



## Synthesis and structure of ferrocenylmethylphosphines, their borane adducts, and some related derivatives

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### ABSTRACT

Syntheses of the known ferrocenylmethylphosphines  $\text{FcCH}_2\text{PH}_2$  (**2**,  $\text{Fc} = (\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$ ),  $(\text{FcCH}_2)_2\text{PH}$  (**3**), and  $(\text{FcCH}_2)_3\text{P}$  (**4**) have been reinvestigated. The reaction of  $[\text{FcCH}_2\text{NMe}_3][\text{I}]$  with  $\text{P}(\text{CH}_2\text{OH})_3$ , generated from  $[\text{P}(\text{CH}_2\text{OH})_4][\text{Cl}]$  and  $\text{KOH}$ , gave a mixture of the major product  $(\text{FcCH}_2)_2\text{P}(\text{CH}_2\text{OH})_2$  (**1**) and over-alkylated  $(\text{FcCH}_2)_2\text{P}(\text{CH}_2\text{OH})$  (**9**). Treatment of pure **9** with  $\text{Na}_2\text{S}_2\text{O}_5$  gave the secondary phosphine **3**; slow addition of  $\text{Na}_2\text{S}_2\text{O}_5$  to **1** gave **2** in improved yield. Reaction of **1** with  $[\text{FcCH}_2\text{NMe}_3][\text{I}]$ , followed by treatment with  $\text{NEt}_3$ , gave the tertiary phosphine  $(\text{FcCH}_2)_3\text{P}$  (**4**), along with the known phosphonium salt  $[(\text{FcCH}_2)_4\text{P}][\text{I}]$  (**5**), which could be prepared in higher yield by adjusting the stoichiometry. Phosphine **4** oxidized slowly in air to yield  $(\text{FcCH}_2)_3\text{P}(\text{O})$  (**12**), was protonated by  $\text{HBF}_4(\text{OMe}_2)$  to give  $[(\text{FcCH}_2)_3\text{PH}][\text{BF}_4]$  (**13**), and reacted with  $\text{Pt}(\text{COD})\text{Cl}_2$  or  $\text{PtCl}_2$  to yield a mixture of *cis*- and *trans*- $\text{Pt}(\text{P}(\text{CH}_2\text{Fc})_3)_2\text{Cl}_2$  (**14**). Silylation of **2** with *n*-BuLi/ $\text{Me}_3\text{SiCl}$  gave  $\text{FcCH}_2\text{P}(\text{CH}_2\text{OSiMe}_3)_2$  (**11**). The phosphine-borane adducts  $\text{FcCH}_2\text{PH}_2(\text{BH}_3)$  (**6**),  $(\text{FcCH}_2)_2\text{PH}(\text{BH}_3)$  (**7**),  $(\text{FcCH}_2)_3\text{P}(\text{BH}_3)$  (**8**) and  $(\text{FcCH}_2)_2\text{P}(\text{CH}_2\text{OSiMe}_3)_2(\text{BH}_3)$  (**15**) were prepared from the corresponding phosphines and  $\text{BH}_3(\text{SMe}_2)$ . The phosphines **2**, **3**, and **4**, phosphonium salts **5** and **13**, phosphine oxide **12**, Pt complex *trans*-**14**, and phosphine-boranes **6**, **7** and **8** were structurally characterized by X-ray crystallography. The solid cone angle of  $(\text{FcCH}_2)_3\text{P}$ ,  $139^\circ$ , in Pt complex **14** showed that **4** was bulkier than  $\text{PPh}_3$ , but less sterically demanding than  $\text{P}(t\text{-Bu})_3$ . The structural changes observed on quaternization of P (shorter P–C bonds and larger angles at P), along with results from NMR and IR spectroscopy and DFT calculations, were consistent with the expected rehybridization at phosphorus. Related observations for analogous methylphosphines suggest that methyl and ferrocenylmethyl phosphorus substituents have similar properties.

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### 1. Introduction

Alkylphosphines are useful ligands for transition metals in coordination and organometallic chemistry and catalysis, but their air-sensitivity and unpleasant smell have discouraged their routine use [1]. For this reason, the recent syntheses of the air-stable ferrocenylmethylphosphine derivatives  $\text{FcCH}_2\text{P}(\text{CH}_2\text{OH})_2$  (**1**,  $\text{Fc} = (\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$ ) [2] and, more strikingly, the primary and secondary phosphines  $\text{FcCH}_2\text{PH}_2$  (**2**) [3] and  $(\text{FcCH}_2)_2\text{PH}$  (**3**) [4] were significant advances in preparing “user-friendly” ligands for various applications [5]. Although these phosphines can be prepared readily from inexpensive, commercially available  $[\text{P}(\text{CH}_2\text{OH})_4][\text{Cl}]$ , their potential as ligands and as building blocks in phosphine synthesis

remains little explored [6]. More recently, the analogous tertiary phosphine  $(\text{FcCH}_2)_3\text{P}$  (**4**) was prepared in a mixture and isolated in 1.5% yield after separation from **2** and **3**; no metal complexes of this potentially useful ligand have yet been reported [4d]. In order to explore structure-property relationships as a basis for further applications of the  $\text{FcCH}_2$  group in phosphine chemistry, we report here synthetic and structural studies of ferrocenylmethylphosphines, their borane adducts, and related derivatives.

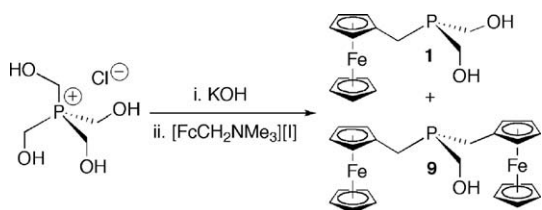
### 2. Results and discussion

#### 2.1. Synthesis of ferrocenylmethylphosphines and some derivatives

As reported previously, treatment of  $[\text{P}(\text{CH}_2\text{OH})_4][\text{Cl}]$  with  $\text{KOH}$ , followed by reaction with  $[\text{FcCH}_2\text{NMe}_3][\text{I}]$  and workup with  $\text{NEt}_3$ , yielded not only  $\text{FcCH}_2\text{P}(\text{CH}_2\text{OH})_2$  (**1**), as originally described [2], but also the over-alkylation byproduct,  $(\text{FcCH}_2)_2\text{P}(\text{CH}_2\text{OH})$  (**9**, Scheme 1) [7]. Earlier, phosphine **9** was characterized only by

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**Scheme 1.** Synthesis of ferrocenylmethyl(hydroxymethyl)phosphines [2,7].

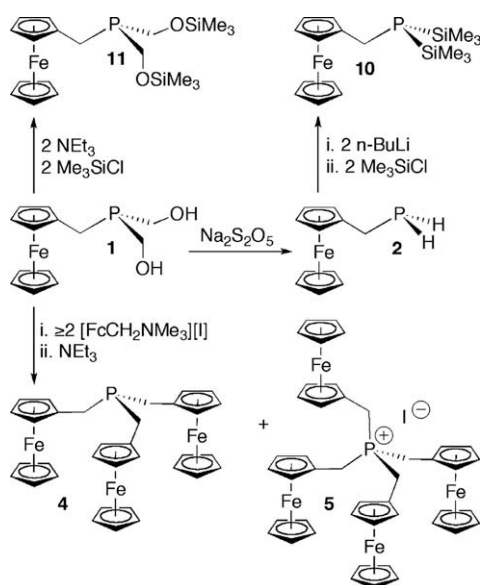
elemental analyses and mass spectroscopy; additional NMR data is given in Section 4.

The original synthesis [3] of **2** was improved by slow addition of  $\text{Na}_2\text{S}_2\text{O}_5$  to **1** (Scheme 2) [8]; the workup could also be performed more conveniently by recrystallization instead of sublimation. These changes enabled synthesis of **2** on a 2-g scale in 79% yield.

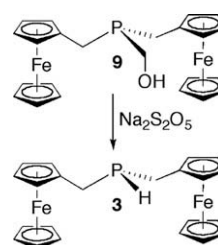
The secondary phosphine **3** was prepared earlier by deformylation of a mixture of hydroxymethylphosphines formed in the reaction of  $[\text{P}(\text{CH}_2\text{OH})_4][\text{Cl}]$  with  $\text{KOH}$  and  $[\text{FcCH}_2\text{NMe}_3][\text{I}]$ , yielding a separable mixture of **2**, **3** and the tertiary phosphine  $(\text{FcCH}_2)_3\text{P}$  (**4**, see below) [4d,8]. Phosphine **3** was more conveniently synthesized by treatment of isolated **9** with  $\text{Na}_2\text{S}_2\text{O}_5$  (Scheme 3). However, because **9** was obtained in only 8.5% yield, an efficient synthesis of **3** is not yet available (the previously reported separation gave it in 21% yield) [4d].

The original synthesis of **4** required multiple recrystallizations before the tertiary phosphine was isolated in low yield from a mixture of the other ferrocenylmethylphosphines [4d]. Instead, heating **1** with 2 equiv. of  $[\text{FcCH}_2\text{NMe}_3][\text{I}]$  in toluene/1-butanol gave a mixture of phosphonium salts. Subsequent treatment with  $\text{NEt}_3$  gave a mixture of **4** and salt **5**, whose low solubility facilitated its separation (Scheme 2). Phosphonium salt **5** could be prepared deliberately in higher yield by adjusting the stoichiometry of this reaction. Previously, **5** was synthesized from  $[\text{FcCH}_2\text{NMe}_3][\text{I}]$  and primary phosphine **2** [4d].

Two other tertiary ferrocenylmethylphosphines were prepared for comparison to **4**. Double deprotonation/silylation of **2** gave the bis(silyl)phosphine  $\text{FcCH}_2\text{P}(\text{SiMe}_3)_2$  (**10**), which underwent hydrolysis rapidly on exposure to traces of water, while a similar sequence with **1** yielded air-stable  $\text{FcCH}_2\text{P}(\text{CH}_2\text{OSiMe}_3)_2$  (**11**, Scheme 2) [9].



**Scheme 2.** Synthesis of ferrocenylmethylphosphines [3,4d,8].



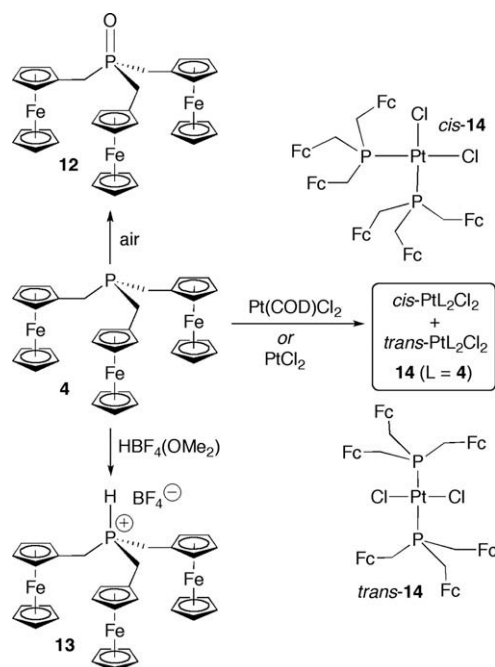
**Scheme 3.** Synthesis of bis(ferrocenylmethyl)phosphine [3,4d,8].

