Base-Free Iron Hydrosilylene Complexes *via* an *α*-Hydride Migration that Induces Spin Pairing

Supporting Information

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General Considerations. All manipulations were carried out using standard Schlenk or inert atmosphere glovebox techniques with an atmosphere of dry dinitrogen. All solvents were dried over activated alumina prior to use. Benzene-d_6 was degassed with 3 freeze-pump-thaw cycles and stored over activated molecular sieves (4 Å) for 24 h prior to use. Cp*H,[1] $^{i}Pr_2MeP$,[2] $DMPSiH_3$,[3] $TripSiH_3$,[4] and $[Mes_2Fe]_2$[5] were prepared by literature procedures. The preparations and characterization of Cp*($^{i}Pr_2MeP$)H_2FeSiHDMP (**10**) and Cp*($^{i}Pr_2MeP$)FeH(N_2) have been described previously.[6]

NMR spectra were recorded using Bruker AVB-400, AVQ-400, AV-500, or AV-600 spectrometers equipped with a 5 mm broad band or TBI probe. Spectra were recorded at room temperature (ca. 22 ºC) and referenced to the residual protoisotopomer of the solvent for ^{1}H unless otherwise noted. $^{31}P\{^{1}H\}$ NMR spectra were referenced relative to 85% H_3PO_4 external standard ($\delta = 0$). $^{13}C\{^{1}H\}$ NMR spectra were calibrated internally with the resonance for the solvent relative to tetramethylsilane. For $^{13}C\{^{1}H\}$ NMR spectra, resonances obscured by the solvent signal were omitted. ^{29}Si NMR spectra were obtained via 2D ^{1}H ^{29}Si HMBC. The following abbreviations have been used to describe infrared features: “s” for strong, “m” for medium, “w” for weak, “v” for very, “b” for broad. Elemental analyses were performed by the College of Chemistry Microanalytical Laboratory at the University of California, Berkeley.

Synthesis of Cp*(^{i}Pr$_2$MeP)FeMes (1). $^{i}Pr_2MeP$ (0.74 mL, 4.0 mmol) was added to $[FeMes_2]_2$ (1.00 g, 1.70 mmol) dissolved in THF (20 mL) with stirring. The solution became lighter orange, and Cp*H (0.56 mL, 3.6 mmol) was added and stirring was continued for 18 h, over which time the solution became brown. Volatile components were removed *in vacuo* to give a dark solid. This was extracted with 3 x 5 mL pentane which was concentrated to ca. 10 mL and stored at -35 °C overnight, giving dark olive crystals. Yield: 1.02 g, 68%. Anal. Calcd. for $C_{26}H_{43}FeP$: C, 70.58; H, 9.80. Found: C, 70.70; H, 9.94. Magnetic moment: 3.6(6) μ_B (Evans). ^{1}H NMR (400 MHz, Benzene-d_6) δ 38.68 (s,

15H, Cp*), 22.38 (s, 2H), 12.36 (s, 3H), 9.20 (s, 3H), 6.68 (s, 6H), -7.03 (s, 6H), -11.63 (s, 6H), -24.41 (s, 2H). FTIR (KBr pellet): 2958 (s), 2901 (s), 2868 (s), 2721 (w), 1605 (m), 1450 (vs, br), 1373 (s), 1311 (m), 1254 (s), 1152 (m), 2098 (m), 1075 (m), 1029 (vs), 890 (vs), 845 (vs), 833 (s), 751 (m), 715 (s), 686 (s), 628 (s), 608 (s) cm^{-1}.

Synthesis of Cp*(^{i}Pr$_2$MeP)(N$_2$)FeSiHPh$_2$/Cp*(^{i}Pr$_2$MeP)FeSiHPh$_2$ (2/3). Ph_2SiH_2 (0.040 g, 0.22 mmol) in 4 mL of pentane was added to **1** (0.10 g, 0.23 mmol) dissolved in 4 mL of pentane, over 30 min. After stirring for 1 h, a small amount of a yellow precipitate formed with a dark orange solution. Volatile components were removed *in vacuo* and the resultant orange residue was extracted with 2 x 5 mL of pentane. This solution was concentrated to 4 mL and stored at -35 °C for 3 days to give orange crystals of **2**. Yield: 0.083 g, 70%. Anal. Calcd. for $C_{29}H_{43}N_2FePSi$: C, 65.16; H, 8.11; N, 5.24. Found: C, 65.10; H, 7.91; N, 5.16. ^{1}H NMR (600 MHz, Benzene-d_6) δ 53.76 (s, **3**), 24.63 (s, **3**), 10.43 (s, **3**), 8.07 (d, J = 7.2 Hz, 2H, **2**), 7.92 (d, J = 7.3 Hz, 2H, **2**), 7.28 (t, J = 7.4 Hz, 2H, **2**), 7.09 (t, J = 7.4 Hz, 1H, **2**), 5.67 (s, J_{Si-H} = 160 Hz, 1H, **2**), 4.49 (s, **3**), 3.45 (s, **3**), 2.15 – 2.04 (m, 1H, **2**), 1.93 (hept, J = 7.3 Hz, 1H, **2**), 1.44 (s, 15H, **2**), 1.04 (dd, J = 14.2, 7.2 Hz, 3H, **2**), 0.95 (dd, J = 13.3, 7.2 Hz, 3H, **2**), 0.84 – 0.77 (m, 6H, **2**), 0.72 (d, J = 7.3 Hz, 3H, **2**), -3.57 (s, 1H, **3**), -3.67 (s, 1H, **3**). ^{13}C NMR (151 MHz, Benzene-d_6) δ 149.29, 147.80, 136.54, 136.47, 132.27, 127.43, 127.35, 127.27, 127.05, 88.88, 29.58 (d, J = 19.1 Hz), 27.38 (d, J = 16.9 Hz), 20.24 (d, J = 2.7 Hz), 19.36 (d, J = 2.1 Hz), 18.60, 18.56 (d, J = 6.1 Hz), 10.22, 5.23 (d, J = 21.3 Hz) ppm. ^{29}Si NMR (80 MHz, Benzene-d_6) δ 39.52 (J = 161 Hz). ^{31}P NMR (162 MHz, benzene-d_6) δ 52.64 (J_{P-Si} = 46 Hz) ppm. FTIR (benzene-d_6): 3061 (m), 3047 (m), 2987 (m), 2960 (s), 2929 (m), 2903 (m), 2048 (sh, ν_{Si-H}), 2034 (s, ν_{N2}), 2013 (sh, w, ν_{Si-H}), 1479 (w), 1425 (m), 1378 (m), 1364 (w), 1283 (w), 1259 (w), 1093 (m), 1065 (m), 1033 (m), 1027 (m), 885 (s) cm^{-1}. FTIR (KBr pellet): 3058 (m), 3041 (m),2960 (s), 2928 (s), 2900 (s), 2872 (s), 2039 (vs, ν_{N2}), 2031 (vs, ν_{N2}), 2013 (m, ν_{SiH}), 1993 (m, ν_{SiH}), 1458 (m), 1448 (m), 1423 (s), 1376 (m), 1361 (w), 1299 (w),

1291 (w), 1259 (w), 1113 (m), 1090 (m), 1064 (m), 1033 (m), 1025 (m), 927 (w), 885 (m), 869 (w), 818 (m), 767 (w), 741 (m), 703 (s), 675 (w) cm^{-1}. These solid state FTIR data do not show the expected 2 bands near 2000 cm^{-1}, but rather 4. This is most consistent with there being multiple crystal morphologies, giving rise to 2 distinct environments for the molecule.

Synthesis of Cp*(^{i}Pr$_2$MeP)(N$_2$)FeSiH$_2$Trip/Cp*(^{i}Pr$_2$MeP)HFe=SiHTrip (4/5). A solution of TripSiH$_3$ (0.105 g, 0.40 mmol) in 2 mL of pentane was added to a solution of **1** (0.200 g, 0.45 mmol) in 4 mL of pentane. The mixture was stirred for 20 min, over which time it darkened from green to deep blue/green. Volatile components were removed *in vacuo* and the blue residue was dissolved in pentane/O(SiMe$_3$)$_2$ (1:1, ca. 2 mL). This solution was filtered and allowed to evaporate at -35 °C, giving yellow blocks of **4**. Yield: 0.100 g, 43%. Anal. Calcd. for $C_{32}H_{57}FeN_2PSi$: C, 65.73; H, 9.82; N, 4.79. Found: C, 66.86; H, 10.04; N, 3.71; this analysis was replicated over several samples and likely reflects a loss of dinitrogen prior to combustion, or partial inclusion of the silylene isomer. Room temperature NMR spectroscopy, under 1 atm N_2: ^{1}H NMR (600 MHz, Benzene-d_6) δ 8.93 (s, br, **5**), 7.21 (s, 2H, **4** *m*-Trip), 6.32 (s, br, **5**), 4.99 (d, *J* = 6.2 Hz, 1H, **4** Si–*H*), 4.75 (s, 1H, **4** Si–*H*), 3.62 (h, *J* = 7.0 Hz, 2H, **4** *m*-TripC*H*Me$_2$), 2.87 (h, *J* = 7.0 Hz, 1H, **4** *p*-TripC*H*Me$_2$), 2.39 (s, br, **5**), 2.22 (h, *J* = 7.2 Hz, 1H, **4** PC*H*Me$_2$), 2.11 – 2.00 (m, 1H, **4** PC*H*Me$_2$), 1.56 (d, *J* = 6.7 Hz, 6H, **4** TripCH*Me*$_2$), 1.53 (d, *J* = 6.7 Hz, 6H, **4** TripCH*Me*$_2$), 1.48 (s, br, **5**), 1.44 (s, 15H, **4** Cp*), 1.34 (s, br, **5**), 1.29 (dd, *J* = 6.9, 6H, **4** TripCH*Me*$_2$), 1.24 (d, *J* = 6.9 Hz, 6H, **4** TripCH*Me*$_2$), 1.05 – 0.95 (m, 12H, **4** P*Me* + PCH*Me*$_2$), 0.92 (dd, *J* = 11.6, 7.1 Hz, 3H, **4** PCH*Me*$_2$), 0.09 (s, br, **5**), -0.03 (s, br, **5**), -7.52 (s, br, **5**) ppm. ^{13}C NMR (151 MHz, 292 K, Benzene-d_6) δ 155.65, 148.36, 138.15, 124.01, 120.37, 88.12, 37.34, 34.89, 29.44 (d, *J* = 19.3 Hz), 28.67 (d, *J* = 17.1 Hz), 25.40, 25.33, 24.48, 24.47, 24.33, 21.45, 20.72, 19.62, 19.00, 18.96, 17.35, 10.06 ppm; presumably all observable resonances in the 292 K ^{13}C NMR spectrum correspond to **4**. ^{29}Si NMR (119 MHz, 292 K, Benzene-d_6) δ -16.2 (*J* = 151 Hz, **4**). ^{31}P NMR (243

MHz, Benzene-d_6) δ 53.68 (J_{Si-P} = 49.5 Hz, **4**) ppm. FTIR (benzene-d_6): 3044 (w), 2957 (vs), 2923 (s), 2898 (s), 2865 (s), 2042 (s, ν_{N2}, **4**), 2025 (sh, ν_{SiH}) , 1653 (br, m), 1595 (m), 1542 (br, m), 1459 (s), 1444 (m), 1417 (m), 1380 (m), 1360 (m), 1279 (w), 1253 (w), 1237 (w), 1205 (w), 1135 (w), 1102 (w), 1066 (m), 1030 (m), 887 (sh), 872 (vs), 745 (m), 701 (br, m), 619 (m), 608 (m) cm^{-1}.

Isolation/characterization of 5. Single crystals of **5** suitable for X-ray diffraction were grown by subjecting a solution of isolated **4** (0.030 g) in 4 mL 1:1 pentane/$O(SiMe_3)_2$ to slight vacuum for 20 min, giving a small amount of deep blue blocks. NMR spectroscopy, freeze-pump-thawed sample of **4**; no resonances attributable to **4** were observed in these spectra at 292 K: ^{1}H NMR (500 MHz, Toluene-d_8, 190 K) δ 7.30 (s, 1H, Trip-*H*), 7.22 (s, 1H, Si*H*), 7.18 (s, 1H, Trip-*H*), 4.70 (s, 1H, Trip-C*H*Me_2), 3.89 (s, 1H, Trip-C*H*Me_2), 3.01 – 2.74 (m, 1H, Trip-C*H*Me_2), 1.79 (s, 15H, Cp*), 1.66 (s, 3H), 1.60 (s, 3H), 1.38 (m, 17H), 1.21 – 1.11 (m, 3H), 1.04 (s, 6H), 0.88 (s, 3H), -19.67 (d, *J* = 23.3 Hz, 1H, Fe*H*); large linewidths in this spectrum (most likely due to high solvent viscosity at 190 K) limited the resolution of resonance multiplicities. ^{13}C NMR (126 MHz, Toluene-d_8, 205 K) δ 152.67, 151.16, 149.46, 141.51, 120.31, 120.09, 82.78, 35.14, 34.61, 34.23, 27.20, 25.71, 24.71, 22.99 (d, *J* = 7.5 Hz), 18.41, 18.05, 17.67, (vs) 12.71. ^{29}Si NMR (119 MHz, 190 K, Toluene-d_8) δ 191 (*J* = 148 Hz). No ^{31}P resonance attributable to **5** was observed at 292 or 205 K.

Synthesis of Cp*(^{i}Pr$_2$MeP)HFe=SiHDMP (6). Solid $DMPSiH_3$ (0.082 g, 0.24 mmol) was added to **1** (0.100 g, 0.23 mmol) dissolved in 5 mL of pentane. This was swirled for ca. 2 min, at which point the deep blue solution was filtered and stored at -35 °C for 18 h to give deep blue blocks. A second crop was collected by concentrating the mother liquor to 2 mL and cooling to -35 °C. Yield: 0.094 g, 63% over two crops. Anal. Calcd. for $C_{41}H_{59}FePSi$: C, 73.85; H, 8.92. Found: C, 73.43; H, 8.92. ^{1}H NMR ^{1}H NMR ^{1}H NMR (600 MHz, Benzene-d_6, 292 K) δ 7.44 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.4 Hz, 2H), 6.81 (s, 4H), 2.61 (s, 15H), 2.28 (s, 12H), 2.19 (s, 6H), 1.81 (s, 2H), 0.99 (d, *J* = 5.3 Hz, 6H), 0.45

(s, 6H). ^{31}P NMR (243 MHz, Benzene-d_6) δ 52.25. (600 MHz, Toluene-d_8, 205K) δ 7.22 (t, J = 7.7 Hz, 1H, DMP-*p*-*H*), 7.03 (d, J = 6.8 Hz, 1H), 6.91 (s, 1H, DMP-Mes*H*), 6.88 (s, 1H, DMP-Mes*H*), 6.77 (s, 1H, DMP-Mes*H*), 6.76 (s, 1H) , DMP-Mes*H*, 6.03 (d, J = 9.4 Hz, 1H, Si*H*), 2.59 (s, 3H, DMP-Mes-*Me*), 2.51 (s, 3H, DMP-Mes-*Me*), 2.21 (m, 12H, DMP-Mes-*Me*), 1.70 (s, 15H, Cp*), 1.39 – 1.33 (m, 3H), 0.95 (q, J = 8.0 Hz, 3H), 0.93 – 0.86 (m, 3H), 0.76 (m, 3H), 0.71 – 0.58 (m, 3H), -20.48 (d, J = 18.2 Hz, 1H, Fe*H*). ^{13}C NMR (126 MHz, Toluene-d_8, 205 K) δ 146.16, 145.67, 140.80, 140.21, 137.05, 136.86, 136.73, 136.44, 136.35, 136.05, 81.88, 35.00, 30.01 (d, J = 24.8 Hz), 29.76 (d, J = 25.7 Hz), 23.60, 23.23, 21.71, 21.57, 19.50, 18.72, 18.12 (d, J = 20.8 Hz), 15.11, 13.13, 10.31, 9.27 (d, J = 13.2 Hz) ppm. ^{29}Si NMR (99 MHz, Toluene-d_8, 205 K) δ 159.95 (J = 147 Hz). FTIR (benzene-d_6): 3028 (w), 2950 (vs), 2911 (vs), 2959 (vs), 2729 (w), 2134 (w), 2063 (s, ν_{SiH}), 1718 (br, m), 1479 (s), 1426 (s), 1278 (m), 1253 (m), 1241 (m), 1109 (m), 1083 (m), 1069 (m), 914 (s), 881 (s), 849 (s), 741 (s), 701 (m), 623 (m), 610 (m) cm^{-1}. UV-Vis (pentane): λ_{max} 660 nm (ε = 510 M^{-1}cm^{-1}), 356 nm (ε = 2720 M^{-1}cm^{-1}).

