

## Electronic Supplementary Information for

### Regioselective Silylphosphination of Methyl Vinyl Ketone with Complexes Containing Cyclic and Linear Iron–Silicon–Phosphorus Reacting Sites

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**Reaction of  $\text{Cp}^*(\text{CO})\text{Fe}\{\kappa^2(\text{Si},\text{P})\text{-SiMe}_2\text{PPh}_2\}$  (**1**) with Methyl Vinyl Ketone.** A Schlenk tube (50 mL) was charged with **1** (30 mg, 0.065 mmol) and pentane (10 mL), to which an excess of methyl vinyl ketone (0.5 mL) was added by syringe at room temperature. After stirring for 30 min, removal of volatiles in vacuo gave a yellow oil of **3**. Yield: 26 mg (75%). NMR spectral data showed that **3** consists of two isomers **3a** and **3b** in a 2:1 molar ratio. Anal. Calc. for  $\text{C}_{29}\text{H}_{37}\text{FeO}_2\text{SiP}$ : C: 65.41, H: 7.00. Found: C: 65.17, H: 7.19. EI-Mass (70 eV)  $m/z$  532 ( $\text{M}^+$ , 22), 504 ( $\text{M}^+ - \text{CO}$ , 9), 489 ( $\text{M}^+ - \text{CO} - \text{Me}$ , 4), 462 ( $\text{M}^+ - \text{CO} - \text{Me} - \text{C}_2\text{H}_5$ , 100).  $^1\text{H}$  NMR (300 MHz, benzene- $d_6$ )  $\delta$  0.96, 0.99 (s, 3Hx2, SiMe<sub>2</sub> for **3a**), 0.99, 1.01 (s, 3Hx2, SiMe<sub>2</sub> for **3b**), 1.11 (d,  $^3J_{\text{PH}} = 12.6$  Hz, 3H, CMe for **3a**), 1.39 (s, 15H, Cp\* for **3b**), 1.40 (s, 15H, Cp\* for **3a**), 1.68 (d,  $^3J_{\text{PH}} = 8.9$  Hz, 3H, CMe for **3b**), 4.94 (ddd,  $^2J_{\text{ab}} = 1.8$  Hz,  $^4J_{\text{PH}} = 2.4$  Hz,  $^3J_{\text{ac}} = 10.4$  Hz, 1H, H<sub>a</sub> for **3b**), 5.00 (ddd,  $^2J_{\text{ab}} = 2.1$  Hz,  $^4J_{\text{PH}} = 2.4$  Hz,  $^3J_{\text{ac}} = 10.4$  Hz, 1H, H<sub>a</sub> for **3a**), 5.38 (ddd,  $^3J_{\text{PH}} = 2.6$  Hz,  $^3J_{\text{ac}} = 10.4$  Hz,  $^3J_{\text{bc}} = 17.0$  Hz, 1H, H<sub>c</sub> for **3b**), 5.56 (ddd,  $^2J_{\text{ab}} = 1.8$  Hz,  $^4J_{\text{PH}} = 2.0$  Hz,  $^3J_{\text{bc}} = 17.0$  Hz, 1H, H<sub>b</sub> for **3b**), 5.63 (ddd,  $^2J_{\text{ab}} = 2.1$  Hz,  $^4J_{\text{PH}} = 2.7$  Hz,  $^3J_{\text{bc}} = 16.8$  Hz, 1H, H<sub>b</sub> for **3a**), 6.05 (ddd,  $^3J_{\text{PH}} = 1.5$  Hz,  $^3J_{\text{ac}} = 10.4$  Hz,  $^3J_{\text{bc}} = 16.8$  Hz, 1H, H<sub>c</sub> for **3a**), 6.93–7.23 (m, Ph), 7.86–8.02 (m, Ph).  $^{13}\text{C}$  NMR (75.5 MHz, benzene- $d_6$ )  $\delta$  9.5 (d,  $^2J_{\text{PC}} = 2.2$  Hz, SiMe for **3b**), 9.7

