

**THE CHEMISTRY OF IRON-  
 TRIS(DIMETHYLPHOSPHINOMETHYL)METHYLSILANE COMPLEXES:  
 CRYSTAL STRUCTURE OF THE COMPOUND  $[\{\text{Fe}((\text{Me}_2\text{PCH}_2)_3\text{SiMe})_2(\mu\text{-H})_2(\mu\text{-C}=\text{CH}_2)\}]$  WITH A VINYLIDENE GROUP WHICH IS DERIVED FROM ETHYLENE \***

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**Summary**

The ability of the tri-tertiary-phosphine tris(dimethylphosphinomethyl)methylsilane (tm<sub>ps</sub>) to act as a ligand in a variety of iron compounds has been explored. Tm<sub>ps</sub> reacts with  $[\text{Fe}(\eta\text{-C}_6\text{H}_6)(\text{PMe}_3)_2]$  giving  $[\text{Fe}(\eta^4\text{-C}_6\text{H}_6)(\text{tm}_ps)]$ . The  $\eta^4\text{-C}_6\text{H}_6$  ligand of this compound is readily displaced by carbon monoxide, cyclopentadiene, cyclohexa-1,3-diene, disubstituted acetylenes or ethylene giving  $[\text{Fe}(\text{tm}_ps)(\text{CO})_2]$ ,  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)\text{H}(\eta^2\text{-tm}_ps)]$ ,  $[\text{Fe}(\eta\text{-C}_6\text{H}_8)(\text{tm}_ps)]$ ,  $[\text{Fe}(\eta\text{-RC}\equiv\text{CR})(\text{tm}_ps)]$  (R, R' = Ph, Ph; Me, Me; Me, Et; Et, Et or Me<sub>3</sub>Si, Me<sub>3</sub>Si) or  $[\{\text{Fe}(\text{tm}_ps)(\mu\text{-H})_2(\mu\text{-C}=\text{CH}_2)\}]$ , respectively. The formation of the  $\mu$ -vinylidene compound directly from ethylene is noteworthy. The crystal structure of the  $\mu$ -vinylidene compound has been determined. The new compounds  $[\text{Fe}(\eta^5\text{-C}_6\text{H}_7)(\text{tm}_ps)]\text{PF}_6$ ,  $[\text{Fe}(\eta\text{-C}_6\text{H}_6)(\text{tm}_ps)][\text{BF}_4]_2$ ,  $[(\text{tm}_ps)\text{Fe}(\mu\text{-Cl})_3\text{Fe}(\text{tm}_ps)]\text{Cl}$ ,  $[(\text{tm}_ps)\text{Fe}(\mu\text{-Cl})_3\text{Fe}(\text{tm}_ps)]\text{BPh}_4$ ,  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{tm}_ps)]\text{-PF}_6$ ,  $[\text{Fe}(\eta\text{-C}_4\text{H}_6)(\text{tm}_ps)]$ ,  $[\text{Fe}(\eta\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{Ph})(\text{tm}_ps)]$ ,  $[\text{Fe}(\eta^5\text{-2-PhCH}_2\text{CH}_2\text{C}_6\text{H}_6)(\text{tm}_ps)]\text{PF}_6$  are also described.

We have set out to explore the properties, as a ligand to transition metals, of the potentially tridentate tertiary-alkylphosphine  $\text{MeSi}(\text{CH}_2\text{PMe}_2)_3(\text{tm}_ps)$ . Tm<sub>ps</sub> is potentially a six-electron donor ligand which can be seen to be broadly analogous to a bulky  $\eta$ -arene ligand such as hexamethylbenzene. Tm<sub>ps</sub> was first prepared by Karsch and Appelt [1] and is readily available on a 50–100 g scale from  $\text{MeSiCl}_3$  and  $\text{LiCH}_2\text{PMe}_2$ .

Here we describe the chemistry of iron-tm<sub>ps</sub> derivatives; a preliminary account of part of this work has been published [2].

\* Dedicated to Professor G.E. Coates on the occasion of his 70th birthday.

## Results and discussion

Treatment of the highly reactive  $[\text{Fe}(\eta^6\text{-C}_6\text{H}_6)(\text{PMe}_3)_2]$  [3] with one equivalent of tmps at room temperature gives red, diamagnetic crystals of  $[\text{Fe}(\eta^4\text{-C}_6\text{H}_6)(\text{tmps})]$  in

TABLE 1  
ANALYTICAL AND SPECTROSCOPIC DATA

| Compound | Analysis<br>(Found(calc)<br>(%)) |                | $^1\text{H}$ , $^{13}\text{C}$ and $^{31}\text{P}$ NMR <sup>a</sup>  |
|----------|----------------------------------|----------------|--|
|          | C                                | H              |  |
| 1        | 47.7<br>(47.8)                   | 8.15<br>(8.27) | $^1\text{H}$ <sup>b</sup> : 5.80 [2H, br, q, $\text{H}_{\text{a,a}'}$ ], 5.50 [2H, t, $J(\text{H-H})$ 3.5, $\text{H}_{\text{c,c}'}$ ], 1.80 [6H, d, $J(\text{P-H})$ 7.0, $\text{P}_\text{a}\text{Me}_2$ ], 1.69 [2H, brm, $\text{H}_{\text{b,b}'}$ ], 0.89 [2H, d, $J(\text{P-H})$ 10.1, $\text{Si}(\text{CH}_2\text{P}_\text{a})$ ], 0.81 [12H, virtually coupled, $J'$ 10.5, $\text{P}_\text{b}\text{Me}_2$ and $\text{P}_\text{c}\text{Me}_2$ ], -0.04 [3H, s, $\text{SiMe}$ ], -0.05 [4H, complex AB system, $\text{Si}(\text{CH}_2\text{P}_\text{b})$ and $\text{Si}(\text{CH}_2\text{P}_\text{c})$ ]. $^{13}\text{C}$ <sup>c</sup> : 129.3 [d, $J(\text{C-H})$ 160, $\text{C}_{\text{c,c}'}$ ], 81.1 [d, $J(\text{C-H})$ 165, $\text{C}_{\text{a,a}'}$ or $\text{C}_{\text{b,b}'}$ ], 48.5 [d, $J(\text{C-H})$ 153, $\text{C}_{\text{b,b}'}$ or $\text{C}_{\text{a,a}'}$ ], 27.9 [qd, $J(\text{C-H})$ 130, $J(\text{P-C})$ 17, $\text{P}_\text{a}\text{Me}_2$ ], 23.8 [q of vt, $J(\text{C-H})$ 126, $J(\text{P-C})$ 7, $\text{P}_\text{b}\text{Me}$ and $\text{P}_\text{c}\text{Me}$ ], 22.1 [q of vt, $J(\text{C-H})$ 126, $J'$ 21.6, $\text{P}_\text{b}\text{Me}$ and $\text{P}_\text{c}\text{Me}$ ], 17.2 [t, $J(\text{C-H})$ 117, $\text{Si}(\text{CH}_2\text{P}_\text{a})$ ], 14.3 [t, $J(\text{C-H})$ 118, $\text{Si}(\text{CH}_2\text{P}_\text{b})$ and $\text{Si}(\text{CH}_2\text{P}_\text{c})$ ], 0.06 [qq, $J(\text{C-H})$ 118, $J(\text{P-C})$ 5.8, $\text{SiMe}$ ]. $^{31}\text{P}\{^1\text{H}\}$ <sup>c</sup> : 26.53 [2P, s], 27.72 [1P, s]. |
| 3        | 38.9<br>(39.1)                   | 8.53<br>(8.64) | $^1\text{H}$ : 7.27 [2H, tq, $J_t(\text{P-H})$ 8.5, $J_q(\text{P-H})$ 3, $\mu\text{-C}=\text{CH}_2$ ], 2.68 [24H, m, $4\text{PMe}_2$ ], 0.82 [4H, vt, $J'$ 8.5, $2\text{Si}(\text{CH}_2\text{P})$ ], 0.74 [12H, vt, $J'$ 6.4, $2\text{PMe}_2$ ], 0.61 [8H, m, $4\text{Si}(\text{CH}_2\text{P})$ ], 0.12 [6H, s, $2\text{SiMe}$ ], -22.58 [2H, tt, $J(\text{P-H})$ 22.5 and 8, $2(\mu\text{-H})$ ].<br>$^{13}\text{C}$ : 290.3 [t, $J(\text{P-C})$ 27, ( $\mu\text{-C}$ )], 118.5 [t, $J(\text{C-H})$ 147, $\text{C}=\text{CH}_2$ ], 29.73 [q, $J(\text{C-H})$ 125, $2\text{PMe}_2$ ], 28.9 [q of vt, $J(\text{C-H})$ 127, $J'$ 20, $2\text{PMe}_2$ ], 22.0 [q, $J(\text{C-H})$ 124, $2\text{PMe}_2$ ], 18.7 [t, $J(\text{C-H})$ 120, $2\text{Si}(\text{CH}_2\text{P})$ ], 17.2 [t, $J(\text{C-H})$ 120, $4\text{Si}(\text{CH}_2\text{P})$ ], 0.54 [q, $J(\text{C-H})$ 120, $2\text{SiMe}$ ]. $^{31}\text{P}\{^1\text{H}\}$ : 34.39 [4P, vt, $J'$ 7], 12.14 [2P,].  |
| 4        | 46.0<br>(46.2)                   | 8.26<br>(8.52) | $^1\text{H}$ : 4.07 [5H, t, $J(\text{P-H})$ 1.5, $\eta\text{-C}_5\text{H}_5$ ], 1.38 [6H, vt, $J'$ 7.5, $2\text{PMe}_\text{a}$ ], 1.26 [6H, vt, $J'$ 7.5, $2\text{PMe}_\text{b}$ ], 0.88 [6H, s, $\text{P}_\text{c}\text{Me}_2$ ], 0.77 [2H, 5 line m, $2\text{Si}(\text{CH}_2\text{P})$ ], 0.63 [2H, 5 line m, $2\text{Si}(\text{CH}_2\text{P})$ ], 0.43 [2H, brs, $\text{Si}(\text{C}_6\text{H}_2\text{P}_\text{c})$ ], 0.06 [3H, s, $\text{SiMe}$ ], -16.82 [1H, t, $J(\text{P-H})$ 75, $\text{Fe-H}$ ].<br>$^{13}\text{C}\{^1\text{H}\}$ : 73.65 [s, $\eta\text{-C}_5\text{H}_5$ ], 30.13 [vt, $J'$ 28, $2\text{PMe}_\text{a}$ ], 25.77 [vt, $J'$ 15, $2\text{PMe}_\text{b}$ ], 23.18 [s, $\text{P}_\text{c}\text{Me}_2$ ], 21.62 [d, $J(\text{P-C})$ 25, $\text{C}_\text{c}$ ], 18.13 [d, $J(\text{P-C})$ 13, $\text{Si}(\text{CH}_2\text{P})_2$ ], 0.80 [s, $\text{SiMe}$ ].<br>$^{31}\text{P}\{^1\text{H}\}$ : 42.26 [2 P, s], -59.43 [1P, s, $\text{P}_\text{c}$ ].  |
| 5        | 47.6<br>(47.5)                   | 8.64<br>(8.72) | $^1\text{H}$ : 4.27 [2H, m $2\eta\text{-CH}$ ], 1.80 [4H, overlapping m, $2\eta\text{-CH}$ and $\text{CH}_2$ ], 1.57 [2H, m, $\text{CH}_2$ ], 1.19 [18H, m, $3\text{PMe}_2$ ], 0.42 [6H, m, $3\text{Si}(\text{CH}_2\text{P})$ ], -0.37 [3H, s, $\text{SiMe}$ ]. $^{13}\text{C}\{^1\text{H}\}$ : 78.74 [s, diene CH], 47.65 [s, diene CH], 27.11 [s, diene $\text{CH}_2$ ], 25.30 [br s, $3\text{PMe}_2$ ], 17.16 [br s, $3\text{Si}(\text{CH}_2\text{P})$ ], 0.08 [br s, $\text{SiMe}$ ].<br>$^{31}\text{P}\{^1\text{H}\}$ : 28.56 [s].  |
| 6        | 57.2<br>(57.4)                   | 7.32<br>(7.42) | $^1\text{H}$ : 7.65 [4H, d, $J(\text{H-H})$ 7.4, <i>ortho</i> -H], 7.25 [4H, t, $J(\text{H-H})$ 7.1, <i>meta</i> -H], 7.08 [2H, t, $J(\text{H-H})$ 7.1, <i>para</i> -H], 1.39 [18H, m, $3\text{PMe}_2$ ], 0.30 [6H, m, $3\text{Si}(\text{CH}_2\text{P})$ ], -0.12 [3H, s, $\text{SiMe}$ ]. $^{13}\text{C}\{^1\text{H}\}$ : 187.4 [s, $\text{C}\equiv\text{C}$ ], 147.4 [s, <i>ipso</i> -C], 127.6 [d, $J(\text{C-H})$ 165, <i>ortho</i> - or <i>meta</i> -C], 126.8 [d, $J(\text{C-H})$ 159, <i>meta</i> - or <i>ortho</i> -C], 124.4 [d, $J(\text{C-H})$ 160, <i>para</i> -C], 27.9 [q of vt $J(\text{C-H})$ 126, $J'$ 23.8, $3\text{PMe}_2$ ], 15.2 [t, $J(\text{C-H})$ 119, $3\text{Si}(\text{CH}_2\text{P})$ ], -0.11 [qq, $J(\text{C-H})$ 120, $J(\text{P-C})$ 7.2, $\text{SiMe}$ ].  |

