in MeOH under a nitrogen atmosphere for >20 h and treated with triethylamine. After workup, the desired hydroxymethylphosphane $RcCH_2P(CH_2OH)_2$ **20** was obtained as a pale-yellow oil in low yield (10%). The entire yield of **20** was refluxed with $Na_2S_2O_5$ in a two-phase system of water and petroleum spirits for 3 h under nitrogen. Recovery of the product from the organic phase gave the desired primary phosphane **21** as a pale-yellow oil in moderate yield (43%), which had a distinctive phosphane odour; workup of the aqueous phase yielded $RcCH_2P(O)(CH_2OH)H$ **22** (*vide infra*).

$RcCH_2PH_2$ **21** was characterised by IR and NMR spectroscopies and ESI MS. The PH stretch was observed at 2290 $cm^{-1}$ as a medium intensity peak, consistent with the values observed for $FcCH_2PH_2$ **1** (2285 $cm^{-1}$) and for the ferrocenyl analogues with extended alkylene spacers e.g. $Fc(CH_2)_nPH_2$ (*vide supra*). The proton-coupled $^{31}P$ NMR spectrum of **21** yielded a triplet at $\delta$ −132.5 with a $^1J_{PH}$ coupling constant of 193 Hz; this is shifted upfield by 3 ppm compared to the corresponding ferrocenyl primary phosphane $FcCH_2PH_2$ **1** [8]. In the $^1H$ NMR spectrum, the phosphane proton signal appeared at $\delta$ 2.9 as a doublet of triplets with $^1J_{PH}$ and $^3J_{HH}$ coupling constants of 194 and 7 Hz respectively. The cyclopentadienyl proton signals were shifted further downfield by an average of 0.5 ppm compared to the corresponding ferrocenyl analogue **1**.

$RcCH_2PH_2$ **21** was also characterised by EI and ESI MS. In the EI mass spectrum, the fragmentation of the molecular ion $[M]^+$ to $[RcCH_2]^+$ and $[CpRu]^+$ followed analogous pathways to those of the ferrocenyl primary phosphane **1**. ESI MS at a capillary exit voltage of 150 V did not yield the molecular ion $[M]^+$ but instead $[M-PH_2]^+$ (*m/z* observed 244.989; calcd. 244.989 for $C_{11}H_{11}Ru$) was observed, with good agreement between observed and calculated isotope patterns. Addition of $AgNO_3$ gave the silver adduct $[M+Ag]^+$ (*m/z* observed 384.885; calcd. 384.884 for $C_{11}H_{13}AgPRu$). Attempted purification of the compound by chromatography or crystallisation was unsuccessful; satisfactory microelemental data and single crystals suitable for an X-ray diffraction study could not be obtained, so the assignment of the compound as $RcCH_2PH_2$ is based on spectroscopic evidence.

A white solid, isolated in low yield (5%) by evaporation of the aqueous phase separated from the reaction mixture in the synthesis of **21**, was tentatively characterised as the new secondary hydroxymethylphosphane oxide $RcCH_2P(O)(CH_2OH)H$ **22** by NMR spectroscopy. The (proton-coupled) $^{31}P$ NMR showed a pseudo doublet of triplets at $\delta$ 35.7 with $^1J_{PH}$ and $^2J_{PH}$ coupling constants




**Scheme 6.** Reaction sequence for the synthesis of the ruthenocene-substituted primary phosphane $RcCH_2PH_2$ **21**.

of 467 and 14 Hz, respectively. The chemical shift and coupling constant are consistent with a secondary phosphane oxide. The cyclopentadienyl and $CH_2$ proton and carbon signals were observed in the same region as $RcCH_2PH_2$ and are also comparable to $[RcCH_2NMe_3]I$ [45]. No further characterisation was done on this compound.

$RcCH_2PH_2$ **21** appears to have some air stability but much less than the corresponding ferrocene analogue $FcCH_2PH_2$ **1** which is stable in air for as long as 2 years in the solid state [8]. Examination of a $CDCl_3$ solution of the compound by $^{31}P$ NMR spectroscopy in a capped NMR tube showed that nearly half of the phosphane had oxidised after around 1 month.

## 3. Conclusions

In summary, we have successfully extended the range of stabilised ferrocenylalkylphosphanes. The compounds can be synthesised from readily accessible precursors, using an extension of previously developed methodologies. In addition, we have prepared the first example of a ruthenocene-derived primary phosphane. Preliminary studies indicate that these new derivatives also show appreciable air-stability.

## 4. Experimental

### 4.1. Instrumentation

ESI mass spectra were recorded either on a VG Platform II instrument (low resolution), or on a Bruker Daltonics MicrOTOF instrument (high resolution), as methanol solutions (unless otherwise stated); the extent of fragmentation was controlled by variation of the cone voltage (Platform) or capillary exit voltage (MicrOTOF). Identification of ions was facilitated by comparison of *m/z* values and isotope patterns of observed and calculated ions, the latter obtained using either an internet-based program (for low resolution matching), [46] or proprietary instrument-based software.

Elemental analyses were performed at the Campbell Microanalytical Laboratory, University of Otago, New Zealand. FTIR spectra were recorded as KBr disks on a Digilab Scimitar FTS 2000 series spectrometer using Varian Resolution software version 4.1.0.101 or Perkin Elmer Spectrum 100 FT-IR spectrometer using Spectrum software. GC–mass spectra were recorded on a Hewlett–Packard 5890 Series 1 gas chromatograph coupled to a Hewlett–Packard 5973 Series Mass Selective Detector, operating at 70 eV, using a HP1 column containing cross-linked methylsilicone gum, 24 m × 0.2 mm × 0.33 μm film thickness. The sample was injected using a HP 7683A Autosampler as a $CH_2Cl_2$ or MeOH solution and eluted using a 50–295 °C temperature ramp, at a rate of 50 °C $min^{-1}$ from 100–150 °C and 10 °C $min^{-1}$ from 150–295 °C with a 2.25 min solvent delay. The samples were freshly prepared prior to analysis either in MeOH or $CH_2Cl_2$.

NMR spectra were recorded in $CDCl_3$ solution on a Bruker Avance DRX 300 or a Bruker Avance DRX 400 spectrometer using TOPSPIN software version 1.3 or a Bruker300AVR or a Bruker400AVR using TOPSPIN software version 3.0. Chemical shifts are referenced to residual solvent lines for $^1H$ and $^{13}C$ NMR spectra, and external aqueous 85% $H_3PO_4$ for $^{31}P$ NMR spectra, and are reported in ppm. Scheme 3 shows the atom numbering scheme used for the ferrocenyl phosphanes, illustrated for the secondary derivatives.

