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

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Reaction of Cp*(CO)Fe{κ^2(Si,P)-SiMe2PPh2} (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 C_{29}H_{37}FeO_{2}SiP: C: 65.41, H: 7.00. Found: C: 65.17, H: 7.19. EI-Mass (70 eV) m/z 532 (M^+, 22), 504 (M^+-CO, 9), 489 (M^+-CO–Me, 4), 462 (M^+-CO–Me–C_2H_5, 100). ^1H NMR (300 MHz, benzene-d_6) δ 0.96, 0.99 (s, 3H, SiMe for 3a), 0.99, 1.01 (s, 3H, SiMe for 3b), 1.11 (d, ^3J_{PH} = 12.6 Hz, 3H, CMe for 3a), 1.39 (s, 15H, Cp for 3a), 1.40 (s, 15H, Cp for 3b), 1.68 (d, ^3J_{PH} = 8.9 Hz, 3H, CMe for 3b), 4.94 (ddd, ^2J_{ab} = 1.8 Hz, ^4J_{PH} = 2.4 Hz, ^3J_{ac} = 10.4 Hz, 1H, H_a for 3a), 5.00 (ddd, ^2J_{ab} = 2.1 Hz, ^4J_{PH} = 2.4 Hz, ^3J_{ac} = 10.4 Hz, 1H, H_a for 3b), 5.38 (ddd, ^3J_{PH} = 2.6 Hz, ^3J_{ac} = 10.4 Hz, ^3J_{bc} = 17.0 Hz, 1H, H_c for 3a), 5.56 (ddd, ^2J_{ab} = 1.8 Hz, ^4J_{PH} = 2.0 Hz, ^3J_{bc} = 17.0 Hz, 1H, H_b for 3b), 5.63 (ddd, ^2J_{ab} = 2.1 Hz, ^4J_{PH} = 2.7 Hz, ^3J_{bc} = 16.8 Hz, 1H, H_b for 3a), 6.05 (ddd, ^3J_{PH} = 1.5 Hz, ^3J_{ac} = 10.4 Hz, ^3J_{bc} = 16.8 Hz, 1H, H_c for 3a), 6.93–7.23 (m, Ph), 7.86–8.02 (m, Ph). ^13C NMR (75.5 MHz, benzene-d_6) δ 9.5 (d, ^2J_{PC} = 2.2 Hz, SiMe for 3b), 9.7
(d, $^2J_{PC} = 2.2$, SiMe for 3a), 9.8 (C$_5$Me$_5$ for 3b), 9.9 (C$_5$Me$_5$ for 3a), 10.4 (d, $^3J_{PC} = 3.3$ Hz, SiMe for 3a), 10.8 (d, $^3J_{PC} = 3.3$ Hz, SiMe for 3b), 26.4 (OCMe for 3b), 27.7 (d, $^2J_{PC} = 10.9$ Hz, OCMe for 3a), 85.7 (d, $^1J_{PC} = 34.9$ Hz, OCMe for 3b), 86.0 (d, $^1J_{PC} = 32.8$, OCMe for 3a), 91.1 (C$_5$Me$_5$ for 3b), 91.4 (C$_5$Me$_5$ for 3a), 112.9 (d, $^3J_{PC} = 5.4$ Hz, CH=CH$_2$ for 3a), 115.9 (d, $^3J_{PC} = 7.6$ Hz, CH=CH$_2$ for 3b), 127.1 (d, $J_{PC} = 7.9$ Hz, Ph), 128.9 (d, $J_{PC} = 8.8$ Hz, Ph), 130.5 (m, Ph), 134.5 (d, $J_{PC} = 27.3$ Hz, Ph), 135.4 (m, Ph), 135.9 (d, $J_{PC} = 27.2$ Hz, Ph), 142.9 (d, $^2J_{PC} = 10.9$ Hz, CH=CH$_2$ for 3b), 143.1 (CH=CH$_2$ for 3a), 221.6 (d, $^2J_{PC} = 21.8$ Hz, CO for 3b), 222.5 (d, $^2J_{PC} = 21.8$ Hz, CO for 3a). $^{31}$P{$^1$H} NMR (121.5 MHz, benzene-$d_6$) δ 122.9 (3b), 124.1 (3a).

$^{29}$Si{$^1$H} NMR (59.6 MHz, benzene-$d_6$) δ 95.9 (d, $J_{PSi} = 39.8$ Hz, 3a), 96.4 (d, $J_{PSi} = 44.8$ Hz, 3b), IR (benzene-$d_6$) 1894 cm$^{-1}$ ($\nu_{CO}$).