Synthesis of Cp*(^{i}Pr$_2$MeP)HFe=GeHDMP (7). Solid DMPGeH$_3$ (0.025 g, 0.064 mmol) was added to **1** (0.030 g, 0.064 mmol) dissolved in 4 mL pentane. The reaction mixture was swirled for ca. 2 min, at which point the deep green solution was filtered and stored at -35 °C for 18 h to give deep green blocks. Yield: 0.025 g, 54%. Anal. Calc. for $C_{41}H_{59}FeGeP$: C, 69.22; H, 8.36. Found: C, 68.93; H, 8.35. ^{1}H NMR (400 MHz, Benzene-d_6) δ 7.27 (t, J = 7.5 Hz, 1H, DMP-*p*-*H*), 7.03 (d, J = 7.5 Hz, 2H, DMP-*m*-*H*), 6.84 (s, 4H, DMPE-Mes*H*), 2.32 (s, 12H, Mes-*o*-*Me*), 2.20 (s, 6HMes-*p*-*Me*), 1.72 (s, 15H, Cp*), 1.48 (hept, J = 7.2 Hz, 2H, PC*H*Me$_2$), 1.14 (s, 3H, P-*Me*), 0.90 (d, J = 6.9 Hz, 6H, PCH*Me*$_2$), 0.71 (d, J = 7.0 Hz, 6H, PCH*Me*$_2$) ppm. ^{13}C NMR (101 MHz, Benzene-d_6) δ 145.22, 140.35, 136.46, 136.34, 128.91, 128.89, 127.51, 84.76, 30.49, 21.82, 21.16, 20.10, 17.82, 12.35 ppm. No ^{31}P resonance was observed at 292 K. FTIR (benzene-d_6): 3026 (w), 2953 (vs), 2916 (vs), 2859 (vs), 2731

(w), 1914 (s, ν_{GeH}), 1883 (sh), 1616 (br, m), 1479 (s), 1377 (vs), 1279 (m), 1255 (w), 1174 (w), 1153 (w), 1080 (m), 1033 (s), 874 (w), 849 (vs), 735 (s), 702 (s), 624 (m), 606 (s) cm^{-1}.

Synthesis of Cp*(^{i}Pr$_2$MeP)H$_2$FeSiHPh$_2$ (9). Ph_2SiH_2 (0.036 g, 0.20 mmol) was dissolved in 2 mL of pentane and added to Cp*(^{i}Pr$_2$MeP)FeH(N_2) (0.040 g, 0.11 mmol) in 4 mL of pentane. This mixture was stirred for 1 h, over which time the color changed from orange to yellow. Volatile components were removed *in vacuo* and the resulting yellow solid was recrystallized from 2 mL of pentane and cooling to -35 °C. Yield: 0.046 g, 79%. Anal. Calcd. for $C_{29}H_{45}FePSi$: C, 68.49; H, 8.92. Found: C, 68.37; H, 9.20. ^{1}H NMR (400 MHz, Benzene-d_6) δ 8.05 – 7.91 (m, 4H, Si*Ph*), 7.34 – 7.25 (m, 4H, Si*Ph*), 7.22 – 7.17 (m, 2H, Si-*p*-*Ph*), 5.96 (s, $J_{Si–H}$ = 182 Hz, 1H, Si*H*), 1.66 (s, 15H, Cp*), 1.05 (hept, *J* = 7.1 Hz, 2H, PC*H*Me$_2$), 0.90 (d, *J* = 7.1 Hz, 3H, P*Me*), 0.85 (dd, *J* = 14.7, 6.9 Hz, 6H, PCH*Me*$_2$), 0.75 (dd, *J* = 13.0, 6.8 Hz, 6H, PCH*Me*$_2$), -14.07 (d, *J* = 53.7 Hz $J_{Si–H}$ = 21 Hz, 2H, Fe*H*). ^{13}C NMR (101 MHz, Benzene-d_6) δ 146.29, 136.73, 127.61, 127.25, 87.61, 28.09 (d, *J* = 25.3 Hz), 18.20 (d, *J* = 2.7 Hz), 16.94, 11.20, 7.03 (d, *J* = 12.7 Hz). ^{31}P NMR (162 MHz, Benzene-d_6) δ 76.14. ^{29}Si NMR (79 MHz, Benzene-d_6) δ 20.4 (*J* = 182, 21 Hz). FTIR (Benzene-d_6): 3057 (m), 3043 (m), 2974 (s), 2954 (s), 2925 (s), 2901 (s), 2864 (s), 2043 (m, br ν_{FeH}), 2018 (m, ν_{SiH}), 1928 (m, br, ν_{FeH}), 1479 (m), 1424 (s), 1379 (m), 1373 (m), 1088 (m), 1067 (w), 1029 (m), 883 (m), 734 (s), 701 (vs), 629 (m), 616 (m) cm^{-1}.

Synthesis of Cp*(^{i}Pr$_2$MeP)H$_2$FeSiH$_2$Trip (10). $TripSiH_3$ (0.067 g, 0.284 mmol) was dissolved in 2 mL of pentane and this solution was then added to Cp*(^{i}Pr$_2$MeP)FeH(N_2) (0.100 g, 0.284 mmol) in 4 mL of pentane. This mixture was stirred for 18 h, over which time the color changed from orange to yellow. Volatile components were removed *in vacuo* and the resulting yellow solid was recrystallized from 4 mL 1:1 pentane/$(SiMe_3)_2O$. Yield: 0.096 g, 60%. Anal. Calcd. for $C_{32}H_{59}FePSi$: C, 68.79; H, 10.64. Found: C, 68.73; H, 10.81. ^{1}H NMR (500 MHz, Benzene-d_6) δ 7.13 (s, 2H, Trip*H*), 5.20 (d, *J* = 5.5 Hz, 2H, Si*H*), 3.98 (hept, *J* = 6.7 Hz, 2H, Trip-*o*-C*H*Me$_2$), 2.83 (hept, *J* = 6.9 Hz, 1H, Trip-*p*-

C*H*Me$_2$), 1.75 (s, 15H, Cp*), 1.65 – 1.45 (m, 14H), 1.27 (d, *J* = 6.9 Hz, 6H, TripCH*Me*$_2$), 1.01 (dd, *J* = 14.6, 7.1 Hz, 6H, PCH*Me*$_2$), 0.82 (dd, *J* = 11.8, 6.9 Hz, 6H, PCH*Me*$_2$), 0.20 (d, *J* = 7.7 Hz, 3H, P*Me*), -14.98 (dd, *J* = 56.0, 5.5 Hz, 2H, Fe*H*). ^{13}C NMR (126 MHz, Benzene-d_6) δ 155.54, 148.91, 120.56, 87.07, 34.86, 32.75, 27.86 (d, *J* = 20.1 Hz), 25.63, 24.46, 19.81 (d, *J* = 3.4 Hz), 18.01 (d, *J* = 3.1 Hz), 10.79. ^{31}P NMR (162 MHz, Benzene-d_6) δ 79.32. ^{29}Si NMR (500 MHz, HMBC, Benzene-d_6) -25.94 (*J* = 178, 8 Hz) ppm.

Synthesis of Cp*(^{i}Pr$_2$MeP)H$_2$FeSiH(SiH-κ^2-C$_{ipso}$,C$_{o\text{-}Me}$-DMP) (13). Crystalline **6** (0.020 g, 30 μmol) was flame sealed in a glass ampoule *in vacuo* and immersed in an oil bath at 100 °C for 2 days, over which time the color changed from blue to yellow. The ampoule was opened in the glovebox and the solid was recrystallized by evaporation of pentane (1 mL) at -35 °C. Yield: 0.005 g, 25%. Anal. Calcd. for $C_{41}H_{59}FePSi$: C, 73.85; H, 8.92. Found: C, 74.12; H, 9.21. ^{1}H NMR (500 MHz, Benzene-d_6) δ 7.35 (d, *J* = 7.8 Hz, 1H, DMP-*m*-*H*), 7.27 (t, *J* = 7.6 Hz, 1H, DMP-*p*-*H*), 7.03 (s, 1H, DMP-*MesH*), 6.99 (s, 1H, DMP-*MesH*), 6.97 (s, 1H, DMP-*MesH*), 6.93 (d, *J* = 7.7 Hz, 1H, DMP-*m*-*H*), 6.91 (s, 1H, DMP-*MesH*), 5.11 (s, $^1J_{Si-H}$ = 180 Hz, 1H, Si*H*), 2.86 (d, *J* = 12.5 Hz, 1H, SiC*H*$_2$), 2.46 (d, *J* = 12.5 Hz, 1H, SiC*H*$_2$), 2.41 (s, 3H, DMP-*Me*), 2.34 – 2.25 (m, 12H, DMP-*Me*), 1.81 (s, 1H, PC*H*Me$_2$), 1.52 (s, 15H, Cp*), 1.43 – 1.32 (m, 1H, PC*H*Me$_2$), 1.04 (m, 3H), 0.92 – 0.76 (m, 3H), 0.53 (m, 6H), 0.11 (d, *J* = 8.1 Hz, 3H), -14.76 (d, *J* = 59.2 Hz, 1H, Fe*H*), -16.76 (d, *J* = 49.4 Hz, 1H, Fe*H*). ^{13}C NMR (126 MHz, Benzene-d_6) δ 146.69, 145.44, 142.85, 141.52, 137.96, 137.35, 136.24, 135.74, 135.38, 134.40, 129.83, 129.76, 129.31, 127.59, 127.32, 87.15 (Cp*), 28.48, 28.35 (DMP *C*H$_2$Si), 28, 22.93, 22.76, 22.70, 21.60, 21.25, 21.19, 20.72 (d, *J* = 4.3 Hz), 20.37 – 20.00 (m), 18.68, 17.81 (d, *J* = 4.6 Hz), 10.79. ^{31}P NMR (202 MHz, Benzene-d_6) δ 77.62.

Reaction of 3 with hydrogen. Crystalline **2** (0.005 g, 9 μmol) was dissolved in 0.5 mL benzene-d6 and loaded in a J-Young tube and subjected to 5 freeze-pump-thaw cycles (sufficient to form primarily

the silyl complex **3**). Afterwards, 1 atm H_2 was added at ambient temperature. The solution changed color from orange to yellow. ^{1}H and ^{31}P NMR spectroscopy were consistent with the formation of the hydrogenation product, **9**, compared to an independently synthesized sample.

Reaction of 5 with hydrogen: A solution of **4** (0.005 g, 8 μmol) in 0.5 mL benzene-d_6 was loaded in a J-Young tube subjected to 5 freeze-pump-thaw cycles (sufficient to form primarily the silylene isomer **5**). Afterwards, 1 atm H_2 was added at ambient temperature. The solution changed color from blue to yellow. ^{1}H and ^{31}P NMR spectroscopy were consistent with the formation of the hydrogenation product, **10**, compared to an independently synthesized sample.

Reaction of 6 with hydrogen: A solution of **6** (0.005 g, 7 μmol) in 0.5 mL benzene-d6 was loaded in a J-Young tube and subjected to 3 freeze-pump-thaw cycles. Afterwards, 1 atm H_2 was added at ambient temperature. The solution changed color from blue to yellow. ^{1}H and ^{31}P NMR spectroscopy were consistent with the formation of the hydrogenation product, **11** (in equilibrium with Cp*(^{i}Pr$_2$MeP)HFe(N_2)).

Reaction of Cp*(^{i}Pr$_2$MeP)HRu=SiHDMP with hydrogen to form Cp*(^{i}Pr$_2$MeP)(H)$_2$RuSiH$_2$DMP (12). A J-Young tube was charged with a solution of Cp*(^{i}Pr$_2$MeP)(H)Ru=SiHDMP (0.020 g, 28 μmol) in 0.5 mL benzene-d_6 and subjected to 3 freeze-pump-thaw cycles. The evacuated tube was opened to 1 atm H_2, sealed, and heated to 60 °C for 18 h. At this point the color had changed from deep red to yellow and the ruthenium silylene complex had been completely consumed (by ^{1}H NMR spectroscopy). Volatile components were removed *in vacuo.* The resulting residue was dissolved in 2 mL of Et_2O and stored at -35 °C to give colorless crystals. Yield: 0.008 g, 40%. ^{1}H NMR (500 MHz, Benzene-d_6) δ 6.98 (d, J = 4.2 Hz, 2H, DMP-*m*-*H*), 6.92 (s, 4H, DMP-Mes*H*), 4.82 (s, 2H, Si*H*), 2.42 (s, 12H, DMP-*o*-*Me*), 2.30 (s, 6H, DMP-*p*-*Me*), 1.63 (s, 15H, Cp*), 1.39 (h, J = 7.0 Hz, 2H, PC*H*Me$_2$), 0.79 (dd, J = 15.1, 7.0 Hz, 6H, PCH*Me*$_2$), 0.73 (dd, J = 12.9,

6.8 Hz, 6H, PCH*Me*$_2$), 0.19 (d, *J* = 8.6 Hz, 3H, P*Me*), -12.53 (d, *J* = 28.7 Hz, 2H, Ru*H*). ^{13}C NMR (126 MHz, Benzene-d_6) δ 149.76, 143.08, 142.04, 136.98, 135.41, 129.82, 129.72, 128.77, 94.47 (d, *J* = 1.6 Hz), 26.81 (d, *J* = 25.0 Hz), 22.30, 21.22, 18.46 (d, *J* = 4.2 Hz), 17.31, 11.64. ^{31}P NMR (243 MHz, Benzene-d_6) δ 11.00. FTIR (Benzene-d_6): 2975 (sh), 2956 (vs), 2913 (vs), 2866 (s), 2093 (m, ν_{SiH}), 2071 (m, ν_{SiH}), 2016 (w, ν_{RuH}), 1972 (m ν_{RuH}), 1376 (m), 1112 (m), 1027 (m), 939 (s), 886 (vs), 846 (m), 739 (m), 711 (w) cm^{-1}.

Equilibrium constant determination for 2 and 3 and Evans method measurement of 3 at 295 K. Crystalline **2** was dissolved in benzene-d_6 containing mesitylene (0.028 M), and the resulting concentration of **2** was determined by integration of the Si–H ^{1}NMR resonance against the mesitylene aromatic resonance. The concentration of **3** was taken as the difference between the weighed amount of **2** and the amount of **2** observed in solution. The concentration of dinitrogen in benzene at various temperatures has been previously reported,[7] and was converted to M from mole fraction data. Evans method magnetic moment measurements of **3** were performed by including a capillary with 0.028 M mesitylene in benzene-d_6 along with the solution of **3**; for these the calculated concentration of **3** was used.

$$K = \frac{[\mathbf{3}][\mathrm{N_2}]}{[\mathbf{2}]} \qquad (2)$$

Total [Fe]	[mes] (M)	[**2**]	[**3**]	[N2]	K (M)	Δν (Hz)	μ_{eff}
0.036	0.028	0.029	0.0077	0.00493	0.0013	44.055	2.836733
0.015	0.028	0.012	0.0034	0.00493	0.0014	18.015	2.752803
0.031	0.028	0.023	0.0077	0.00493	0.0016	32.395	2.429498

Table S1: Concentrations of species involved in the dinitrogen binding equilibrium between **2** and **3** and values computed using these data.

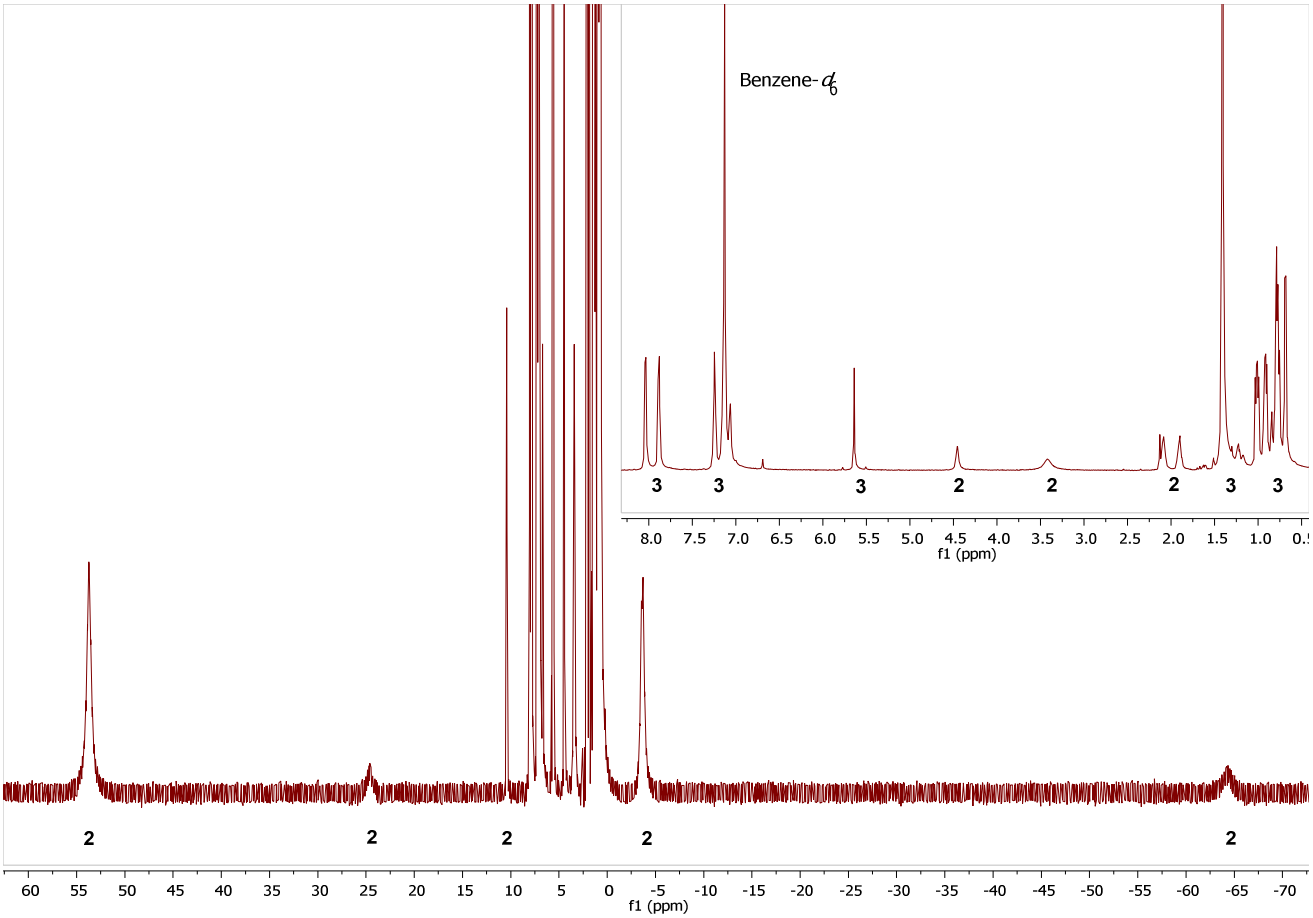

Figure S1: Representative 1H NMR spectrum of an equilibrium mixture of **2** and **3** at 1 atm, 292 K.