### 4.2. Materials

The following chemicals were obtained from commercial sources and used as supplied: ferrocene (Aldrich), $[P(CH_2OH)_4]Cl$ (Retardol C) as an 80% w/w aqueous solution (Albright & Wilson Ltd., Oldbury, UK), $CH_3I$ (May and Baker Ltd.), $p$-$BrCH_2C_6H_4NO_2$ (BDH), KOH (Ajax. Finechem. Pty Ltd.), $NEt_3$ (Aldrich), $Na_2S_2O_5$ (Ajax Finechem. Pty Ltd.) and $BH_3(SMe_2)$ (2 M solution in THF, Aldrich).

The following compounds were prepared *via* the literature procedures: $[FcCH_2NMe_3]I$, [47] $FcCH_2P(CH_2OH)_2$, [39] $Fc(CH_2)_4Br$, [48] $Fc(CH_2)_6Br$, [49] $Fc(CH_2)_{11}Br$, [50] $[Ru(\eta^5\text{-}C_5H_5)_2]$ [51] and $[RcCH_2NMe_3]^+I^-$ [45]. $[CyP(CH_2OH)_3]^+Cl^-$ was prepared from $CyPH_2$ (Strem) by reaction with HCl/HCHO and recrystallisation of the product from isopropanol [36].

Unless otherwise specified, reactions were carried out under nitrogen using standard Schlenk line techniques and dry deoxygenated solvents (obtained from a PureSolv SP-SD-5 Solvent Purification System). The work-ups were performed at room temperature in air unless otherwise stated. Petroleum spirits refers to the fraction of boiling range 60–80 °C and diethyl ether was obtained from a PureSolv SP-SD-5 solvent purification system. Hexane refers throughout to *n*-hexane, which was of AR grade. Water was singly distilled prior to use.

Thin layer chromatography was performed on 70 × 15 mm Merck Kieselgel 60 $F_{254}$ silica gel plates. Preparative thin layer chromatography (TLC) plates were prepared from silica gel (Merck Kieselgel 60 $PF_{254}$) following established methods.

#### 4.2.1. Synthesis of $FcCH_2P(CH_2OH)Cy$ **6**

KOH (1.61 g, 28.70 mmol) was added to a solution of $[CyP(CH_2OH)_3]Cl$ (7.12 g, 29.34 mmol) in methanol (40 mL). The mixture was stirred for 1 h at room temperature before being added dropwise to a solution of $[FcCH_2NMe_3]I$ (3.60 g, 9.35 mmol) in methanol (40 mL). The reaction mixture was refluxed for 21 h. After cooling, the solvent was reduced to about 8 mL and distilled water (30 mL), diethyl ether (70 mL) and triethylamine (30 mL) were added. The mixture was stirred for 1 h. The aqueous layer was removed and re-extracted with diethyl ether (30 mL). The combined organic layers were washed with distilled water (3 × 20 mL) and then filtered. Removal of the solvent under reduced pressure gave **6** as a red oil (5.25 g), which was partly characterised and used directly for the synthesis of $FcCH_2PHCy$. ESI-MS (MeOH, cone voltage 20 V, with added $AgNO_3$) *m/z* 344 $[M]^+$, 796 $[2M+Ag]^+$. $^{31}P\{^1H\}$ NMR: $\delta$ −11.3 (s).

#### 4.2.2. Synthesis of $FcCH_2PHMe$ **7**

MeI (0.13 mL, 2.08 mmol) was added dropwise to a solution of $FcCH_2P(CH_2OH)_2$ (0.63 g, 2.16 mmol) in methanol (15 mL). The mixture was stirred for 15 min. at 50 °C. The solvent was removed under vacuum and distilled water (60 mL), petroleum spirits (60 mL), triethylamine (2 drops) and $Na_2S_2O_5$ (0.47 g, 2.47 mmol) were added sequentially. The mixture was refluxed for 3 h in air. After cooling, the aqueous layer was removed and re-extracted with petroleum spirits (30 mL). The combined organic extracts were washed with distilled water (4 × 20 mL). The solvent was reduced to 8 mL and cooled at −18 °C for 16 h. An unidentified yellow precipitate was removed by filtration. The filtrate was concentrated to about 2 mL and subjected to chromatography with a preparative TLC plate, eluting with diethyl ether/petroleum spirits (1:10). The yellow band at $R_f$ 0.86 gave **7** as a yellow oil (0.17 g, 33%). $C_{12}H_{15}FeP$ requires: C, 58.57; H, 6.14. Found: C, 59.00; H, 6.19%. IR: $\nu$P–H 2276s $cm^{-1}$. $^{31}P$ NMR $\delta$ −73.5 (*P*H, d, $^1J_{PH}$ 199). $^1H$ NMR $\delta$ 1.7 (C*H*$_3$, unresolved m, 3H), 2.7 (C*H*$_2$, d of m, 2H), 3.1 (P*H*, d of q, $^1J_{PH}$ 194, $^3J_{HH}$ 4, 1H), 4.06 ($H_3$, t, $^3J_{HH}$ 2, 2H), 4.08 ($H_2$, t, $^3J_{HH}$ 2, 2H), 4.11 ($H_4$, s, 5H). $^{13}C\{^1H\}$ NMR: $\delta$ 19.8 ($CH_2$, d, $^1J_{PC}$ 14), 31.2 ($CH_3$, d, $^1J_{PC}$ 8), 67.3 ($C_3$, s, CH), 68.3 ($C_2$, d, $^3J_{PC}$ 4, CH), 68.8 ($C_4$, s, CH), 87.0 ($C_1$, d, $^2J_{PC}$ 6, C).

*4.2.3. Synthesis of $FcCH_2PH(CH_2C_6H_4NO_2)$* ***8***

A mixture of $FcCH_2P(CH_2OH)_2$ (2.04 g, 6.98 mmol) and *p*-$BrCH_2C_6H_4NO_2$ (1.82 g, 8.44 mmol) in methanol (60 mL) was refluxed for 22 h. After cooling, the solvent was removed under vacuum. Distilled water (30 mL), toluene (30 mL), triethylamine (1 mL) and $Na_2S_2O_5$ (1.33 g, 7.01 mmol) were added and the mixture was refluxed for 5 h. After cooling, the aqueous phase was removed and re-extracted with toluene (60 mL). The combined organic layer was washed with distilled water (5 × 20 mL) and then filtered. Removal of the solvent under reduced pressure gave a red solid (2.43 g), which was chromatographed with a preparative TLC plate, eluting with dichloromethane/light petroleum (1:1), giving orange and yellow bands. Removal of the solvent of the orange band at $R_f$ 0.57 gave $FcCH_2PH(CH_2C_6H_4NO_2)$ **8** as a red oil (0.46 g, 18%) which solidified at −18 °C. $C_{18}H_{18}FeNO_2P$ requires: C, 58.88; H, 4.94; N, 3.81. Found: C, 59.63; H, 4.92; N, 3.95%. IR: *ν*PH 2278 m *ν*NO 1515vs, 1342vs $cm^{-1}$. $^{31}P$ NMR $\delta$ −49.1 (*P*H, d, $^1J_{PH}$ 192). $^1H$ NMR $\delta$ 2.6 (C$H_2$, m, 2H), 3.0 (C$H_2$, m, 2H), 3.4 (P*H*, d of p, $^1J_{PH}$ 198, $^3J_{HH}$ 7, 1H), 4.08 ($H_3$, unresolved m, 2H), 4.10 ($H_2$, unresolved m, 2H), 4.11 ($H_4$, s, 5H), 7.3 (C*H*, d, $^3J_{HH}$ 8, 2H), 8.1 (C*H*, d, $^3J_{HH}$ 8, 2H). $^{13}C\{^1H\}$ NMR $\delta$ 21.6 (*C*H$_2$, d, $^1J_{PC}$ 14), 28.8 (*C*H$_2$, d, $^1J_{PC}$ 17), 68.1 ($C_3$, s), 68.6 ($C_2$, d, $^3J_{PC}$ 4), 68.9 ($C_4$, s), 85.6 ($C_1$, d, $^2J_{PC}$ 7), 123.9 (*C*H, s), 129.3 (*C*H, d, $^3J_{PC}$ 4), 129.5 (*C*, s), 148.7 (*C*, d, $^2J_{PC}$ 3). ESI MS (MeOH): *m/z* 367.043 $[M]^+$ observed; 367.042 calcd. for $C_{18}H_{18}FeNO_2P$.