TABLE 1 (continued)

| Compound        | Analysis<br>(Found(calc)<br>(%)) |                | <sup>1</sup> H, <sup>13</sup> C and <sup>31</sup> P NMR <sup>a</sup>   |
|-----------------|----------------------------------|----------------|--|
|                 | C                                | H              |  |
| 7 <sup>d</sup>  |                                  |                | <sup>1</sup> H: 3.11 [2H, q, <i>J</i> (H–H) 7.5, CH <sub>2</sub> of Et], 2.81 [3H, s, CH <sub>3</sub> ], 1.44 [18H, m, 3PMe <sub>2</sub> ], 0.96 [3' H, br. t, <i>J</i> (H–H) 7.5, CH <sub>3</sub> of Et], 0.41 [6H, m, 3Si(CH <sub>2</sub> P)], –0.07 [3H, s, SiMe]. <sup>13</sup> C: 187.37 [s, alkyne C], 180.92 [s, alkyne C], 28.65 [br q, <i>J</i> (C–H) 127, 3PMe <sub>2</sub> ], 28.08 [t, <i>J</i> (C–H) 120, CH <sub>2</sub> of Et], 20.01 [q, <i>J</i> (C–H) 124, CH <sub>3</sub> of Et], 15.75 [t, <i>J</i> (C–H) 119, 3Si(CH <sub>2</sub> P)], 15.47 [q, <i>J</i> (C–H) 126, CH <sub>3</sub> ], 0.19 [qd, <i>J</i> (C–H) 119, <i>J</i> (P–C) 6.3, SiMe].<br><sup>31</sup> P{ <sup>1</sup> H}: 37.87 [s].      |
| 8               |                                  |                | <sup>1</sup> H: 3.17 [4H, q, <i>J</i> (H–H) 7.4, CH <sub>2</sub> of Et], 1.44 [18 H, m, 3PMe <sub>2</sub> ], 0.40 [6H, m, 3SiCH <sub>2</sub> P], –0.07 [3H, s, SiMe, ca. 1.5 [Me of Et partially obscured].<br><sup>13</sup> C{ <sup>1</sup> H}: 186.7 [br s, C≡C], 28.97 [s, PMe <sub>2</sub> ], 28.28 [br s, CH <sub>2</sub> ], 15.85 [br s, Si(CH <sub>2</sub> P)], 15.66 [s, CH <sub>3</sub> ], 0.12 [s, SiMe].<br><sup>31</sup> P{ <sup>1</sup> H}: 32.49 [s].  |
| 9               |                                  |                | <sup>1</sup> H: 1.37 [18H, vt, <i>J'</i> 6.6, 3PMe <sub>2</sub> ], 0.57 [18 H, s, 2SiMe <sub>3</sub> ], 0.36 [6H, m, 3Si(CH <sub>2</sub> P)], –0.07 [3 H, s, SiMe].<br><sup>13</sup> C: 203.57 [s, C≡C], 29.02 [q of vt, <i>J</i> (C–H) 126, <i>J'</i> 16.2, 3PMe <sub>2</sub> ], 15.94 [t, <i>J</i> (C–H) 119, 3Si(CH <sub>2</sub> P)], 2.75 [q, <i>J</i> (C–H) 118, 2SiMe <sub>3</sub> ], –0.11 [qq, <i>J</i> (C–H) 119, <i>J</i> (P–C) 5.6, SiMe].<br><sup>31</sup> P{ <sup>1</sup> H}: 33.81 [s].  |
| 11              | 35.2<br>(35.1)                   | 6.13<br>(6.25) | <sup>1</sup> H <sup>c</sup> : 5.99 [1H, tq, <i>J</i> (H–H) 5.2, <i>J</i> (P–H) 1.2, H <sub>c</sub> ], 4.72 [2H, br m, H <sub>d</sub> ], 2.58 [1H, dt, <sup>2</sup> <i>J</i> (H <sub>b</sub> –H <sub>a</sub> ) 14.1, <sup>3</sup> <i>J</i> (H <sub>b</sub> –H <sub>c</sub> ) 6.5, H <sub>b</sub> ], 2.34 [2H, br t, <i>J</i> (H <sub>c</sub> –H <sub>a</sub> ) = <i>J</i> (H <sub>c</sub> –H <sub>b</sub> ) 6.5, H <sub>c</sub> ], 1.75 [1H, dt, <sup>2</sup> <i>J</i> (H <sub>a</sub> –H <sub>b</sub> ) 14.1, <sup>3</sup> <i>J</i> (H <sub>a</sub> –H <sub>c</sub> ) 6.5, H <sub>a</sub> ], 1.66 [18H, br s, 3PMe <sub>3</sub> ], 1.04 [6H, br s, 3Si(CH <sub>2</sub> P)], –0.23 [3H, br s, SiMe].                        |
| 12              | 34.2<br>(33.8)                   | 6.34<br>(5.80) | <sup>1</sup> H <sup>c</sup> : 6.20 [6H, q, <i>J</i> (P–H) 2.0, η-C <sub>6</sub> H <sub>6</sub> ], 1.85 [18H, m, 3PMe <sub>2</sub> ], 0.95 [6H, m, 3Si(CH <sub>2</sub> P)], 0.25 [3H, s, SiMe].   |
| 13 and 14       |                                  |                | <sup>1</sup> H <sup>b</sup> : 1.54 [18H, br s, 3PMe <sub>2</sub> ], 0.61 [6H, br s, 3SiCH <sub>2</sub> P], 0.13 [3H, s, SiMe].   |
| 15              | 33.9<br>(33.7)                   | 5.96<br>(6.21) | <sup>1</sup> H <sup>c</sup> : 4.50 [5H, q, <i>J</i> (P–H) 1.8, η-C <sub>3</sub> H <sub>5</sub> ], 1.75 [18H, m, 3PMe <sub>2</sub> ], 0.98 [6H, m, 3Si(CH <sub>2</sub> P)], 0.21 [3H, s, SiMe].   |
| 16              | 44.2<br>(44.5)                   | 8.62<br>(8.79) | <sup>1</sup> H: 4.57 [2H, br s, 2η-CH], 1.19 [18H, br m, 3PMe <sub>2</sub> ], 0.75 [2H, brs, <i>syn</i> -H of η-CH <sub>2</sub> ], 0.43 [6H, br s, 3Si(CH <sub>2</sub> P)], –0.03 [3H, s, SiMe], –0.97 [2H, br, m, <i>anti</i> -H of η-CH <sub>2</sub> ]. <sup>13</sup> C{ <sup>1</sup> H}: 77.48 [br s, 2diene CH], 30.73 [br s, 2 diene CH <sub>2</sub> ], 25.44 [br s, 3PMe <sub>2</sub> ], 16.96 [br s, 3SiCH <sub>2</sub> P], 0.14 [br s, SiMe].<br><sup>31</sup> P{ <sup>1</sup> H}: 29.8 [s]; at –30 °C in toluene- <i>d</i> <sub>8</sub> : 31.42 [1P, t, <i>J</i> (P–P) 14], 30.05 [2P, d, <i>J</i> (P–P) 14],   |
| 17 <sup>j</sup> |                                  |                | <sup>1</sup> H <sup>s</sup> : 7.09 [5H, m, phenyl], 5.79 [1H, br d, H <sub>d</sub> ], 5.54 [1H, br d, H <sub>c</sub> ], 5.12 [1H, br s, H <sub>a</sub> ], 2.69 [2H, complex m, H <sub>a,r</sub> ], 2.21 [2H, m, H <sub>h,i</sub> ], 1.63 [1H, m, H <sub>b</sub> ], 1.46 [1H, m, H <sub>e</sub> ], 1.74 [6H, d, <i>J</i> (P–H) 7.8, PMe <sub>2</sub> ], 0.94 [2H, d, <i>J</i> (P–H) 9.4, Si(CH <sub>2</sub> P)], 0.87 [6H, d, <i>J</i> (P–H) 7.8, PMe <sub>2</sub> ], 0.81 [6H, d, <i>J</i> (P–H) 7.8, PMe <sub>2</sub> ], 0.00 [4H, complex m, 2Si(CH <sub>2</sub> P)], 0.03 [3H, s, SiMe]. <sup>31</sup> P{ <sup>1</sup> H} at –50 °C: 29.28 [1P, s], 26.71 [1P, d, <i>J</i> (P–P) 54], 25.38 [1P, d, <i>J</i> (P–P) 54]. |

