

Silane-Allyl Coupling Reactions of $\text{Cp}^*(^i\text{Pr}_2\text{MeP})\text{Fe}(\eta^3\text{-C}_3\text{H}_5)$ and
Synthetic Access to the Hydrido-Dinitrogen Complex



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 dried by vacuum distillation from Na/K alloy. Cp*H,¹ ⁱPr₂MeP,² DMPSiH₃,³ and Mes₂SiH₂⁴ were prepared by literature procedures. Fe(acac)₂ was purchased from Sigma-Aldrich and sublimed prior to use.

NMR spectra were recorded using Bruker AVB 400, AV-500, or AV-600 spectrometers equipped with a 5 mm broad band probe. Spectra were recorded at room temperature (ca. 22 °C) and referenced to the residual protonated solvent for ¹H. ³¹P{¹H} NMR spectra were referenced relative to 85% H₃PO₄ external standard ($\delta = 0$). ¹³C{¹H} NMR spectra were calibrated internally with the resonance for the solvent relative to tetramethylsilane. For ¹³C{¹H} NMR spectra, resonances obscured by the solvent signal are omitted. ²⁹Si NMR spectra were obtained via 2D ¹H ²⁹Si HMBC unless otherwise specified. 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.

X-ray Diffraction Experiments. Single crystal X-ray diffraction experiments were carried out at the UC Berkeley CHEXRAY crystallographic facility. Measurements of compounds were performed on a Bruker APEX-II CCD area detector using Mo K radiation ($\lambda = 0.71073\text{\AA}$) monochromated using QUAZAR multilayer mirrors. Specific details of each experiment can be found below, in section 5 at the end of this document and in the included crystallographic information files.

Synthesis of Cp*(ⁱPr₂MeP)Fe(η^3 -C₃H₅) (1). To a stirred solution of Cp*H (0.80 g, 5.91 mmol) in THF (60 mL) was added 1.6 M n-BuLi (3.69 mL, 5.91 mmol). This was stirred for 20 m, after which the mixture was transferred *via* cannula to a flask containing Fe(acac)₂ (1.50 g, 5.91 mmol) in THF (20 mL) that had been cooled to -78 °C. To the resulting deep red mixture, ⁱPr₂MeP (0.78 g, 5.91 mmol)

was added *via* syringe. The cooling bath was removed, and the mixture was allowed to warm to room temperature with stirring. After the solution was stirred at room temperature for 20 min, it was cooled to -78 °C and then 2.6 M (C₃H₅)MgBr in THF was added in one portion (7.5 mL, 15 mmol). The cooling bath was again removed and the mixture was allowed to warm to room temperature with stirring, and for an additional 20 min, before the solvent was removed under reduced pressure. The resulting deep brown residue was extracted with hexane (2 x 50 mL), hexane was removed under reduced pressure from the combined extracts, and the resulting deep red oil was crystallized from pentane at -35 °C to give the product as deep red plates. The combined yield from 3 crops: 1.18 g, 3.24 mmol, 55%. ¹H NMR (benzene-*d*₆): δ = -0.13 (m, 5H, C₃H₅ and P*Me*); 0.99 (dd, 6H, CH*Me*₂, *J*_{HP} = 10.0 Hz, *J* = 7.0 Hz); 0.99 (dd, 6H, CH*Me*₂, *J*_{HP} = 13.8 Hz, *J* = 7.2 Hz); 1.54 (s, 15H, Cp*); 2.13 (m, 4H, PCH*Me*₂ and C₃H₅) 3.28 (m, 1H, C₃H₅) ppm. ¹³C{¹H} NMR (benzene-*d*₆): δ = 0.99 (d, *J*_{CP} = 21.50 Hz); 10.51; 18.91 (d, *J*_{CP} = 3.93 Hz); 20.71 (d, *J*_{CP} = 4.98 Hz); 29.24 (d, *J*_{CP} = 15.43 Hz); 33.14 (d, *J*_{CP} = 8.88 Hz); 74.00 (d, *J*_{CP} = 2.59 Hz); 82.77 (s) ppm. ³¹P NMR (400 MHz, benzene-*d*₆): δ = 67 ppm. FTIR (KBr pellet): 3037 (m), 2974 (s), 2958 (s), 2904 (s), 2860 (s), 2718 (w), 1462 (m), 1373 (s), 1357 (m), 1284 (m), 1260 (w), 1198 (m), 1153 (w), 1093 (m), 1066 (m), 1044 (m), 1026 (s), 990 (m), 883 (s), 804 (w), 760 (w), 702 (m), 601 (m), 470 (m) cm⁻¹. Anal. Calc. For C₂₀H₃₇PFe: C, 65.93; H, 10.24. Found: C, 65.85; H, 10.08.