(d,  $^2J_{\text{PC}} = 2.2$ , SiMe for **3a**), 9.8 ( $\text{C}_5\text{Me}_5$  for **3b**), 9.9 ( $\text{C}_5\text{Me}_5$  for **3a**), 10.4 (d,  $^3J_{\text{PC}} = 3.3$  Hz, SiMe for **3a**), 10.8 (d,  $^3J_{\text{PC}} = 3.3$  Hz, SiMe for **3b**), 26.4 (OCMe for **3b**), 27.7 (d,  $^2J_{\text{PC}} = 10.9$  Hz, OCMe for **3a**), 85.7 (d,  $^1J_{\text{PC}} = 34.9$  Hz, OCMe for **3b**), 86.0 (d,  $^1J_{\text{PC}} = 32.8$ , OCMe for **3a**), 91.1 ( $\text{C}_5\text{Me}_5$  for **3b**), 91.4 ( $\text{C}_5\text{Me}_5$  for **3a**), 112.9 (d,  $^3J_{\text{PC}} = 5.4$  Hz, CH=CH<sub>2</sub> for **3a**), 115.9 (d,  $^3J_{\text{PC}} = 7.6$  Hz, CH=CH<sub>2</sub> for **3b**), 127.1 (d,  $J_{\text{PC}} = 7.9$  Hz, Ph), 128.9 (d,  $J_{\text{PC}} = 8.8$  Hz, Ph), 130.5 (m, Ph), 134.5 (d,  $J_{\text{PC}} = 27.3$  Hz, Ph), 135.4 (m, Ph), 135.9 (d,  $J_{\text{PC}} = 27.2$  Hz, Ph), 142.9 (d,  $^2J_{\text{PC}} = 10.9$  Hz, CH=CH<sub>2</sub> for **3b**), 143.1 (CH=CH<sub>2</sub> for **3a**), 221.6 (d,  $^2J_{\text{PC}} = 21.8$  Hz, CO for **3b**), 222.5 (d,  $^2J_{\text{PC}} = 21.8$  Hz, CO for **3a**).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.5 MHz, benzene-*d*<sub>6</sub>)  $\delta$  122.9 (**3b**), 124.1 (**3a**).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (59.6 MHz, benzene-*d*<sub>6</sub>)  $\delta$  95.9 (d,  $J_{\text{PSi}} = 39.8$  Hz, **3a**), 96.4 (d,  $J_{\text{PSi}} = 44.8$  Hz, **3b**), IR (benzene-*d*<sub>6</sub>) 1894 cm<sup>-1</sup> ( $\nu_{\text{CO}}$ ).

**Reaction of Cp\*(CO)<sub>2</sub>FeSiMe<sub>2</sub>PPh<sub>2</sub> (2) with Methyl Vinyl Ketone.** A Schlenk tube (50 mL) was charged with **2** (202 mg, 0.412 mmol) and toluene (10 mL), to which an excess of methyl vinyl ketone (1.0 mL) was added by syringe at room temperature. After stirring for 30 min, volatiles were removed under reduced pressure. Cooling of the residue at -30 °C allowed the growth of yellow crystals of **4**. Yield: 150 mg (65%). Anal. Calc. for C<sub>30</sub>H<sub>37</sub>FeO<sub>3</sub>PSi: C: 64.28, H: 6.65. Found: C: 64.23, H: 6.70. EI-Mass (70 eV)  $m/z$  560 ( $\text{M}^+$ , 2), 532 ( $\text{M}^+ - \text{CO}$ , 2), 504 ( $\text{M}^+ - 2\text{CO}$ , 2), 313 ( $\text{M}^+ - 2\text{CO} - \text{Cp}^* - \text{Fe}$ , 100).  $^1\text{H}$  NMR (300 MHz, benzene-*d*<sub>6</sub>)  $\delta$  0.75 (s, 6H, SiMe<sub>2</sub>), 1.55 (s, 15H, Cp\*), 1.77 (d,  $^5J_{\text{PH}} = 3.2$  Hz, 3H, OCMe), 3.18 (d,  $^3J_{\text{HH}} = 7.4$  Hz, 2H, CH<sub>2</sub>), 4.56 (pseudo q,  $J = 7.2$  Hz, CH), 7.03–7.21 (m, 6H, *m,p*-Ph), 7.62 (m, 4H, *o*-Ph).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz, chloroform-*d*)  $\delta$  8.8 (SiMe<sub>2</sub>), 10.0 ( $\text{C}_5\text{Me}_5$ ), 23.1 (OCMe), 24.8 (d,  $^1J_{\text{PC}} = 10.6$  Hz, CH<sub>2</sub>), 95.4 ( $\text{C}_5\text{Me}_5$ ), 101.4 (d,  $^2J_{\text{PC}} = 9.1$  Hz, CH), 128.2 (br s, *m,p*-Ph), 132.8 (d,  $^2J_{\text{PC}} = 17.4$  Hz, *o*-Ph), 139.3 (d,  $^1J_{\text{PC}} = 15.1$  Hz, *ipso*-Ph), 150.0 (d,  $^3J_{\text{PC}} = 9.8$  Hz, OCMe), 216.9 (CO).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (benzene-*d*<sub>6</sub>, 75.5 MHz)  $\delta$  68.2.  $^{31}\text{P}\{^1\text{H}\}$  NMR (benzene-*d*<sub>6</sub>, 59.6 MHz)  $\delta$  -14.3. IR (benzene-*d*<sub>6</sub>) 1921, 1977 cm<sup>-1</sup> ( $\nu_{\text{CO}}$ ).