The yellow band at $R_f$ 0.33 gave $(FcCH_2)_2PCH_2C_6H_4NO_2$ **11** as a red oil (0.02 g, 0.8%). $^{31}P\{^1H\}$ NMR $\delta$ −12.3 (s). $^1H$ NMR $\delta$ 2.5 (C$H_2$, q of d, $^4J_{HH}$ 8, 6H), 4.03 (C*H*, unresolved m, $^3J_{HH}$ 2, 4H), 4.06 (C*H*, unresolved m, $^3J_{HH}$ 2, 4H), 4.08 ($H_4$, s, 10H), 7.3 (C*H*, d of d, $^{3,4}J_{HH}$ 8, 1, 2H), 8.1 (C*H*, d, $^3J_{HH}$ 9, 2H). $^{13}C\{^1H\}$ NMR $\delta$ 27.9 (*C*H$_2$, d, $^1J_{PC}$ 19), 34.4 (*C*H$_2$, d, $^1J_{PC}$ 21), 67.7 (*C*H, d, $^3J_{PC}$ 4), 68.9 (*C*H, d, $^4J_{PC}$ 3), 68.9 ($C_5$, s, CH), 83.6 ($C_1$, d, $^2J_{PC}$ 10), 123.6 (*C*H, s), 129.9 (*C*H, d, $^3J_{PC}$ 6), 146.2 (*C*, s), 147.0 (*C*, d, $^2J_{PC}$ 7).

Another by-product $FcCH_2P(CH_2C_6H_4NO_2)_2$ **12** was obtained as a red solid (0.84 g, 24%) from the orange fraction at $R_f$ 0.66. $C_{25}H_{23}FeN_2O_4P$ requires: C, 59.76; H, 4.62; N, 5.58. Found: C, 59.79; H, 4.78; N, 5.71%. IR: *ν*NO 1513vs, 1343vs $cm^{-1}$. $^{31}P\{^1H\}$ NMR $\delta$ −8.7 (s). $^1H$ NMR $\delta$ 2.6 (C$H_2$, s, 2H), 2.9 (C$H_2$, q, $^4J_{HH}$ 19, 4H), 4.03 (C*H*, unresolved m, 2H), 4.08 ($H_5$, s, 5H), 4.11 (C*H*, unresolved m, 2H), 7.3 (C*H*, d, $^3J_{HH}$ 8, 4H), 8.1 (C*H*, d, $^3J_{HH}$ 8, 4H). $^{13}C\{^1H\}$ NMR $\delta$ 27.7 (*C*H$_2$, d, $^1J_{PC}$ 19), 34.1 (*C*H$_2$, d, $^1J_{PC}$ 19), 68.0 (*C*H, s), 68.9 (*C*H, d, $^3J_{PC}$ 3), 69.0 (*C*H, s), 82.2 (*C*, d, $^2J_{PC}$ 8), 123.9 (*C*H, s), 129.9 (*C*H, d, $^3J_{PC}$ 6), 145.5 (*C*, t, $^2J_{PC}$ 4), 146.5 (*C*, s). ESI MS (MeOH with $AgNO_3$ added): *m/z* 502.074 $[M]^+$ observed; 502.073 calcd. for $C_{25}H_{23}FeN_2O_4P$; 608.978 $[M+Ag]^+$ observed; 608.979 calcd. for $C_{25}H_{23}AgFeN_2O_4P$.

*4.2.4. Synthesis of $FcCH_2PHCy$* ***9***

$Na_2S_2O_5$ (2.44 g, 12.83 mmol) was added to a solution of $FcCH_2P(CH_2OH)Cy$ **6** (5.25 g, 15.26 mmol) in a two-phase mixture of water (60 mL) and petroleum spirits (60 mL). The mixture was refluxed for 3 h in air. After cooling, the aqueous layer was removed and the organic layer was washed with distilled water (3 × 20 mL). Removal of the solvent from the organic layer under reduced pressure gave a red oil (2.21 g; a trace of $CyPH_2$ was observed by $^{31}P$ NMR of the crude product at $\delta$ −110.2, t, $^1J_{PH}$ 194 Hz). The red oil was extracted with a solvent mixture of diethyl ether (30 mL) and petroleum spirits (30 mL) which resulted in an immediate precipitation of a yellow solid which was collected by filtration, washed with cold diethyl ether (2 mL) and identified by $^1H$ and $^{31}P$ NMR spectroscopy and ESI MS as **10** (0.15 g, 3%). The organic filtrates were combined and the solvents were removed under reduced pressure. The residue was subjected to chromatography with a preparative TLC plate, eluting with diethyl ether/*n*-hexane (1:10). The orange band at $R_f$ 0.91 gave the pure **9** as a red oil (0.55 g, 19% based on $[FcCH_2NMe_3]I$ used) which solidified at −18 °C. $C_{17}H_{23}FeP$ requires: C, 64.99; H, 7.38. Found: C, 65.18; H, 7.56%. IR: *ν*PH 2268s $cm^{-1}$. $^{31}P$ NMR $\delta$ −41.1 (*P*H, d, $^1J_{PH}$ 199). $^1H$ NMR $\delta$ 1.3–1.7 (C$_6H_{11}$, unresolved m, 11H), 2.7 (C$H_2$, d of m, $^2J_{PH}$ 37, 2H), 3.1 (P*H*, d, $^1J_{PH}$ 198), 4.06 ($H_3$, t, $^3J_{HH}$ 2, 2H), 4.09 ($H_2$, unresolved m, 2H), 4.1 ($H_4$, s, 5H). $^{13}C\{^1H\}$ NMR $\delta$ 19.8 (*C*H$_2$, d, $^1J_{PC}$ 13), 27.0 (*C*H$_2$, d, $^2J_{PC}$ 8), 31.2 (*C*H$_2$, d, $^1J_{PC}$ 7), 32.0 (br), 67.3 ($C_3$, s, CH), 68.3 ($C_2$, br s, CH), 68.8 ($C_4$, s, CH), 87.0 ($C_1$, d, $^2J_{PC}$ 5, C). ESI MS (cone voltage 20 V, $AgNO_3$ added): *m/z* 314 $[M]^+$, 422 $[M+Ag]^+$, 736 $[2M+Ag]^+$.