TABLE 1 (continued)

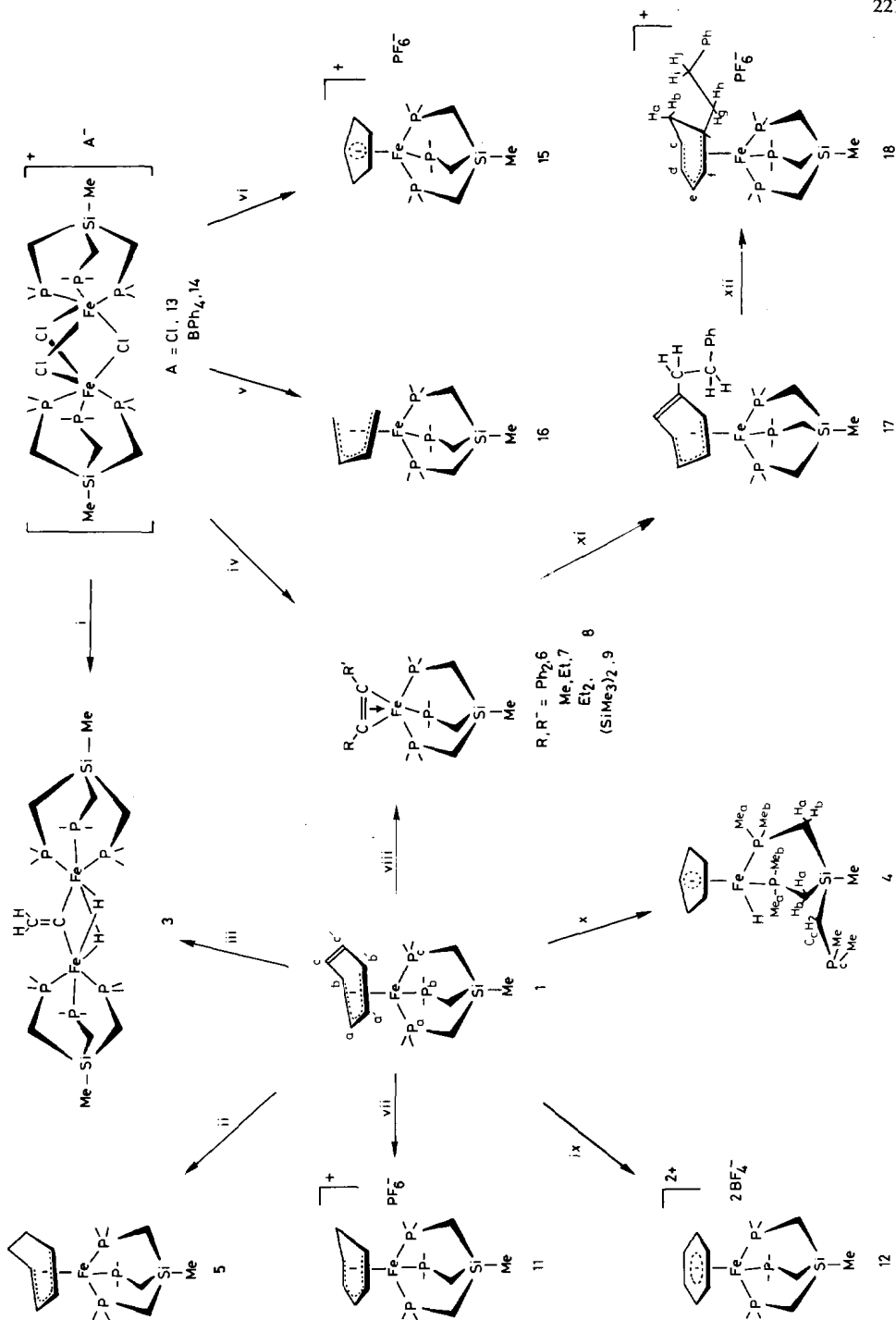
| Compound  | Analysis<br>(Found(calc)<br>(%)) |                | <sup>1</sup> H, <sup>13</sup> C and <sup>31</sup> P NMR <sup>a</sup>  |
|-----------|----------------------------------|----------------|---|
|           | C                                | H              |   |
| <b>18</b> | 44.0<br>(44.2)                   | 6.78<br>(6.79) | <sup>1</sup> H <sup>h</sup> : 7.26 [2H, t, <i>J</i> (H-H) 6.8, 2 <i>meta</i> -H], 7.18 [1H, t, <i>J</i> (H-H) 6.8, <i>para</i> -H], 7.06 [2H, d, <i>J</i> (H-H) 6.8, <i>ortho</i> -H], 5.75 [1H, m, H <sub>c</sub> ], 4.45 [1H, br m, H <sub>d</sub> ], 4.11 [1H, br m, H <sub>f</sub> ], 2.66 [1H, ddd, <sup>2</sup> <i>J</i> (H-H) 13.2, <sup>3</sup> <i>J</i> (H-H) 5.14, 9.26, H <sub>h</sub> ], 2.39 [1H, ddd, <sup>2</sup> <i>J</i> (H-H) 13.6, <sup>3</sup> <i>J</i> (H-H) 7.35 and 8.82, H <sub>j</sub> ], 2.26 [1H, br m, H <sub>b</sub> ], 2.24 [1H, br m, H <sub>c</sub> ], 2.11 [1H, br m, H <sub>a</sub> ], 2.02 [1H, ddd, <sup>2</sup> <i>J</i> (H-H) 13.2, <sup>3</sup> <i>J</i> (H-H) 5.14 and 9.26, H <sub>g</sub> ], 1.81 [1H, ddd, <sup>2</sup> <i>J</i> (H-H) 13.6, <sup>3</sup> <i>J</i> (H-H) 9.26 and 5.14, H <sub>i</sub> ], 2.01 [3H, d, <i>J</i> (P-H) 8.0, PMe], 1.97 [3H, d, <i>J</i> (P-H) 8.0, PMe], 1.38 [3H, d, <i>J</i> (P-H) 8.0, PMe], 1.33 [3H, d, <i>J</i> (P-H) 8.0, PMe], 1.19 [2H, m, Si(CH <sub>2</sub> P)], 1.17 [3H, d, <i>J</i> (P-H) 8.0, PMe], 0.99 [3H, d, <i>J</i> (P-H) 8.0, PMe], 0.56 [4H, complex, 10 lines, 2Si(CH <sub>2</sub> P)]. <sup>13</sup> C <sup>i</sup> : 130.6 [s, <i>ipso</i> -C of Ph group], 118.2 [d, <i>J</i> (C-H) 158, 2 <i>meta</i> -C], 118.2 [d, <i>J</i> (C-H) 158, 2 <i>ortho</i> -C], 116.0 [d, <i>J</i> (C-H) 162, <i>para</i> -C], 84.6 [d, <i>J</i> (C-H) 163, C <sub>f</sub> ], 83.5 [d, <i>J</i> (C-H) 164, C <sub>d</sub> ], 61.5 [d, <i>J</i> (C-H) 172, C <sub>e</sub> ], 58.0 [s, C <sub>k</sub> ], 30.9 [d, <i>J</i> (C-H) 163, C <sub>c</sub> ], 30.8 [t, <i>J</i> (C-H) 129, CH <sub>a</sub> H <sub>b</sub> ], 23.4 [t, <i>J</i> (C-H) 129, CH <sub>i</sub> H <sub>j</sub> or CH <sub>g</sub> H <sub>h</sub> ], 20.5 [t, <i>J</i> (C-H) 134, CH <sub>g</sub> H <sub>h</sub> or CH <sub>i</sub> H <sub>j</sub> ], the C atoms of the tm <sub>ps</sub> ligand were broad due to fluxionality except for -11.09 [q, <i>J</i> (C-H) 117, SiMe] |