The reactivity of tertiary phosphine **4** was briefly surveyed (Scheme 4). In contrast to air-stable primary and secondary phosphines **2** and **3**, it slowly oxidized in air to yield phosphine oxide **12**. Protonation of **4** with  $\text{HBF}_4(\text{OMe}_2)$  gave the air-stable phosphonium salt **13**. Although it was reported that **4** did not react with some Ta, Mo, and W complexes [4d], treatment of  $\text{Pt}(\text{COD})\text{Cl}_2$  or  $\text{PtCl}_2$  with two equiv of **4** yielded the complex  $\text{Pt}(\text{P}(\text{CH}_2\text{Fc})_3)_2\text{Cl}_2$  (**14**) as a mixture of *cis* and *trans* isomers. Although we have not investigated in detail the dependence of product ratio on starting material, or the possibility of *cis*–*trans* isomerization, using  $\text{PtCl}_2$  resulted in enrichment of the *trans* isomer, which was isolated by recrystallization.

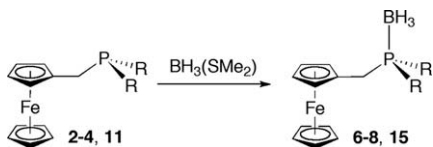
Treatment of phosphines **2**, **3**, **4**, and **11** with  $\text{BH}_3(\text{SMe}_2)$  gave the phosphine–borane adducts **6**, **7**, **8** and **15** (Scheme 5). Although the secondary and tertiary phosphine derivatives **7** and **8** were robust and could be purified by chromatography on silica gel, treatment of  $\text{FcCH}_2\text{P}(\text{H})_2(\text{BH}_3)$  (**6**) with water or attempted chromatography removed the borane to regenerate **2**.

## 2.2. X-ray crystallographic and computational studies of ferrocenylmethylphosphines and their derivatives

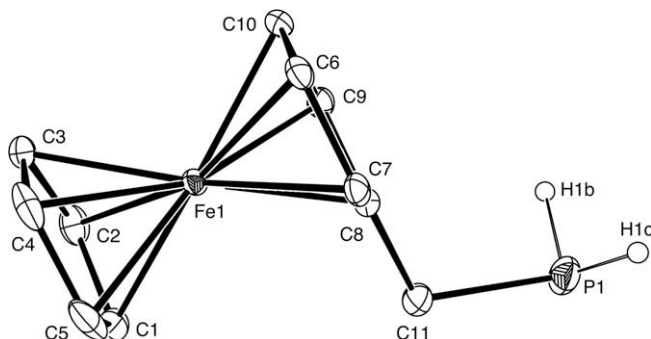
The crystal structures of phosphines **2** and **4**, phosphine–boranes **6**, **7**, and **8**, phosphine oxide **12**, and Pt complex **14** are shown in Figs. 1–7. We also determined the structures of secondary phosphine **3** and of salt **5**. While this work was in progress, the struc-



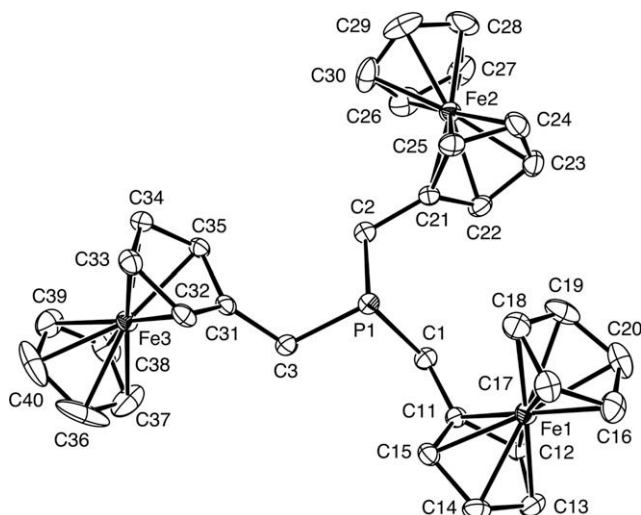
**Scheme 4.** Reactions of tertiary phosphine **4**.



**Scheme 5.** Synthesis of ferrocenylmethylphosphine(boranes) ( $\text{PR}_2 = \text{PH}_2$  (**2** and **6**),  $\text{PH}(\text{CH}_2\text{Fc})$  (**3** and **7**),  $\text{P}(\text{CH}_2\text{Fc})_2$  (**4** and **8**),  $\text{P}(\text{CH}_2\text{OSiMe}_3)_2$  (**11** and **15**)).



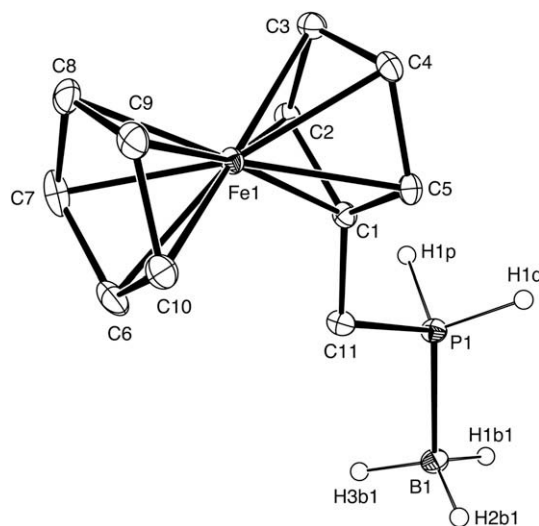
**Fig. 1.** ORTEP diagram of  $\text{FcCH}_2\text{PH}_2$  (**2**). Only the P–H hydrogen atoms are shown. Ellipsoids in this and the other figures are drawn at 30% probability.



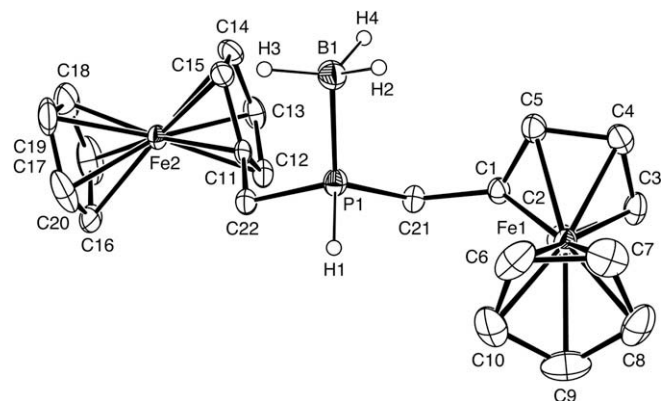
**Fig. 2.** ORTEP diagram of  $(\text{FcCH}_2)_3\text{P}$  (**4**).

tures of **3** and of the  $\text{CHCl}_3$  solvate of **5** were reported [4d]. Therefore, these structures, as well as that of phosphonium salt **13**, which was suitable only to establish its composition, are included only in Supplementary material. Crystallographic data for **2**, **4**, **6–8**, **12** and **14** is given in Table 1, and selected bond lengths and angles appear in Table 2. For additional details, see Section 4 and Supplementary material.

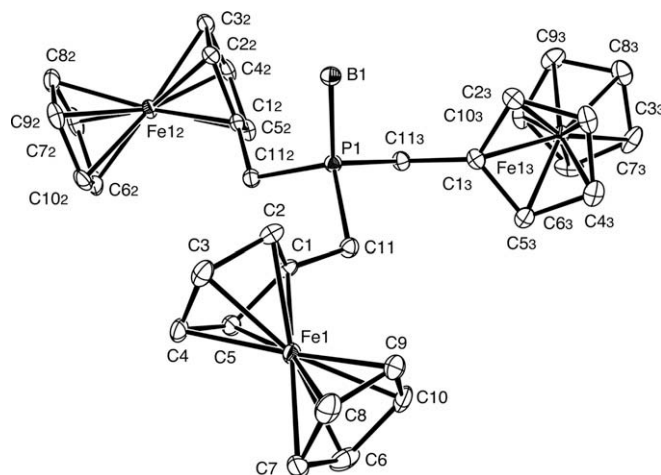
The crystal structure of primary phosphine **2** was reported previously [3]. However, the difficulty in locating hydrogens by X-ray crystallography resulted in some structural parameters which appeared unusual for a primary phosphine [10], including an anomalously large HPH angle ( $129.2(4)^\circ$ ) and unequal P–H distances of 1.23(2) and 1.12(2) Å (Table 2) [3]. Since the remarkable air-stability of **2** might be correlated with an unusual structure, we confirmed the lattice parameters in space group  $P2_1/c$  and redetermined the structure at low temperature. The results for the  $\text{FcCH}_2\text{P}$  fragment were similar, but the new structure included a reduced HPH angle ( $110(2)^\circ$ ) and equivalent P–H bond lengths of



**Fig. 3.** ORTEP diagram of  $\text{FcCH}_2\text{PH}_2(\text{BH}_3)$  (**6**). Only the PH and BH hydrogens are shown.



**Fig. 4.** ORTEP diagram of  $(\text{FcCH}_2)_2\text{PH}(\text{BH}_3)$  (**7**). Only the PH and BH hydrogens are shown. They were located and refined with the restriction that the B–H bonds be the same length.



**Fig. 5.** ORTEP diagram of  $(\text{FcCH}_2)_3\text{P}(\text{BH}_3)$  (**8**).

1.29(4) and 1.26(4) Å. However, the CPH angles of  $98.2(16)$  and  $114.5(17)^\circ$  were unexpectedly different, raising doubts about the reliability of the H atom positions, especially because HPH and

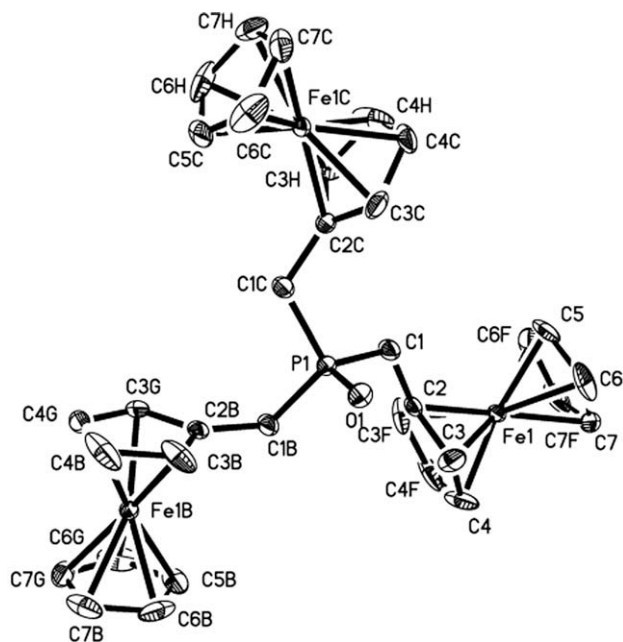


Fig. 6. ORTEP diagram of  $(\text{FcCH}_2)_3\text{P}(\text{O})$  (**12**).