Selective inversion recovery kinetics for 6. Experiments were performed on samples of **6** dissolved in 0.5 mL of toluene-d_8 using a method that has been described previously.[8] Mixing times were chosen to properly sample around experimentally determined T1 relaxation times for the nuclei of interest and spaced based on powers of 2. Magnetization vs. mixing time data were fit using CIFIT 2.0.[9]

Parameter	Value, Fe–H excited	Value, Si–H excited
1/T1 Site 1	4.2(2)	6.3(3)
1/T1 Site 2	4(2)	3(1)
M(inf) Site 1	11600(200)	10100(100)
M(inf) Site 2	12400(200)	9200(100)
M(0)-M(inf) Site 1	-18700(200)	-11900(100)
M(0)-M(inf) Site2	-100(300)	-100(100)
k	11(3)	12(3)

Table S2: CIFIT parameters fit for the Fe–H/Si–H exchange of **6** at 205 K.

VT NMR fitting of 5, 6, and 7. All spectra were recorded in toluene-d_8 at concentrations of ca. 20 mg mL^{-1}. Peak positions were extracted by fitting in MestReNova v 11.0.4. The probe temperature was calibrated using an external standard of neat methanol.[10] Curve fitting was performed using Igor Pro version 6.2.0.0 using the equation f(T) = S+1000000*C/(T*(3+exp(E/(0.001986*T))))).[11,12]

T (K)	*p*-Ph	*m*-Mes	Cp*	Mes-Me	P-^{i}Pr	Ph-m-H
205	7.2304	6.82465	1.6834	2.2231	0.7147	7.0087
216	7.2473	6.82335	2.6856	2.2206	0.7007	6.997
226	7.2662	6.8208	1.7032	2.2178	0.6818	6.9956
237	7.2811	6.8107	1.7742	2.2118	0.6575	6.9865
248	7.298	6.8064	1.8594	2.2061	0.6269	6.97805
258	7.319	6.799	1.973	2.2008	0.5896	6.9678
269	7.3388	6.7904	2.1038	2.1944	0.5518	6.95565
279	7.3606	6.7816	(obscured)	2.188	0.5121	6.9421
290	7.3854	6.7713	2.3941	2.1806	0.4641	6.926
300	7.4163	6.7567	2.5815	2.1703	0.4044	6.9045
311	7.4442	6.7459	2.746	2.1628	0.3529	6.88715
321	7.4751	6.7333	2.934	2.1543	0.2967	6.8672
332	7.5069	6.7211	3.118	2.1461	0.2394	6.84765

Table S3: VT NMR chemical shifts for 6 resonances of **6**

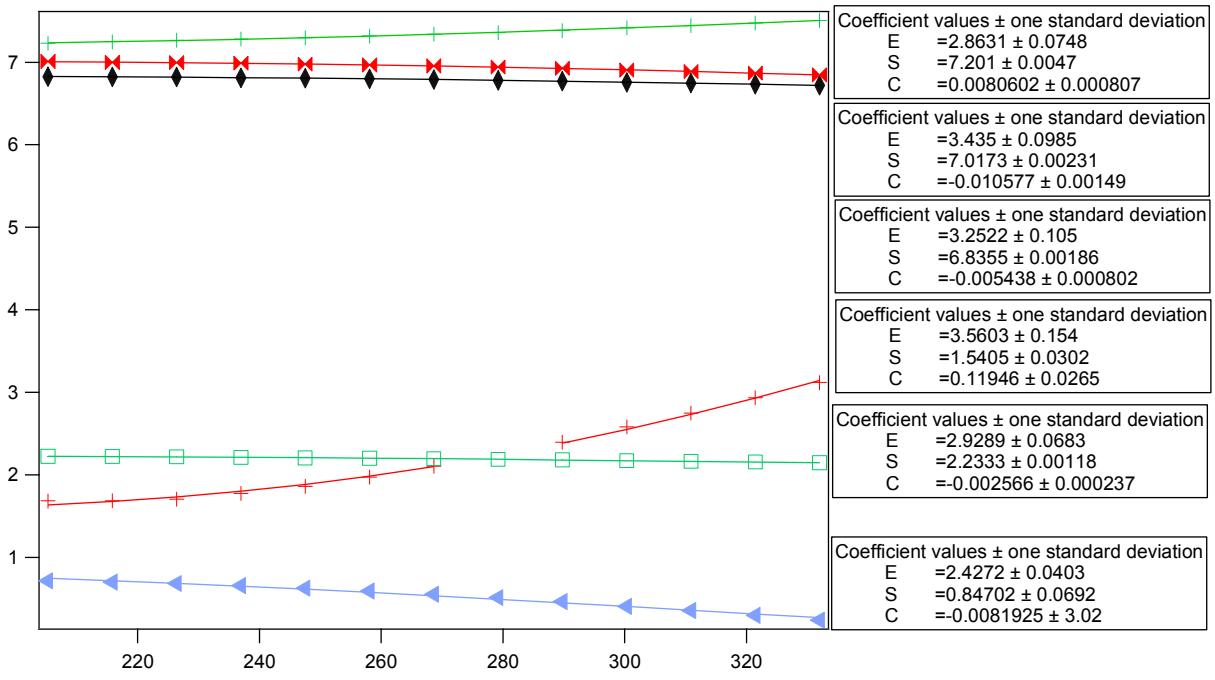

Figure S2: Fits of data presented in Table S2 with fit coefficients displayed in boxes at right.

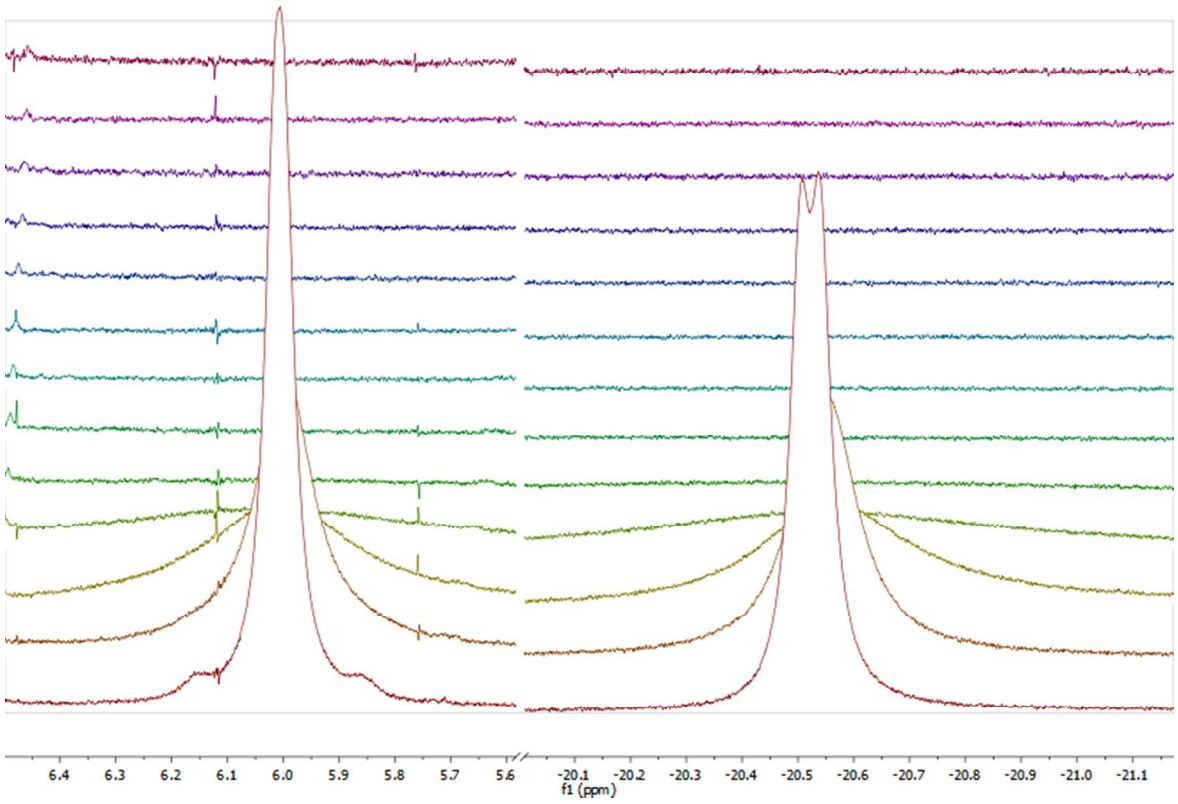

Figure S3: Si–H and Fe–H resonances of **6** showing decoalescence behavior; 205–332 K.

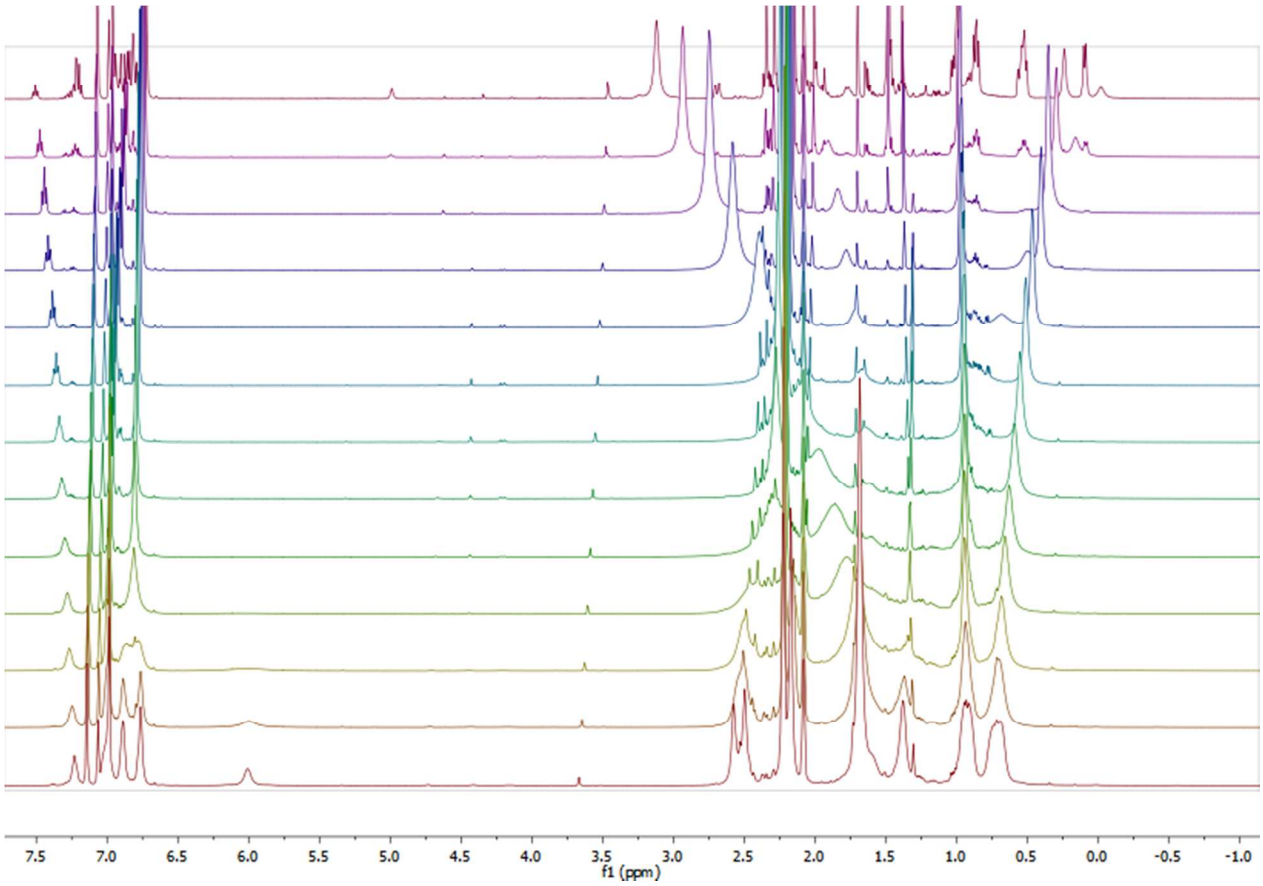

Figure S4: VT NMR spectra of **6** showing temperature dependence of chemical shifts; 205–332 K.

T (K)	Trip p-CH	Trip 0-CH	Trip m-H
195	2.8688	4.29225	7.240965
216	2.8688	4.2845	7.21721
226	2.8688	4.2637	7.17335
237	2.8428	4.19765	7.10511
248	2.7946	4.19625	7.00291
258	2.734	3.96	6.67228
269	2.7112	3.7124	6.51488
279	2.6859	3.472	6.40057
290	2.663	2.4117	6.27201
300	2.6383	3.2501	6.16271
311	2.617	3.1374	6.06199
321	2.591	3.0032	5.96156

Table S4: VT NMR chemical shifts for 3 resonances of **5**

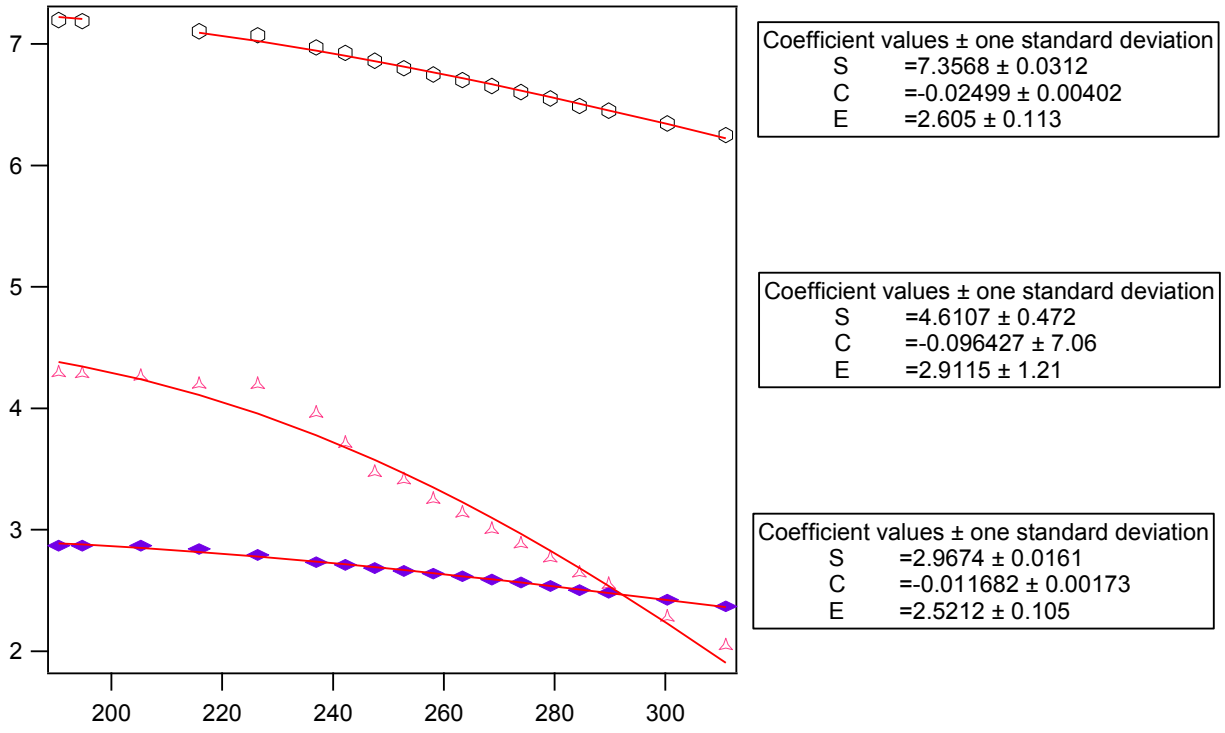

Figure S5: Fits of data presented in Table S3 with fit coefficients displayed in boxes at right.