*4.2.4.1. Characterisation data for* ***10****.* $^{31}P\{^1H\}$ NMR $\delta$ −7.6 (s); $^1H$ NMR $\delta$ 1.2–1.8 (C$_6H_{11}$, unresolved m, 11H), 2.5 (C$H_2$, s, 4H), 4.1 (*CH*, s, 18H). ESI MS (cone voltage 20 V, $AgNO_3$ added): *m/z* 620 $[M+Ag]^+$, 1132 $[2M+Ag]^+$). Decomposition of **10** occurred over a period of 2 weeks in $CDCl_3$ solution at room temperature in a capped NMR tube.

*4.2.5. Synthesis of $Fc(CH_2)_4P(CH_2OH)_2$* ***13***

KOH (1.85 g, 32.97 mmol) was added to a solution of $[P(CH_2OH)_4]Cl$ (8.29 g, 34.80 mmol) in methanol (19 mL). The mixture was stirred for 1 h before being added dropwise to a solution of $Fc(CH_2)_4Br$ (3.63 g, 11.31 mmol) in methanol (20 mL). The reaction mixture was refluxed for 21 h. After cooling, the solvent was removed under reduced pressure. Distilled water (25 mL), diethyl ether (60 mL) and triethylamine (25 mL) were added and the mixture stirred for 1 h. The aqueous layer was removed and re-extracted with diethyl ether (30 mL). The combined organic layers were washed with distilled water (3 × 20 mL) and filtered. Removal of the solvent under reduced pressure gave **13** as a red oil (3.36 g, 89%). $C_{16}H_{23}FePO_2$ requires: C, 57.49; H, 6.94; N, 0.00. Found: C, 58.84; H, 6.73; N, <0.2%. $^{31}P\{^1H\}$ NMR $\delta$ −22.7 (s). $^1H$ NMR $\delta$ 1.6 (C$H_2$, m, 2H), 1.7 (C$H_2$, m, 2H), 1.8 (C$H_2$, m, 2H), 2.4 (C$H_2$, m, 2H), 4.05 (C*H*, m, 4H), 4.10 (C*H*, s, 5H), 4.2 (C$H_2$, d of m, $^2J_{PH}$ 85, 4H). $^{13}C\{^1H\}$ NMR $\delta$ 16.7 (d, $^1J_{PC}$ 9, *C*H$_2$), 25.8 (d, $^2J_{PC}$ 15, *C*H$_2$), 29.3 (s, *C*H$_2$), 32.7 (d, $^3J_{PC}$ 12, *C*H$_2$), 61.9 (d, $^1J_{PC}$ 21, *C*H$_2$), 67.1 (s, *C*H), 68.1 (s, *C*H), 68.5 (s, *C*H), 89.1 (*C*, s). ESI MS (MeOH with $AgNO_3$ added): *m/z* 334.078 $[M]^+$ observed; 334.078 calcd. for $C_{16}H_{23}FeO_2P$; 440.984 $[M+Ag]^+$ observed; 440.983 calcd. for $C_{16}H_{23}AgFeO_2P$; 775.061 $[2M+Ag]^+$ observed; 775.061 calcd. for $C_{32}H_{46}AgFe_2O_4P_2$.

*4.2.6. Synthesis of $Fc(CH_2)_6P(CH_2OH)_2$* ***14***

KOH (1.91 g, 34.04 mmol) was added to a solution of $[P(CH_2OH)_4]Cl$ (7.71 g, 32.37 mmol) in methanol (20 mL). The mixture was stirred for 1 h before being added dropwise to a solution of $Fc(CH_2)_6Br$ (2.06 g, 5.89 mmol) in 95% ethanol (20 mL) and the reaction mixture was refluxed for 20.5 h. After cooling, the solvent was removed under reduced pressure. Water (25 mL), diethyl ether (40 mL) and triethylamine (12 mL) were added and the mixture was stirred for 2 h. The aqueous layer was removed and re-extracted with diethyl ether (30 mL). The combined organic layers were washed with water (3 × 20 mL). Removal of the solvent under reduced pressure gave **14** as a red oil (2.02 g, 95%). $^{31}P\{^1H\}$ NMR $\delta$ −22.9 (s). $^1H$ NMR $\delta$ 1.4–1.5 (C$H_2$, m, 8H), 1.8 (C$H_2$, m, 2H), 2.3 (C$H_2$, t, $^3J_{HH}$ 8, 2H), 4.04 ($H_{2,3}$, unresolved m, 4H), 4.09 ($H_4$, s, 5H), 4.2 (C$H_2$, d of m, $^2J_{PH}$ 92, 4H). $^{13}C\{^1H\}$ NMR $\delta$ 16.8 (d, $^1J_{PC}$ 8, *C*H$_2$), 25.8 (d, $^2J_{PC}$ 15, *C*H$_2$), 29.3 (s, *C*H$_2$), 29.5 (s, *C*H$_2$), 31.0 (s, *C*H$_2$), 31.2 (d, $^3J_{PC}$ 12, *C*H$_2$), 61.9 (d, $^1J_{PC}$ 20, *C*H$_2$), 67.0 (s, *C*H), 68.1 (s, *C*H), 68.5 (s, *C*H), 89.4 (*C*, s). ESI MS (MeOH with $AgNO_3$ added): *m/z* 362.108 $[M]^+$ observed; 362.109 calcd. for $C_{18}H_{27}FeO_2P$; 385.099 $[M+Na]^+$ observed; 385.099 calcd. for $C_{18}H_{27}FeNaO_2P$; 469.014 $[M+Ag]^+$ observed; 469.014 calcd. for $C_{18}H_{27}AgFeO_2P$; 831.123 $[2M+Ag]^+$ observed; 831.124 calcd. for $C_{36}H_{54}AgFe_2O_4P_2$.