Synthesis of Cp*Fe(*μ*-H)Si^{''}PrMes(*η*³-CH₂C₆H₂Me₂) (2). To a stirred solution of **1** (0.100 g, 0.275 mmol) in 4 mL of pentane was added Mes₂SiH₂ (0.075 g, 0.280 mmol) in 2 mL of pentane. The resulting solution was stirred at room temperature for 18 h, after which all solvent was removed under reduced pressure. The resulting deep purple residue was dissolved in pentane (6 mL), which was allowed to slowly evaporate at -35 °C to give deep purple blocks. Yield: 0.087 g, 63%. ¹H NMR (500 MHz, benzene-*d*₆) δ = -15.85 (t, *J* = 3.4 Hz, 1H, FeH*Si*), -0.47 (t, *J* = 4.1 Hz, 1H), 0.88 (q, *J* = 7.0 Hz,

2H), 0.99 (t, $J = 6.9$ Hz, 3H), 1.58 (s, 15H), 1.97 (s, 3H), 2.08 (s, 3H), 2.20 (s, 3H), 2.57 (d, $J = 3.7$ Hz, 4H), 2.61 (s, 3H), 6.39 (s, 1H), 6.61 (s, 1H), 6.76 (s, 1H), 6.99 (s, 1H) ppm. ^{13}C NMR (126 MHz, benzene- d_6) $\delta = 10.34, 18.94, 19.98, 20.37, 21.04, 21.74, 24.10, 24.28, 25.37, 28.46, 61.68, 80.50, 102.23, 124.58, 128.58, 128.70, 128.76, 137.23, 138.45, 143.29, 144.85, 149.76$ ppm. ^{29}Si NMR (500 MHz, benzene- d_6): $\delta = -27$ ppm. FTIR (KBr pellet): $\nu = 3013$ (w), 2959 (s), 2902 (s), 2866 (s), 1701 (wb), 1618 (m), 1604 (m), 1516 (w), 1448 (sb), 1409 (m), 1376 (s), 1331 (w), 1316 (w), 1225 (w), 1067 (s), 1029 (s), 991 (w), 891 (m), 847 (m), 831 (m), 798 (w), 719 (m), 689 (m) cm^{-1} . Anal. Calc. for $\text{C}_{31}\text{H}_{44}\text{FeSi}$: C, 74.38; H, 8.86. Found: C, 74.65; H, 8.86.

Synthesis of $\text{Cp}^*\text{Fe}(\mu\text{-H})\text{SiH}(\text{DMP})(\eta^3\text{-CHCHCH}_2)$ (3). To a stirred solution of **1** (0.080 g, 0.220 mmol) in 4 mL of pentane was added DMPSiH_3 (0.076 g, 0.220 mmol) in 8 mL of pentane. The resulting solution was allowed to stir at room temperature for 3 h, after which all the solvent was removed under reduced pressure. The resulting deep red residue was dissolved in pentane (6 mL), which was allowed to slowly evaporate at -35°C to give deep red plates. Yield: 0.044 g, 0.088 mmol, 40 %. ^1H NMR (600 MHz, benzene- d_6): $\delta = -16.72$ (td, $J = 4.0, {}^1J_{\text{SiH}} = 94$ Hz, 2.6 Hz, 1H, FeH), -0.18 (dt, $J = 9.3, 3.1$ Hz, 1H), 1.41 (s, 15H, Cp^*), 1.98 (dt, $J = 6.6, 2.0$ Hz, 1H), 2.14 (s, 6H), 2.16 (s, 6H, o-CH_3), 2.31 (s, 6H), 2.34 (d, $J = 2.5$ Hz, 1H), 3.84 (dt, $J = 9.0, 7.0$ Hz, 1H), 4.59 (d, $J = 2.5$ Hz, ${}^1J_{\text{SiH}} = 222$ Hz, 1H, SiH), 6.79 (d, $J = 7.6$ Hz, 2H), 7.00 (s, 4H), 7.10 (t, $J = 7.6$ Hz, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (400 MHz, benzene- d_6): $\delta = 10.16, 21.18, 21.34, 21.40, 32.96, 39.17, 83.13, 91.57, 128.84, 128.93, 130.10, 136.10, 136.60, 136.68, 140.80, 149.74$ ppm. ^{29}Si NMR (600 MHz, benzene- d_6): $\delta = -34$ ppm. FTIR (KBr pellet): $\nu = 3021$ (m), 2970 (s), 2946 (s), 2912 (s), 2855 (m), 2728 (w), 2127 (s, ν_{SiH}), 1735 (bw), 1610 (m), 1556 (m), 1479 (m), 1443 (s), 1378 (s), 1296 (w), 1260 (w), 1293 (w), 1176 (w), 1116 (m), 1085 (w), 1066 (w), 1048 (w), 1031 (m), 988 (w), 852 (vs), 804 (s), 780 (m), 739 (s), 731 (m), 650 (m) cm^{-1} . Anal. Calc. For $\text{C}_{37}\text{H}_{44}\text{SiFe}$: C, 77.60; H, 7.74. Found: C, 77.63; H, 7.84.