CPH angles in the few structurally characterized primary phosphines were usually  $\leq 100^\circ$  [10,11].

Therefore, we investigated the structure of **2** computationally using Density Functional Theory [12]. Using the hybrid B3LYP functional and the LACV3P\*\*++ basis set gave the results shown in Table 2, with HPH ( $93.4^\circ$ ) and HPC ( $96.8^\circ$ ) angles and a P–H bond length (1.423 Å) as expected for a primary phosphine [10,11]. Moreover, the DFT calculations predicted gas-phase P–H stretching vibrations for **2** at 2289 and 2282  $\text{cm}^{-1}$ , which is consistent with experimental results ( $\nu_{\text{PH}} = 2285 \text{ cm}^{-1}$  for **2** in KBr) [3]. In contrast, single point energy calculations on both crystal structures found them to be significantly higher in energy, and vibrational calculations on these structures produced many imaginary frequencies. Therefore, we conclude that the DFT structure is more reliable than the crystal structure data, at least for the  $\text{PH}_2$  portion of **2**.

The P–H hydrogen in secondary phosphine **3** was disordered over two positions, as reported earlier [4d]. Despite this disorder,

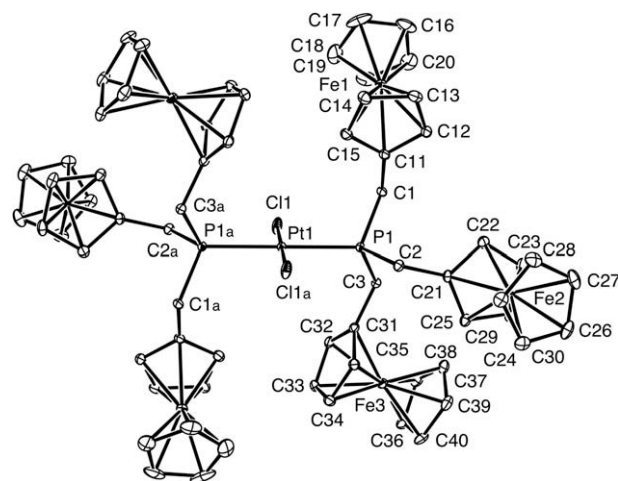


Fig. 7. ORTEP diagram of  $\text{trans-Pt}((\text{FcCH}_2)_3\text{P})_2\text{Cl}_2 \cdot 2\text{CHCl}_3$  (**14**). The solvent molecules are not shown. Selected bond lengths (Å) and angles ( $^\circ$ ): Pt–P 2.3125(12), Pt–Cl 2.3209(12), P(1)–Pt–Cl(1) 86.47(5), P(1)–Pt–Cl(1a) 93.53(5).

and in contrast to the results for **2**, the metrical data for the P–H bond were consistent with those for other secondary phosphines [10], and they were reproduced computationally (Table 2). Similarly, the structure of tertiary phosphine **4** was in good agreement with the DFT results (Table 2).

Only a few primary phosphine-boranes analogous to **6** have been structurally characterized; its geometry and bond lengths were similar to those reported earlier [13]. Although intermolecular P–H...H–B contacts were observed by X-ray crystallography in  $\text{PH}_2\text{R}(\text{BH}_3)$  (R = Ph, *p*- $\text{CF}_3\text{C}_6\text{H}_4$ , (–)-menthyl), they were absent in **6** [13]. The crystal structures of phosphine-boranes **6**, **7**, and **8** were also consistent with the computational results.

In contrast, DFT results for phosphine oxide **12** were slightly different from those obtained by crystallography (Table 2). The calculations predicted a larger CPO angle and smaller CPC angles than those observed. However, benchmark DFT calculations on the model phosphine oxides  $\text{Me}_3\text{P}(\text{O})$  and  $(\text{PhCH}_2)_3(\text{O})$  gave results similar to those for **12**. For these models, the computed CPC and CPO angles were in good agreement with the experimental X-ray crystal structures (Table 3) [14], while the calculations appear to consistently overestimate the P–C bond lengths. The crystallographic disorder observed for **12** (see Section 4 and Supplementary

Table 1  
Crystallographic data for ferrocenylmethylphosphines **2** and **4**, phosphine(boranes) **6**–**8**, phosphine oxide **12**, and Pt complex **14** · 2CHCl<sub>3</sub>.

Complex	<b>2</b>	<b>4</b>	<b>6</b>	<b>7</b>	<b>8<sup>b</sup></b>	<b>12</b>	<b>14</b> · 2CHCl <sub>3</sub>
Formula	C <sub>11</sub> H <sub>13</sub> FeP	C <sub>33</sub> H <sub>33</sub> Fe <sub>3</sub> P	C <sub>11</sub> H <sub>16</sub> BF <sub>2</sub> FeP	C <sub>22</sub> H <sub>26</sub> BF <sub>2</sub> Fe <sub>2</sub> P	C <sub>33</sub> H <sub>36</sub> BF <sub>2</sub> Fe <sub>3</sub> P	C <sub>33</sub> H <sub>33</sub> Fe <sub>3</sub> OP	C <sub>74</sub> H <sub>80</sub> Cl <sub>8</sub> Fe <sub>6</sub> P <sub>2</sub> Pt
Formula weight	232.03	628.11	245.87	443.91	641.95	644.11	1845.11
Space group	<i>P</i> 2(1)/ <i>c</i>	<i>Pbca</i>	<i>P</i> 2(1)/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>R</i> 3	<i>P</i> 6(3)/ <i>m</i>	<i>P</i> 1
<i>a</i> (Å)	13.596(3)	10.5933(7)	6.1012(8)	32.974(9)	20.391(3)	12.2228(6)	10.444(7)
<i>b</i> (Å)	7.4827(17)	20.8019(13)	18.912(2)	5.8832(15)	20.391(3)	12.2228(6)	12.417(8)
<i>c</i> (Å)	10.546(3)	24.2842(15)	9.9134(13)	24.187(6)	5.9512(19)	10.1744(10)	14.485(10)
$\alpha$ ( $^\circ$ )	90	90	90	90	90	90	70.051(9)
$\beta$ ( $^\circ$ )	107.085(4)	90	95.450(2)	124.245(4)	90	90	79.901(8)
$\gamma$ ( $^\circ$ )	90	90	90	90	120	120	81.261(8)
<i>V</i> (Å <sup>3</sup> )	1025.5(4)	5351.3(6)	1138.7(3)	3878.6(18)	2142.9(8)	1316.38(16)	1730(2)
<i>Z</i>	4	8	4	8	3	2	1
<i>D</i> (calcd) (g/cm <sup>3</sup> )	1.503	1.559	1.434	1.520	1.492	1.625	1.771
$\mu$ (MoK $\alpha$ ) (mm <sup>-1</sup> )	1.574	1.686	1.420	1.581	1.580	1.719	3.635
Temperature (K)	100(2)	100(2)	100(2)	208(2)	100(2)	120(2)	100(2)
<i>R</i> ( <i>F</i> ) (%) <sup>a</sup>	3.03	2.76	2.58	6.69	3.14	4.31	2.24
<i>Rw</i> ( <i>F</i> <sup>2</sup> ) (%) <sup>a</sup>	7.87	7.00	7.23	18.86	7.10	9.61	5.42

<sup>a</sup> Quantity minimized:  $R_w(F^2) = \sum [w(F_o^2 - F_c^2)^2] / \sum [(wF_o^2)^2]^{1/2}$ ;  $R = \sum A / \sum (F_o)$ ,  $A = |F_o - F_c|$ ,  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ ,  $P = [2F_c^2 + \text{Max}(F_o^2, 0)]/3$ . A Bruker CCD diffractometer was used in all cases.

<sup>b</sup> Absolute structure parameter = 0.03(2).

**Table 2**Selected bond lengths (Å) and angles (°) for ferrocenylmethylphosphines **2–4**, salt **5**, phosphine(boranes) **6–8**, phosphine oxide **12** and Pt complex **14** from X-ray crystallographic and computational results.