*4.2.7. Synthesis of $Fc(CH_2)_{11}P(CH_2OH)_2$* ***15***

KOH (3.40 g, 60.6 mmol) was added to a solution of $[P(CH_2OH)_4]Cl$ (15.28 g, 64.15 mmol) in methanol (20 mL). The mixture was stirred for 1 h before adding dropwise to a solution of $Fc(CH_2)_{11}Br$ (8.68 g, 20.69 mmol) in methanol (20 mL) and the reaction mixture refluxed for 20.5 h. After cooling, the solvent was reduced to ~13 mL under reduced pressure. Water (12 mL), diethyl ether (34 mL) and triethylamine (14 mL) were added and the solution stirred for 2 h. The aqueous layer was removed and re-extracted with diethyl ether (10 mL). The combined organic layer was washed with water (6 × 10 mL). Removal of the solvent under reduced pressure gave a red oil (8.29 g, 93%). Recrystallisation of the crude product by addition of petroleum spirits (b.p. 40–60 °C) to a dichloromethane-methanol solution followed by cooling to −18 °C gave **15** as a yellow solid. $C_{23}H_{37}FeO_2P$ requires: C, 63.87; H, 8.63; N, 0.00. Found: C, 63.95; H, 8.76; N, 0.47%. ESI MS (MeOH with added $AgNO_3$): *m/z* 432.186 $[M]^+$ observed; 432.187 calcd. for $C_{23}H_{37}FeO_2P$; 539.093 $[M+Ag]^+$ observed; 539.092 calcd. for $C_{23}H_{37}AgFeO_2P$. $^{31}P\{^1H\}$ NMR $\delta$ −22.7 (s). $^1H$ NMR $\delta$ 1.4–1.5 (C$H_2$, m, 18H), 1.8 (C$H_2$, m, 2H), 2.3 (C$H_2$, t, $^3J_{HH}$ 8, 2H), 4.04 (C*H*, m, 4H), 4.09 (C*H*, s, 5H), 4.2 (C$H_2$, d of m, $^2J_{PH}$ 89, 4H). $^{13}C\{^1H\}$ NMR $\delta$ 16.9 (d, $^1J_{PC}$ 8, $CH_2$), 25.9 (d, $^2J_{PC}$ 15, $CH_2$), 28.2–31.1 (s, $CH_2$), 31.3 (d, $^3J_{PC}$ 12, $CH_2$), 61.8 (d, $^1J_{PC}$ 20, $CH_2$), 67.0 (s, CH), 68.1 (s, CH), 68.5 (s, CH), 89.6 (*C*, s).

*4.2.8. Synthesis of $Fc(CH_2)_4PH_2$* ***16***

$Na_2S_2O_5$ (0.03 g, 0.16 mmol) was added to a solution of $Fc(CH_2)_4P(CH_2OH)_2$ **13** (0.07 g, 0.21 mmol) in a two-phase solvent system of water (5 mL) and petroleum spirits (5 mL) and the mixture was refluxed for 2 h. After cooling, the aqueous layer was removed and re-extracted with petroleum spirits (10 mL). The combined organic layer was washed with water (3 × 10 mL). Removal of the solvent under reduced pressure gave a red oil which was chromatographed with a preparative TLC plate, eluting with petroleum spirits. Removal of the solvent from the yellow band at $R_f$ 1.0 gave **16** as a yellow oil (0.02 g, 35%). IR: *v*PH 2289s $cm^{-1}$. $^{31}P$ NMR $\delta$ −136.9 (P$H_2$, t, $^1J_{PH}$ 194). $^1H$ NMR $\delta$ 1.5–1.6 (C$H_2$, m, 6H), 2.3 (C$H_2$, t, $^3J_{HH}$ 7, 2H), 2.7 (P$H_2$, d of t, $^1J_{PH}$ 194, $^3J_{HH}$ 7, 2H), 4.05 (C*H*, two unresolved singlets, 4H), 4.1 ($H_4$, s, 5H). $^{13}C\{^1H\}$ NMR $\delta$ 13.7 ($CH_2$, d, $^1J_{PC}$ 7), 29.2 (C$H_2$, s), 32.0 (d, $^2J_{PC}$ 6), 32.8 ($CH_2$, d, $^3J_{PC}$ 3), 67.1 ($C_3$, s, CH), 68.1 ($C_2$, s, CH), 68.5 ($C_4$, s, CH), 89.1 ($C_1$, s). GC–MS: *m/z* 56 $[Fe]^+$, 121 $[CpFe]^+$, 199 $[FcCH_2]^+$, 274 $[M]^+$. ESI MS ($CH_2Cl_2$/MeOH): *m/z* 274.056 $[M]^+$ observed; 274.056 calcd. for $C_{14}H_{19}FeP$. A sample for elemental analysis was obtained by distillation under $10^{-6}$ torr at 65 °C for 12 h. $C_{14}H_{19}FeP$ requires: C, 61.34; H, 6.99. Found: C, 61.64; H, 6.61%.

*4.2.9. Synthesis of $Fc(CH_2)_6PH_2$* ***17***

$Na_2S_2O_5$ (1.08 g, 5.66 mmol) was added to a solution of $Fc(CH_2)_6P(CH_2OH)_2$ **14** (2.04 g, 5.64 mmol) in a two-phase solvent system of water (30 mL) and petroleum spirits (30 mL) and the mixture was refluxed for 4 h in air. After cooling, the aqueous layer was removed. The organic layer was washed with water (3 × 10 mL) and filtered. Removal of the solvent under reduced pressure gave a red oil (1.42 g, 83%). A sample for microelemental analysis was obtained by chromatography on a preparative TLC plate, eluting with ether/petroleum spirits (1:1). Removal of the solvent of the fraction at $R_f$ 0.70 gave **17** as a yellow oil. $C_{16}H_{23}FeP$ requires: C, 63.58; H, 7.68. Found: C, 62.04; H, 7.99%. IR: *v*PH 2283 m $cm^{-1}$. $^{31}P$ NMR $\delta$ −136.5 (P$H_2$, t of t, $^1J_{PH}$ 195, $^2J_{PH}$ 6). $^1H$ NMR $\delta$ 1.3–1.6 (C$H_2$, m, 10H), 2.3 (C$H_2$, t, $^3J_{HH}$ 8, 2H), 2.7 (P$H_2$, d of t, $^1J_{PH}$ 195, $^3J_{HH}$ 7, 2H), 4.05 (C*H*, unresolved m, $^3J_{HH}$ 2, 4H), 4.09 ($H_4$, s, 5H). $^{13}C\{^1H\}$ NMR $\delta$ 13.7 ($CH_2$, d, $^1J_{PC}$ 7), 29.2 (C$H_2$, s), 29.6 (C$H_2$, s), 30.5 (C$H_2$, d, $^2J_{PC}$ 6), 31.0 ($CH_2$, s), 32.9 ($CH_2$, d, $^3J_{PC}$ 4), 67.0 (C*H*, s), 68.1 (C*H*, s), 68.5 (C*H*, s), 89.4 (*C*, s). GC–MS: *m/z* 56 $[Fe]^+$, 121 $[CpFe]^+$, 199 $[FcCH_2]^+$, 302 $[M]^+$. ESI MS ($CH_2Cl_2$/MeOH): *m/z* 302.088 $[M]^+$ observed; 302.088 calcd. for $C_{16}H_{23}FeP$.