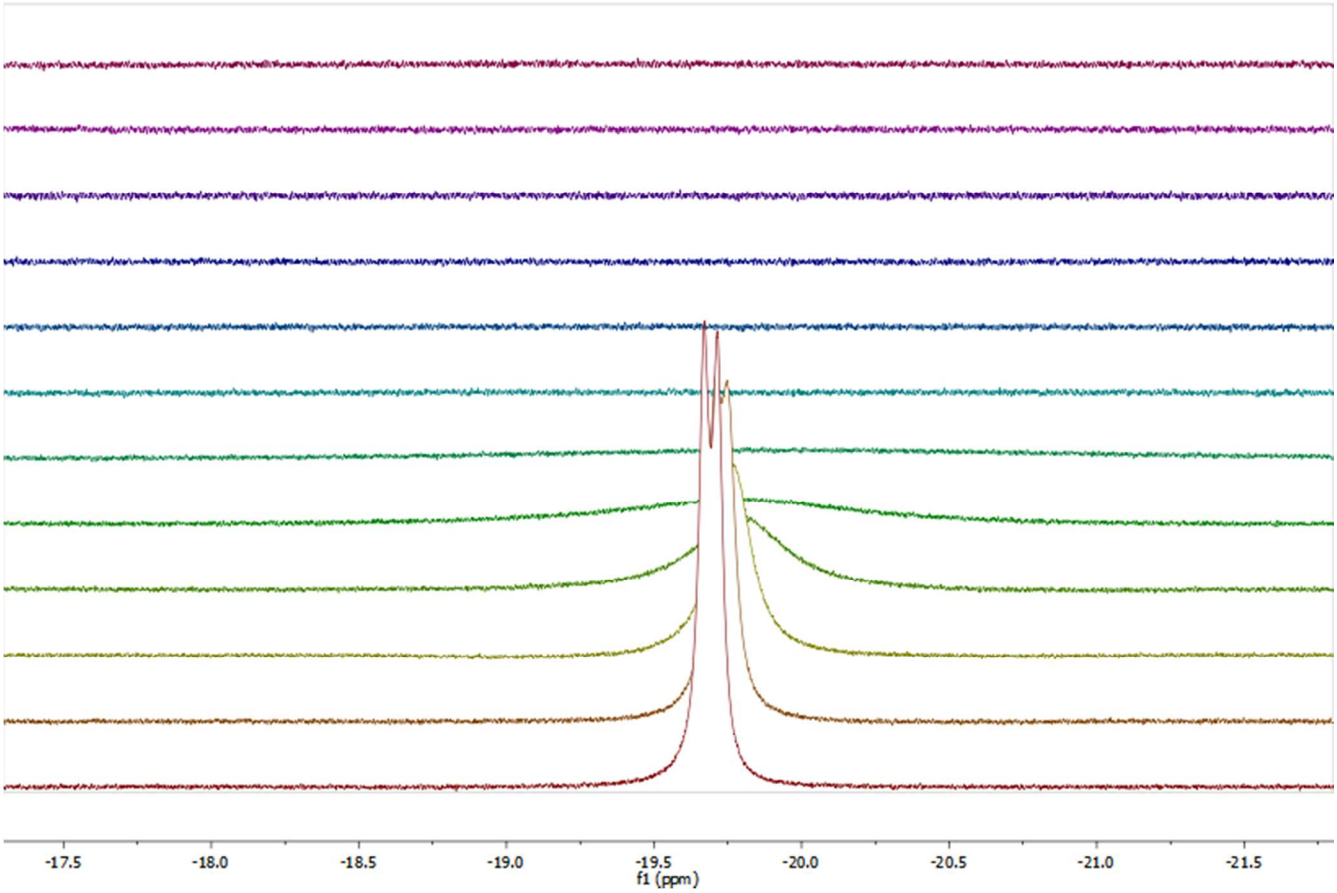

Figure S6: Fe–H resonance of **5** showing decoalescence behavior; 195-321 K. The corresponding Si–H resonance is obscured by solvent residual ^{1}H signal.

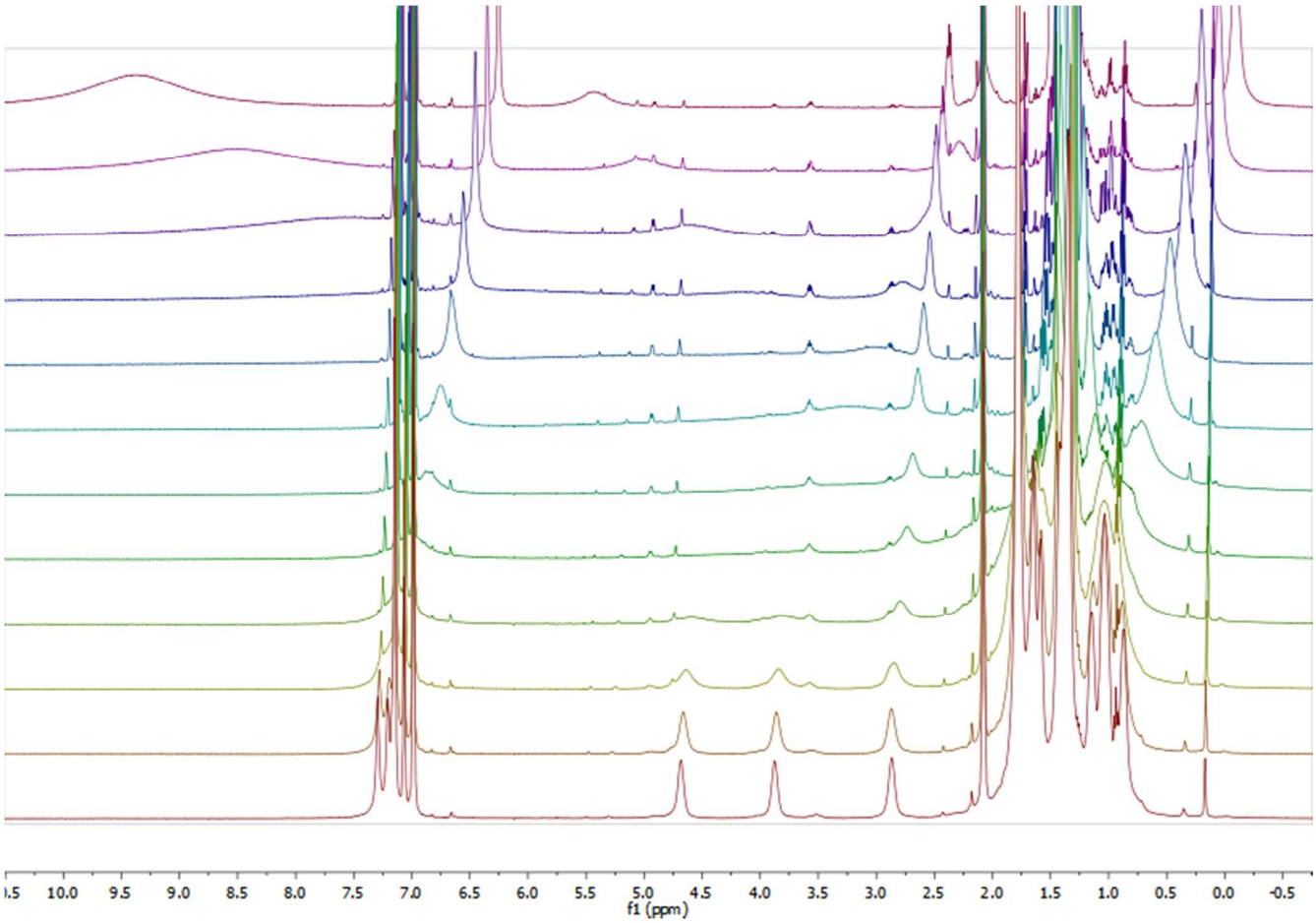

Figure S7: VT NMR spectra of **5** showing temperature dependence of chemical shifts; 195-321 K.

Temperature	Cp*
194.71	1.609
205.271	1.602
215.832	1.598
226.393	1.598
236.954	1.6
247.515	1.609
258.076	1.622
268.637	1.635
279.198	1.651
289.759	1.67
300.32	1.692
310.881	1.717
321.442	1.747
332.003	1.782
342.564	1.821
353.125	1.865
363.686	1.913
374.247	1.971

Table S5: VT NMR chemical shifts for the Cp* resonance of **7.**

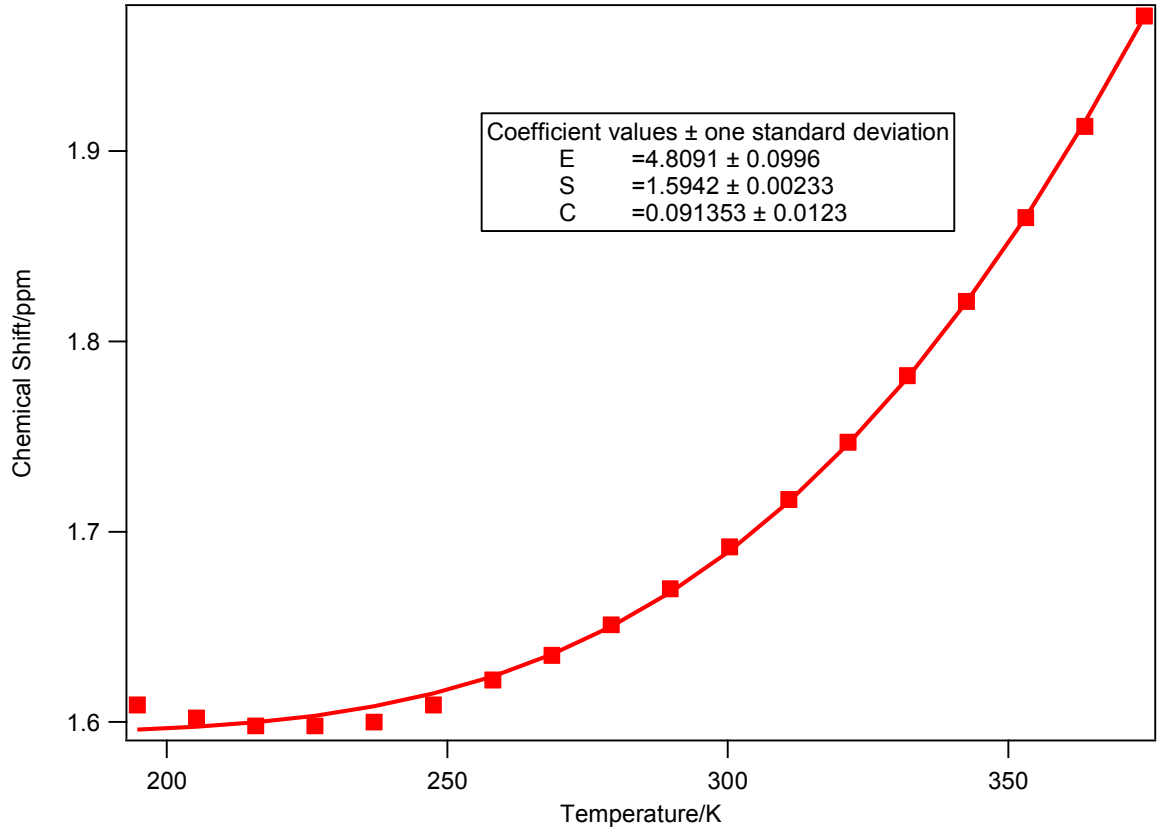

Figure S8: Fits of data presented in Table S4 with fit coefficients.

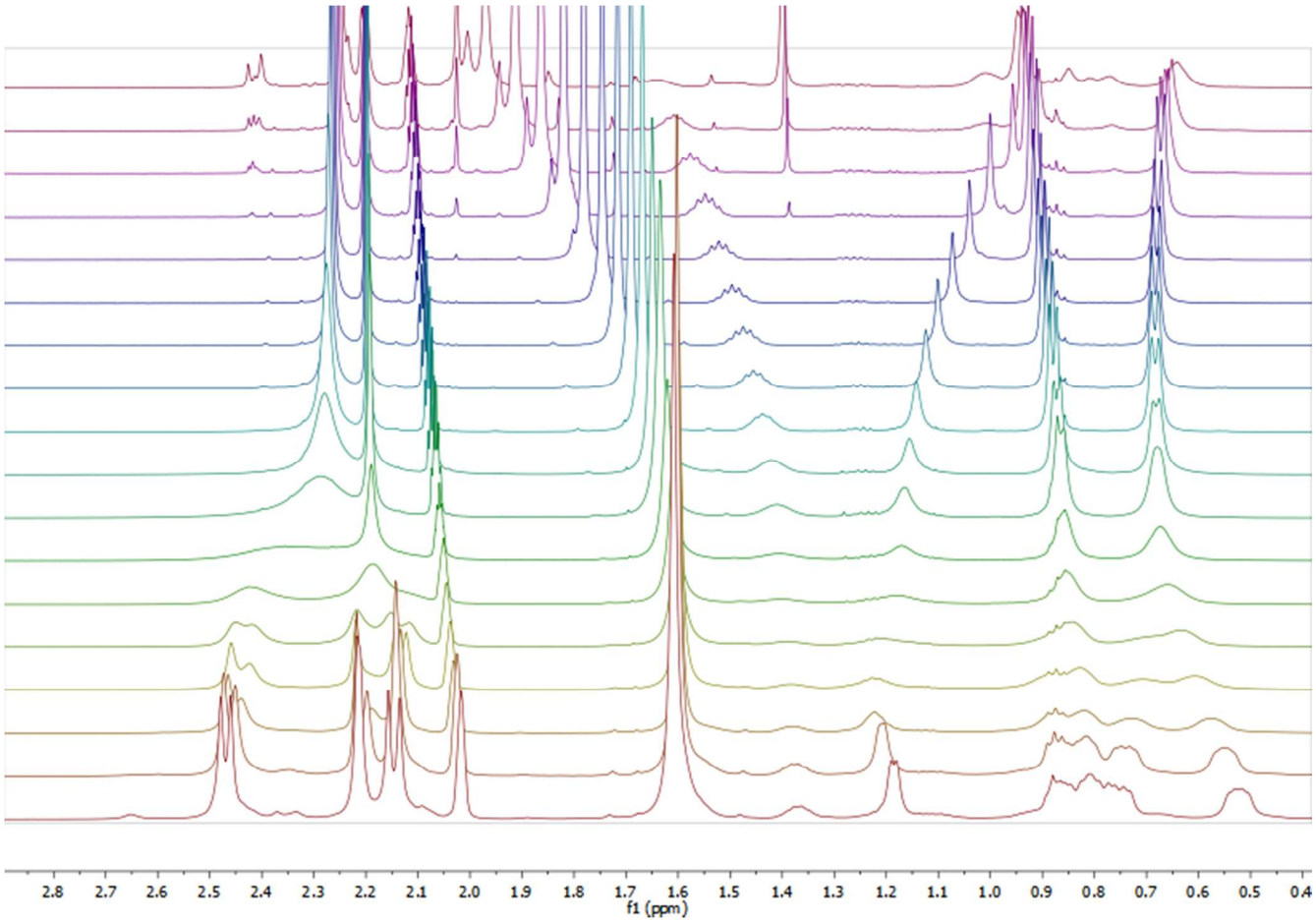

Figure S9: VT NMR spectra of **7** showing temperature dependence of chemical shifts; 195-380 K.

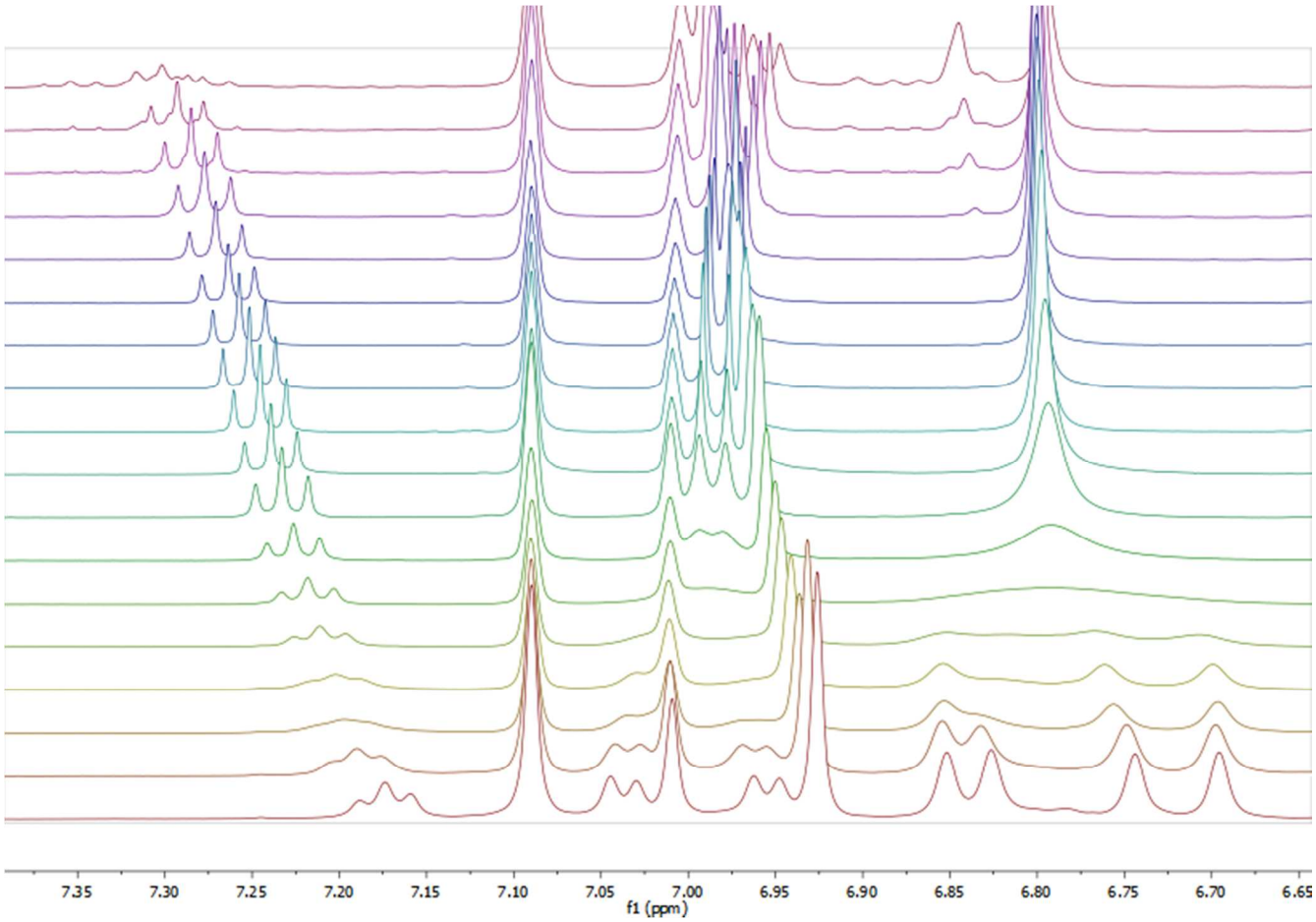

Figure S10: VT NMR spectra of **7** showing temperature dependence of chemical shifts; 195-380 K.