Compound (no.)	P–C	P–H	P–B	HPH	CPH	CPC	HPB	CPB	PBH
FcCH <sub>2</sub> PH <sub>2</sub> ( <b>2</b> ) <sup>a</sup>	1.850(3)	1.23(2)		129.2(4)	107.36				
		1.12(2)			109.10				
FcCH <sub>2</sub> PH <sub>2</sub> ( <b>2</b> ) <sup>b</sup>	1.861(2)	1.29(4)		110(2)	98.2(16)				
		1.26(4)			114.5(17)				
FcCH <sub>2</sub> PH <sub>2</sub> ( <b>2</b> ) <sup>c</sup>	1.889	1.423		93.39	96.81				
FcCH <sub>2</sub> PH <sub>2</sub> (BH <sub>3</sub> ) ( <b>6</b> ) <sup>b</sup>	1.8233(15)	1.29(2)	1.9230(17)	102.2(13)	104.7(9)		115.7(9)	113.01(7)	106.1(10)
		1.30(2)			104.0(9)		115.8(9)		102.6(10)
									109.1(11)
FcCH <sub>2</sub> PH <sub>2</sub> (BH <sub>3</sub> ) ( <b>6</b> ) <sup>c</sup>	1.855	1.412	1.940	99.61	102.57		116.76	116.05	104.44
(FcCH <sub>2</sub> ) <sub>2</sub> PH ( <b>3</b> ) <sup>b</sup>	1.8547(19)	1.38(6)			95(2), 97(2)	100.96(11)			
(FcCH <sub>2</sub> ) <sub>2</sub> PH ( <b>3</b> ) <sup>c</sup>	1.891	1.424			96.5	98.68			
(FcCH <sub>2</sub> ) <sub>2</sub> PH(BH <sub>3</sub> ) ( <b>7</b> ) <sup>b</sup>	1.806(6)	1.28(4)	1.916(8)		98(2)	104.5(3)	119.3(19)	116.4(3)	111(3)
	1.818(6)				104.8(19)			111.5(3)	100(5)
									103(4)
(FcCH <sub>2</sub> ) <sub>2</sub> PH(BH <sub>3</sub> ) ( <b>7</b> ) <sup>c</sup>	1.860	1.413	1.935		102.16	103.41	116.94	115.09	104.85
(FcCH <sub>2</sub> ) <sub>3</sub> P ( <b>4</b> ) <sup>b</sup>	1.853(3)					99.43(14)			
	1.864(3)					98.48(14)			
	1.868(3)					99.36(13)			
(FcCH <sub>2</sub> ) <sub>3</sub> P ( <b>4</b> ) <sup>c</sup>	1.886					98.93			
(FcCH <sub>2</sub> ) <sub>3</sub> P(BH <sub>3</sub> ) ( <b>8</b> ) <sup>b</sup>	1.817(3)		1.897(6)			105.80(12)		112.93(11)	117(2)
(FcCH <sub>2</sub> ) <sub>3</sub> P(BH <sub>3</sub> ) ( <b>8</b> ) <sup>c</sup>	1.859		1.937			103.67		114.78	105.30
[(FcCH <sub>2</sub> ) <sub>4</sub> P][I] ( <b>5</b> ) <sup>b</sup>	1.812(4) <sup>d</sup>					109.45(18) <sup>d</sup>			
(FcCH <sub>2</sub> ) <sub>3</sub> P(O) ( <b>12</b> ) <sup>b</sup>	1.767(5)		1.500(8) <sup>e</sup>			109.82(11)		109.12(11) <sup>e</sup>	
(FcCH <sub>2</sub> ) <sub>3</sub> P(O) ( <b>12</b> ) <sup>c</sup>	1.851		1.502 <sup>e</sup>			105.13		113.53 <sup>e</sup>	
<i>trans</i> -Pt((FcCH <sub>2</sub> ) <sub>3</sub> P) <sub>2</sub> Cl <sub>2</sub> · 2CHCl <sub>3</sub> ( <b>14</b> )	1.836(3)					100.95(13)		112.79(9) <sup>f</sup>	
	1.844(3)					105.91(13)		112.63(10)	
	1.849(3)					105.61(13)		117.39(10)	

<sup>a</sup> X-ray crystallographic structural data from Ref. [3].<sup>b</sup> X-ray crystallographic structural data, this work.<sup>c</sup> Computational results (average values), this work.<sup>d</sup> Average value.<sup>e</sup> P–O bond length; CPO bond angle.<sup>f</sup> CPPT bond angles.**Table 3**

Selected bond distances (Å) and angles (°) in tertiary phosphine oxides: comparison of X-ray crystallographic and DFT results.

Compound (no.)	P–C	P–O	CPC	CPO
(FcCH <sub>2</sub> ) <sub>3</sub> P(O) ( <b>12</b> ) <sup>a</sup>	1.767(5)	1.500(8)	109.82(11)	109.12(11)
(FcCH <sub>2</sub> ) <sub>3</sub> P(O) ( <b>12</b> ) <sup>b</sup>	1.851	1.502	105.13	113.53
Me <sub>3</sub> P(O) <sup>c</sup>	1.772(6)	1.489(6)	105.6(3)	112.2(2)
	1.770(10)		106.2(3)	114.0(4)
Me <sub>3</sub> P(O) <sup>b</sup>	1.830	1.500	104.9	113.7
(PhCH <sub>2</sub> ) <sub>3</sub> P(O) <sup>d</sup>	1.823(3)	1.488(4)	103.8 <sup>e</sup>	114.7(1)
(PhCH <sub>2</sub> ) <sub>3</sub> P(O) <sup>b</sup>	1.851	1.503	105.0	113.6

<sup>a</sup> X-ray crystallographic results, this work.<sup>b</sup> Computational results (average values), this work.<sup>c</sup> See Ref. [14a].<sup>d</sup> See Ref. [14b].<sup>e</sup> No esd was reported.

material) may make the structure less reliable than the DFT results, or the bond angles in **12** may differ from those in the model compounds as a result of steric effects involving intramolecular interactions of the FcCH<sub>2</sub> groups, or crystal packing forces.

The crystal structure and the  $J_{Pt-P}$  coupling constant of Pt complex **14** were similar to those of the related complexes *trans*-PtL<sub>2</sub>Cl<sub>2</sub> (L = P(CH<sub>2</sub>Ph)<sub>3</sub>, PEt<sub>3</sub>, P(*i*-Pr)<sub>3</sub>) [15], suggesting that tertiary phosphine **4** is sterically and electronically similar to these ligands. To provide more quantitative information on the properties of **4** as a ligand, its solid cone angle in **14** was found to be 139°, with the Pt–P bond length normalized to 2.28 Å [16]. In comparison to related phosphines whose solid cone angles were calculated by the same method, ligand **4** was bulkier than PPh<sub>3</sub> (128°), but not as large as P(*t*-Bu)<sub>3</sub> (157°) [17].

### 2.3. Structure and bonding in ferrocenylmethylphosphines and their derivatives

Trends in the structural effects of phosphorus substituents and of quaternization at P are evident from the data in Table 2. As expected, systematically replacing H with bulkier FcCH<sub>2</sub> groups at the phosphorus center led to increased angles at P. However, this substitution did not result in significant changes in P–C or P–B bond lengths. On quaternization by borane complexation, oxidation, formation of phosphonium salts, or complexation to Pt, the P–C bond lengths shortened and the angles at phosphorus increased. These observations are consistent with a change in hybridization at P on quaternization from approximately unhybridized (s + 3p) to sp<sup>3</sup>; the decreased P–C bond lengths can then be rationalized as a result of increased P–C s-character [18].

The DFT studies are in agreement with this qualitative explanation. Natural bond orbital (NBO) analyses provided the data shown in Table 4. The phosphorus orbitals used to form the P–H and P–C bonds in phosphines **2**, **3**, and **4** have mostly p-character, while the lone pair has greater s-character. In the borane adducts **6–8** and phosphine oxide **12**, the s-character of the P orbitals involved in P–H and P–C bonding increased, while that of the P–B and P–O bonds is reduced, in comparison to the lone pair in the phosphine precursors.

The nature of the P–H and P–C bonds in the phosphines before and after complexation can also be probed by IR and NMR spectroscopy (Table 5) [19]. On adduct formation, both  $^1J_{PH}$  and  $^1J_{PC}$  couplings increased dramatically, while the stretching frequency  $\nu_{PH}$  also increased. Similar trends have been observed previously and ascribed to the hybridization changes discussed above [18].

Very similar structural [20] and spectroscopic [21] results have been observed for the analogous primary, secondary, and tertiary

**Table 4**  
NBO analyses of hybridization in ferrocenylmethylphosphines and derivatives.

Compound (no.)	Phosphorus orbital composition			
	P–H	P–C	P–B <sup>a</sup>	Lone Pair
FcCH <sub>2</sub> PH <sub>2</sub> ( <b>2</b> )	sp <sup>5.98</sup>	sp <sup>5.18</sup>		sp <sup>0.80</sup>
FcCH <sub>2</sub> PH <sub>2</sub> (BH <sub>3</sub> ) ( <b>6</b> )	sp <sup>4.09</sup>	sp <sup>3.33</sup>	sp <sup>1.62</sup>	
(FcCH <sub>2</sub> ) <sub>2</sub> PH ( <b>3</b> )	sp <sup>6.31</sup>	sp <sup>5.60</sup>		sp <sup>0.76</sup>
(FcCH <sub>2</sub> ) <sub>2</sub> PH(BH <sub>3</sub> ) ( <b>7</b> )	sp <sup>4.12</sup>	sp <sup>3.56</sup>	sp <sup>1.69</sup>	
(FcCH <sub>2</sub> ) <sub>3</sub> P ( <b>4</b> )		sp <sup>5.67</sup>		sp <sup>0.79</sup>
(FcCH <sub>2</sub> ) <sub>3</sub> P(BH <sub>3</sub> ) ( <b>8</b> )		sp <sup>3.63</sup>	sp <sup>1.80</sup>	
(FcCH <sub>2</sub> ) <sub>3</sub> P(O) ( <b>12</b> )		sp <sup>3.12</sup>	sp <sup>2.48</sup>	

<sup>a</sup> P–O for **12**.

**Table 5**  
Selected NMR and IR spectroscopic data for ferrocenylmethylphosphines and some derivatives.<sup>a</sup>

Compound	$\nu(\text{PH})$	$J_{\text{PH}}$	$J_{\text{PC}}(\text{CH}_2)$
FcCH <sub>2</sub> PH <sub>2</sub> ( <b>2</b> ) <sup>b</sup>	2285	192	9
FcCH <sub>2</sub> PH <sub>2</sub> (BH <sub>3</sub> ) ( <b>6</b> )	2408 2398	357	33
(FcCH <sub>2</sub> ) <sub>2</sub> PH ( <b>3</b> )	2286	193	14
(FcCH <sub>2</sub> ) <sub>2</sub> PH(BH <sub>3</sub> ) ( <b>7</b> )	2355	352	30
(FcCH <sub>2</sub> ) <sub>3</sub> P ( <b>4</b> )			18
[(FcCH <sub>2</sub> ) <sub>4</sub> P][I] ( <b>5</b> )			40
(FcCH <sub>2</sub> ) <sub>3</sub> P(BH <sub>3</sub> ) ( <b>8</b> )			28
(FcCH <sub>2</sub> ) <sub>3</sub> P(O) ( <b>12</b> )			60
[(FcCH <sub>2</sub> ) <sub>3</sub> PH][BF <sub>4</sub> ] ( <b>13</b> )	<sup>c</sup>	486	39

<sup>a</sup> Coupling constants in Hz. IR data in cm<sup>-1</sup>, for KBr pellets. Solvents for NMR data: CDCl<sub>3</sub> for **2**, **4**, **5**, **8**, **12**, **13**, C<sub>6</sub>D<sub>6</sub> for **3**, **6**, **7**.

<sup>b</sup> Data for **2** is from Ref. [3].

<sup>c</sup> Not observed.

methylphosphines and their borane adducts. For example, on conversion of PH<sub>2</sub>Me to PH<sub>2</sub>Me(BH<sub>3</sub>),  $J_{\text{PH}}$  doubled from 186 to 375 Hz and  $\nu(\text{PH})$  increased from 2309 and 2305 cm<sup>-1</sup> to 2422 and 2404 cm<sup>-1</sup>, while the P–C bond shortened from 1.863 to 1.809(6) Å, and the HPH angle increased from 93.23 to 99.4(4)°. Similarly, the structures of tertiary phosphine-boranes PMe<sub>3</sub>(BH<sub>3</sub>) and (FcCH<sub>2</sub>)<sub>3</sub>P(BH<sub>3</sub>) include identical P–B and P–C distances (1.901(7) vs. 1.897(6) Å; 1.819(10) vs. 1.817(3) Å, respectively) and CPC angles (105.0(4) vs. 105.80(12)°). From these and related observations, methyl- and ferrocenylmethylphosphines and their borane adducts appear to have similar properties.