*4.2.10. Synthesis of $Fc(CH_2)_{11}PH_2$* ***18***

$Na_2S_2O_5$ (0.11 g, 0.57 mmol) was added to a solution of $Fc(CH_2)_{11}P(CH_2OH)_2$ **15** (0.25 g, 0.64 mmol) in a two-phase mixture of water (10 mL) and petroleum spirits (10 mL) and the mixture was refluxed for 3 h. After cooling, the solvents were removed with a syringe. The yellow precipitate was washed with water (4 × 10 mL). After drying under vacuum, the residue (0.26 g) was extracted with dichloromethane and filtered. The filtrate was subjected to chromatography with a preparative TLC plate, eluting with dichloromethane/petroleum spirits (5:6). Removal of the solvent from the yellow fraction at $R_f$ 0.93 gave **18** as a yellow oil (0.06 g, 28%). $C_{21}H_{33}FeP$ requires: C, 67.73; H, 8.94; N, 0.00. Found: C, 71.08; H, 9.36; N, <0.2%. IR: *v*PH 2290 m $cm^{-1}$. $^{31}P$ NMR $\delta$ −136.7 (P$H_2$, t of t, $^1J_{PH}$ 195, $^2J_{PH}$ 6). $^1H$ NMR $\delta$ 1.3–1.5 (C$H_2$, m, 22H), 2.3 (C$H_2$, t, $^3J_{HH}$ 8, 2H), 2.7 (P$H_2$, d of t, $^1J_{PH}$ 195, $^3J_{HH}$ 7, 2H), 4.04 (C*H*, unresolved m, 4H), 4.09 (C*H*, s, 5H). $^{13}C\{^1H\}$ NMR $\delta$ 13.7 ($CH_2$, d, $^1J_{PC}$ 7), 29.2 (C$H_2$, s), 29.6 (C$H_2$, s), 30.6 (C$H_2$, d, $^2J_{PC}$ 6), 31.1 (C$H_2$, s), 32.9 (C$H_2$, d, $^3J_{PC}$ 3), 67.0 (C*H*, s), 68.1 (C*H*, s), 68.5 (C*H*, s), 89.6 (*C*, s). GC–MS: *m/z* 121 $[CpFe]^+$, 199 $[FcCH_2]^+$, 372 $[M]^+$. ESI MS ($CH_2Cl_2$/MeOH): *m/z* 372.165 $[M]^+$ observed; 372.166 calcd. for $C_{21}H_{33}FeP$.

*4.2.11. Synthesis of $Fc(CH_2)_6PH_2(BH_3)$* ***19***

Under a nitrogen atmosphere a solution of $Fc(CH_2)_6PH_2$ **17** (0.05 g, 0.17 mmol) in dry hexane (10 mL) was cooled to −63 °C. $BH_3(SMe_2)$ in THF (0.5 mL, 5.63 mmol) was added and the mixture stirred at −63 °C for 15 min. Volatiles were removed under vacuum, and the residue recrystallised from dry *n*-hexane at −20 °C. Orange needles of **19** (13.8 mg, 26%) were collected and washed with cold hexane (2 × 1 mL). $C_{16}H_{26}BFeP$ requires: C, 60.75; H, 8.29. Found: C, 60.84; H, 8.19%. ESI MS ($CH_2Cl_2$/MeOH): *m/z* 316.1195 $[M]^+$ (calcd. for $C_{16}H_{26}BFeP$ *m/z* 316.1209); 339.1096 $[M+Na]^+$ observed; 339.1110 calcd. for $C_{16}H_{26}BFeNaP$; 355.0588 $[M+K]^+$ observed; 355.0846 calcd. for $C_{16}H_{26}BFeKP$. $^{31}P$ NMR ($CDCl_3$) $\delta$ −52.32 (broad t, $^1J_{PH}$ 362). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.26–1.53 (C$H_2$ and B$H_3$, m, 13H), 1.76–1.86 (C$H_2$, m, 2H), 2.33 (CpC$H_2$, t, $^3J_{HH}$ 7.8, 2H), 4.05–4.10 (Cp*H*, s, 11H), 4.50 (P$H_2$, d of sextets, $^1J_{PH}$ 360, $^3J_{HH}$ 1.32). $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 16.5 ($CH_2PH_2$, $^1J_{PC}$ 35.4), 28.9 ($CpCH_2CH_2CH_2$, s), 28.9 ($CH_2CH_2CH_2PH_2$, d, $^3J_{PC}$ 5.75), 29.5 (CpC$H_2$, s), 30.2 ($CH_2CH_2PH_2$, d, $^2J_{PC}$ 10.5), 31.0 ($CpCH_2CH_2$, s), 67.2 ($C_3$, s, CH), 68.2 ($C_2$, s, CH), 68.7 ($C_5H_5$, s, CH), 89.5 ($C_1$, s).

*4.2.12. Synthesis of $RcCH_2P(CH_2OH)_2$* ***20***

KOH (1.30 g, 23.13 mmol) was added to a solution of $[P(CH_2OH)_4]Cl$ (5.37 g, 22.54 mmol) in methanol (15 mL). The mixture was stirred for 1 h before being added dropwise to a solution of $[RcCH_2NMe_3]I$ (1.95 g, 4.53 mmol) in methanol (15 mL) and the reaction mixture was refluxed for 20 h. After cooling, the solvent was removed under reduced pressure. Water (10 mL), diethyl ether (25 mL) and triethylamine (5 mL) were added and the solution was stirred for 1 h. The aqueous layer was removed and re-extracted with diethyl ether (20 mL). The combined organic layers were washed with water (5 × 10 mL). Removal of the solvent under reduced pressure gave **20** as a pale-yellow oil with some white solids (0.95 g, 62%) which was used in the synthesis of $RcCH_2PH_2$ **21** without further purification or characterisation.