**Reaction of Cp*(CO)$_2$FeSiMe$_2$PPh$_2$ (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 ºC allowed the growth of yellow crystals of 4. Yield: 150 mg (65%). Anal. Calc. for C$_{30}$H$_{37}$FeO$_3$PSi: C: 64.28, H: 6.65. Found: C: 64.23, H: 6.70. EI-Mass (70 eV) m/z 560 (M$^+$, 2), 532 (M$^+$–CO, 2), 504 (M$^+$–2CO, 2), 313 (M$^+$–2CO–Cp*–Fe, 100). $^1$H NMR (300 MHz, benzene-$d_6$) δ 0.75 (s, 6H, SiMe$_2$), 1.55 (s, 15H, Cp*), 1.77 (d, $^5J_{PH} = 3.2$ Hz, 3H, OCMe), 3.18 (d, $^3J_{HH} = 7.4$ Hz, 2H, CH$_2$), 4.56 (pseudo q, $J = 7.2$ Hz, CH), 7.03–7.21 (m, 6H, m,p-Ph), 7.62 (m, 4H, o-Ph). $^{13}$C{$^1$H} NMR (75.5 MHz, chloroform-$d$) δ 8.8 (SiMe$_2$), 10.0 (C$_5$Me$_5$), 23.1 (OCMe), 24.8 (d, $^1J_{PC} = 10.6$ Hz, CH$_2$), 95.4 (C$_5$Me$_5$), 101.4 (d, $^2J_{PC} = 9.1$ Hz, CH), 128.2 (br s, m,p-Ph), 132.8 (d, $^2J_{PC} = 17.4$ Hz, o-Ph), 139.3 (d, $^1J_{PC} = 15.1$ Hz, ipso-Ph), 150.0 (d, $^3J_{PC} = 9.8$ Hz, OCMe), 216.9 (CO). $^{29}$Si{$^1$H} NMR (benzene-$d_6$, 75.5 MHz) δ 68.2. $^{31}$P{$^1$H} NMR (benzene-$d_6$, 59.6 MHz) δ –14.3. IR (benzene-$d_6$) 1921, 1977 cm$^{-1}$ ($\nu_{CO}$).

**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 °C gave yellow crystals of 5. Yield: 85 mg (60%). Anal. Calc. for C_{29}H_{37}FeO_2PSi: C: 65.41, H: 7.00. Found: C: 65.42, H: 7.11. EI-Mass (70 eV) m/z 532 (M^+, 14), 504 (M^–CO, 37), 489 (M^–CO–Me, 2), 462 (M^–CO–Me–C_3H_3, 6), 262 (100). 1H NMR (300 MHz, benzene-\(d_6\)) δ 0.92, 1.15 (s, 3Hx2, SiMe2), 1.37 (s, 15H, Cp*), 1.85 (d, \(^5J_{PH} = 5.9\) Hz, 3H, OCMe), 2.76 (ddd, \(J_{gem} = 13.1\) Hz, \(J_{vic} = 6.5\) Hz, \(^2J_{PH} = 13.1\) Hz, 1H, PCH2), 3.64 (ddd, \(J_{gem} = 13.1\) Hz, \(J_{vic} = 8.0\) Hz, \(^2J_{PH} = 6.5\) Hz, 1H, PCH2), 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). 13C{1H} NMR (75.5 MHz, dichloromethane-\(d_2\)) δ 9.6 (C_5Me_5), 9.9, 10.9 (SiMe_2), 21.8 (d, \(^4J_{PC} = 3.0\) Hz, OCMe), 35.5 (d, \(^1J_{PC} = 31.0\) Hz, CH_2PPh_2), 91.7 (C_5Me_5), 96.6 (d, \(^2J_{PC} = 6.8\) Hz, CH=CMe), 127.6 (d, \(^3J_{PC} = 4.5\) Hz, m-Ph), 127.7 (d, \(^3J_{PC} = 4.5\) Hz, m-Ph), 128.7 (p-Ph), 129.6 (p-Ph), 132.6 (d, \(^2J_{PC} = 8.3\) Hz, o-Ph), 134.3 (d, \(^2J_{PC} = 10.6\), o-Ph), 135.8 (d, \(^1J_{PC} = 34.7\) Hz, ipso-Ph), 138.2 (d, \(^1J_{PC} = 26.4\) Hz, ipso-Ph), 155.1 (d, \(^3J_{PC} = 9.1\) Hz, CH=CMe), 221.3 (d, \(^2J_{PC} = 22.7\), CO). 29Si{1H} NMR (59.6 MHz, benzene-\(d_6\)) δ 79.3 (d, \(J_{PSi} = 43.5\) Hz). 31P{1H} NMR (121.5 MHz, benzene-\(d_6\)) δ 65.9. IR (benzene-\(d_6\)) 1896 cm\(^{-1}\) (\(\nu_{CO}\)).

**X-ray Diffraction Study of 3, 4 and 5.** Cooling the pentane solutions of 3, 4, and 5 at –30 °C allowed the growth of single crystals suitable for x-ray diffraction study. Intensity data for the analysis were collected at –123 °C on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo 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 \(R^2\) data (SHELXL-97). Crystallographic data are available as CIF files.