### 3. Conclusions

Spectroscopic and structural studies of ferrocenylmethylphosphines and their borane adducts suggest that this substituent gives rise to normal pyramidal phosphines and approximately tetrahedral phosphine-boranes which are similar to the analogous methylphosphines. The anomalous air-stability of the primary and secondary phosphines **2** and **3** remains unexplained, especially in comparison to tertiary phosphine **4**, which is moderately air-sensitive in solution [22]. Although an earlier study reported that **4** did not react with some early transition metal complexes [4d], and octahedral complexes have not yet been obtained, it readily formed square planar Pt(P(CH<sub>2</sub>Fc)<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (**14**) as a mixture of *cis* and *trans* isomers. The solid cone angle of **4** in *trans*-**14**, determined crystallographically, is in between those of PPh<sub>3</sub> and P(*t*-Bu)<sub>3</sub>, so **4** may be useful as a medium-sized trialkylphosphine ligand. Similarly, primary and secondary phosphines **2** and **3** are attractive precursors to polydentate phosphines, and their borane adducts **6** and **7** are potential substrates for dehydrocoupling to yield phosphino-borane polymers [23]. We are currently investigating these possibilities.

### 4. Experimental

Unless otherwise noted, all reactions and manipulations were performed in dry glassware under a nitrogen atmosphere at 20 °C in a dry box or using standard Schlenk techniques. Petroleum ether (bp 38–53 °C), ether, THF, toluene, and CH<sub>2</sub>Cl<sub>2</sub> were dried using columns of activated alumina [24]. NMR spectra were recorded using Varian 300 or 500 MHz spectrometers. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are reported vs. Me<sub>4</sub>Si and were determined by reference to the residual <sup>1</sup>H and <sup>13</sup>C solvent peaks. <sup>31</sup>P NMR chemical shifts are reported vs. H<sub>3</sub>PO<sub>4</sub> (85%) used as an external reference. Coupling constants are reported in Hz as absolute values. Unless indicated, peaks in NMR spectra are singlets. IR spectra were recorded on KBr disks and are reported in cm<sup>-1</sup>. Elemental analyses were provided by Quantitative Technologies Inc. Mass spectra were recorded at the University of Illinois Urbana-Champaign. Reagents were from commercial suppliers, except for K[B(Ar<sub>F</sub>)<sub>4</sub>] (Ar<sub>F</sub> = 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) [25] and Pt(COD)Cl<sub>2</sub> [26], which were prepared by literature methods.

#### 4.1. Synthesis and separation of (FcCH<sub>2</sub>)P(CH<sub>2</sub>OH)<sub>2</sub> (**1**) and (FcCH<sub>2</sub>)<sub>2</sub>P(CH<sub>2</sub>OH) (**9**) [2,7]

A solution of [FcCH<sub>2</sub>NMe<sub>3</sub>][I] (40.00 g, 103.9 mmol) in 250 mL of degassed methanol was heated to reflux under N<sub>2</sub> at 65 °C. In a separate Schlenk flask, to 4.67 equiv. of [P(CH<sub>2</sub>OH)<sub>4</sub>][Cl] (115.62 g of 80% w/w solution in water, 486 mmol) under N<sub>2</sub>, 150 mL of degassed methanol and KOH pellets (25.56 g, 456 mmol) were then added. The slurry was stirred for 1 h under N<sub>2</sub>, vented with a needle. This solution was then added slowly to the refluxing solution of [FcCH<sub>2</sub>NMe<sub>3</sub>][I] via cannula. This mixture was refluxed under N<sub>2</sub> for 72 h to give a mixture of yellow solution and white precipitate. The solvent was removed under vacuum and the residue was stirred for 1 h in a biphasic mixture of 250 mL of ether, 100 mL of water, and 80 mL of NEt<sub>3</sub>. The organic layer was then separated and washed 3 times with water in a separatory funnel, then collected and dried over anhydrous MgSO<sub>4</sub>. After filtration over a frit to remove the magnesium sulfate and any residual solid, the solvent was removed under vacuum.

This crude product was recrystallized from hot toluene and then hot 50/50 methanol/methylene chloride layered with petroleum ether to yield yellow crystals of pure compound **1**. Repeating the two recrystallizations on the combined mother liquors gave a second crop, total yield = 21.5 g, 70%. The mother liquor was concentrated under vacuum to give a solid, which contained mostly compound **9**. This solid was recrystallized overnight at 10 °C from hot 50/50 methanol/methylene chloride layered with petroleum ether to yield yellow crystals of pure **9**; repeating this procedure on the mother liquor gave a second crop, total yield = 2.02 g, 8.5% based on [FcCH<sub>2</sub>NMe<sub>3</sub>][I].

Data for (FcCH<sub>2</sub>)<sub>2</sub>P(CH<sub>2</sub>OH) (**9**): Anal. Calc. for C<sub>23</sub>H<sub>25</sub>PFe<sub>2</sub>O: C, 60.04; H, 5.48. Found: C, 60.01; H, 5.54%. HRMS calcd for C<sub>23</sub>H<sub>26</sub>PFe<sub>2</sub>O [(MH)<sup>+</sup>]: *m/z* 461.0420. Found: *m/z* 461.0422. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  -16.7. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  4.15–4.10 (m, 18H, Cp), 3.81 (dd,  $J_{\text{H-OH}} = 2$ ,  $J_{\text{PH}} = 6$ , 2H, CH<sub>2</sub>OH), 2.69–2.59 (AB pattern,  $\delta_{\text{A}} = 2.67$ ,  $\delta_{\text{B}} = 2.61$ ,  $J_{\text{AB}} = 14$ ,  $J_{\text{PH(B)}} = 3.5$ , 4H, CH<sub>2</sub>). The hydroxyl proton signal was not observed. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  84.5 (d,  $J = 10$ , quat Cp), [27] 69.1 (Cp), 69.0 (d,  $J = 3$ , Cp), 68.9 (d,  $J = 3$ , Cp), 68.0 (Cp), 67.9 (Cp), 60.5 (d,  $J = 20$ , CH<sub>2</sub>OH), 24.8 (d,  $J = 16$ , CH<sub>2</sub>).

#### 4.2. FcCH<sub>2</sub>PH<sub>2</sub> (**2**)

This procedure is a modification of the ones in Refs. [3,8]; spectroscopic data for the product matched literature values. A solution

of  $\text{Na}_2\text{S}_2\text{O}_5$  (1.30 g, 0.0068 mol) in 10 mL of water was added dropwise over a period of 2 h to a stirred, refluxing mixture (100 °C oil bath) of 30 mL of heptane, 20 mL of water, and  $\text{FcCH}_2\text{P}(\text{CH}_2\text{OH})_2$  (2 g, 0.0068 mol). The mixture was stirred rapidly throughout the addition; refluxing and stirring was continued for an additional hour. The solution was then allowed to cool to room temperature for approximately one hour. The aqueous layer was separated and extracted with 10 mL of petroleum ether. The combined organic layers were washed three times with 10 mL of water, and dried with  $\text{MgSO}_4$ . The solvent was removed under vacuum. The remaining red oil was dissolved in a minimal amount of warm petroleum ether (<2 mL) in a warm water bath. The solution was then placed in the refrigerator leading to the formation of dark orange crystals (1.25 g, 0.0054 mol, 79%).

#### 4.3. $\text{FcCH}_2\text{PD}_2$ (**2-D**)

A solution of 50 mg (0.22 mmol) of  $\text{FcCH}_2\text{PH}_2$  in 1.0 mL of  $\text{C}_6\text{D}_6$  was treated with 5 drops of  $\text{D}_2\text{O}$  and a catalytic amount of  $\text{Me}_3\text{SiCl}$  (5 mol%, 0.011 mmol, 1.5  $\mu\text{L}$ ). The NMR tube was shaken for approximately 15 min yielding a mixture of  $\text{FcCH}_2\text{PHD}$  and  $\text{FcCH}_2\text{PD}_2$ .  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  -130.5 (1:1:1 3-line pattern,  $J = 29$ ,  $\text{FcCH}_2\text{PHD}$ , 15%), -131.8 (5-line pattern,  $J = 30$ ,  $\text{FcCH}_2\text{PD}_2$ , 85%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): No  $\text{PH}_2$  signals detected. IR (Nujol): the PH stretch was not observed, but the expected PD stretch could not be identified.

#### 4.4. $(\text{FcCH}_2)_2\text{PH}$ (**3**) [4d]

A solution of  $(\text{FcCH}_2)_2\text{P}(\text{CH}_2\text{OH})$  (**9**, 500 mg, 1.08 mmol) in 25 mL of toluene was heated to 65 °C under a nitrogen atmosphere. A solution of  $\text{Na}_2\text{S}_2\text{O}_5$  (3 g, 15.8 mmol) in 15 mL of degassed water was added to the stirring toluene solution, which was refluxed overnight. The reaction mixture was then separated and the organic layer was washed 3 times in a separatory funnel. The organic layer was then dried over magnesium sulfate and filtered through a 2-inch silica plug on a frit. The resultant solution was reduced to a solid under vacuum and then recrystallized from minimal hot hexanes to yield small orange crystals of pure bis(ferrocenylmethyl)phosphine (250 mg, 0.648 mmol, 60%). Recrystallization from hot acetonitrile gave larger and more regular crystals. Spectroscopic and analytical data were consistent with the literature [4d].

#### 4.5. $(\text{FcCH}_2)_2\text{PD}$ (**3-D**)

A solution of 10 mg (0.023 mmol) of  $(\text{FcCH}_2)_2\text{PH}$  in 1.0 mL of  $\text{C}_6\text{D}_6$  was treated with 5 drops of  $\text{D}_2\text{O}$  and a catalytic amount of  $\text{Me}_3\text{SiCl}$  (5 mol%, 0.0012 mmol, 0.25  $\mu\text{L}$ ). The solution initially showed only partial deuterium exchange, but standing overnight resulted in almost full conversion.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  -54.0 (1:1:1 3-line pattern,  $J = 30$ ,  $(\text{FcCH}_2)_2\text{PD}$ , >95%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): No PH signals detected. IR (KBr): no PH stretch at 2286  $\text{cm}^{-1}$ . The expected PD stretch could not be identified.