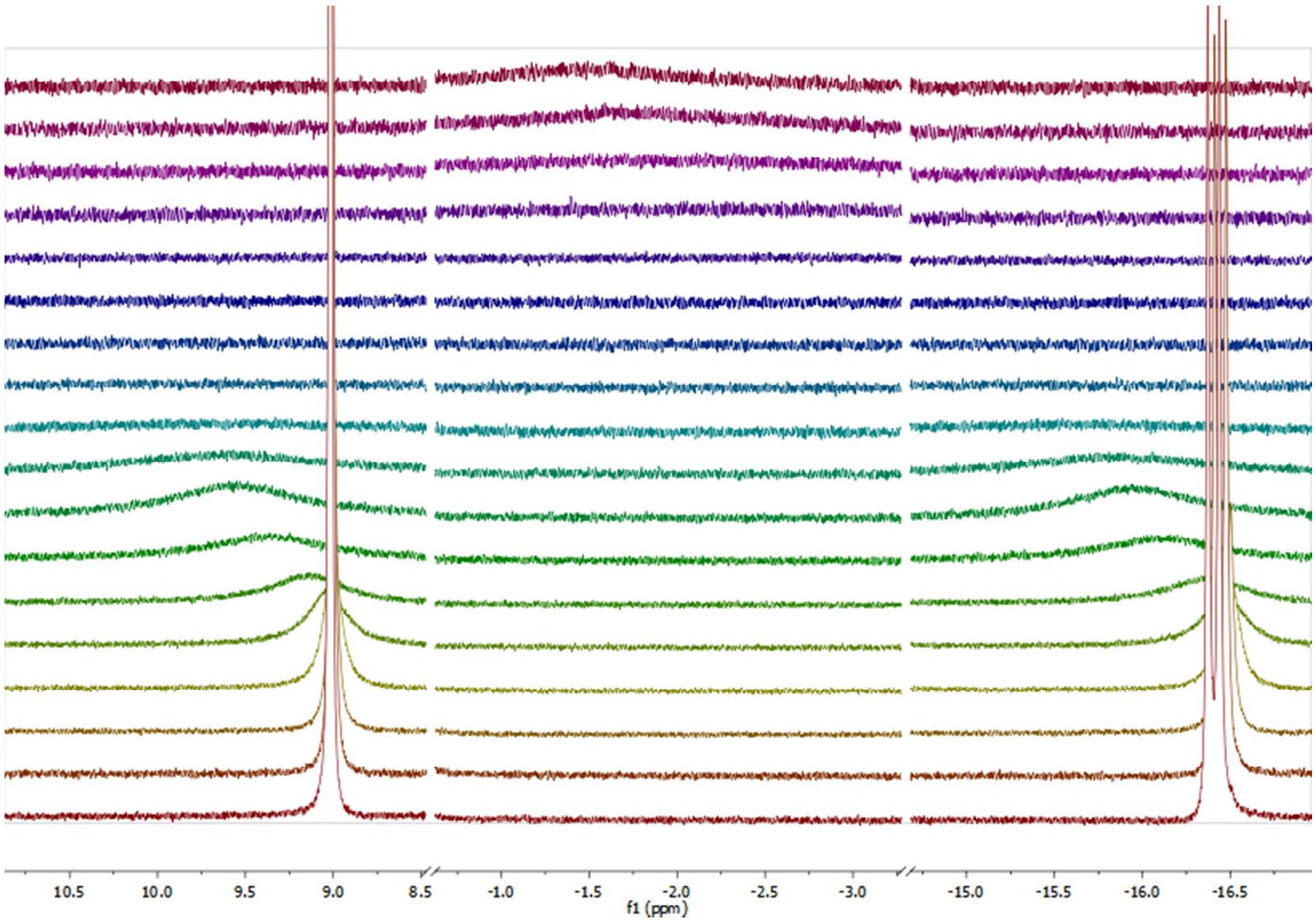

Figure S11: VT NMR spectra of **7** showing temperature dependence of chemical shifts; 195-380 K.

X-ray Diffraction Experiments. Single crystal X-ray diffraction experiments were carried out at the UC Berkeley CHEXRAY crystallography facility. Measurements of compounds were performed on a Bruker APEX-II CCD area detector using Mo K radiation (λ = 0.71073Å) monochromated using QUAZAR multilayer mirrors. Structure solution, modeling and refining was performed using Olex2[13] with the SHELX suite of programs.[14–16] Specific details of each experiment can be found below and in the included crystallographic information files.

Structural determination of 1: The structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation.

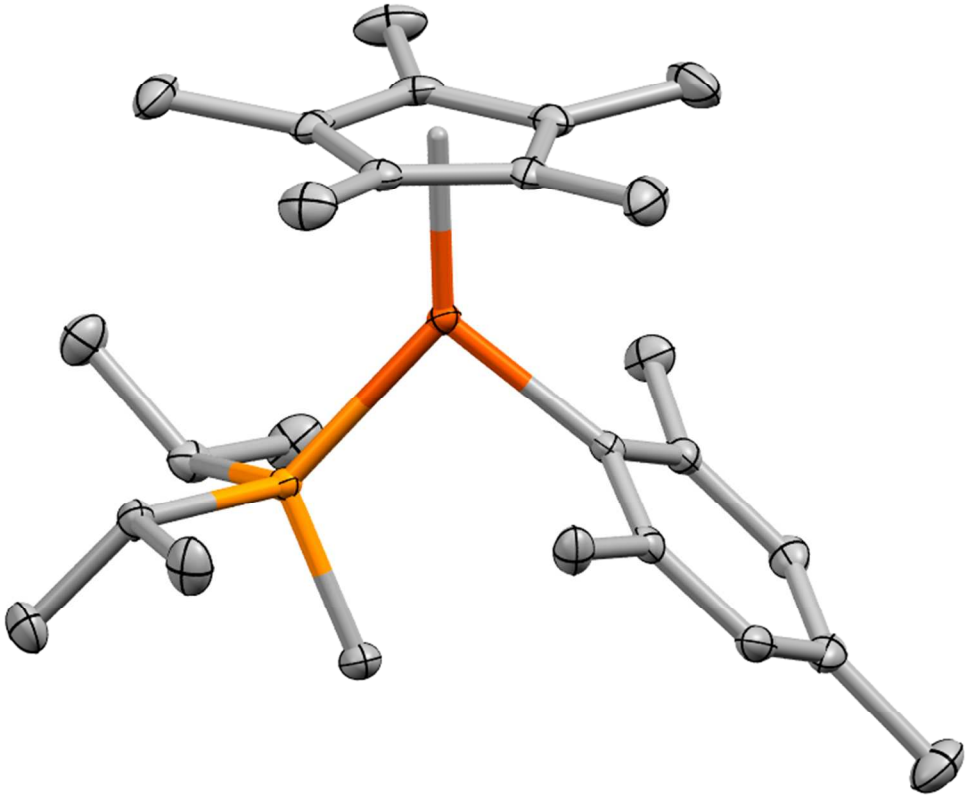

Figure S12: Ellipsoid drawing of **1.** Thermal ellipsoids are drawn at 50% probability; C–bound hydrogen atoms are omitted for clarity. Atoms are color coded as follows: Fe, red-orange; P, orange; Si, tan; N, blue; C, gray; H, white.

Table S6 Crystal data and structure refinement for **1**

Empirical formula	$C_{26}H_{43}PFe$
Formula weight	442.42
Temperature/K	100.02
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.6511(3)
b/Å	22.3002(9)
c/Å	12.8632(6)
α/°	90
β/°	95.8418(19)
γ/°	90
Volume/Å^3	2468.70(17)
Z	4
ρ_{calc}g/cm^3	1.190
μ/mm^{-1}	0.685
F(000)	960.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.652 to 50.78
Index ranges	$-10 \leq h \leq 10$, $-26 \leq k \leq 26$, $-13 \leq l \leq 15$
Reflections collected	26907
Independent reflections	4538 [R_{int} = 0.0311, R_{sigma} = 0.0219]
Data/restraints/parameters	4538/0/266
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0272, wR_2 = 0.0677
Final R indexes [all data]	R_1 = 0.0316, wR_2 = 0.0703
Largest diff. peak/hole / e Å^{-3}	0.32/-0.26

Structural determination of 2: The structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimization.

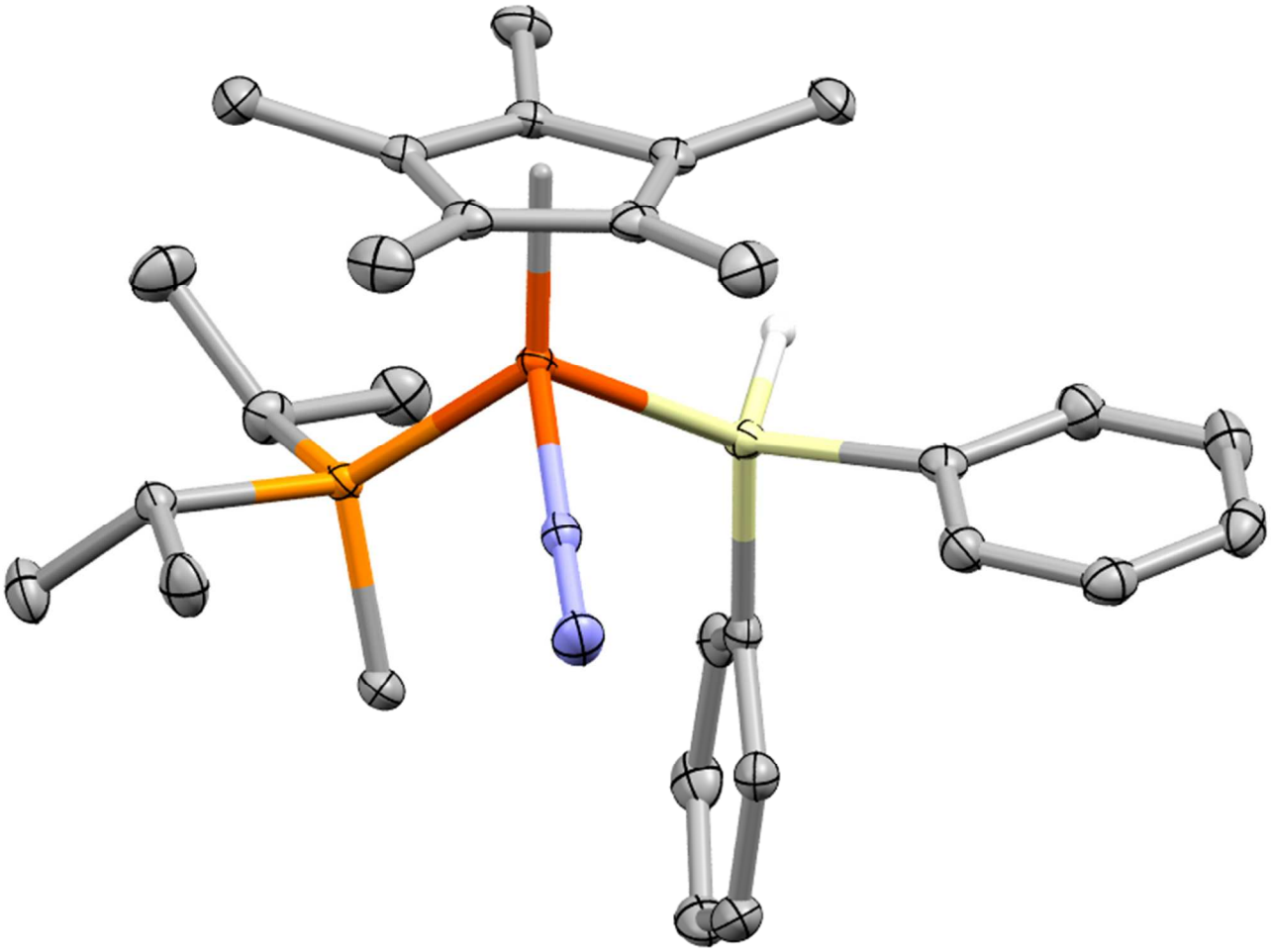

Figure S13: Ellipsoid drawing of **2.** Thermal ellipsoids are drawn at 50% probability; C–bound hydrogen atoms are omitted for clarity, and all displayed hydrogens were located on the Fourier difference map. Atoms are color coded as follows: Fe, red-orange; P, orange; Si, tan; N, blue; C, gray; H, white.

Table S7 Crystal data and structure refinement for **2**

Empirical formula	$C_{29}H_{43}FeN_2PSi$
Formula weight	534.56
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	10.3308(12)
b/Å	10.7423(12)
c/Å	13.3532(15)
α/°	77.326(2)
β/°	83.547(2)
γ/°	74.207(2)
Volume/Å^3	1389.0(3)
Z	2
ρ_{calc}g/cm^3	1.278
μ/mm^{-1}	0.664
F(000)	572.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.132 to 50.692
Index ranges	$-12 \le h \le 12$, $-12 \le k \le 12$, $-16 \le l \le 16$
Reflections collected	31237
Independent reflections	5069 [R_{int} = 0.0293, R_{sigma} = 0.0176]
Data/restraints/parameters	5069/0/321
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0257, wR_2 = 0.0645
Final R indexes [all data]	R_1 = 0.0272, wR_2 = 0.0660
Largest diff. peak/hole / e Å^{-3}	0.33/-0.31

Structural determination of 4: The structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimization. The data were modeled with a twin component [-1 0 0 0 -1 0 0 0 1] with freely refined BASF = 0.4342.

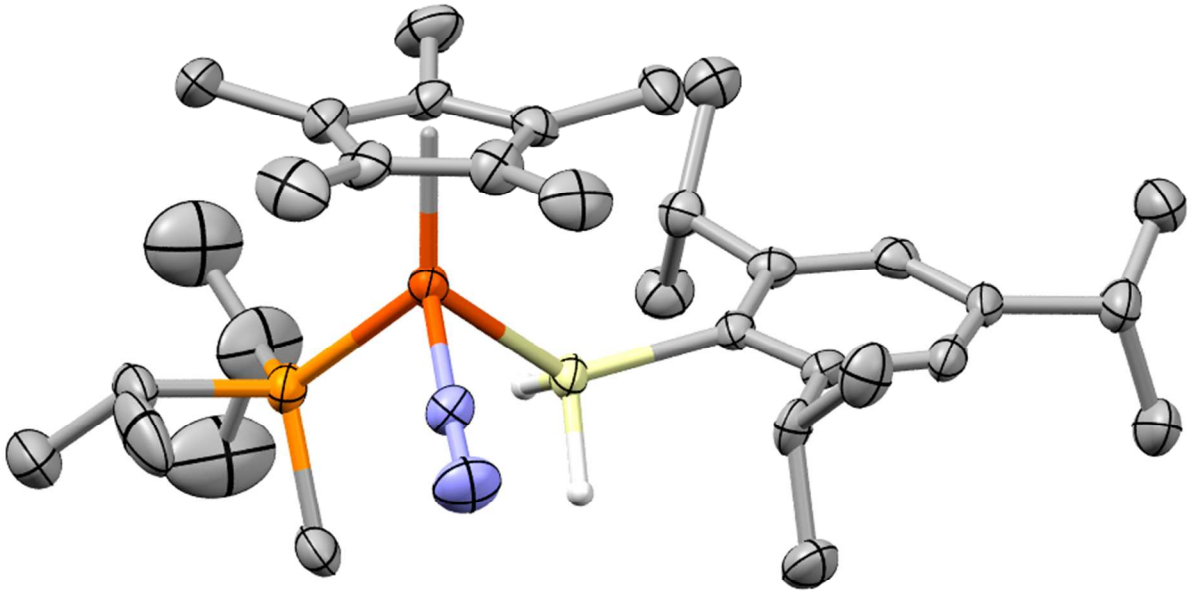

Figure S14: Ellipsoid drawing of **4.** Thermal ellipsoids are drawn at 50% probability; C–bound hydrogen atoms are omitted for clarity, and all displayed hydrogens were located on the Fourier difference map. Atoms are color coded as follows: Fe, red-orange; P, orange; Si, tan; N, blue; C, gray; H, white.