<sup>a</sup> Given as: chemical shift ( $\delta$ ) [relative intensity, multiplicity (*J* in Hz), assignment], unless otherwise stated <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra were measured at 300, 62.89 and 101.26 MHz respectively, at r.t. in benzene-*d*<sub>6</sub>. *J*' = separation between outer lines for virtual triplets. <sup>b</sup> In toluene-*d*<sub>8</sub> at -60 °C. <sup>c</sup> In toluene-*d*<sub>8</sub> at -65 °C. <sup>d</sup> *m/e*: 392 (*M*<sup>+</sup>), 324 (*M*<sup>+</sup> - pent-2-yne). **8**: *m/e*: 406 [*P*<sup>+</sup>]. **9**: *m/e*: 494 [*P*<sup>+</sup>]. <sup>e</sup> In acetone-*d*<sub>6</sub>. <sup>f</sup> In dichloromethane-*d*<sub>2</sub> at r.t. <sup>g</sup> in toluene-*d*<sub>8</sub> at -50 °C. <sup>h</sup> In dichloromethane-*d*<sub>2</sub> at -40 °C. <sup>i</sup> In dichloromethane-*d*<sub>2</sub> at 125.7 MHz and r.t. *j* *m/e*: 506 [*P*<sup>+</sup>].

high yield (**1**). The analytical and NMR data characterising **1**, and all other new compounds described below are given in Table 1. This data will not be discussed further unless the interpretation is not straightforward. The structures proposed for the new compounds are shown in Scheme 1.

The  $\eta^4$ -coordination mode of the benzene ligand in this complex is confirmed by the low temperature <sup>1</sup>H, <sup>13</sup>C {<sup>1</sup>H} and <sup>31</sup>P {<sup>1</sup>H} NMR spectra. In particular, the observation of three non-equivalent pairs of proton and carbon resonances for the benzene ligand in **1** confirms that the C<sub>6</sub>H<sub>6</sub> moiety is bonded in an  $\eta^4$ -fashion. The  $\eta^4$ -mode of the benzene ligand in **1** contrasts with the observed  $\eta^6$ -hexamethylbenzene rings in the 20e bis( $\eta$ -hexamethylbenzene)iron [4], and is a rare example of  $\eta^4$ -coordination by benzene. The only other example of an  $\eta^4$ -areneiron compound is [Fe(CO)<sub>3</sub>( $\eta^4$ -1,2-C<sub>6</sub>(CF<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)<sub>4</sub>)] [5]. Other examples of  $\eta^4$ -arene derivatives are [Ru( $\eta$ -C<sub>6</sub>Me<sub>6</sub>)( $\eta^4$ -C<sub>6</sub>Me<sub>6</sub>)] [6], [Ru( $\eta$ -C<sub>6</sub>H<sub>6</sub>)( $\eta^4$ -C<sub>6</sub>Ph<sub>6</sub>)] [7], {Rh( $\eta$ -C<sub>5</sub>H<sub>5</sub>)}( $\eta^4$ -C<sub>6</sub>(CF<sub>3</sub>)<sub>6</sub>)] + [8], [M( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)( $\eta^4$ -C<sub>6</sub>Me<sub>6</sub>)] [9] (M = Rh or Ir) and [Os( $\eta$ -C<sub>6</sub>H<sub>6</sub>)( $\eta^4$ -C<sub>6</sub>H<sub>6</sub>)] [10].

The compound **1** readily undergoes displacement of the  $\eta^4$ -benzene ligand. Treatment of **1** with carbon monoxide at one atmosphere gives quantitative yields of [Fe(tm<sub>ps</sub>)(CO)<sub>2</sub>] (**2**). When **1** is heated to 50 °C with ethylene, the bridging  $\mu$ -vinylidene- $\mu$ -dihydrido complex [{Fe(tm<sub>ps</sub>)}<sub>2</sub>( $\mu$ -H)<sub>2</sub>( $\mu$ -C=CH<sub>2</sub>)] (**3**), is formed in moderate yield. The crystal structure of **3** has been determined. The molecular



SCHEME 1. (i) Ethylene (1.5 atm) and sodium amalgam at r.t. for 2 d, 57%. (ii) Cyclohexa-1,3-diene in toluene at 80 °C for 2 h, 82%. (iii) Ethylene (7 atm) in toluene for 12 h at 50 °C, ca. 50%. (iv) PhC=CPh and sodium amalgam in toluene at r.t. for 1 h, 60%. (v) Mg(C<sub>4</sub>H<sub>6</sub>)·2thf in thf at r.t. for 6 h, > 70%. (vi) NaC<sub>5</sub>H<sub>5</sub> in thf at r.t. for 2 h, 60%. (vii) NH<sub>4</sub>PF<sub>6</sub> in wet thf, 84%. (viii) RC≡CR (R, R' = Ph<sub>2</sub>, Me; Et, Et<sub>2</sub>; or (Me<sub>2</sub>Si)<sub>2</sub>) in toluene at 70 °C for 15 h, 50–70%. (ix) AgBF<sub>4</sub> in thf at r.t. for 30 min, > 95%. (x) Cyclopentadiene in toluene at 100 °C for 15 h, > 30%. (xi) H<sub>2</sub> (1 atm) for 15 min, > 95%. (xii) HCl for 5 min, then NH<sub>4</sub>PF<sub>6</sub>, 94%.

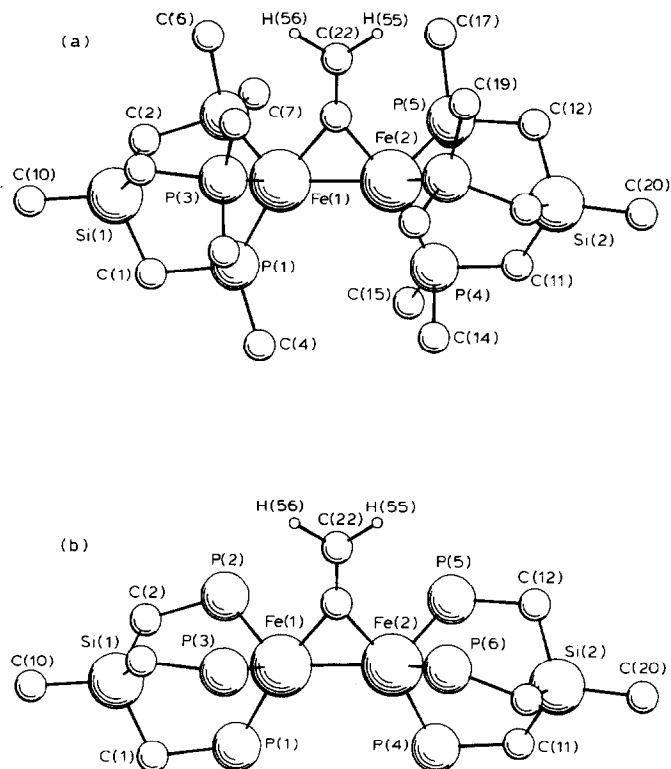


Fig. 1. (a) Molecular structure of **3**, the positions of the H(55) and H(56) hydrogen atoms are calculated. (b) Molecular structure of **3** with the P-methyl groups omitted, for clarity.

structure of **3** is shown in Fig. 1 and selected distances and angles are given in Table 2. Fractional atomic coordinates for all non-hydrogen atoms are in Table 3. The molecule contains two (tm<sub>ps</sub>)Fe groups bridged by one  $\mu$ -vinylidene and two  $\mu$ -hydrido ligands. The coordination geometry around the iron atoms is that of two

TABLE 2  
SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR **3**

|                  |          |                   |          |
|------------------|----------|-------------------|----------|
| Fe(1)–Fe(2)      | 2.428(1) | Fe(2)–P(5)        | 2.154(2) |
| Fe(1)–P(1)       | 2.216(2) | Fe(2)–P(6)        | 2.157(2) |
| Fe(1)–P(2)       | 2.156(2) | Fe(1)–C(21)       | 1.920(8) |
| Fe(1)–P(3)       | 2.162(2) | Fe(2)–C(21)       | 1.928(8) |
| Fe(2)–P(4)       | 2.214(2) | C(21)–C(22)       | 1.35(1)  |
| P(1)–Fe(1)–P(2)  | 94.31(9) | P(4)–Fe(2)–P(6)   | 94.53(9) |
| P(1)–Fe(1)–P(3)  | 93.7(1)  | P(5)–Fe(2)–P(6)   | 94.5(1)  |
| P(2)–Fe(1)–P(3)  | 94.77(8) | P(4)–Fe(2)–C(21)  | 166.1(2) |
| P(1)–Fe(1)–C(21) | 167.0(2) | P(5)–Fe(2)–C(21)  | 97.0(3)  |
| P(2)–Fe(1)–C(21) | 93.3(3)  | P(6)–Fe(2)–C(21)  | 93.9(2)  |
| P(3)–Fe(1)–C(21) | 96.1(3)  | Fe(1)–C(21)–Fe(2) | 78.2(3)  |
| P(4)–Fe(2)–P(5)  | 93.3(1)  |                   |          |