*4.2.13. Synthesis of $RcCH_2PH_2$* ***21***

$Na_2S_2O_5$ (0.54 g, 2.83 mmol) was added to a solution of crude $RcCH_2P(CH_2OH)_2$ **20** (0.95 g, 2.83 mmol) in a two-phase mixture of water (20 mL) and petroleum spirits (25 mL) and the mixture was refluxed for 3 h. After cooling, the aqueous layer was removed. The organic layer was washed with water (5 × 10 mL). Removal of

the solvent from the organic layer under reduced pressure gave a pale yellow oil with some white solids (0.34 g, 43%). The crude product was partially purified by chromatography with a preparative TLC plate, eluting with dichloromethane/petroleum spirits (1:1). Removal of the solvent of the pale yellow fraction at $R_f$ 0.76 gave **21** as a pale-yellow oil (0.08 g, 10%). Satisfactory microanalytical data could not be obtained: $C_{11}H_{13}PRu$ requires: C, 47.65; H, 4.73. Found: C, 45.03; H, 4.44%. IR: $\nu$PH 2290 m cm$^{-1}$. $^{31}$P NMR $\delta$ −132.5 (*P*H$_2$, t, $^1J_{PH}$ 193). $^1$H NMR $\delta$ 2.5 (C*H*$_2$, m, $^3J_{HH}$ 4, 2H), 2.9 (P*H*$_2$, d of t, $^1J_{PH}$ 194, $^3J_{HH}$ 7, 2H), 4.5 (C*H*, t, $^3J_{HH}$ 2, 2H), 4.56 (C*H*, s, 5H), 4.57 (C*H*, t, $^3J_{HH}$ 2, 2H). $^{13}$C{$^1$H} NMR $\delta$ 14.0 (*C*H$_2$, d, $^1J_{PC}$ 8), 69.5 (*C*H, s), 70.7 (*C*H, s), 70.9 (*C*H, d, $^3J_{PC}$ 3), 92.6 (C$_1$, unresolved m). GC–MS: *m/z* 167 [CpRu]$^+$, 245 [RcCH$_2$]$^+$, 278 [M]$^+$. ESI MS (MeOH): *m/z* 244.989 [M−PH$_2$]$^+$ observed; 244.989 calcd. for $C_{11}H_{11}Ru$; (MeOH with added $AgNO_3$): *m/z* 384.885 [M+Ag]$^+$ observed; 384.884 calcd. for $C_{11}H_{13}AgPRu$.

A by-product which was tentatively identified as RcCH$_2$-P(O)H(CH$_2$OH) **22** was obtained as a white solid (0.05 g, 5%) from the aqueous phase of the reaction mixture. $^{31}$P NMR $\delta$ 35.7 (*P*H, d of t, $^1J_{PH}$ 467, $^2J_{PH}$ 14). $^1$H NMR $\delta$ 3.0 (C*H*$_2$, d of t, $^3J_{HH}$ 13, $^4J_{HH}$ 4, 2H), 4.0 (C*H*$_2$, m, 2H), 4.5 (C*H*, d, $^3J_{HH}$ 1, 2H), 4.6 (C*H*, s, 5H), 4.7 (C*H*, unresolved m, 2H), 6.8 (P*H*, broad d, $^1J_{PH}$ 467, 1H). $^{13}$C{$^1$H} NMR $\delta$ 26.7 (*C*H$_2$), 58.7 (*C*H$_2$, d, $^1J_{PC}$ 74), 70.6 (*C*H), 71.2 (*C*H), 71.9 (*C*H), 80.0 (*C*).

### 4.3. X-ray structure determination on Fc(CH$_2$)$_6$PH$_2$(BH$_3$) **19**

Crystals of **19** were obtained by recrystallisation from *n*-hexane, slowly cooling at −18 °C. Intensity data were obtained on a Bruker SMART diffractometer with Mo Kα X-rays and corrected for absorption using a multi-scan procedure [52]. The structure was solved by direct methods and developed and refined on $F_o^2$. All calculations were with the SHELX97 programs [53,54] run under WINGX [55]. Figures were generated with ORTEP-3 [56].

#### 4.3.1. Crystal data for Fc(CH$_2$)$_6$PH$_2$(BH$_3$) **19**

$C_{16}H_{26}BFeP$; $M_r$ = 316.00; monoclinic; space group $P2_1/n$; $a$ = 14.9861(4) Å; $b$ = 5.8093(1) Å; $c$ = 19.7607(5) Å; $\beta$ = 110.711(1)°; $V$ = 1609.17(7) Å$^3$; $Z$ = 4; $T$ = 89(2) K; $\lambda$(Mo Kα) = 0.71073 Å; $\mu$(Mo Kα) = 1.021 mm$^{-1}$; $D_{calc}$ = 1.304 g cm$^{-3}$; 20240 reflections collected; 3871 unique ($R_{int}$ = 0.0300). H atoms on the (CH$_2$)$_6$ chain and the cyclopentadienyl rings were in calculated positions; the PH$_2$ and BH$_3$ hydrogen atoms were located and refined with isotropic temperature factors. Final refinement gave $R_1$ = 0.0243, $wR_2$ = 0.0616 for data with [$I > 2\sigma(I)$] and $R_1$ = 0.0289, $wR_2$ = 0.0645 for all data. Residual electron density (e$^-$ Å$^{-3}$) maximum/minimum: 0.440/−0.211.

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## Appendix A. Supplementary material

CCDC 971461 contains the supplementary crystallographic data for Fc(CH2)6PH2(BH3). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2014.01.049.