Synthesis of $\text{Cp}^*(^i\text{Pr}_2\text{MeP})\text{FeH}_2(\text{SiH}_2\text{DMP})$ (4**). Method A:** The mother liquor from the recrystallization of **2** was allowed to evaporate further at $-35\text{ }^\circ\text{C}$, to provide **4** as yellow needles. Yield: $< 0.01\text{ g}$, $< 10\%$ **Method B:** A solution of **1** (0.200 g , 0.549 mmol) in pentane (5 mL) was stirred under 1 atm of hydrogen for 40 min . To the resulting solution was added solid DMPSiH_3 (0.157 g , 0.456 mmol), and this solution was stirred under hydrogen for 2 h , at which point a yellow precipitate had formed. The solvent was removed under reduced pressure, and the resulting yellow powder was recrystallized twice from pentane at $-35\text{ }^\circ\text{C}$ to give yellow needles. Yield: 0.061 g , 20% . The NMR spectra of **4** (benzene- d_6 , N_2 atmosphere) contain resonances for DMPSiH_3 and **5**. Spectra for **4**: ^1H NMR (600 MHz , benzene- d_6) $\delta = -15.00$ (d, $J_{\text{HP}} = 57.1\text{ Hz}$, 2H , FeH), 0.04 (d, $J_{\text{HP}} = 8.0\text{ Hz}$, 3H , PMe), 0.80 (dd, $J_{\text{HP}} = 12.2$, $J = 6.7\text{ Hz}$, 6H PCHMe), $0.97 - 0.83$ (m, **5** PMe , **5** PCHMe , and **4** PCHMe), 1.54 (m, 17H , Cp^* and PCHMe_2), 2.29 (s, 6H , $p\text{-Mes}$), 2.41 (s, 12H , $o\text{-Mes}$), 4.87 (s, 2H , SiH_2), 6.90 (s, 4H , $m\text{-Mes}$), 6.96 (d, $J = 7.8\text{ Hz}$, 2H , $m\text{-C}_6\text{H}_3$), 7.22 (t, $J = 7.4\text{ Hz}$, 1H , $p\text{-C}_6\text{H}_3$) ppm. ^{13}C NMR (151 MHz , benzene- d_6) $\delta = 9.70$ (d, $J_{\text{CP}} = 25.5\text{ Hz}$), 11.77 , 18.16 , 19.50 (d, $J_{\text{CP}} = 2.2\text{ Hz}$), 22.34 , 27.51 (d, $J_{\text{CP}} = 19.3\text{ Hz}$), 87.75 , 129.02 , 130.13 , 135.44 , 137.05 , 143.14 , 143.28 , 149.83 ppm. ^{31}P NMR (400 MHz , benzene- d_6): $\delta = 75\text{ ppm}$. ^{29}Si NMR (600 MHz , benzene- d_6): $\delta = -23\text{ ppm}$. Anal. Calcd. For $\text{C}_{41}\text{H}_{61}\text{FePSi}$: C, 73.63 ; H, 9.19 ; N, 0.00 . Found: C, 73.55 ; H, 8.87 ; N, 0.47 ; The nitrogen content is likely due to cocrystallization with a small amount of the dinitrogen complex **5**, with which **4** is in equilibrium in solution.