TABLE 3  
FRACTIONAL ATOMIC COORDINATES FOR ALL NON-HYDROGEN ATOMS FOR 3

| Atom  | x           | y           | z          |
|-------|-------------|-------------|------------|
| Fe(1) | -0.16869(8) | 0.07104(8)  | 0.12281(4) |
| Fe(2) | -0.32790(8) | -0.06239(8) | 0.12048(4) |
| P(1)  | -0.2168(2)  | 0.2515(2)   | 0.1299(1)  |
| P(2)  | -0.0507(2)  | 0.0988(2)   | 0.05967(8) |
| P(3)  | -0.0372(2)  | 0.0811(2)   | 0.18192(8) |
| P(4)  | -0.5021(2)  | 0.0122(2)   | 0.12941(9) |
| P(5)  | -0.3798(2)  | -0.1682(2)  | 0.05691(9) |
| P(6)  | -0.3546(2)  | -0.1911(2)  | 0.17817(9) |
| Si(1) | 0.0447(2)   | 0.2941(2)   | 0.1245(1)  |
| Si(2) | -0.5882(2)  | -0.2321(2)  | 0.1249(1)  |
| C(1)  | -0.0978(9)  | 0.3526(7)   | 0.1449(4)  |
| C(2)  | 0.0259(8)   | 0.2358(8)   | 0.0585(3)  |
| C(3)  | 0.0834(8)   | 0.1776(9)   | 0.1697(3)  |
| C(4)  | -0.3235(9)  | 0.2999(9)   | 0.1779(5)  |
| C(5)  | -0.2757(9)  | 0.3248(9)   | 0.0727(4)  |
| C(6)  | 0.0732(8)   | 0.006(1)    | 0.0475(4)  |
| C(7)  | -0.1155(9)  | 0.0908(9)   | -0.0047(3) |
| C(8)  | -0.086(1)   | 0.1303(9)   | 0.2454(4)  |
| C(9)  | 0.0425(9)   | -0.043(1)   | 0.2047(4)  |
| C(10) | 0.1587(9)   | 0.4044(9)   | 0.1260(4)  |
| C(11) | -0.6274(7)  | -0.0793(8)  | 0.1159(3)  |
| C(12) | -0.4933(8)  | -0.2751(9)  | 0.0695(3)  |
| C(13) | -0.5037(9)  | -0.2458(8)  | 0.1857(4)  |
| C(14) | -0.5450(9)  | 0.059(1)    | 0.1945(4)  |
| C(15) | -0.5464(9)  | 0.1359(8)   | 0.0921(5)  |
| C(16) | -0.443(1)   | -0.094(1)   | 0.0007(3)  |
| C(17) | -0.274(1)   | -0.256(1)   | 0.0218(4)  |
| C(18) | -0.3163(9)  | -0.1467(9)  | 0.2441(3)  |
| C(19) | -0.278(1)   | -0.3275(9)  | 0.1767(5)  |
| C(20) | -0.7211(9)  | -0.322(1)   | 0.1284(5)  |
| C(21) | -0.1642(6)  | -0.0902(6)  | 0.1154(3)  |
| C(22) | -0.0889(8)  | -0.1770(7)  | 0.1101(4)  |

octahedra which share a face. Even though the Fe(1)–Fe(2) distance is short at 2.428(1) Å, electron counting considerations suggest that there is no need to invoke a direct Fe–Fe bond.

The Fe–P bond lengths fall into two sets. The Fe–P distances *trans* to hydride ligands average to 2.157(4) Å, and those *trans* to the vinylidene ligand to 2.215(2) Å. Thus the vinylidene ligand exerts a greater *trans* influence on the phosphine ligands than the hydride ligands.

Binuclear compounds containing  $\mu$ -vinylidene groups have been structurally characterised previously, e.g. {[Mn( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sub>2</sub>( $\mu$ -C=CHR)} [11], {[Co( $\eta$ -C<sub>5</sub>H<sub>5</sub>)CO]<sub>2</sub>( $\mu$ -C=CH<sub>2</sub>)} [12], {[M( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>( $\mu$ -CO)( $\mu$ -C=CH<sub>2</sub>)] (M = Fe [13], Ru [14])} {[Fe(CO)<sub>4</sub>]<sub>2</sub>( $\mu$ -C=CPh<sub>2</sub>)} [15], [( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(PPr<sup>i</sup><sub>3</sub>)Mn( $\mu$ -CO)( $\mu$ -C=CH<sub>2</sub>)Rh(PPr<sup>i</sup><sub>3</sub>)( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] [16], and {[Rh( $\eta$ -indenyl)CO]<sub>2</sub>( $\mu$ -C=CH<sub>2</sub>)} [17]. Comparison with these data shows that vinylidene C=C distance of 1.34 Å lies in the range (1.29–1.35 Å) observed for these related compounds. Similarly, the Fe– $\mu$ -C(21) distance and Fe(1)C(21)Fe(2) angle were within the range observed for

the iron compounds containing bridging vinylidene groups. The compound **3** is the first example where a  $\mu$ -vinylidene is accompanied by  $\mu$ -hydrido ligands.

Treatment of **1** with cyclopentene or cyclopentadiene gives the yellow complex  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)\text{H}(\eta^2\text{-tmps})]$  (**4**) in which the tmps ligand is coordinated by only two of the three  $\text{PMe}_2$  groups.

When **1** is heated under  $\text{H}_2$  (10 atm,  $60^\circ\text{C}$ , 7 d) the major product is the cyclohexa-1,3-diene derivative,  $[\text{Fe}(\eta\text{-C}_6\text{H}_8)\text{tmps}]$  (**5**). A minor product of the hydrogenation reaction was an unidentified hydride-containing species. The compound **5** could be prepared more conveniently by treating **1** with cyclohexa-1,3-diene.

The disubstituted acetylenes  $\text{RC}\equiv\text{CR}'$  ( $\text{R}, \text{R}' = \text{Ph}, \text{Ph}; \text{Me}, \text{Me}; \text{Me}, \text{Et}; \text{Et}, \text{Et}$  or  $\text{Me}_3\text{Si}, \text{Me}_3\text{Si}$ ) react with **1** at elevated temperatures to give the complexes  $[\text{Fe}(\eta\text{-RC}\equiv\text{CR})(\text{tmps})]$  ( $\text{R}, \text{R}' = \text{Ph}, \text{Ph}$  (**6**);  $\text{Me}, \text{Me}$  (**7**);  $\text{Et}, \text{Et}$  (**8**) or  $\text{Me}_3\text{Si}, \text{Me}_3\text{Si}$  (**9**), respectively). The compound **6** is a crystalline solid, while **7–9** are oils at room temperature which may be purified by sublimation under high vacuum. In order to achieve an 18-electron count for the compounds **6–9**, the acetylene ligands must act as 4-electron donors. In support of this proposal, the  $^{13}\text{C}$  NMR spectra of **6–9** show peaks assignable to the acetylenic carbons in the range 180 to 203 ppm. These chemical shifts are in good agreement with those observed in other complexes that contain 4-electron donor acetylene ligands, such as  $[\text{W}(\text{CO})(\text{S}_2\text{CET}_2)_2(\text{RC}\equiv\text{CR})]$  (**10**) [18]. The complexes **6–9** do not react with excess disubstituted acetylenes or olefins under thermolysis or photolysis.

The complex **1** is readily protonated by aqueous solutions of  $\text{NH}_4\text{PF}_6$  to give the  $\eta$ -cyclohexadienyl complex  $[\text{Fe}(\eta\text{-C}_6\text{H}_7)(\text{tmps})]\text{PF}_6$  (**11**). The observation that **1** is so easily protonated indicates strong basicity. The complex **1** also reacts instantly with two equivalents of  $\text{AgBF}_4$  to give the yellow di-cation  $[\text{Fe}(\eta\text{-C}_6\text{H}_6)(\text{tmps})][\text{BF}_4]_2$  (**12**). The cyclic voltammogram of **1** in thf showed an irreversible reduction wave at  $-1.0$  V vs. N.H.E.

When one equivalent of tmps was stirred with one equivalent of  $\text{FeCl}_2(\text{thf})_2$ , a purple crystalline material rapidly precipitated from solution. This material has the stoichiometry  $[\text{Fe}(\text{tmps})\text{Cl}_2]$  (**13**). In the preliminary communication of these results [2], we formulated this compound as a monomeric material. However, treatment of **12** with  $\text{NaBPh}_4$  gives the salt  $[(\text{tmps})\text{Fe}(\mu\text{-Cl})_3\text{Fe}(\text{tmps})]\text{BPh}_4$  (**14**), whose solution NMR data are virtually identical with that of **13**. Therefore, we reformulate **12** as the dimer  $[(\text{tmps})\text{Fe}(\mu\text{-Cl})_3\text{Fe}(\text{tmps})]\text{Cl}$  (**13**), which is analogous to the previously described  $[(\text{etripfos})\text{Fe}(\mu\text{-Cl})_3\text{Fe}(\text{etripfos})]\text{BPh}_4$  (etripfos =  $\text{MeC}(\text{CH}_2\text{PEt}_2)_3$  [19]), whose crystal structure has been determined.