## References

[1] M. Brynda, M. Geoffroy, G. Bernardinelli, Chem. Commun. (1999) 961.
[2] R.M. Hiney, L.J. Higham, H. Müller-Bunz, D.G. Gilheany, Angew. Chem., Int. Ed. Engl. 45 (2006) 7248.
[3] K.R. Prabhu, N. Pillarsetty, H. Gali, K.V. Katti, J. Am. Chem. Soc. 122 (2000) 1554.
[4] M. Brynda, Coord. Chem. Rev. 249 (2005) 2013.
[5] R.J. Baker, M. Brym, C. Jones, M. Waugh, J. Organomet. Chem. 689 (2004) 781.
[6] M. Brynda, G. Bernardinelli, C. Dutan, M. Geoffroy, Inorg. Chem. 42 (2003) 6586.
[7] N. Pillarsetty, K. Raghuraman, C.L. Barnes, K.V. Katti, J. Am. Chem. Soc. 127 (2005) 331.
[8] N.J. Goodwin, W. Henderson, B.K. Nicholson, J. Fawcett, D.R. Russell, J. Chem. Soc., Dalton Trans. (1999) 1785.
[9] W. Henderson, S.R. Alley, J. Organomet. Chem. 656 (2002) 120.
[10] M.A. Pet, M.F. Cain, R.P. Hughes, D.S. Glueck, J.A. Golen, A.L. Rheingold, J. Organomet. Chem. 694 (2009) 2279.
[11] C. Spang, F.T. Edelmann, M. Noltemeyer, H.W. Roesky, Chem. Ber. 122 (1989) 1247.
[12] R. Kalio, P. Lönnecke, J. Reinhold, E. Hey-Hawkins, Organometallics 26 (2007) 3884.
[13] S.I.M. Paris, F.R. Lemke, R. Sommer, P. Lönnecke, E. Hey-Hawkins, J. Organomet. Chem. 690 (2005) 1807.
[14] R. Kalio, P. Lönnecke, A. Cinquantini, P. Zanello, E. Hey-Hawkins, Z. Anorg. Allg. Chem. 633 (2007) 2470.
[15] S.I.M. Paris, J.L. Petersen, E. Hey-Hawkins, M.P. Jensen, Inorg. Chem. 45 (2006) 5561.
[16] S.I.M. Paris, U.A. Laskay, S. Liang, O. Pavlyuk, S. Tschirschwitz, P. Lönnecke, M.C. McMills, G.P. Jackson, J.L. Petersen, E. Hey-Hawkins, M.P. Jensen, Inorg. Chim. Acta 363 (2010) 3390.
[17] R. Sommer, P. Lönnecke, J. Reinhold, P.K. Baker, E. Hey-Hawkins, Organometallics 24 (2005) 5256.
[18] R. Kalio, P. Lönnecke, E. Hey-Hawkins, J. Organomet. Chem. 693 (2008) 590.
[19] M.M. Dell'Anna, U. Englert, M. Latronico, P. Lorenzo Luis, P. Mastorilli, D. Giardina Papa, C.F. Nobile, M. Peruzzini, Inorg. Chem. 45 (2006) 6892.
[20] M. Peruzzini, P. Barbaro, V. Bertolasi, C. Bianchini, I. DelosRios, N. Mantovani, L. Marvelli, R. Rossi, Dalton Trans. (2003) 4121.
[21] M.M. Dell'Anna, P. Mastrorilli, C.F. Nobile, B. Calmuschi-Cula, U. Englert, M. Peruzzini, Dalton Trans. (2008) 6005.
[22] M.M. Dell'Anna, D. Giardina-Papa, S. Ibáñez, A. Martin, P. Mastrorilli, C.F. Nobile, M. Peruzzini, Eur. J. Inorg. Chem. (2009) 4454.
[23] B.J. Anderson, M.A. Guino-o, D.S. Glueck, J.A. Golen, A.G. DiPasquale, L.M. Liable-Sands, A.L. Rheingold, Org. Lett. 10 (2008) 4425.
[24] M.F. Cain, R.P. Hughes, D.S. Glueck, J.A. Golen, C.E. Moore, A.L. Rheingold, Inorg. Chem. 49 (2010) 7650.
[25] R. Sommer, P. Lönnecke, P.K. Baker, E. Hey-Hawkins, Inorg. Chem. Commun. 5 (2002) 115.
[26] A.A. Karasik, R.N. Naumov, R. Sommer, O.G. Sinyashin, E. Hey-Hawkins, Polyhedron 21 (2002) 2251.
[27] A.A. Karasik, Y.S. Spiridonova, D.G. Yakhvarov, O.G. Sinyashin, P. Lönnecke, R. Sommer, E. Hey-Hawkins, Mendeleev Commun. 15 (2005) 89.
[28] F. Labrue, B. Pons, L. Ricard, A. Marinetti, J. Organomet. Chem. 690 (2005) 2285.
[29] B. Stewart, A. Harriman, L.J. Higham, Organometallics 30 (2011) 5338.
[30] A.R. Seibert, M.F. Cain, D.S. Glueck, C. Nataro, J. Organomet. Chem. 696 (2011) 2259.
[31] M.D. Sliger, G.A. Broker, S.T. Griffin, R.D. Rogers, K.H. Shaughnessy, J. Organomet. Chem. 690 (2005) 1478.
[32] G.M. Kosolapoff, L. Maier, Organic Phosphorus Compounds, vol. 1, Wiley-Interscience, New York, 1972.
[33] See for example W. Henderson, A.G. Oliver, A.J. Downard, Polyhedron 15 (1996) 1165.
[34] W. Henderson, J.S. McIndoe, Mass Spectrometry of Inorganic, Coordination and Organometallic Compounds – Tools-Techniques-Tips, John Wiley & Sons, 2005.
[35] W. Henderson, G.M. Olsen, Polyhedron 17 (1998) 577.
[36] W. Henderson, G.M. Olsen, Polyhedron 15 (1996) 2105.
[37] M.G. Fitzpatrick, L.R. Hanton, W. Henderson, P.E. Kneebone, E.G. Levy, L.J. McCaffrey, D.A. McMorran, Inorg. Chim. Acta 281 (1998) 101.
[38] G.C. Welch, T. Holtrichter-Roessmann, D.W. Stephan, Inorg. Chem. 47 (2008) 1904.
[39] N.J. Goodwin, W. Henderson, B.K. Nicholson, J.K. Sarfo, J. Fawcett, D.R. Russell, J. Chem. Soc., Dalton Trans. (1997) 4377.
[40] A. Staubitz, A.P.M. Robertson, M.E. Sloan, I. Manners, Chem. Rev. 110 (2010) 4023.
[41] A.V. Polukeev, S.A. Kuklin, P.V. Petrovskii, S.M. Peregudova, A.F. Smol'yakov, F.M. Dolgushin, A.A. Koridze, Dalton Trans. 40 (2011) 7201;
A.A. Koridze, A.V. Polezhaev, S.V. Safronov, A.M. Sheloumov, F.M. Dolgushin, M.G. Ezernitskaya, B.V. Lokshin, P.V. Petrovskii, A.S. Peregudov, Organometallics 29 (2010) 4360;
S.A. Kuklin, A.M. Sheloumov, F.M. Dolgushin, M.G. Ezernitskaya, A.S. Peregudov, P.V. Petrovskii, A.A. Koridze, Organometallics 25 (2006) 5466.
[42] H.C.L. Abbenhuis, U. Burckhardt, V. Gramlich, A. Martelletti, J. Spencer, I. Steiner, A. Togni, Organometallics 15 (1996) 1614.
[43] M. Watanabe, Tetrahedron Lett. 36 (1995) 8991.

[44] See for example S. Barlow, A. Cowley, J.C. Green, T.J. Brunker, T. Hascall, Organometallics 20 (2001) 5351.
[45] M.C. Grossel, D.G. Hamilton, J.I. Fuller, E. Millan-Barios, J. Chem. Soc., Dalton Trans. (1997) 3471.
[46] http://fluorine.ch.man.ac.uk/research/tools.php.
[47] D. Lednicer, C.R. Hauser, Org. Synth. Coll. 5 (1973) 434.
[48] C.J. Yu, H. Wang, Y. Wan, H. Yowanto, J.C. Kim, L.H. Donilon, C. Tao, M. Strong, Y. Chong, J. Org. Chem. 66 (2001) 2937.
[49] G. Zotti, S. Zecchin, G. Schiavon, A. Berlin, G. Pagani, A. Canavesi, Chem. Mater. 7 (1995) 2309.
[50] M. Tazaki, K. Okada, K. Yakata, K. Nakano, M. Sakai, T. Yonemitsu, Phosphorus, Sulfur, Silicon Relat. Elem. 167 (2000) 239.
[51] E.P. Kündig, F.R. Monnier, Adv. Synth. Catal. 346 (2004) 901.
[52] R.H. Blessing, Acta Crystallogr., Sect. A 51 (1995) 33.
[53] G.M. Sheldrick, SHELX-97 Programs for the Solution and Refinement of Crystal Structures (Release 97-2), University of Göttingen, Germany, 1997.
[54] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.
[55] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.
[56] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.