Synthesis of $\text{Cp}^*(^i\text{Pr}_2\text{MeP})\text{FeH}(\text{N}_2)$ (5**).** Compound **1** (0.240 g , 0.485 mmol) was dissolved in 20 mL pentane and placed in a 500 mL Teflon-stoppered Schlenk flask. The solution was subjected to 3 freeze-pump-thaw cycles, after which a hydrogen atmosphere was introduced. The resulting solution was stirred at room temperature for 40 min , at which point it had turned bright yellow. The solution was frozen, after which the flask was evacuated and backfilled with nitrogen. The solution was allowed

to warm to room temperature with stirring, and stirring was continued for an additional 20 min, after which the solvent was removed to give a red oily residue. This was recrystallized by slow evaporation of a pentane-hexamethyldisiloxane (1:1, 2 mL total) solution at -35 ° C to give **5** as orange blocks. Yield: 0.146 g, 62 %. ^1H NMR (600 MHz, benzene- d_6): δ = -12.14 (d, J_{HP} = 80.5 Hz, 1H), 0.90 – 0.84 (m, 6H), 0.93 (dd, J_{HP} = 14.4, J = 6.8 Hz, 3H), 1.02 (dd, J_{HP} = 14.5, J = 6.7 Hz, 3H), 1.18 (dd, J_{HP} = 15.0, J = 7.2 Hz, 3H), 1.55-1.65 (m, 1H), 1.73 (s, 15H), 1.90 – 1.81 (m, 1H) ppm. ^{13}C NMR (151 MHz, benzene- d_6) δ = 7.19 (d, J_{CP} = 15.4 Hz), 11.12, 16.34 (d, J_{CP} = 4.6 Hz), 17.02 (d, J_{CP} = 2.9 Hz), 17.86 (d, J_{CP} = 2.4 Hz), 18.83 (d, J_{CP} = 4.3 Hz), 24.52 (d, J_{CP} = 18.1 Hz), 28.74 (d, J_{CP} = 27.5 Hz), 87.62 ppm. ^{31}P NMR (400 MHz, benzene- d_6): δ = 75.84 ppm. FTIR (KBr pellet): ν = 2956 (s), 2929 (m), 2911 (m), 2869 (m), 2733 (w), 2047 (m, ν_{N_2}), 1711 (w), 1635 (m), 1469 (m), 1444 (m), 1373 (m), 1302 (m), 1262 (w), 1173 (m), 1143 (s), 1088 (s), 929 (m), 891 (m), 807 (m), 754 (m), 674 (m). Anal. Calcd. For $\text{C}_{17}\text{H}_{33}\text{N}_2\text{FeP}$: C, 57.96; H, 9.44; N, 7.95. Found: C, 57.79; H, 9.80; N, 7.60.

Hydrogenolysis of 1 in benzene- d_6 . A solution of **1** (0.010 g, 0.02 mmol) was dissolved in benzene- d_6 (0.5 mL). The solution was freeze-pump-thawed three times, after which it was backfilled with hydrogen. Every 20 min for the next 1 h, the solution was frozen and the hydrogen atmosphere was removed and refilled to replenish the consumed hydrogen. The solution was allowed to react for a further hour before a ^1H NMR spectrum was recorded. A single product assigned as $\text{Cp}^*(^i\text{Pr}_2\text{MeP})\text{FeH}_3$ was observed by ^1H NMR spectroscopy. ^1H NMR (600 MHz, benzene- d_6) δ = -12.25 (m, 3H, FeH_3), 1.04 – 0.78 (m, 21H, MeCH_2Me , PMe , PCHMe_2), 1.30 – 1.18 (m, 2H, MeCH_2Me), 1.37 (m, 2H, PCHMe_2), 1.95 (s, 15H, Cp^*) ppm.

Reaction of 5 with DMPSiH_3 . Compound **5** (0.025 g, 0.071 mmol) was dissolved in benzene- d_6 (0.5 mL) and the resulting solution was added to solid DMPSiH_3 (0.024 g, 0.071 mmol). The mixture was swirled until all DMPSiH_3 had dissolved, over which time the solution turned from orange to

yellow. The ^1H NMR spectrum of this solution matched that for crystals of **4**.

NMR spectroscopy of **4 in degassed benzene- d_6 :** Benzene- d_6 (0.5 mL) was degassed by 3 freeze-pump-thaw cycles. The degassed solvent was vacuum-transferred onto crystals of **4** (0.008 g, 0.012 mmol) and ferrocene (0.0023 g, 0.012 mmol) as an internal standard. The spectrum is shown in Figure S1.