Table S8 Crystal data and structure refinement for **4**

Empirical formula	$C_{64}H_{114}Fe_2N_4P_2Si_2$
Formula weight	1169.41
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.6114(11)
b/Å	26.303(2)
c/Å	16.3706(12)
α/°	90
β/°	90.0230(10)
γ/°	90
Volume/Å^3	6722.1(9)
Z	4
ρ_{calc}g/cm^3	1.155
μ/mm^{-1}	0.554
F(000)	2544.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.488 to 50.748
Index ranges	$-15 \le h \le 17$, $-13 \le k \le 31$, $-19 \le l \le 19$
Reflections collected	24471
Independent reflections	11475 [R_{int} = 0.0595, R_{sigma} = 0.0852]
Data/restraints/parameters	11475/0/712
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0592, wR_2 = 0.1238
Final R indexes [all data]	R_1 = 0.0860, wR_2 = 0.1419
Largest diff. peak/hole / e Å^{-3}	1.05/-0.43

Structural determination of 5: Twinned crystals were selected; the twin components were resolved using Cell Now and data were scaled using Twinabs. The structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimization.

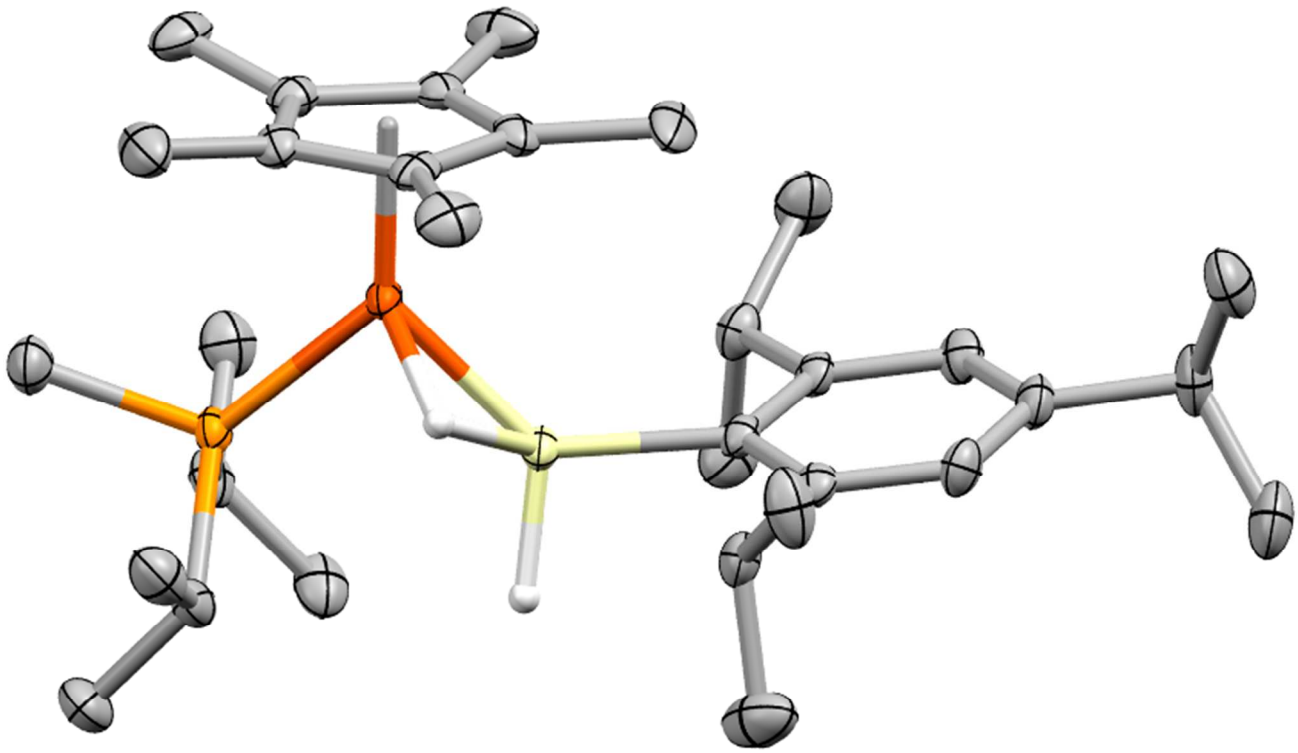

Figure S15: Ellipsoid drawing of **5.** Thermal ellipsoids are drawn at 50% probability; C–bound hydrogen atoms are omitted for clarity, and all displayed hydrogens were located on the Fourier difference map. Atoms are color coded as follows: Fe, red-orange; P, orange; Si, tan; N, blue; C, gray; H, white.

Table S9 Crystal data and structure refinement for **5**

Empirical formula	$C_{32}H_{57}FePSi$
Formula weight	556.68
Temperature/K	100.01
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.1407(9)
b/Å	10.2012(7)
c/Å	26.3408(19)
α/°	90
β/°	90.418(5)
γ/°	90
Volume/Å^3	3262.2(4)
Z	4
ρ_{calc}g/cm^3	1.133
μ/mm^{-1}	0.566
F(000)	1216.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.092 to 50.796
Index ranges	$-14 \leq h \leq 14$, $0 \leq k \leq 12$, $0 \leq l \leq 31$
Reflections collected	20347
Independent reflections	5865 [R_{int} = 0.2120, R_{sigma} = 0.1047]
Data/restraints/parameters	5865/0/339
Goodness-of-fit on F^2	1.164
Final R indexes [I>=2σ (I)]	R_1 = 0.0634, wR_2 = 0.1493
Final R indexes [all data]	R_1 = 0.0774, wR_2 = 0.1570
Largest diff. peak/hole / e Å^{-3}	0.60/-0.50

Structural determination of 6: The structure was solved with the ShelXS structure solution program using Patterson Method and refined with the ShelXL refinement package using Least Squares minimisation. The molecule was found to be disordered over a special position, resulting in duplication of the whole molecule necessitating modeling of all atoms at ½ occupancy. Furthermore, the phosphine ligand was found to be rotationally disordered around the Fe–P bond, with occupancy modeled as FVAR/2 and (1-FVAR)/2 with FVAR = 0.57054 (summing to ½ occupancy in line with the rest of the structure). Eleven total C atoms in the phosphine, DMP, and Cp* required restraint using ISOR due to proximity to other disordered C atoms.

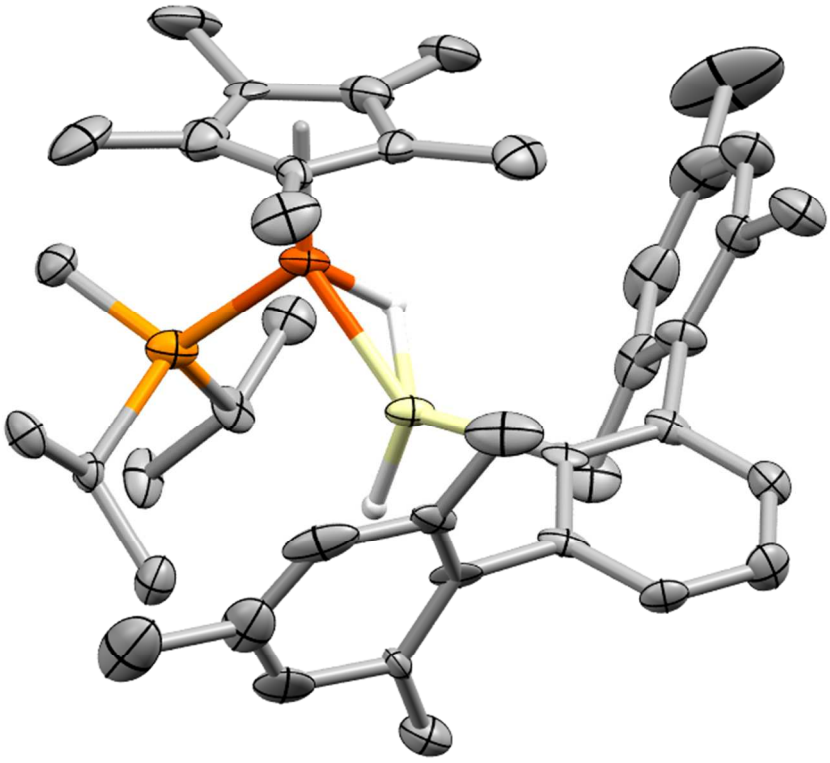

Figure S16: Ellipsoid drawing of **6.** Thermal ellipsoids are drawn at 50% probability; C–bound hydrogen atoms are omitted for clarity, and all displayed hydrogens were located on the Fourier difference map. Atoms are color coded as follows: Fe, red-orange; P, orange; Si, tan; N, blue; C, gray; H, white.

Table S10 Crystal data and structure refinement for **6**

Empirical formula	$C_{41.01}H_{60.01}FePSi$
Formula weight	667.87
Temperature/K	99.99
Crystal system	orthorhombic
Space group	Pnma
a/Å	27.887(3)
b/Å	11.5982(13)
c/Å	11.5654(10)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3740.7(7)
Z	4
ρ_{calc}g/cm^3	1.186
μ/mm^{-1}	0.505
F(000)	1444.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.92 to 50.712
Index ranges	$-33 \leq h \leq 33$, $-12 \leq k \leq 13$, $-12 \leq l \leq 13$
Reflections collected	21681
Independent reflections	3567 [R_{int} = 0.0773, R_{sigma} = 0.0715]
Data/restraints/parameters	3567/84/489
Goodness-of-fit on F^2	1.139
Final R indexes [I>=2σ (I)]	R_1 = 0.0665, wR_2 = 0.1031
Final R indexes [all data]	R_1 = 0.1114, wR_2 = 0.1137
Largest diff. peak/hole / e Å^{-3}	0.22/-0.30

Structural determination of 13: The structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation. Disorder of one phosphine-bound isopropyl group was treated by refinement against a free variable with final FVAR = 0.4005.

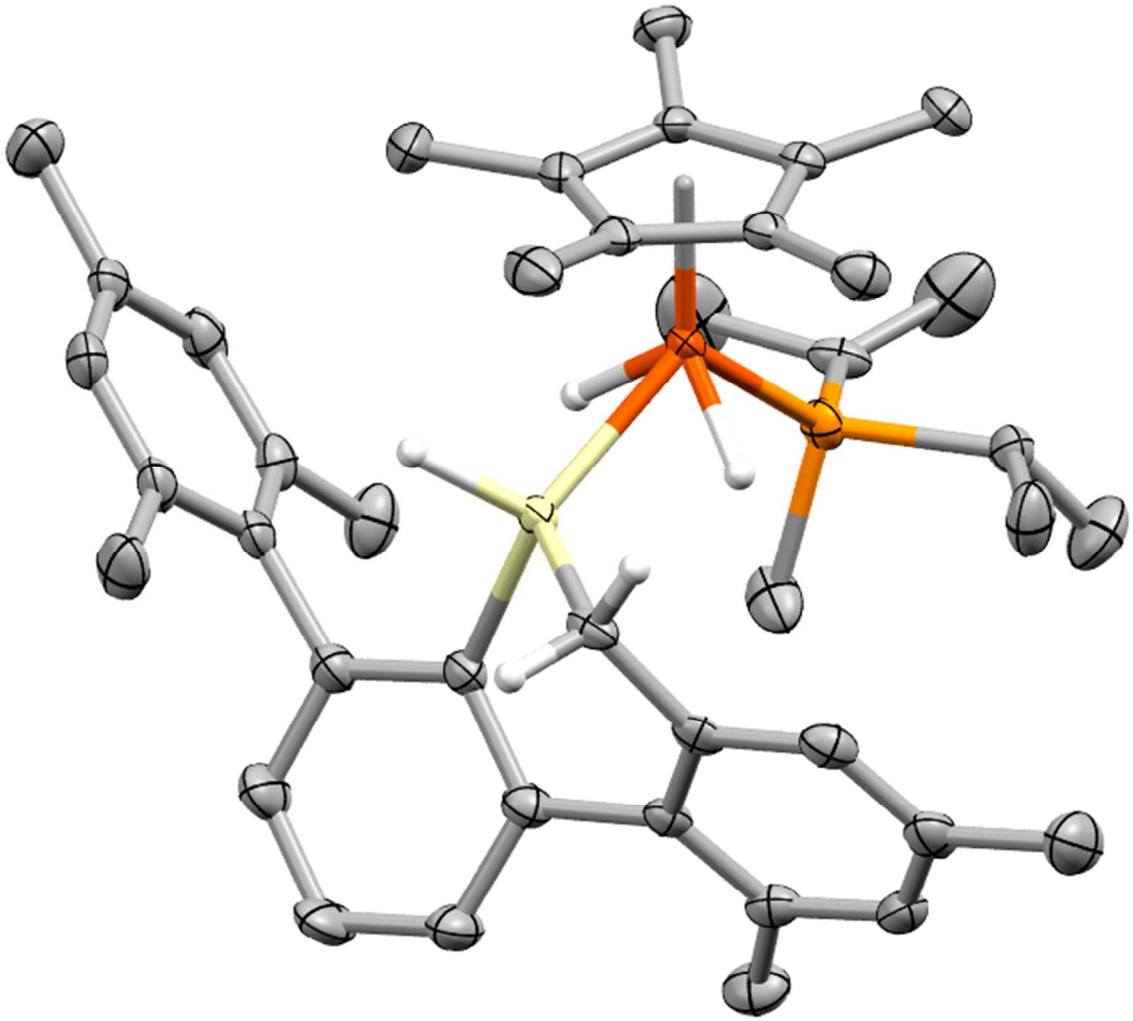

Figure S17: Ellipsoid drawing of **13.** Thermal ellipsoids are drawn at 50% probability; C–bound hydrogen atoms are omitted for clarity, and all displayed hydrogens were located on the Fourier difference map. Atoms are color coded as follows: Fe, red-orange; P, orange; Si, tan; N, blue; C, gray; H, white.

Table S11 Crystal data and structure refinement for **13**

Empirical formula	$C_{82}H_{118}Fe_2P_2Si_2$
Formula weight	1333.58
Temperature/K	100.02
Crystal system	orthorhombic
Space group	Pbca
a/Å	14.0318(3)
b/Å	15.6740(3)
c/Å	33.3126(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	7326.6(2)
Z	4
ρ_{calc}g/cm^3	1.209
μ/mm^{-1}	0.515
F(000)	2880.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.446 to 50.876
Index ranges	$-16 \leq h \leq 16$, $-18 \leq k \leq 18$, $-40 \leq l \leq 37$
Reflections collected	66365
Independent reflections	6763 [R_{int} = 0.0470, R_{sigma} = 0.0285]
Data/restraints/parameters	6763/0/444
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0353, wR_2 = 0.0848
Final R indexes [all data]	R_1 = 0.0481, wR_2 = 0.0920
Largest diff. peak/hole / e Å^{-3}	0.48/-0.32

Computational Studies: All calculations were performed using Q Chem 5.0.0[17] on the Tiger cluster at UC Berkeley Molecular Graphics and Computing Facility. Geometry optimizations for the silylene isomer were performed starting from coordinates taken from the crystal structure of **5**. This was truncated for computational expediency by replacement of Trip with a 2,6-xylyl substituent (**A**). The initial geometry for the corresponding silyl isomer (**B**) was generated by placement of hydrides on Si to form a nearly tetrahedral coordination with Si–H distances of ca. 1.8 Å; other coordinates were unchanged. All calculations were performed using the all-electron def2-TZVP[18] basis set on all atoms. Geometry optimizations and frequency calculations for both molecules were performed using both the ωB97X-D3[19] (long-range separated hybrid GGA) and B97-D3[20] (pure GGA) functionals with empirical dispersion correction. TDDFT for the silylene isomer was performed using the ωB97X-D3 functional.