The dimer **13** is a convenient precursor to some of the complexes that were obtained from **1** and also to other mononuclear derivatives of the  $\text{Fe}(\text{tmps})$  moiety. Treatment of **13** with an excess of sodium cyclopentadienide in thf, followed by addition of ammonium hexafluorophosphate, gives the compound  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{tmps})]\text{PF}_6$  (**15**) in good yields. The compound **13** also reacts readily with  $[\text{Mg}(\text{C}_4\text{H}_6)(\text{thf})_2]$  giving the  $\eta$ -butadiene compound  $[\text{Fe}(\eta\text{-C}_4\text{H}_6)(\text{tmps})]$  (**16**) as yellow, pentane soluble crystals.

Reduction of **13** with sodium amalgam in the presence of ethylene (2 atm) gives the green  $\mu$ -vinylidene dihydride complex **3**. Similarly, reduction of **13** in the presence of the dialkylacetylenes  $\text{RC}\equiv\text{CR}'$  gives the acetylene complexes **6–9**. Attempts to prepare dinitrogen compounds by the reduction of **13** under  $\text{N}_2$  gave



only an intractable brown oil that had an  $^1\text{H}$  NMR spectrum similar to the product of thermolysis of **1**.

The complex  $[\text{Fe}(\eta\text{-PhC}\equiv\text{CPh})(\text{tmps})]$  (**6**) undergoes an unusual reaction with  $\text{H}_2$  in which the carbon-carbon triple bond is hydrogenated and the resulting 1,2-diphenylethane remains coordinated to the iron through one of the phenyl groups, in an  $\eta^4$ -fashion. The reaction proceeds to completion in seconds, and produces a single isomer  $[\text{Fe}(\eta^4\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{Ph})(\text{tmps})]$  (**17**) in essentially quantitative yields ( $^1\text{H}$  NMR). Like the parent complex **1**, **17** is readily protonated with dilute aqueous HCl giving, after anion metathesis with  $\text{NH}_4\text{PF}_6$ , the substituted cyclohexadiene complex  $[\text{Fe}(\eta^5\text{-2-PhCH}_2\text{CH}_2\text{C}_6\text{H}_6)(\text{tmps})]\text{PF}_6$  (**18**). Only one isomer of **18** is formed in the protonation reaction, as determined from the  $^1\text{H}$ - $^1\text{H}$  phase sensitive COSY 2D NMR spectrum of the complex.

The observation that many of the new compounds **1**–**17** have only one resonance in their  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra at r.t. suggests that they are fluxional at r.t. This is presumably due to rotation of the  $\eta$ -hydrocarbon ligands. This fluxional behaviour has been investigated by variable temperature NMR spectroscopy. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **5** is a sharp singlet at r.t., but at  $-75^\circ\text{C}$  two resonances are observed. However, it appears that the slow exchange limit is not reached even at  $-90^\circ\text{C}$ . The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **16**, which shows only a singlet at r.t., resolved on cooling to give two sets of bands, in a 1/2 ratio, which may be assigned as a first-order  $\text{AX}_2$  spin system. Similarly, the low temperature  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **17** shows, as expected, that the three  $^{31}\text{P}$  nuclei are in different environments. Two of these are strongly coupled to each other, but neither show coupling to the third. The acetylene complexes **6**–**9** show only one resonance in their  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra, even at  $-90^\circ\text{C}$ , which indicates that acetylene rotation cannot be frozen out on the NMR timescale. This is not surprising because there is no electronic preference for the acetylene orientation, and any steric barrier would be expected to be small.

In addition to ring rotation, compound **1** also undergoes degenerate haptotropic ring shifts of the  $\eta$ -benzene ligand. The 60 MHz  $^1\text{H}$  NMR spectrum of **1** in benzene- $d_6$  at r.t. shows only one broad, featureless band at 5.65 ppm in the low field region. In the 300 MHz  $^1\text{H}$  NMR spectrum at  $-20^\circ\text{C}$  the haptotropic ring shift is frozen out, and three separate resonances are observed for the  $\eta^4$ -benzene ligand. However, resonances due to the tmps ligand remain broad, due to rotation of the  $\eta^4$ -benzene ring. At  $-60^\circ\text{C}$ , this ring rotation is also frozen out, and the  $^1\text{H}$ ,  $^{31}\text{P}$  and  $^{13}\text{C}$  NMR data may be assigned (Table 1) in terms of the rigid structure shown in Scheme 1. For example, two bands in the ratio of 2/1 is observed in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, but there is no resolvable  $^{31}\text{P}$ – $^{31}\text{P}$  coupling. The activation energies at coalescence for the ring rotation in **1** and **16** [20] are given in Table 4, along with an upper limit for **5**, and for comparison, some other selected analogous complexes.

The degenerate haptotropic ring shift in **1** has been investigated by magnetization transfer NMR experiments using a  $180^\circ$ - $t$ - $90^\circ$  pulse sequence. When one set of hydrogens was irradiated, magnetization was transferred into the other two sets of ring hydrogens. A plot of normalized peak intensity vs. time shows that the initial rate of transfer of magnetization into the two non-irradiated peaks of the benzene is the same for both peaks. This observation rules out a 1,2-shift mechanism because such a mechanism requires the exchange between  $\text{H}_{\text{a,a}'}$  and  $\text{H}_{\text{b,b}'}$  to occur at twice

TABLE 4  
 ROTATIONAL ENERGY BARRIERS FOR SOME IRON- $\eta$ -DIENE COMPOUNDS

|   | $G$ (kcal mol <sup>-1</sup> ) | Ref.      | $T_c$ (K)          |
|---|-------------------------------|-----------|--------------------|
| [Fe( $\eta^4$ -C <sub>6</sub> H <sub>6</sub> )(tmps)] (1)                               | 13.4                          | This work | 28                 |
| [Fe( $\eta$ -C <sub>4</sub> H <sub>6</sub> )(tmps)] (16)                                | 13.0                          | This work | 273                |
| [Fe( $\eta^4$ -1,3-C <sub>6</sub> H <sub>8</sub> )(tmps)] (5)                           | < 12.8 <sup>a</sup>           | This work | < 198 <sup>a</sup> |
| [Fe( $\eta^4$ -1,3-C <sub>6</sub> H <sub>8</sub> )[P(OMe) <sub>3</sub> ] <sub>3</sub> ] | 14.6                          | 25        |                    |
| [Fe( $\eta$ -C <sub>4</sub> H <sub>6</sub> )[P(OMe) <sub>3</sub> ] <sub>3</sub> ]       | 11.4                          | 26        |                    |
| [Fe( $\eta$ -C <sub>4</sub> H <sub>6</sub> )(CO) <sub>3</sub> ]                         | 12.0                          | 27        |                    |

<sup>a</sup> Low-temperature limit not achieved, estimate is an upper limit.

the rate of that between H<sub>a,a'</sub> and H<sub>c,c'</sub>. A 1,3-shift mechanism is, however, consistent with the observed rate data. Mingos [21] has shown, by Perturbation Molecular Orbital Theory arguments, that a 1,2-shift mechanism should be disallowed for such ring shifts in 18e, [M( $\eta^4$ -C<sub>6</sub>H<sub>6</sub>)L<sub>3</sub>] complexes. Although the complexity of three site exchange precluded a rigorous quantitative analysis of the data it appears from the variable temperature <sup>1</sup>H and <sup>31</sup>P NMR data, that the haptotropic ring shift is more than an order of magnitude slower than the ring rotation.

### Experimental

All preparations and reactions described were carried out under an atmosphere of nitrogen (< 10 ppm oxygen or water) using standard Schlenk tube, and vacuum line technique or in a dry box. Nitrogen was purified by passage through a gas drying column containing BASF catalyst and 5 Å molecular sieves.

All solvents were thoroughly deoxygenated before use by repeated pumping followed by admission of nitrogen. Solvents were pre-dried over activated molecular sieves and then distilled from potassium (toluene, benzene, tetrahydrofuran, cyclohexane), sodium-potassium alloy (pentane, 40–60 °C petroleum ether, diethyl ether,) or phosphorus pentoxide (dichloromethane), under an inert atmosphere of nitrogen. Deuteriated solvents for NMR were stored in Rotaflo ampoules over activated molecular sieves or a potassium film and transferred by vacuum distillation.

Elemental analyses were performed by the Analysis Department in this laboratory, or in the case of very air-sensitive materials, by Analytische Laboratorien, 5270 Gummersbach, 1 Elbach, W. Germany.

Infrared spectra were recorded on a Pye Unicam SP2000 double beam, grating spectrophotometer, or on a Perkin-Elmer 1510 FT interferometer. Abbreviations used in relative intensities are (vs) very strong, (s) strong, (m) medium, (w) weak, (br) broad; frequencies in cm<sup>-1</sup>.

NMR spectra were recorded on the following instruments: <sup>1</sup>H NMR 250 MHz, Bruker AM-250; 300 MHz, Bruker WH-300, 500 MHz, Bruker AM-500. <sup>13</sup>C NMR: 62.8 MHz, Bruker AM-250; 125.6 MHz; Bruker AM-500. <sup>31</sup>P NMR: 101.2 MHz, Bruker AM-250. Abbreviations used in multiplicities are; s singlet, d doublet, t triplet, q quartet, quin quintet, sex sextet, sept septet, m multiplet, vt virtual triplet, and br broad.