#### 4.6. $(\text{FcCH}_2)_3\text{P}$ (**4**)

Under nitrogen,  $\text{FcCH}_2\text{P}(\text{CH}_2\text{OH})_2$  (**1**, 500 mg, 1.71 mmol) and 2.1 equiv. (1.40 g, 3.64 mmol) of  $[\text{FcCH}_2\text{NMe}_3][\text{I}]$  were dissolved in 25 mL of a degassed 50:50 mixture of toluene and *n*-butanol. The solution was stirred rapidly and refluxed for 14 h (oil bath temperature 100 °C); the solution became homogeneous as it reached its refluxing temperature. At the completion of the reflux, the solution was cloudy with some precipitate. A portion of the still hot solution (soluble layer) was analyzed by  $^{31}\text{P}$  NMR spectroscopy, which revealed the presence of three peaks in a ratio of 6:39:5, including  $\delta$  23.8, tentatively assigned to  $[(\text{FcCH}_2)_2\text{P}(\text{CH}_2\text{OH})_2][\text{I}]$ ,  $\delta$  21.4, tentatively assigned to  $[(\text{FcCH}_2)_3\text{P}(\text{CH}_2\text{OH})][\text{I}]$ , and  $\delta$  18.7, corresponding to the tetrakis salt  $[(\text{FcCH}_2)_4\text{P}][\text{I}]$ . The chemical shifts for these compounds in  $\text{CDCl}_3$  have been previously reported as  $\delta$  24.7, 20.6, and 17.6, respectively [4d]. The hot solution was treated with 10 mL of degassed  $\text{NEt}_3$ , and the reflux was continued for 75 min to facilitate deprotonation of the salts. More precipitation was observed, and a hot portion of the slurry was analyzed by  $^{31}\text{P}$  NMR spectroscopy, which revealed three peaks at  $\delta$  18.9, -17.4 (with a shoulder at -17.6), and -31.8 corresponding to the tetrakis salt, the tertiary phosphine, and an unidentified compound in a ratio of 17:71:12. The reaction mixture was allowed to cool to approximately 40 °C before the soluble layer was removed by cannula filtration and discarded. (Note: if the solution was cooled to room temperature and allowed to stand, then some of the tertiary phosphine was converted to  $[(\text{FcCH}_2)_3\text{P}(\text{CH}_2\text{OH})][\text{I}]$ .) The insoluble layer was subjected to three separate toluene extractions ( $3 \times \sim 25$  mL, 9 total). The toluene solution was then pumped down under vacuum, and the resulting crude orange solid was recrystallized from chloroform layered with petroleum ether at -30 °C to yield dark orange crystals in three crops (498 mg, 0.793 mmol, 46%). These crystals were suitable for X-ray analysis. Additional crops contained the salt  $[(\text{FcCH}_2)_3\text{P}(\text{CH}_2\text{OH})][\text{I}]$  as an impurity.

The solid remaining after the three toluene extractions, according to  $^{31}\text{P}$  NMR spectroscopy ( $\text{CHCl}_3$ ), was 91%  $[(\text{FcCH}_2)_4\text{P}][\text{I}]$  and also contained  $(\text{FcCH}_2)_3\text{P}$  and  $[(\text{FcCH}_2)_3\text{P}(\text{CH}_2\text{OH})][\text{I}]$ . The solid was washed with water to remove  $[\text{NEt}_3\text{H}][\text{I}]$ . After recrystallization of the residue from methylene chloride layered with petroleum ether at -30 °C, the salt **5** was isolated (170 mg, 0.178 mmol, 10%, see below for data). Spectroscopic data for tertiary phosphine **4** were consistent with literature values [4d].

#### 4.7. $[(\text{FcCH}_2)_4\text{P}][\text{I}]$ (**5**)

This salt was prepared previously from primary phosphine **2** and  $[\text{FcCH}_2\text{NMe}_3][\text{I}]$  [4d]. Since **2** was prepared from hydroxymethylphosphine **1**, starting with **1** was somewhat more convenient.  $\text{FcCH}_2\text{P}(\text{CH}_2\text{OH})_2$  (**1**, 0.50 g, 1.7 mmol) and 2 equiv. of  $[\text{FcCH}_2\text{NMe}_3][\text{I}]$  (1.32 g, 3.42 mmol) were dissolved in a mixture of 100 mL of *n*-butanol, 2 mL of  $\text{NEt}_3$ , and 5 mL of methanol. The solution was brought to reflux under nitrogen at 100 °C (oil bath temperature). The reaction was monitored by  $^{31}\text{P}$  NMR spectroscopy. After six hours, several peaks were observed:  $\delta$  20.8, 17.8, -18.2, -18.4, and -21.2 in a ratio of 4:1:2:8:8. After 24 h, the following singlets were observed:  $\delta$  23.3 ( $[(\text{FcCH}_2)_2\text{P}(\text{CH}_2\text{OH})_2][\text{I}]$ , tentative assignment), 20.7 ( $[(\text{FcCH}_2)_3\text{P}(\text{CH}_2\text{OH})][\text{I}]$ , tentative assignment), 17.8 ( $[(\text{FcCH}_2)_4\text{P}][\text{I}]$ ), -18.4 ( $(\text{FcCH}_2)_3\text{P}$ ), -21.2 ( $(\text{FcCH}_2)_2\text{P}(\text{CH}_2\text{OH})_2$ ), -55.0 ( $(\text{FcCH}_2)\text{PH}$ ) in a ratio of 1:10:5:10:10:2 [4d]. After 30 h, little change was observed, so 2 mL of  $\text{NEt}_3$  was added. After 48 h, the same peaks were observed. The ratio was now 1:4:2:8:7 with disappearance of the secondary phosphine. Additional  $[\text{FcCH}_2\text{NMe}_3][\text{I}]$  (1.32 g, 3.42 mmol, 2 equiv.), plus 2 mL of  $\text{NEt}_3$ , 50 mL of BuOH, and 5 mL of MeOH were added, and reflux was continued for another 24 h, until the peak due to  $\text{FcCH}_2\text{P}(\text{CH}_2\text{OH})_2$  was no longer observed. The major species in solution was the salt  $[(\text{FcCH}_2)_4\text{P}][\text{I}]$ . The mixture was filtered to give a flakey yellow-orange solid (1.10 g, 1.15 mmol, 67%). Recrystallization from  $\text{CH}_2\text{Cl}_2$ /petroleum ether gave analytically pure crystals, while recrystallization from  $\text{CH}_2\text{Cl}_2$ /ether yielded crystals suitable for X-ray crystallography.

$^{31}\text{P}$  and  $^{13}\text{C}$  NMR data were consistent with the literature; elemental analyses and high-resolution mass spectra were not reported earlier [4d]. Anal. Calc. for  $\text{C}_{44}\text{H}_{44}\text{PFe}_4$ : C, 55.39; H, 4.65. Found: C, 55.26; H, 4.55%. HRMS:  $m/z$  calcd for  $\text{C}_{44}\text{H}_{44}\text{PFe}_4$ : 827.0579. Found:  $m/z$  827.0580.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  4.22 (br m, 8H), 4.19 (br m, 8H), 4.18 (20H), 3.48 (d,  $J = 12$ , 8H,  $\text{CH}_2$ ). Note:

the recently reported  $^1\text{H}$  NMR spectrum of this compound [4d] is mostly consistent with these results, but it also included an extra peak at 2.83 (d,  $J_{\text{PH}} = 4.9$  Hz,  $\text{CH}_2$ ), which we did not observe. Our assignment was consistent with a  $^{13}\text{C}$ - $^1\text{H}$  correlation spectrum. Note, however, that the  $\text{CH}_2$   $^1\text{H}$  NMR signal in the  $[\text{B}(\text{Ar}_F)_4]$  salt described below was observed at  $\delta$  2.88.

#### 4.8. Ion exchange: synthesis of $[(\text{FcCH}_2)_4\text{P}][\text{B}(\text{Ar}_F)_4]$

The iodide salt **5** was soluble only in chlorinated solvents. We prepared the  $[\text{B}(\text{Ar}_F)_4]$  salt, which dissolved in THF, by ion exchange. To a solution of iodide salt **5** (500 mg, 0.524 mmol) in 100 mL of methylene chloride, in a separatory funnel, was added a slurry of  $[\text{K}][\text{B}(\text{Ar}_F)_4]$  ( $\text{Ar} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$ , 473 mg, 0.524 mmol) in 100 mL of water. The funnel was shaken to allow the layers to mix. They became cloudy, and the organic layer was separated, washed with water ( $3 \times 100$  mL), and then dried with  $\text{MgSO}_4$ . The solution was filtered on a frit to remove the salt and any other insoluble material. The remaining solution was pumped down to give a crude orange oily solid (794 mg, 0.470 mmol, 90%).

$^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  18.5.  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -62.5.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.75 (8H, Ar), 7.55 (4H, Ar), 4.30 (8H, Fc), 4.10 (20H, Fc), 4.02 (8H, Fc), 2.88 (d,  $J = 11$ , 8H,  $\text{CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  162.0 (q,  $J = 50$ ), 135.1, 129.2 (q with fine structure,  $J = 30$ ), 124.9 (q,  $J = 273$ ), 117.8, 72.6 (quat Cp) [27], 70.3 (Cp), 70.0 (Cp), 69.4 (Cp), 21.8 (d,  $J = 38$ ,  $\text{CH}_2$ ).

#### 4.9. $\text{FcCH}_2\text{PH}_2(\text{BH}_3)$ (**6**)

A solution of ferrocenylmethylphosphine (**2**, 500 mg, 2.15 mmol) in 20 mL of dry petroleum ether under  $\text{N}_2$  was cooled to  $-78$  °C.  $\text{BH}_3(\text{SMe}_2)$  (2 M in THF, 1.5 mL, 3 mmol, 1.4 equiv.) was then added via syringe. A bright yellow precipitate formed immediately. It was collected by filtration in air and washed with cold petroleum ether. This material was dissolved in  $\text{CH}_2\text{Cl}_2$  and stirred in air for 15 min. The solution was filtered on a frit to remove any insoluble boron-containing impurities. The solvent was then removed under vacuum and the residue was recrystallized overnight by diffusion of hexanes vapors into a concentrated THF solution to give large orange-brown crystals (350 mg, 66% yield).