**UV Irradiation of 4 in Pentane.** A Pyrex tube (20 mm o.d.) equipped with a greaseless

vacuum valve was charged with **4** (150 mg, 0.268 mmol). Pentane (25 mL) was introduced into this tube under high vacuum by the trap-to-trap transfer technique. After sealing the tube off from the vacuum line, the contents were irradiated using a 450 W medium pressure Hg lamp for 30 min. In the course of the photoreaction, the color of the solution changed from yellow to brown. Volatiles were removed under reduced pressure, and recrystallization of the residue from pentane at  $-30\text{ }^{\circ}\text{C}$  gave yellow crystals of **5**. Yield: 85 mg (60%). Anal. Calc. for  $\text{C}_{29}\text{H}_{37}\text{FeO}_2\text{PSi}$ : C: 65.41, H: 7.00. Found: C: 65.42, H: 7.11. EI-Mass (70 eV)  $m/z$  532 ( $\text{M}^+$ , 14), 504 ( $\text{M}^+ - \text{CO}$ , 37), 489 ( $\text{M}^+ - \text{CO} - \text{Me}$ , 2), 462 ( $\text{M}^+ - \text{CO} - \text{Me} - \text{C}_2\text{H}_5$ , 6), 262 (100).  $^1\text{H}$  NMR (300 MHz, benzene- $d_6$ )  $\delta$  0.92, 1.15 (s, 3Hx2, SiMe<sub>2</sub>), 1.37 (s, 15H, Cp\*), 1.85 (d,  $^5J_{\text{PH}} = 5.9\text{ Hz}$ , 3H, OCMe), 2.76 (ddd,  $J_{\text{gem}} = 13.1\text{ Hz}$ ,  $J_{\text{vic}} = 6.5\text{ Hz}$ ,  $^2J_{\text{PH}} = 13.1\text{ Hz}$ , 1H, PCH<sub>2</sub>), 3.64 (ddd,  $J_{\text{gem}} = 13.1\text{ Hz}$ ,  $J_{\text{vic}} = 8.0\text{ Hz}$ ,  $^2J_{\text{PH}} = 6.5\text{ Hz}$ , 1H, PCH<sub>2</sub>), 4.08 (m, 1H, CH=CMe), 6.96–7.06 (m, 4H, Ph), 7.09–7.26 (m, 2H, *o*-Ph), 7.39–7.49 (m, 2H, Ph), 7.74–7.83 (m, 2H, Ph).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz, dichloromethane- $d_2$ )  $\delta$  9.6 ( $\text{C}_5\text{Me}_5$ ), 9.9, 10.9 (SiMe<sub>2</sub>), 21.8 (d,  $^4J_{\text{PC}} = 3.0\text{ Hz}$ , OCMe), 35.5 (d,  $^1J_{\text{PC}} = 31.0\text{ Hz}$ , CH<sub>2</sub>PPh<sub>2</sub>), 91.7 ( $\text{C}_5\text{Me}_5$ ), 96.6 (d,  $^2J_{\text{PC}} = 6.8\text{ Hz}$ , CH=CMe), 127.6 (d,  $^3J_{\text{PC}} = 4.5\text{ Hz}$ , *m*-Ph), 127.7 (d,  $^3J_{\text{PC}} = 4.5\text{ Hz}$ , *m*-Ph), 128.7 (*p*-Ph), 129.6 (*p*-Ph), 132.6 (d,  $^2J_{\text{PC}} = 8.3\text{ Hz}$ , *o*-Ph), 134.3 (d,  $^2J_{\text{PC}} = 10.6$ , *o*-Ph), 135.8 (d,  $^1J_{\text{PC}} = 34.7\text{ Hz}$ , *ipso*-Ph), 138.2 (d,  $^1J_{\text{PC}} = 26.4\text{ Hz}$ , *ipso*-Ph), 155.1 (d,  $^3J_{\text{PC}} = 9.1\text{ Hz}$ , CH=CMe), 221.3 (d,  $^2J_{\text{PC}} = 22.7$ , CO).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (59.6 MHz, benzene- $d_6$ )  $\delta$  79.3 (d,  $J_{\text{PSi}} = 43.5\text{ Hz}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.5 MHz, benzene- $d_6$ )  $\delta$  65.9. IR (benzene- $d_6$ )  $1896\text{ cm}^{-1}$  ( $\nu_{\text{CO}}$ ).

**X-ray Diffraction Study of **3**, **4** and **5**.** Cooling the pentane solutions of **3**, **4**, and **5** at  $-30\text{ }^{\circ}\text{C}$  allowed the growth of single crystals suitable for x-ray diffraction study. Intensity data for the analysis were collected at  $-123\text{ }^{\circ}\text{C}$  on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo  $\text{K}\alpha$  radiation. The structure was solved by Patterson and Fourier transform methods (SHELXS-97) and refined by full matrix least-squares techniques on all  $F^2$  data (SHELXL-97). Crystallographic data are available as CIF files.