Spectra were referenced internally using the residual protio solvent resonance (<sup>1</sup>H, <sup>13</sup>C) relative to tetramethylsilane ( $\delta = 0$  ppm), or externally using trimeth-

ylphosphate in D<sub>2</sub>O (<sup>31</sup>P). All chemical shifts are quoted in δ (ppm), and coupling constants in hertz (Hz).

All multiple pulse and 2-dimensional NMR experiments were acquired using standard Bruker software, and processed using either ASPECT 2000 or ASPECT 3000 computers.

Crystal structures were determined on an Enraf Nonius CAD4F-circle diffractometer, using Mo radiation. Structures were solved and refined using the CRYSTALS [22] crystallography package and plotted using the CHEMGRAF [23] programmes on a VAX 11/750 computer. The source of the structure factor data is given in ref. 24.

Low resolution mass spectra were recorded on an AEI M.S. 902 mass spectrometer, updated by a data handling system supplied by Mass Spectroscopy Services Ltd.

Photoelectron spectra were recorded on a P.E.S. laboratories 0078 spectrometer using a heated inlet system. The spectrometer was calibrated using He, Xe, and N<sub>2</sub> ionisation potentials.

#### *η<sup>4</sup>-Benzene(tris(dimethylphosphinomethyl)methylsilane)iron (1)*

The compound [Fe(η-C<sub>6</sub>H<sub>6</sub>)(PMe<sub>3</sub>)<sub>2</sub>] [2] (2.84 g, 9.92 mmol) in petroleum ether (b.p. 40–60 °C, 60 cm<sup>3</sup>) was treated with tris(dimethylphosphinomethyl)methylsilane (tmps) (2.66 g, 9.91 mmol) in toluene (ca. 30 cm<sup>3</sup>). The reaction mixture was stirred and rapidly became a lighter shade of red. The reaction was stirred at r.t. for 6 h, and the volatiles were removed under reduced pressure. The solid red residue was extracted with pentane (2 × 30 cm<sup>3</sup>). The combined extracts were filtered, concentrated to ca. 15 cm<sup>3</sup>, and cooled to –20 °C giving red plate-like crystals of [Fe(η<sup>4</sup>-C<sub>6</sub>H<sub>6</sub>)(tmps)]. Yield: 2.7 g, 68%.

#### *Dicarbonyl(tris(dimethylphosphinomethyl)methylsilane)iron (2)*

A solution of [Fe(η<sup>4</sup>-C<sub>6</sub>H<sub>6</sub>)(tmps)] (0.15 g, 0.37 mmol) in petroleum ether (b.p. 40–60 °C, 30 cm<sup>3</sup>) was stirred under 1 atm. of CO. There was an instantaneous reaction giving a bright yellow solution. This was filtered, and concentrated to ca. 3 cm<sup>3</sup>. Cooling the concentrate (–40 °C) gave yellow crystals which were collected and dried in vacuo. Yield: > 90%.

#### *Di(μ-hydrido)(μ-vinylidene){bis[(tris(dimethylphosphinomethyl)methylsilane)iron]} (3)*

(a) A solution of [Fe(η<sup>4</sup>-C<sub>6</sub>H<sub>6</sub>)(tmps)] (0.65 g, 1.6 mmol) in toluene ca. 20 cm<sup>3</sup> in a thick-walled glass pressure bottle was pressurized to ca. 7 atm with ethylene. The red solution was heated at 55 °C for 15 h. The red solution slowly turned green. The volatiles were removed under reduced pressure leaving a green oily residue. The residue was extracted with pentane ca. 40 cm<sup>3</sup>, and the extract was filtered, concentrated to ca. 5 cm<sup>3</sup>, and cooled to –25 °C giving green needles. A second crop of these crystals were obtained by cooling the mother liquor to –80 °C. The overall yield was cal. 0.21 g, 40%.

(b) A suspension of {[ (tmps)Fe]<sub>2</sub>(μ-Cl)<sub>3</sub>}Cl (1.1 g, 2.8 mmol) in toluene (65 cm<sup>3</sup>) was added to sodium-amalgam (0.64 g, 28 mmol Na in ca. 64 g, Hg) under argon. The argon was evacuated and replaced by ethylene (1.5 atm). The mixture was then stirred vigorously for 2 days. Vigorous stirring was essential to ensure the stated yield. During this time the purple solid disappeared, and a dark green solution

formed. The solution was filtered, and the residue was extracted with petroleum ether (b.p. 40–60 °C, 2 × 50 cm<sup>3</sup>). The extracts were combined with the toluene filtrate, and the volatiles removed under reduced pressure leaving a green residue. The product was isolated as described in (a). Yield: 0.54 g, 57%.

*η-Cyclopentadienyl(tris(dimethylphosphinomethyl)methylsilane)hydridoiron (4)*

Cyclopentadiene (1.0 cm<sup>3</sup>) was vacuum-distilled into a frozen solution of [Fe(η<sup>4</sup>-C<sub>5</sub>H<sub>6</sub>)(tmps)] (0.20 g, 0.49 mmol) in toluene (20 cm<sup>3</sup>). The mixture was heated to 100 °C for 15 h. The volatiles were removed from the resultant yellow solution and black precipitate. The residue was extracted with pentane (40 cm<sup>3</sup>) and the extract was filtered and then concentrated to ca. 5 cm<sup>3</sup>. Cooling of the concentrate to –80 °C gave yellow microcrystals. Yield: 0.15 g, 77%. When the cyclopentadiene was replaced by cyclopentene, the same product was isolated but in lower yield, ca. 30%.

*η-Cyclohexa-1,3-diene[tris(dimethylphosphinomethyl)methylsilane]iron (5)*

A solution of cyclohexa-1,3-diene (0.21 g, 2.6 mmol) in toluene (5 cm<sup>3</sup>) was added to [Fe(η-C<sub>6</sub>H<sub>6</sub>)(tmps)] (0.35 g, 0.87 mmol) in toluene (20 cm<sup>3</sup>). The mixture was then heated to 80 °C for 2 h giving a yellow solution and a black precipitate. After cooling to r.t. the volatiles were removed under reduced pressure. The residue was extracted with pentane (30 cm<sup>3</sup>) and the extract was filtered and concentrated to ca. 5 cm<sup>3</sup>. Cooling the concentrate (to –40 °C) gave large yellow-brown prisms. Yield: 0.25 g, 72%.

*Diphenylacetylene(tris(dimethylphosphinomethyl)methylsilane)iron (6)*

(a) Diphenylacetylene (0.22 g, 1.24 mmol) in toluene (10 cm<sup>3</sup>) was added to a solution of [(η<sup>4</sup>-C<sub>6</sub>H<sub>6</sub>)Fe(tmps)] (0.50 g, 1.24 mmol) in toluene (20 cm<sup>3</sup>). The resultant mixture was heated to 60 °C for 6 h. The solution slowly turned dark green. The volatiles were removed under reduced pressure leaving a green solid which was extracted with pentane (2 × 30 cm<sup>3</sup>). The combined extracts were filtered, concentrated to ca. 25 cm<sup>3</sup> and cooled to –25 °C giving green needles. Yield: 0.48 g, 77%.

(b) A mixture of diphenylacetylene (0.20 g, 1.1 mmol) and {[(tmps)Fe]<sub>2</sub>Cl<sub>3</sub>}Cl (0.44 g, 1.1 mmol) was dissolved and suspended respectively in toluene (50 cm<sup>3</sup>) and then added to sodium amalgam (0.26 g, 11 mmol Na and ca. 40 g Hg). The mixture was stirred vigorously, and the solution turned dark green over 1 h. The reaction mixture was filtered, and the amalgam residue was extracted with petroleum ether (b.p. 40–60 °C). The extract was filtered and the filtrate was combined with the toluene filtrate. The volatile components were removed under reduced pressure, and the resulting green residue was crystallized as described in (a). Yield: 0.33 g, 60%.

*η-Pent-3-yne(tris(dimethylphosphinomethyl)methylsilane)iron (7)*

The compound [Fe(η<sup>4</sup>-C<sub>6</sub>H<sub>6</sub>)(tmps)] (0.35 g, 0.87 mmol) in toluene (10 cm<sup>3</sup>) was treated with pent-2-yne (0.25 cm<sup>3</sup>) and the mixture was heated to 70 °C for 15 h. The solution slowly turned deep blue. The volatile components were removed under reduced pressure giving a dark blue oil which was extracted with petroleum ether (b.p. 40–60 °C). The extract was filtered and the solvent was removed from the filtrate under reduced pressure giving a blue oil. This was distilled (120 °C, 10<sup>–5</sup>

torr) onto a cooled ( $-196^{\circ}\text{C}$ ) probe. The resulting oily distillate was washed from the probe with petroleum ether ( $40\text{--}60^{\circ}\text{C}$ ,  $20\text{ cm}^3$ ) and the solvent was removed under reduced pressure giving a blue oil. Yield: 0.20 g, 58%.

*$\eta$ -Hex-3-yne(tris(dimethylphosphinomethyl)methylsilane)iron (8)*

Hex-3-yne ( $0.25\text{ cm}^3$ ) was added to  $[\text{Fe}(\eta^4\text{-C}_6\text{H}_6)(\text{tmps})]$  (0.3 g, 0.74 mmol) in toluene ( $10\text{ cm}^3$ ). The solution was heated at  $70^{\circ}\text{C}$  for 15 h and it became dark blue. The reaction mixture was filtered and the product was isolated in the same fashion as the pent-2-yne analogue. Yield: 0.15 g, 50% as a blue oil.