Optimized geometry of A at ωB97X-D3/def2-TZVP:

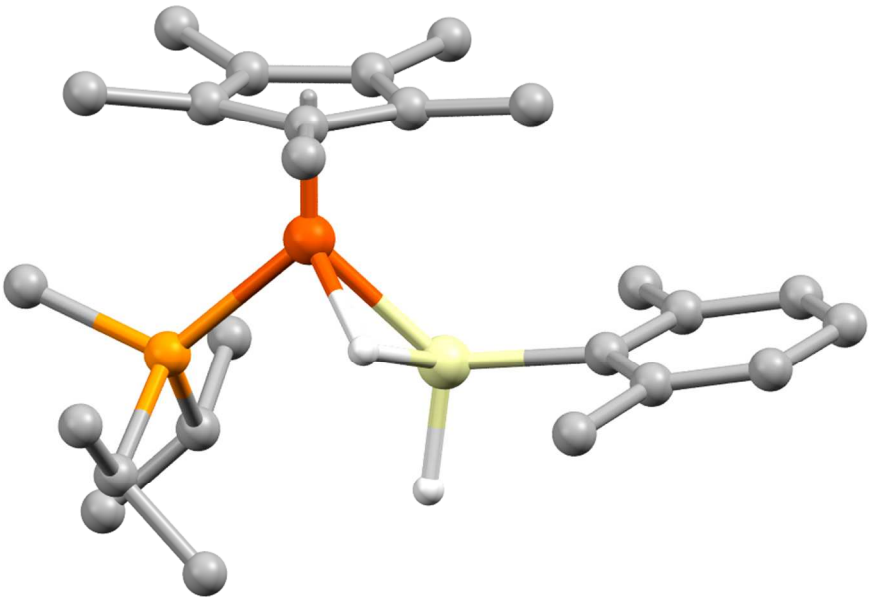

Figure S18: Geometry of **A** optimized at ωB97X-D3/def2-TZVP.

Fe	-0.2728106056	-1.2698022301	-0.5510383782
P	-0.0432793978	-2.6186974883	1.2197435029
Si	0.3239599717	0.4551169590	0.5736449468
H	0.3553345605	0.5811474724	2.0699949402
C	-1.6460170384	-1.3421285807	-2.1111180839
C	1.6113847876	2.8082591626	-0.3804778785
C	0.6214840185	-1.1283132128	-2.4162100628
C	0.5378811587	4.9059848815	-0.8865336701
H	0.5917709355	5.9219184296	-1.2602295966
C	0.3858031967	2.2723611536	0.0415119663
C	-0.7562294451	3.0909188285	0.0364498935
C	-0.6671397119	4.3959870086	-0.4313012095
H	-1.5549184510	5.0193158173	-0.4400175095
C	0.0971437295	-4.4160752275	0.8929546521
H	-0.7499409772	-4.7554356073	0.3037505122
H	0.1229207424	-4.9846347037	1.8227937590
H	1.0048237000	-4.6200002182	0.3284343276
C	-0.6053670500	-0.4077871057	-2.4050658047
C	1.6725938124	4.1172766110	-0.8506534986
H	2.6218883497	4.5186230418	-1.1893794081
C	1.4498468025	-2.3656152227	2.3048670010
H	1.3621672107	-1.3241566552	2.6242180131
C	0.3465582538	-2.4900432243	-2.1295073852
C	-1.0729826596	-2.6240285981	-1.9670047069

C	2.8867559032	2.0099034657	-0.2823243545
C	2.7265137226	-2.4829948151	1.4721391151
H	2.9077010864	-3.5159507755	1.1628588481
H	3.5914320087	-2.1647692155	2.0589377019
H	2.6718753295	-1.8605272328	0.5773631176
C	-1.4555285002	-2.6569046399	2.4342175435
H	-1.2362355492	-3.4813156990	3.1200288496
C	1.9660543360	-0.5847902389	-2.7746201042
H	2.0124276622	0.4943699386	-2.6319722598
H	2.1937281236	-0.7920136892	-3.8247890388
H	2.7523699384	-1.0370355680	-2.1686633154
C	-1.6008861137	-1.3770255405	3.2509158764
H	-0.6893730761	-1.1132124504	3.7889711145
H	-2.3991932679	-1.4986692152	3.9872604218
H	-1.8629984291	-0.5334294583	2.6105613699
C	-2.7631069138	-2.9711748548	1.7107138447
H	-2.9846585577	-2.1982522043	0.9711330646
H	-3.5904844560	-3.0082447848	2.4234337664
H	-2.7303002829	-3.9327671727	1.1963194435
C	-0.8151363693	1.0088088037	-2.8368508416
H	-1.6323129450	1.4839599986	-2.2936698804
H	-1.0676945820	1.0422314467	-3.9008009494
H	0.0698788257	1.6255127806	-2.6864364799
C	1.5331752751	-3.2434584222	3.5511787224
H	0.6587417545	-3.1450474255	4.1955261936
H	2.4060205182	-2.9591389386	4.1443385527
H	1.6508370735	-4.2994423765	3.2978843612
C	1.3553248323	-3.5925853585	-2.2222830303
H	2.2539701868	-3.3725431896	-1.6425409184
H	1.6629693864	-3.7440903412	-3.2609985299
H	0.9542648535	-4.5401892522	-1.8650298170
C	-3.1087227951	-1.0352286495	-2.0660969953
H	-3.6434438761	-1.7325814837	-1.4203754182
H	-3.5514645133	-1.1023446798	-3.0645326194
H	-3.2956841517	-0.0282144616	-1.6920813914
C	-1.8589788682	-3.8965544934	-1.8990866618
H	-1.2226404812	-4.7614014490	-1.7176859284
H	-2.3655395718	-4.0680743657	-2.8529737993
H	-2.6262506462	-3.8701770678	-1.1244186692
H	-1.1895520538	-0.2144295669	0.3555953041
C	-2.0840573474	2.5784503932	0.5312772886
H	3.6149903539	2.3248817375	-1.0310539204
H	2.7088321277	0.9396149005	-0.4144817092
H	3.3470371926	2.1422323417	0.7009122681
H	-2.8135697046	3.3852185014	0.6053555161
H	-1.9878320009	2.1187966765	1.5182655328
H	-2.4937313311	1.8136668008	-0.1334075070

Optimized geometry of B at ωB97X-D3/def2-TZVP:

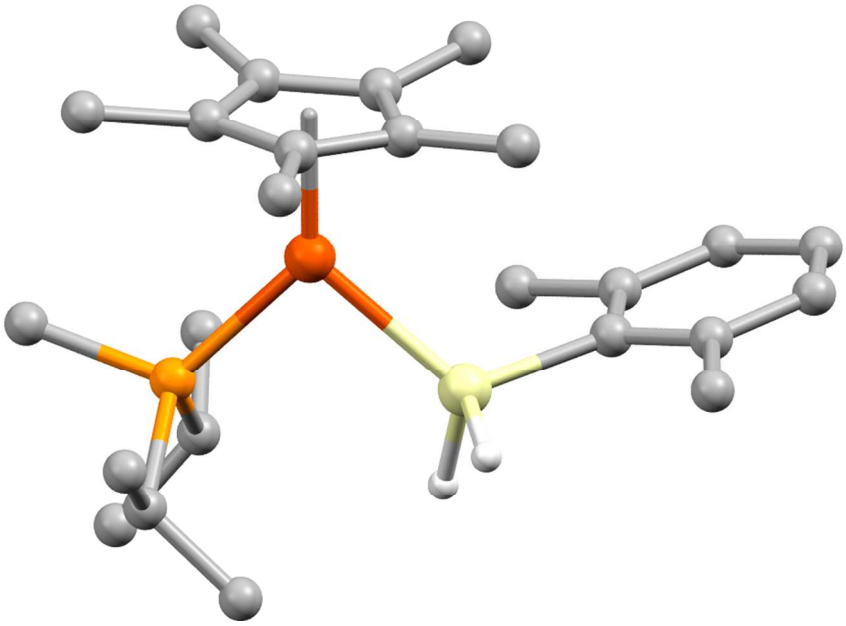

Figure S19: Geometry of **B** optimized at ωB97X-D3/def2-TZVP.

Fe	-0.3823805821	-1.3248746022	-0.4997654530
P	-0.0553296221	-2.6807837518	1.2940621749
Si	-0.4118580488	0.6914381608	0.7930904606
H	0.2575652160	0.6216407990	2.1385555427
C	-1.8626690880	-1.6986128143	-2.1212299595
C	1.7432984802	2.3312929406	-0.1123058980
C	0.2405251789	-0.8073563458	-2.4680616000
C	1.6030468320	4.5621463137	-1.0098485503
H	2.0809597002	5.4353681464	-1.4384539516
C	0.3492573454	2.2925680201	0.0775796084
C	-0.4011180896	3.4339917852	-0.2612298927
C	0.2350618686	4.5462638977	-0.8066502961
H	-0.3571895915	5.4159433427	-1.0708990218
C	0.2105471032	-4.4599174684	0.9525195279
H	-0.6831437077	-4.8893406393	0.5062447373
H	0.4427234515	-5.0115071662	1.8641762412
H	1.0285046954	-4.5831506399	0.2438113210
C	-1.1519339766	-0.4892151319	-2.3156560993
C	2.3540058882	3.4571883171	-0.6531186205
H	3.4291330090	3.4618756224	-0.7982510282
C	1.4521104956	-2.2628287192	2.2810463817
H	1.3147863244	-1.2066763262	2.5251306999
C	0.3806284757	-2.2079715853	-2.3222998675
C	-0.9248187387	-2.7537896382	-2.0939398529
C	2.6025693415	1.1570524571	0.2709649565

C	2.6903609404	-2.3822069025	1.3907235542
H	2.9283756519	-3.4272056150	1.1775237195
H	3.5576090508	-1.9427642050	1.8877582591
H	2.5579324414	-1.8677417380	0.4373583686
C	-1.4535801499	-2.7889698920	2.5043883372
H	-1.2134000501	-3.6302628503	3.1635166869
C	1.3046698961	0.1530057342	-2.8968205910
H	1.1411282420	1.1499125739	-2.4876553114
H	1.3239685119	0.2406349608	-3.9873013166
H	2.2959465929	-0.1740650421	-2.5800469514
C	-1.6326851704	-1.5352152455	3.3553426590
H	-0.7225042319	-1.2454591009	3.8807565473
H	-2.4090760174	-1.7103112624	4.1040350197
H	-1.9453698740	-0.6856214623	2.7470509767
C	-2.7484830580	-3.1090925828	1.7565017211
H	-3.0115861773	-2.2919803968	1.0804941486
H	-3.5700795097	-3.2384571084	2.4645145473
H	-2.6777412699	-4.0236938607	1.1648345090
C	-1.7702141487	0.8481596683	-2.5633926498
H	-2.7087601938	0.9588817205	-2.0192807026
H	-1.9906680396	0.9731475124	-3.6278262076
H	-1.1071028811	1.6596509091	-2.2665445060
C	1.6351440262	-3.0503751072	3.5755616804
H	0.7831185526	-2.9555199942	4.2495475773
H	2.5147453590	-2.6806469731	4.1077892936
H	1.7999834361	-4.1131680338	3.3841697435
C	1.6441961270	-2.9886995483	-2.5154265236
H	2.5161667297	-2.4369335944	-2.1604041678
H	1.8114375613	-3.2164488694	-3.5723473201
H	1.6206979719	-3.9386094537	-1.9795078475
C	-3.3469040809	-1.8277226509	-1.9764036326
H	-3.6230960515	-2.7579062556	-1.4783034476
H	-3.8407871058	-1.8208862449	-2.9525655493
H	-3.7662594715	-1.0052115320	-1.3942284371
C	-1.2778163638	-4.2077803540	-2.0652919479
H	-0.4219618658	-4.8333975719	-1.8167985408
H	-1.6342256853	-4.5241161624	-3.0495970021
H	-2.0739732501	-4.4233607513	-1.3505231014
H	-1.8191160206	1.0355738821	1.1814601213
C	-1.8888605193	3.5185508328	-0.0277600207
H	3.6321802594	1.2907786570	-0.0620838178
H	2.2183837195	0.2340393750	-0.1708790494
H	2.6107218751	1.0106945779	1.3544939333
H	-2.2877333197	4.4512823866	-0.4281043366
H	-2.1203234533	3.4793421674	1.0385104486
H	-2.4253709464	2.6927504302	-0.4948804344

Optimized geometry of A at B97-D3/def2-TZVP:

Fe	-0.2667594250620319	-1.2530656018237574	-0.4943805183548359
P	-0.0335606200958487	-2.6258813575380002	1.2121164423329338
Si	0.3233883618311630	0.4773657323107425	0.6037229927958565
H	0.3177349551345333	0.6245724866624742	2.1036307188685002
C	-1.6578918773540052	-1.3074607207669307	-2.0672651002826861
C	1.6261160124996550	2.8287151327772926	-0.4033028844703195
C	0.6294518989548572	-1.1038168246640150	-2.3703031844643481
C	0.5364862898698106	4.9281968014076245	-0.9558536132353457
H	0.5878573379621745	5.9436495069045190	-1.3444879243207484
C	0.3915114909171478	2.2899646564909513	0.0257905467414510
C	-0.7677618638274120	3.1036287041657729	-0.0137051784390964
C	-0.6806875893739931	4.4103787211995735	-0.5087744749092613
H	-1.5772894994663391	5.0282004026158438	-0.5455981415755436
C	0.1158335848916701	-4.4404684461378441	0.8636205056691993
H	-0.7021981082305694	-4.7619879862086787	0.2209106724854080
H	0.0854343439757559	-5.0217606994589046	1.7910793968116094
H	1.0587415890504108	-4.6357024269218927	0.3491113611080782
C	-0.6033196147816098	-0.3731231325926597	-2.3690388767732187
C	1.6843021293299092	4.1403494191242443	-0.8961937223904445
H	2.6396972906896163	4.5431423467203160	-1.2307710318967513
C	1.4753558019580399	-2.3954678465487387	2.3305819071923244
H	1.3751516736266434	-1.3612648486093362	2.6823770879345461
C	0.3363400515565175	-2.4807059111280956	-2.0982324843693654
C	-1.0934769558377546	-2.6075653400996126	-1.9470258562179561
C	2.9109879707468531	2.0344074555635254	-0.2879758807870491
C	2.7681539640334889	-2.4819520593246898	1.5002440788546629
H	2.9498114738158963	-3.5072801848485455	1.1532539143312237
H	3.6294378769426578	-2.1881079734726576	2.1149039473699798
H	2.7252285039800812	-1.8230755370065561	0.6257061332064159
C	-1.4620227084690511	-2.6912302639056391	2.4484833778546249
H	-1.2284081770370121	-3.5193334284518265	3.1318677951939242
C	1.9839977235094997	-0.5739472083270963	-2.7287645909293023
H	2.0466373312313548	0.5054898646967421	-2.5677308540492390
H	2.2137885369581576	-0.7728356670024601	-3.7870624040103387
H	2.7613271809156545	-1.0515104748132704	-2.1223572212151764
C	-1.6124587469665770	-1.4044315177151316	3.2676397670513886
H	-0.6976813090075439	-1.1453175785606524	3.8105300879384236
H	-2.4218064718712515	-1.5222479280261605	4.0006851829921297
H	-1.8667171549767145	-0.5598775026390795	2.6183251802373806
C	-2.7714613942607107	-3.0178091297197578	1.7147668151733242
H	-2.9797109638946480	-2.2519193565620594	0.9580867395681272
H	-3.6077896108955994	-3.0419378497728982	2.4262127925170773
H	-2.7301854858266248	-3.9915934527506574	1.2147650642086534
C	-0.8169324039536614	1.0410115852924275	-2.8202885414130794
H	-1.5868561813060806	1.5456249378141926	-2.2300978114059111

H	-1.1475998833684051	1.0517359555759205	-3.8700850135377736
H	0.0906634200570746	1.6459121990995849	-2.7509830299647446
C	1.5610330078409527	-3.3160268765458776	3.5580246937633881
H	0.6849955193029412	-3.2322819274457060	4.2094447149004184
H	2.4433182774393787	-3.0499632673955452	4.1560662069330947
H	1.6740537244255347	-4.3671264071624423	3.2672986415175278
C	1.3392813353617938	-3.5923149527484837	-2.2087403457223087
H	2.2347630539920473	-3.3935234807368042	-1.6084057385978552
H	1.6651283346800105	-3.7122715281730128	-3.2530902851425836
H	0.9243430347672339	-4.5504471340868715	-1.8848038055237595
C	-3.1249770189970407	-0.9981977859299662	-2.0438105299901679
H	-3.6604560818720078	-1.6629226665091994	-1.3576349246965485
H	-3.5667956597541375	-1.1275943089459828	-3.0441463975796390
H	-3.3137642391277380	0.0340846998988630	-1.7327072344421539
C	-1.9035518542385388	-3.8710943337039150	-1.9121859775297363
H	-1.2804473230011784	-4.7612093598399721	-1.7887326826198764
H	-2.4479403266995452	-3.9890394022823537	-2.8610443691485821
H	-2.6505160900291571	-3.8623627973101740	-1.1119496051584916
H	-1.2231805584600561	-0.2740438247778538	0.3540100063670737
C	-2.1040292081057772	2.5843367358033396	0.4762038727447444
H	3.6254484719889977	2.3076824397920817	-1.0734108854007509
H	2.7317223767560455	0.9522945825426067	-0.3534361520743849
H	3.3952322680636184	2.2218076155104591	0.6808123058451698
H	-2.8837496314168338	3.3496228112588771	0.3947844488117593
H	-2.0460418791751849	2.2706403014739029	1.5279482976313352
H	-2.4323302823166686	1.7035432142900870	-0.0907884243122812

Optimized geometry of B at B97-D3/def2-TZVP:

Fe	-0.3626158614103132	-1.2963750073737759	-0.4667418186132181
P	-0.0260265315094986	-2.6395497368332625	1.2696981564391838
Si	-0.4097735367017559	0.7085201646072217	0.7852869959845511
H	0.2392115127326797	0.6556248881320590	2.1452501696079449
C	-1.8946251420695239	-1.7272936369475778	-2.0601780164360344
C	1.8014125775486289	2.2606894254877274	-0.1877318744877004
C	0.1723237638188773	-0.7422851906636319	-2.4610675143288794
C	1.7391846126397099	4.5268365536916297	-1.0533368296623937
H	2.2492707654353539	5.3886801314634480	-1.4799335586521669
C	0.4002775929760932	2.2848190046458567	0.0398871382837542
C	-0.3152529946891066	3.4697003795936880	-0.2744491520207935
C	0.3650430236088093	4.5677757517795268	-0.8234890442250984
H	-0.1930141279700442	5.4721551726493196	-1.0640458541610718
C	0.3147354979418029	-4.4302384008260134	0.9204923846665479
H	-0.5610187044534334	-4.8950253113936784	0.4658616915381731
H	0.5621827449009362	-4.9710230664144017	1.8401887462641080
H	1.1495230093355373	-4.5121009932683824	0.2199214624680454
C	-1.2364442447076520	-0.4780926283068339	-2.2642764672710696
C	2.4543165736943187	3.3756089479292974	-0.7275262903948918
H	3.5294744753763201	3.3359810814759543	-0.8983886993967719
C	1.4407983549232994	-2.2242542395330487	2.3746268629202629
H	1.2928803736494485	-1.1642024684806809	2.6098663944906608
C	0.3700163564713586	-2.1533701573577577	-2.3404791327845618
C	-0.9130218328749985	-2.7562118698866649	-2.0912765984395842
C	2.6083622164194651	1.0264130047424225	0.1413846801319606
C	2.7509885553475386	-2.3612836159405513	1.5767035917229675
H	2.9808449121013076	-3.4144978224918709	1.3735356119238382
H	3.5857600628081245	-1.9471669811252814	2.1566153579396081
H	2.7116465288008764	-1.8299429091355448	0.6204633805331459
C	-1.4771936513425037	-2.8250420136519270	2.4535597063815593
H	-1.2067934209726703	-3.6563168868126814	3.1206770096630816
C	1.1719551695418253	0.2639969782167816	-2.9456659128451612
H	1.0198052754999516	1.2395026252397083	-2.4769279280457348
H	1.0834590062207219	0.3957441038267307	-4.0348966419425709
H	2.1994567411105184	-0.0506545758085583	-2.7368493949948993
C	-1.7443616292316599	-1.5724190596902781	3.3002092071705036
H	-0.8532330283180900	-1.2164745556705061	3.8253411362475989
H	-2.5151509660192737	-1.7967926681094462	4.0495399288355953
H	-2.1144805432766804	-0.7491947398499379	2.6799788022348392
C	-2.7426126645755802	-3.2113030646251026	1.6696923454454891
H	-3.0169586364376233	-2.4107770579475782	0.9734612566903621
H	-3.5807255940774332	-3.3628318051795416	2.3626316845962041
H	-2.6170473146797302	-4.1334598052979752	1.0907245134851551
C	-1.9102062731081779	0.8396541375663181	-2.4940690596075501

H	-2.8523334112173049	0.9104570518537443	-1.9407375880758904
H	-2.1437324429296907	0.9698971669472861	-3.5618199492410230
H	-1.2691297011614660	1.6708360383012875	-2.1899013644250838
C	1.5303642765022718	-3.0131351286092971	3.6900828849369840
H	0.6371663135627919	-2.9005656655113032	4.3119766749912447
H	2.3872968222677757	-2.6503936560730676	4.2735578608381699
H	1.6922943779798723	-4.0831147440790865	3.5130863222681263
C	1.6608312819992872	-2.8846979575613125	-2.5715513414057103
H	2.5186668898044280	-2.3034791873777323	-2.2154823925537310
H	1.8229194502464523	-3.0843795451556648	-3.6419937203738000
H	1.6778393747084184	-3.8501322953797867	-2.0544991948163536
C	-3.3717037259464524	-1.9153737738670689	-1.8691750692266067
H	-3.5973815871954806	-2.8615354978648413	-1.3669448802226505
H	-3.8995832574128380	-1.9224075889284435	-2.8350976311782539
H	-3.8052069570671194	-1.1063668469856636	-1.2693781156263424
C	-1.2151887507888097	-4.2257328822885194	-2.0920849247265672
H	-0.3367275303389841	-4.8289046220381779	-1.8495246452402085
H	-1.5592751316523634	-4.5347669506429389	-3.0905369803492686
H	-2.0131336974229033	-4.4838323532721294	-1.3869628857979022
H	-1.8325730718544238	1.0618905997737011	1.1133548241661100
C	-1.7998890226610142	3.6133224867222440	-0.0031033144304082
H	3.6446328269197776	1.1142130940088872	-0.2033165481402013
H	2.1641361270234900	0.1388636095398648	-0.3312441461423478
H	2.6220362988680455	0.8308666210010754	1.2220165998904968
H	-2.1611432011045619	4.5977914897405325	-0.3214336841045832
H	-2.0185567354569378	3.4990815284890400	1.0659156623675672
H	-2.3916288200500651	2.8513969273321900	-0.5216408809366782

TDDFT of A:

Character	Energy (eV)	Wavelength (nm)	Strength (arb)
(triplet)	1.1344	1092.941966	0
(triplet)	1.1893	1042.490008	0
(triplet)	1.6978	730.2587857	0
(singlet)	1.8735	661.7738812	0.00256
(triplet)	1.9122	648.3805911	0
(singlet)	1.9333	641.3041775	0.004579
(triplet)	2.0746	597.625261	0
(singlet)	2.3051	537.8653275	0.000387
(triplet)	2.6245	472.4074553	0
(singlet)	2.8534	434.5108875	0.00408
(triplet)	2.9436	421.1962788	0
(singlet)	3.1408	394.7508171	0.001535
(singlet)	3.3898	365.7541349	0.015065
(triplet)	4.0261	307.9489745	0
(singlet)	4.0919	302.9969858	0.10761
(triplet)	4.2071	294.7002368	0
(triplet)	4.3017	288.2193938	0
(triplet)	4.4819	276.631198	0
(triplet)	4.6257	268.0315123	0
(singlet)	4.6897	264.3737054	0.022902
(triplet)	4.6947	264.0921393	0
(triplet)	4.7527	260.8692672	0
(singlet)	4.8114	257.6866123	0.12999
(triplet)	4.8564	255.2988564	0
(triplet)	4.9331	251.3294615	0
(triplet)	5.007	247.6200053	0
(singlet)	5.0312	246.4289566	0.007097
(triplet)	5.066	244.736156	0
(triplet)	5.072	244.4466416	0
(singlet)	5.1011	243.0521586	0.008775
(triplet)	5.1898	238.8981014	0
(singlet)	5.2249	237.2932241	0.017015
(singlet)	5.3042	233.7455915	0.005377
(triplet)	5.3321	232.522527	0
(triplet)	5.3873	230.1400268	0
(singlet)	5.4056	229.3609158	0.010061
(singlet)	5.5012	225.3750757	0.028657
(singlet)	5.5399	223.8006763	0.065701
(triplet)	5.5647	222.8032718	0

(singlet)	5.6126	220.9017864	0.003884
(singlet)	5.6316	220.1565037	0.126825
(triplet)	5.7219	216.6821102	0
(singlet)	5.7663	215.0136771	0.016885
(triplet)	5.769	214.9130467	0
(triplet)	5.8568	211.6912591	0
(triplet)	5.9077	209.8673539	0
(singlet)	5.9162	209.5658305	0.002823
(singlet)	5.9399	208.7296699	0.020401
(triplet)	5.9446	208.5646413	0
(singlet)	5.9519	208.3088369	0.003093
(triplet)	6.0193	205.9763372	0
(singlet)	6.0438	205.1413625	0.07115
(triplet)	6.0483	204.9887351	0
(singlet)	6.0919	203.5216216	0.009599
(singlet)	6.1194	202.6070148	0.040656
(singlet)	6.1506	201.5792551	0.011403
(singlet)	6.2354	198.8378238	0.0102
(singlet)	6.3157	196.3097307	0.006954
(singlet)	6.3456	195.3847337	0.017989
(singlet)	6.4735	191.5244252	0.009473

Table S12: TDDFT excitation energies and impulses for **A** at the ωB97X-D3/def2-TZVP level of theory.

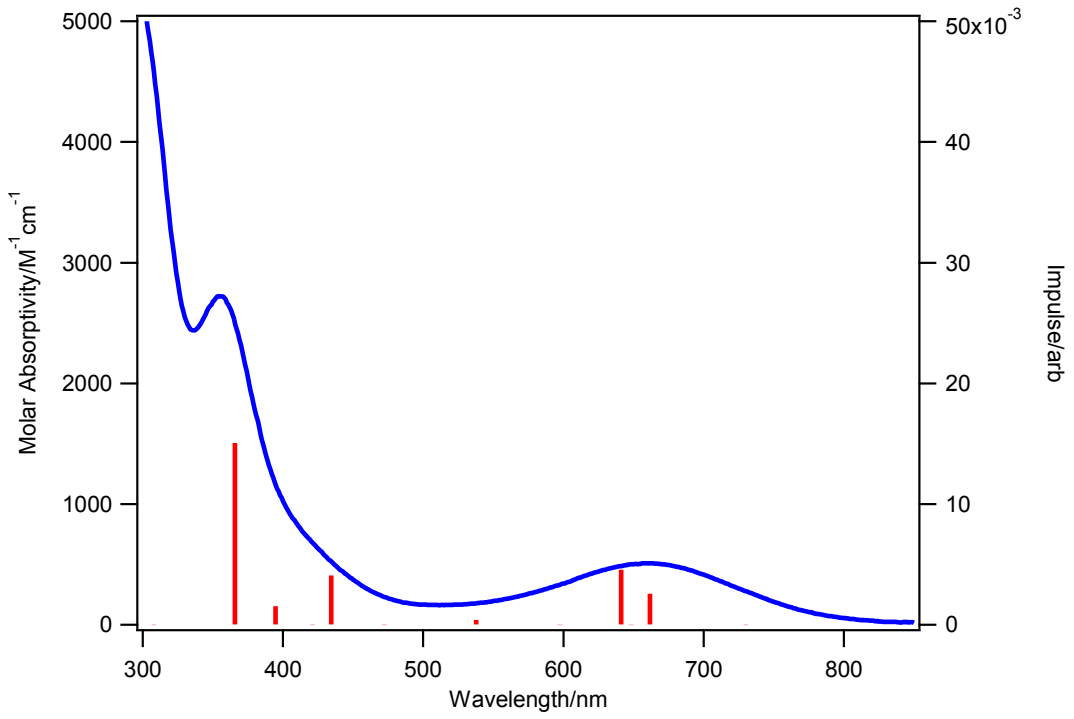

Figure S20: Experimental UV-Vis spectrum of **6** (blue) with TDDFT impulses (red).

Thermochemical parameters for A and B (in kcal mol^{-1}):

wB97X-D3	H	S	G
A	413.322	211.505	-1802670
B	413.472	215.799	-1802681
Δ	-10.3682	1.26673	-11.6355
B97-D3			
A	401.583	216.88	-1802693
B	402.441	211.667	-1802691
Δ	0.45454	-1.537835	1.993157

Table S13: Thermochemical parameters for **A** and **B**.

References

(1) Threlkel, R. S.; Bercaw, J. E.; Seidler, P. F.; Stryker, J. M.; Bergman, R. G. *Org. Synth.* **1987**, *65*, 42.

(2) Betley, T. A.; Peters, J. C. *Inorg. Chem.* **2003**, *42*, 5074–5084.

(3) Simons, R. S.; Haubrich, S. T.; Mork, B. V.; Niemeyer, M.; Power, P. P. *Main Gr. Chem.* **1998**, *2*, 275–283.

(4) Glaser, P. B.; Tilley, T. D. *Organometallics* **2004**, 5799–5812.

(5) Seidel, V. W.; Lattermann, K.-J. *Z. Anorg. Allg. Chem* **1982**, *74*, 69–74.

(6) Smith, P. W.; Tilley, T. D. *Organometallics* **2015**, *34*, 2134–2138.

(7) Battino, R.; Rettich, T. R.; Tominaga, T. *J. Phys. Chem. Ref. Data* **1984**, *13*, 563–600.

(8) Bain, A. D.; Fletcher, D. A. *Mol. Phys.* **1998**, *95*, 1091–1098.

(9) Bain, A. D.; Cramer, J. A. *J. Magn. Reson. - Ser. A* **1996**, *118*, 21–27.

(10) Ammann, C.; Meier, P.; Merbach, A. *J. Magn. Reson.* **1982**, *46*, 319–321.

(11) Lemon, C. M.; Huynh, M.; Maher, A. G.; Anderson, B. L.; Bloch, E. D.; Powers, D. C.; Nocera, D. G. *Angew. Chemie - Int. Ed.* **2016**, *55*, 2176–2180.

(12) Guennic, B. Le; Floyd, T.; Galan, B. R.; Autschbach, J.; Keister, J. B. *Inorg. Chem.* **2009**, *48*, 5504–5511.

(13) Dolomanov, O. V; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.

(14) Sheldrick, G. M. *Acta Crystallogr. Sect. A* **2015**, *71*, 3–8.

(15) Sheldrick, G. M. *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122.

(16) Sheldrick, G. M. *Acta Crystallogr. Sect. C* **2015**, *71*, 3–8.

(17) Shao, Y.; Gan, Z.; Epifanovsky, E.; Gilbert, A. T. B.; Wormit, M.; Kussmann, J.; Lange, A. W.; Behn, A.; Deng, J.; Feng, X.; Ghosh, D.; Goldey, M.; Horn, P. R.; Jacobson, L. D.; Kaliman, I.; Khaliullin, R. Z.; Kuš, T.; Landau, A.; Liu, J.; Proynov, E. I.; Rhee, Y. M.; Richard, R. M.; Rohrdanz, M. A.; Steele, R. P.; Sundstrom, E. J.; Woodcock, H. L.; Zimmerman, P. M.; Zuev, D.; Albrecht, B.; Alguire, E.; Austin, B.; Beran, G. J. O.; Bernard, Y. A.; Berquist, E.; Brandhorst, K.; Bravaya, K. B.; Brown, S. T.; Casanova, D.; Chang, C. M.; Chen, Y.; Chien, S. H.; Closser, K. D.; Crittenden, D. L.; Diedenhofen, M.; Distasio, R. A.; Do, H.; Dutoi, A. D.; Edgar, R. G.; Fatehi, S.; Fusti-Molnar, L.; Ghysels, A.; Golubeva-Zadorozhnaya, A.; Gomes, J.; Hanson-Heine, M. W. D.; Harbach, P. H. P.; Hauser, A. W.; Hohenstein, E. G.; Holden, Z. C.; Jagau, T. C.; Ji, H.; Kaduk, B.; Khistyaev, K.; Kim, J.; Kim, J.; King, R. A.; Klunzinger, P.; Kosenkov, D.; Kowalczyk, T.; Krauter, C. M.; Lao, K. U.; Laurent, A. D.; Lawler, K. V.; Levchenko, S. V.; Lin, C. Y.; Liu, F.; Livshits, E.; Lochan, R. C.; Luenser, A.; Manohar, P.; Manzer, S. F.; Mao, S. P.; Mardirossian, N.; Marenich, A. V.; Maurer, S. A.; Mayhall, N. J.; Neuscamman, E.; Oana, C. M.; Olivares-Amaya, R.; Oneill, D. P.; Parkhill, J. A.; Perrine, T. M.; Peverati, R.; Prociuk, A.; Rehn, D. R.; Rosta, E.; Russ, N. J.; Sharada, S. M.; Sharma, S.; Small, D. W.; Sodt, A.; Stein, T.; Stück, D.; Su, Y. C.; Thom, A. J. W.; Tsuchimochi, T.; Vanovschi, V.; Vogt, L.; Vydrov, O.; Wang, T.; Watson, M. A.; Wenzel, J.; White, A.; Williams, C. F.; Yang, J.; Yeganeh, S.; Yost, S. R.; You, Z. Q.; Zhang, I. Y.; Zhang, X.; Zhao, Y.; Brooks, B. R.; Chan, G. K. L.; Chipman, D. M.; Cramer, C. J.; Goddard, W. A.; Gordon, M. S.; Hehre, W. J.; Klamt, A.; Schaefer, H. F.; Schmidt, M. W.; Sherrill, C. D.; Truhlar, D. G.; Warshel, A.; Xu, X.; Aspuru-Guzik, A.; Baer, R.; Bell, A. T.; Besley, N. A.; Chai, J. Da; Dreuw, A.; Dunietz, B. D.; Furlani, T. R.; Gwaltney, S. R.; Hsu, C. P.; Jung, Y.; Kong, J.; Lambrecht, D. S.; Liang, W.;

Ochsenfeld, C.; Rassolov, V. A.; Slipchenko, L. V.; Subotnik, J. E.; Van Voorhis, T.; Herbert, J. M.; Krylov, A. I.; Gill, P. M. W.; Head-Gordon, M. *Mol. Phys.* **2015**, *113*, 184–215.

(18) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

(19) Lin, Y. S.; Li, G. De; Mao, S. P.; Chai, J. Da. *J. Chem. Theory Comput.* **2013**, *9*, 263–272.

(20) Grimme, S. *J. Comput. Chem.* **2009**, *27*, 1787–1799.