Anal. Calc. for  $\text{C}_{11}\text{H}_{16}\text{BPFe}$ : C, 53.73; H, 6.56. Found: C, 53.78; H, 6.50%. HRMS calcd for  $\text{C}_{11}\text{H}_{16}\text{BPFe}$ :  $m/z$  246.0432. Found:  $m/z$  246.0418.  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  -40.5 (broad td,  $J_{\text{P-B}} = 43$ ,  $J_{\text{PH}} = 357$ ).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  3.82 (5H, Cp), 3.80 (d of sextets,  $J_{\text{PH}} = 357$ ,  $J_{\text{HH}} = 6.5$ , 7.2, 2H,  $\text{PH}_2$ ), 3.79 (t,  $J = 2$ , 2H, Cp), 3.63 (t,  $J = 2$ , 2H, Cp), 2.15 (dt,  $J_{\text{HH}} = 6.5$ ,  $J_{\text{PH}} = 8$ , 2H,  $\text{CH}_2$ ), 1.73-1.14 (broad q,  $J = 105$ , 3H,  $\text{BH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  82.0 (d,  $J = 6$ , quat Cp), 69.1 (Cp), 68.2 (d,  $J = 3$ , Cp), 68.2 (Cp), 18.8 (d,  $J = 33$ ,  $\text{CH}_2$ ). IR: 2408, 2398, 2380, 2340, 2245, 1130, 1052, 1000, 928, 900, 837, 823, 782, 728, 647. Similarly, treatment of **2-D**<sub>2</sub> with  $\text{BH}_3\text{-SMe}_2$  gave **6-D**<sub>2</sub>, but NMR spectroscopy suggested that H-D exchange had occurred and this material contained only about 50% D in the  $\text{PH}_2$  position. Therefore, definitive assignments of the P-H and B-H stretches from the IR spectrum of this material were not possible.

#### 4.10. $(\text{FcCH}_2)_2\text{PH}(\text{BH}_3)$ (**7**)

To a solution of bis(ferrocenylmethyl)phosphine (**3**, 86 mg, 0.2 mmol) in 10 mL of dry THF under  $\text{N}_2$  was added  $\text{BH}_3(\text{SMe}_2)$  (2 M in THF, 0.2 mL, 0.4 mmol, 2 equiv.) and the solution was stirred for 20 min. The solvent was removed under vacuum and the residue was redissolved in methylene chloride. This solution was filtered through a silica plug, the filtrate was concentrated under vacuum, and the residue was recrystallized by diffusion of petro-

leum ether vapors into a concentrated THF solution to yield small orange needle-like crystals (60 mg, 67%).

Anal. Calc. for  $\text{C}_{22}\text{H}_{26}\text{PBFe}_2$ : C, 59.52; H, 5.90. Found: C, 59.20; H, 5.70%. HRMS calcd for  $\text{C}_{22}\text{H}_{26}\text{PBFe}_2$ :  $m/z$  444.0564. Found:  $m/z$  444.0564.  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.4 (broad d,  $J = 352$ ).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  4.38 (d of apparent sextets,  $J_{\text{PH}} = 352$ ,  $J_{\text{HH}} = 7.5$ , 9.5, 1H, PH), 3.91 (m, 2H, Cp), 3.85 (m, 4H, Cp), 3.85 (10H, Cp, overlapping previous peak), 3.83 (m, 2H, Cp), 2.47-2.38 (apparent  $\text{A}_2\text{B}_2\text{MX}$  pattern,  $\delta_{\text{A}} = 2.59$ ,  $\delta_{\text{B}} = 2.49$ ,  $J_{\text{AB}} = 15$ ,  $J_{\text{PH(A)}} = 7.5$ ,  $J_{\text{PH(B)}} = 9.5$ ,  $J_{\text{P(H)-H(A)}} = 5$ ,  $J_{\text{P(H)-H(B)}} = 6$ , 4H,  $\text{PCH}_2\text{Cp}$ ), 2.0-1.2 (br q,  $J = 57$ ,  $\text{BH}_3$ ) [28].  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  86.7 (d,  $J = 7$ , quat Cp), 69.3 (d,  $J = 2$ , Cp), 69.2 (Cp), 68.9 (d,  $J = 2$ , Cp), 68.3 (Cp), 68.2 (Cp), 22.4 (d,  $J = 30$ ,  $\text{CH}_2$ ). IR: 2384 (broad), 2355 (shoulder), 1122, 1081, 1045, 1020, 950, 918, 834, 500.

#### 4.11. $(\text{FcCH}_2)_3\text{P}(\text{BH}_3)$ (**8**)

To a solution of phosphine **4** (90 mg, 0.14 mmol) in toluene (50 mL) was added 1.75 equiv. of  $\text{BH}_3(\text{SMe}_2)$  (125  $\mu\text{L}$ , 2 M, 0.25 mmol) via syringe. After 2 h of stirring, the solvent was removed under vacuum to yield a crude yellow solid ( $^{31}\text{P}$  NMR ( $\text{CH}_2\text{Cl}_2$ ):  $\delta$  18.2 (broad)). Recrystallization from warm methylene chloride layered with petroleum ether at  $-20$  °C gave two crops of yellow needle-like crystals (78 mg, 76%). Large yellow crystals for X-ray crystallography were grown by vapor diffusion of petroleum ether into a  $\text{CH}_2\text{Cl}_2$  solution.

Anal. Calc. for  $\text{C}_{33}\text{H}_{36}\text{PBFe}_3$ : C, 61.74; H, 5.65. Found: C, 61.49; H, 5.60%. HRMS calcd for  $\text{C}_{33}\text{H}_{36}\text{PBFe}_3$ :  $m/z$  642.0696. Found:  $m/z$  642.0688.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  18.2 (broad).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  4.17 (d,  $J = 2$ , 6H, Cp), 4.15 (6H, Cp), 4.09 (15H, Cp), 2.59 (d,  $J = 10$ , 6H,  $\text{CH}_2$ ). Signals due to the  $\text{BH}_3$  protons were not observed.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  79.1 (d,  $J = 6$ , quat Cp), 69.9 (d,  $J = 2$ , Cp), 69.2 (Cp), 68.3 (Cp), 25.2 (d,  $J = 28$ ,  $\text{CH}_2$ ). IR (Nujol): 2921, 2851, 2357, 2332, 2257 (w), 1456, 1375.

#### 4.12. $\text{FcCH}_2\text{P}(\text{SiMe}_3)_2$ (**10**)

To a solution of ferrocenylmethylphosphine (300 mg, 1.29 mmol) in 10 mL of dry THF at  $-78$  °C under  $\text{N}_2$ , *n*-butyllithium (2 M in cyclohexane, 2.6 mL, 5.2 mmol, 2 equiv. per P-H) was added dropwise via syringe. The solution was stirred for 30 min, while a deep rust color evolved. Twelve equivalents of dry  $\text{Me}_3\text{SiCl}$  (2.0 mL, 15.5 mmol) was then added via syringe. The solution was stirred at  $-78$  °C for 15 min, then warmed to room temperature. The solvent was removed under vacuum; the residue was dissolved in ether and filtered through Celite on a frit. The solvent was again removed under vacuum yielding an air-sensitive deep red oil (471 mg, 97%) which contained  $\text{FcCH}_2\text{PH}(\text{SiMe}_3)$  ( $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  -141.2) as an impurity.

MS: the calculated mass ( $m/z$  375) was not observed. Instead, peaks due to the protonolysis products  $\text{FcCH}_2\text{PH}_2$  and  $\text{FcCH}_2\text{PH}(\text{SiMe}_3)$  were found at  $m/z$  232.1 and 304.0, respectively.  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  -158.6.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  4.13 (apparent td,  $J = 2$ , 1, 2H, Cp), 3.96 (5H, Cp), 3.88 (apparent t,  $J = 2$ , 2H, Cp), 2.77 (2H,  $\text{CH}_2$ ), 0.16 (d,  $J = 5$ , 18H,  $\text{SiMe}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  89.3 (d,  $J = 13$ , quat Cp), 69.3 (d,  $J = 4$ , Cp), 69.0 (Cp), 67.5 (Cp), 16.2 (d,  $J = 18$ ,  $\text{CH}_2$ ), 1.1 (d,  $J = 12$ ,  $\text{SiMe}_3$ ).

#### 4.13. $\text{FcCH}_2\text{P}(\text{CH}_2\text{OSiMe}_3)_2$ (**11**)

(Ferrocenylmethyl)bis(hydroxymethyl)phosphine (**9**, 400 mg, 1.37 mmol) and triethylamine (552 mg, 5.46 mmol, 2 equiv. per OH) were dissolved in 40 mL of dry ether under  $\text{N}_2$ . Chlorotrimethylsilane (4.25 g, 5 mL, 7.8 mmol, 2.8 equiv. per OH) was added via syringe, causing immediate precipitation of a white salt. After stirring for 20 min, the solvent was removed from the mixture under



vacuum at room temperature. When only an oily/solid residue remained, it was redissolved in ether, dried over magnesium sulfate, and filtered through a frit to remove the salt. The resultant solution was pumped down under vacuum at room temperature to give  $\text{FcCH}_2\text{P}(\text{CH}_2\text{OSiMe}_3)_2$  as an analytically pure oil (565 mg, 94%).

Anal. Calc. for  $\text{C}_{19}\text{H}_{33}\text{PFeO}_2\text{Si}_2$ : C, 52.29; H, 7.62. Found: C, 52.69; H, 7.22%. HRMS calcd for  $\text{C}_{19}\text{H}_{34}\text{PFeO}_2\text{Si}_2$  [(MH)<sup>+</sup>]: *m/z* 437.1184. Found: *m/z* 437.1184.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -21.4.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  4.13 (5H, Cp), 4.12 (apparent t, *J* = 2, 2H, Cp), 4.06 (apparent t, *J* = 2, 2H, Cp), 3.87 (ABX pattern,  $\delta_{\text{A}} = 3.91$ ,  $\delta_{\text{B}} = 3.83$ ,  $J_{\text{AB}} = 12$ ,  $J_{\text{PH(A)}} = 5$ ,  $J_{\text{PH(B)}} = 7$ , 4H,  $\text{CH}_2\text{OSiMe}_3$ ), 2.59 (2H,  $\text{CH}_2$ ), 0.15 (18H,  $\text{SiMe}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  84.8 (d, *J* = 12, quat Cp), 69.1 (d, *J* = 3, Cp), 69.0 (Cp), 67.6 (Cp), 58.3 (d, *J* = 11,  $\text{CH}_2\text{O}$ ), 21.4 (d, *J* = 13,  $\text{CH}_2$ ), 0.3 ( $\text{SiMe}_3$ ).

#### 4.14. $(\text{FcCH}_2)_3\text{P}(\text{O})$ (**12**)

A solution of 25 mg (0.040 mmol) of  $(\text{FcCH}_2)_3\text{P}$  was dissolved in  $\text{CDCl}_3$  and stirred in a vial exposed to the air. Complete oxidation, which was monitored by  $^{31}\text{P}$  NMR spectroscopy, took place in 6 days. (Note: heating the sample accelerated oxidation but also gave an unidentified dark impurity ( $^{31}\text{P}$  NMR:  $\delta$  44.8), which could be removed by addition of aqueous  $\text{NaHCO}_3$  and separation of the organic layer). Recrystallization from  $\text{CDCl}_3$  layered with petroleum ether at  $-20^\circ\text{C}$  gave a light brown solid, but also some dark orange needle-like crystals (12 mg, 48%). Both were the phosphine oxide. Crystals suitable for X-ray analysis were obtained by dissolving the oxide in a minimal amount of THF followed by layering with petroleum ether at  $-20^\circ\text{C}$ .