*Bis(trimethylsilyl)acetylene(tris(dimethylphosphinomethyl)methylsilane)iron (9)*

The compound  $[\text{Fe}(\eta^4\text{-C}_6\text{H}_6)(\text{tmps})]$  (0.32 g, 0.79 mmol) in toluene ( $15\text{ cm}^3$ ) was treated with bis(trimethylsilyl)acetylene (0.25 g, 1.9 mmol). The mixture was heated to  $80^{\circ}\text{C}$  for 12 h and became green. The volatile component were removed under reduced pressure to give a green oil. The oil was dissolved in ca.  $20\text{ cm}^3$  of pentane, and filtered. Removal of the pentane under reduced pressure gave a green oil. Yield ca. 50%.

*$\eta$ -Cyclohexadienyl(tris(dimethylphosphinomethyl)methylsilane)iron hexafluorophosphate (11)*

The compound  $\text{NH}_4\text{PF}_6$  (0.10 g, 0.61 mmol) in wet thf ( $20\text{ cm}^3$ ) was added to a  $[\text{Fe}(\eta^4\text{-C}_6\text{H}_6)(\text{tmps})]$  (0.15 g, 0.37 mmol) in thf ( $10\text{ cm}^3$ ) giving a yellow precipitate. The mixture was stirred overnight, and the thf was then removed under reduced pressure. The residue was washed with water ( $30\text{ cm}^3$ ) and diethyl ether ( $40\text{ cm}^3$ ) and dissolved in methanol ( $40\text{ cm}^3$ ). The extract was filtered, and the filtrate was concentrated to ca.  $10\text{ cm}^3$ . Cooling to  $-20^{\circ}\text{C}$  afforded yellow prismatic crystals. Yield: 0.17 g, 84%.

*$\eta$ -Benzene(tris(dimethylphosphinomethyl)methylsilane)iron bis(tetrafluoroborate)  $\cdot \frac{1}{4}$  acetonitrile (12)*

$\text{AgBF}_4$  (0.29 g, 1.5 mmol) in thf ( $20\text{ cm}^3$ ) was added to a solution of  $[\text{Fe}(\eta\text{-C}_6\text{H}_6)(\text{tmps})]$  (0.30 g, 0.75 mmol) in thf ( $20\text{ cm}^3$ ) giving a bright yellow precipitate. After stirring for ca. 30 min the precipitate was collected, dried under reduced pressure, and dissolved in ca.  $10\text{ cm}^3$   $\text{CH}_3\text{CN}$ . The extract was filtered, and concentrated to ca.  $5\text{ cm}^3$ . Addition of diethyl ether ( $15\text{ cm}^3$ ) precipitated the product as yellow microcrystals. Yield  $> 95\%$ .

*{Bis[(tris(dimethylphosphinomethyl)methylsilane)iron]( $\mu$ -trichloro)}chloride (13)*

A solution of tmps (1.95 g, 7.38 mmol) in toluene  $10\text{ cm}^3$  was added to a stirred suspension of  $\text{FeCl}_2 \cdot 2\text{thf}$  in  $\text{CH}_2\text{Cl}_2$  ( $30\text{ cm}^3$ ). There was an instantaneous reaction to form a dark purple solution. The  $\text{FeCl}_2 \cdot 2\text{thf}$  dissolved within ca. 5 min, and within 15 min a purple microcrystalline solid precipitated. The mixture was stirred for 24 h, and the precipitate was collected and dried under reduced pressure. The volatiles were removed from the solution to give a purple powder which was washed with petroleum ether (b.p.  $40\text{--}60^{\circ}\text{C}$ ). Yield  $> 95\%$ .

*{Bis[(tris(dimethylphosphinomethyl)methylsilane)iron]( $\mu$ -trichloro)} tetraphenylborate (14)*

This complex was synthesized following the procedure described by Bianchini et al. [19] except using tmps and  $\text{FeCl}_2 \cdot 2\text{thf}$ . Yield  $> 80\%$ .

*$\eta$ -Cyclopentadienyl(tris(dimethylphosphinomethyl)methylsilane)iron hexafluoro-phosphate (15)*

Sodium cyclopentadienide (0.5 g, 5.68 mmol) in thf (20 cm<sup>3</sup>) was added to a suspension of [(tmps)Fe( $\mu$ -Cl)<sub>3</sub>Fe(tmps)]Cl (0.50 g, 0.63 mmol) in thf (30 cm<sup>3</sup>). There was an immediate reaction giving a yellow-brown solution. After stirring for 2 h the volatile components were removed under reduced pressure, and the residue was treated with water (40 cm<sup>3</sup>). Solid NH<sub>4</sub>PF<sub>6</sub> (0.25 g, 1.5 mmol) was added giving a bright yellow precipitate. This was collected, and washed with water (20 cm<sup>3</sup>) then with diethyl ether (40 cm<sup>3</sup>). The product was recrystallized from methanol as yellow crystals. Yield: 0.41 g, 60%.

*$\eta$ -Buta-1,3-diene(tris(dimethylphosphinomethyl)methylsilane)iron (16)*

A suspension of Mg(C<sub>4</sub>H<sub>6</sub>)<sub>2</sub>·2thf (0.42 g, 1.9 mmol) in thf (20 cm<sup>3</sup>) was cooled to 0 °C and added to a suspension of [MeSi(CH<sub>2</sub>PMe<sub>2</sub>)<sub>3</sub>Fe( $\mu$ -Cl)<sub>3</sub>Fe(tmps)]Cl (0.42 g, 0.53 mmol) in thf (30 cm<sup>3</sup>) at 0 °C. The reaction mixture turned yellow-brown as it was allowed to warm to r.t. The reaction was stirred for a further 6 h at room temperature, and then the volatiles were removed under reduced pressure. The residue was extracted with pentane (2 × 50 cm<sup>3</sup>), and the combined extracts were filtered and concentrated to ca. 5 cm<sup>3</sup>. Cooling to -80 °C gave yellow microcrystals. Yield: 0.10 g, 25%. The low yield is due to the solubility of the complex. Removal of solvent from the mother liquor of the crystallization gives a further 0.20 g of product which is at least 90% pure.

*exo-(2-Phenylethyl)- $\eta$ -cyclohexadienyl(tris(dimethylphosphinomethyl)methylsilane)iron (17)*

The compound [Fe( $\eta$ -PhC≡CPh)(tmps)] (0.23 g, 0.46 mmol) in petroleum ether (b.p. 40–60 °C, 20 cm<sup>3</sup>) was stirred under an atmosphere of H<sub>2</sub>. Within seconds of exposure to H<sub>2</sub>, the green solution turned bright red. After stirring for ca. 15 min, the solution was filtered and the solvent was removed under reduced pressure giving an involatile red oil. Yield: > 95%.

*5-exo-(2-Phenylethyl)- $\eta$ -cyclohexa-1,3-diene(tris(dimethylphosphinomethyl)methylsilane)iron (18)*

The compound [Fe( $\eta^4$ -C<sub>14</sub>H<sub>14</sub>)(tmps)] (0.20 g, 0.39 mmol) was treated with excess dilute aqueous HCl (15 cm<sup>3</sup>, 0.5 M) for ca. 5 min. Solid NH<sub>4</sub>PF<sub>6</sub> (0.25 g, 1.6 mmol) was added giving a yellow-orange precipitate which was washed with water (10 cm<sup>3</sup>), diethyl ether (15 cm<sup>3</sup>), and, finally, recrystallized from methanol as yellow-orange crystals. Yield: 0.24 g, 94%.

*Crystal structure determination*

*Crystal data for 3.* C<sub>22</sub>H<sub>58</sub>Fe<sub>2</sub>P<sub>6</sub>Si<sub>2</sub>, *M* = 676.4, orthorhombic, space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* 11.573(2), *b* 11.804(1), *c* 25.805(6) Å, *V* 3549.6 Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> 1.265 g cm<sup>-3</sup>, *F*(000) = 1440, graphite monochromated (Mo-*K*<sub>α</sub>) radiation,  $\lambda$  0.71069 Å,  $\mu$ (Mo-*K*<sub>α</sub>) 11.816 cm<sup>-1</sup>.

A crystal of compound 3 (0.2 × 0.3 × 0.45 mm) was mounted in a Lindemann glass capillary under N<sub>2</sub> and was mounted on a CAD4 diffractometer. Accurate cell dimensions were determined from the position of 24 carefully centred reflections. Data were collected out to 22.5° in  $\theta$ , using an  $\omega$ -2 $\theta$  scan with variable scan angle

of  $(1.0 + 0.35 \tan \theta)^\circ$ . During data collection three intensity control reflections were measured every hour and three orientation controls were checked after each 250 measurements. There was no variation in intensity controls during data collection.

The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was also applied [22]. The equivalent reflections were merged ( $R_m$  4.32%) and only those for which  $I > 3\sigma(I)$  were included in refinement yielding 2172 observed. The structure was solved by the heavy-atom method. All the non-hydrogen atoms were refined anisotropically using full matrix least-squares methods. The two highest peaks in the final difference Fourier maps of 0.61 and 0.46  $e/\text{\AA}^3$  were located in positions consistent with the bridging hydride ligands, but were not included in refinement. The remaining hydrogen atoms were placed in calculated positions and included in structure factor calculations, but were not refined. At convergence  $R, R' = 0.0325, 0.0431$ . The final positional parameters for the compound are recorded in Table 4.

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