We could not obtain satisfactory elemental analysis data for this compound, despite repeated attempts. This may be a result of cocrystallization with variable amounts of water, which was observed by  $^1\text{H}$  NMR spectroscopy. For example, Anal. Calc. for  $\text{C}_{33}\text{H}_{33}\text{Fe}_3\text{PO}(\text{H}_2\text{O})$ : C, 59.86; H, 5.33. Found: C, 59.65; H, 5.03%. NMR spectra of **12** are included in the [Supplementary material](#). HRMS: *m/z* calcd for  $\text{C}_{33}\text{H}_{33}\text{Fe}_3\text{PO}$ : 644.0315. Found: 644.0317.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  40.7.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  4.19 (br, 6H, Fc), 4.16 (d, *J* = 2, 6H, Fc), 4.09–4.07 (br, 15H, CH), 2.68 (d, *J* = 13, 6H,  $\text{CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  78.5 (quat Cp), 69.7 (d, *J* = 2, Cp), 69.2 (Cp), 68.4 (Cp), 29.5 (d, *J* = 60,  $\text{CH}_2$ ).

#### 4.15. $[(\text{FcCH}_2)_3\text{PH}][\text{BF}_4]$ (**13**)

A solution of  $(\text{FcCH}_2)_3\text{P}$  (57 mg, 0.091 mmol) in 3 mL of  $\text{CHCl}_3$  was treated with  $\text{HBF}_4 \cdot \text{OMe}_2$  (30  $\mu\text{L}$ , 0.29 mmol) and stirred for 2 h. The reaction mixture was concentrated under vacuum;  $^{31}\text{P}$  NMR spectroscopy ( $\text{CDCl}_3$ ) showed complete conversion to the product ( $\delta$  14.6). Recrystallization from  $\text{CDCl}_3$  layered with petroleum ether at  $-30^\circ\text{C}$  gave orange crystals in quantitative yield (65 mg, 0.091 mmol).

Anal. Calc. for  $\text{C}_{33}\text{H}_{34}\text{BF}_4\text{Fe}_3\text{P}(\text{H}_2\text{O})$ : C, 54.00; H, 4.94. Found: C, 53.74; H, 4.91%. The presence of water in the analytical sample, which was recrystallized in the air, was confirmed by  $^1\text{H}$  NMR integration. HRMS: *m/z* calcd for  $\text{C}_{33}\text{H}_{34}\text{Fe}_3\text{P}$ : ( $\text{M}-\text{H}$ )<sup>+</sup>: 628.0389. Found: 628.0369.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  15.8.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  5.64 (dm, *J* = 486, 1H, PH), 4.24 (apparent t, *J* = 2, 9H, FcH), 4.18 (18H, FcH), 3.35 (m, 6H,  $\text{CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  75.2 (d, *J* = 3, quat Cp), 69.8 (Cp), 69.5 (Cp), 69.4 (d, *J* = 2, Cp), 19.4 (d, *J* = 39,  $\text{CH}_2$ ).  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -150.1. IR (Nujol): 2923, 2853, 1457, 1377, 1023, 759, 721. The P–H stretch was not observed.

#### 4.16. $\text{Pt}(\text{P}(\text{CH}_2\text{Fc})_3)_2\text{Cl}_2$ (**14**)

(a)  $\text{Pt}(\text{COD})\text{Cl}_2$  (10 mg, 0.027 mmol) and  $(\text{FcCH}_2)_3\text{P}$  (34 mg, 0.054 mmol, 2 equiv.) were dissolved in  $\text{CH}_2\text{Cl}_2$ . The orange solu-

tion was stirred for 30 min, then pumped down under vacuum. The crude orange solid was washed three times with petroleum ether to remove the COD.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  10.3 ( $J_{\text{Pt-P}} = 3692$ , cis, 57%), 8.0 ( $J_{\text{Pt-P}} = 2456$ , trans, 43%), 1.6 (unidentified impurity). The crude orange solid was recrystallized from chloroform layered with petroleum ether to give the product (32 mg, 78%).

(b) A solution of  $\text{PtCl}_2$  (10 mg, 0.038 mmol) in 2 mL of  $\text{CH}_2\text{Cl}_2$  was treated with a solution of  $(\text{FcCH}_2)_3\text{P}$  (47 mg, 0.075 mmol) in 5 mL of  $\text{CH}_2\text{Cl}_2$ . The brown-orange solution was stirred for 30 min, then pumped down under vacuum. The resulting  $^{31}\text{P}$  NMR spectrum revealed that the crude product was significantly (87%) enriched in the trans form and <1% of an unidentified impurity ( $\delta$  1.6) was present. The NMR tube was allowed to stand for several hours, but no isomerization occurred. After pumping down the solution, the crude product was recrystallized from  $\text{CHCl}_3/\text{ether}$  at  $-20^\circ\text{C}$ , resulting in orange needles (27 mg, 0.018 mmol, 47%), which were free of the impurity and highly enriched (98%) in the trans form. A second recrystallization gave 2 more mg for a total of 29 mg, 0.019 mmol, 51%. Crystals of a chloroform solvate suitable for X-ray analysis were obtained by diffusion of ether into a chloroform solution at  $-20^\circ\text{C}$ .

As observed in the crystal structure, a sample for elemental analysis, prepared in the same way, also contained 2 equiv. of  $\text{CHCl}_3$ . Anal. Calc. for  $\text{C}_{66}\text{H}_{66}\text{Cl}_2\text{Fe}_6\text{P}_2\text{Pt} \cdot 2\text{CHCl}_3$ : C, 46.38; H, 3.89. Found: C, 46.68; H, 3.50%. HRMS: *m/z* calcd for  $\text{C}_{66}\text{H}_{66}\text{Cl}_2\text{Fe}_6\text{P}_2\text{Pt}$ : 1520.977. Found: 1520.976.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.0 ( $J_{\text{Pt-P}} = 2456$ ), <2% cis  $\delta$  10.3 ( $J_{\text{Pt-P}} = 3692$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  4.31 (t, *J* = 2, 12H, Fc), 4.15 (t, *J* = 2, 12H, Fc), 4.12 (30H, Fc), 2.92 (t, *J* = 3, 12H,  $\text{CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  80.6 (quat Cp), 70.6 (Cp), 69.4 (Cp), 68.0 (Cp), 22.3 (t, *J* = 13,  $\text{CH}_2$ ).

#### 4.17. $\text{FcCH}_2\text{P}(\text{BH}_3)(\text{CH}_2\text{OSiMe}_3)_2$ (**15**)

$\text{BH}_3(\text{SMe}_2)$  (2 M in THF, 0.5 mL, 1.0 mmol, 1.6 equiv.) was added via syringe to a solution of  $\text{FcCH}_2\text{P}(\text{CH}_2\text{OSiMe}_3)_2$  (257 mg, 0.62 mmol) in 20 mL of dry THF under  $\text{N}_2$ . After stirring for 20 min, the solvent was removed from the mixture under vacuum. When only a solid residue remained, it was dissolved in ether and filtered through a 2-inch silica plug. The solvent was then removed under vacuum and the resultant crude solid was recrystallized from hot heptane. This quickly yielded extremely fine fibrous yellow crystals of pure  $\text{FcCH}_2\text{P}(\text{BH}_3)(\text{CH}_2\text{OSiMe}_3)_2$  (240 mg, 86%).

Anal. Calc. for  $\text{C}_{19}\text{H}_{36}\text{PFeBO}_2\text{Si}_2$ : C, 50.68; H, 8.06. Found: C, 50.79; H, 7.66%. HRMS calcd for  $\text{C}_{19}\text{H}_{36}\text{PFeBO}_2\text{Si}_2$ : *m/z* 450.1434. Found: *m/z* 450.1436.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  23.0 (d,  $J_{\text{P-B}} = 53$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  4.20 (broad t, *J* = 2, 2H, Cp), 4.14 (5H, Cp), 4.12 (broad t, *J* = 2, 2H, Cp), 3.87 (ABX pattern,  $\delta_{\text{A}} = 3.89$ ,  $\delta_{\text{B}} = 3.87$ ,  $J_{\text{AB}} = 12$ ,  $J_{\text{PH(A)}} = 2$ ,  $J_{\text{PH(B)}} = 3$ , 4H,  $\text{CH}_2\text{OSiMe}_3$ ), 2.88 (2H, *J* = 11,  $\text{CH}_2$ ), 0.15 (18H,  $\text{SiMe}_3$ ). Signals due to the  $\text{BH}_3$  protons were not observed.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  78.8 (quat Cp), 69.8 (d, *J* = 6, Cp), 69.1 (Cp), 68.1 (Cp), 55.7 (d, *J* = 42,  $\text{CH}_2\text{OSiMe}_3$ ), 20.8 (d, *J* = 30,  $\text{CH}_2$ ), 0.8 ( $\text{SiMe}_3$ ).

#### 4.18. X-ray crystallography

Data collection and structure solutions followed standard procedures with no difficulties, in most cases; see [Supplementary material](#) for details. The structure of phosphine oxide **12** was disordered over two positions. Possible merohedral twinning in **12** was considered and rejected because of the successful solution and refinement of the disordered structure, which contains two well-behaved molecules. Reducing the symmetry by removing the mirror plane perpendicular to the threefold axis removed the disorder, but resulted in severe distortions in the Cp rings. The crystal of sec-

ondary phosphine–borane **7** was a cellophane-thin plate with 180° rotational twinning, resulting in an increased  $R_W$  value.

#### 4.19. DFT computations

Gas phase structures were optimized using the hybrid B3LYP functional [29] and the triple- $\zeta$  LACV3P\*\*++ basis set [30], which uses extended core potentials on heavy atoms and a 6-311G\*\*++ basis for other atoms, as implemented in the JAGUAR [12] suite of programs. Natural Bond Orbital (NBO), Natural Resonance Theory (NRT), and Natural Population Analyses (NPA) [31] are also integrated with the Jaguar program, and were run on B3LYP/LACV3P\*\*++ optimized structures. All computed structures were confirmed as energy minima by calculating the vibrational frequencies by second derivative analytic methods, and confirming the absence of imaginary frequencies. Although scaled frequencies were not calculated directly, the P–H vibrations reported in the text were scaled by the factor of 0.9614 recommended for the B3LYP functional [32]. Thermodynamic quantities were calculated assuming an ideal gas, and are zero point energy corrected.

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#### Appendix A. Supplementary material

CCDC 712974, 712975, 712976, 712977, 712978, 712979, 712980, 712981, 712982 and 712983 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.03.015.

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