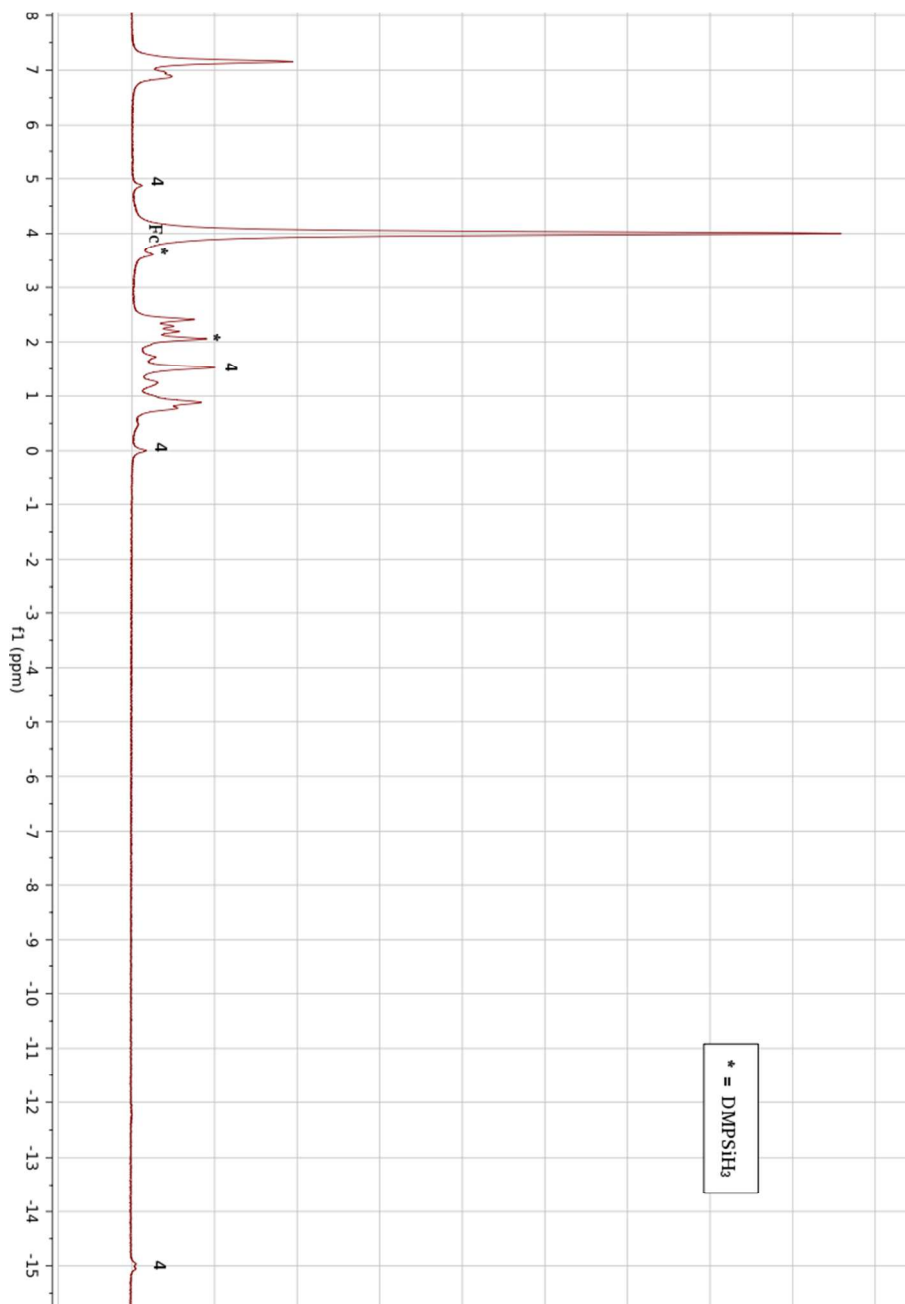


Figure S1: ^1H NMR spectrum of crystals of **4** dissolved in degassed benzene- d_6 .

Determination of the equilibrium constant and ΔG° : Crystals of **3** were dissolved in 0.5 mL of benzene- d_6 containing 1,3,5-tris(trifluoromethyl)benzene at a concentration of 5.3 mM as an internal standard. The ^1H NMR spectrum of each sample was recorded; a sample spectrum is given in Figure S2. Integration of selected resonances against the internal standard was used to determine the concentrations of **4**, **5**, and DMPSiH_3 . The integration regions, as well as the total number of protons associated with each region, are given in Table S1. The concentration of dinitrogen in benzene at various temperatures has been previously reported.⁵ The averages of the integrated concentrations for each sample are given in Table S2; these concentrations were used for further calculations. The equilibrium constant for each sample was determined by the equation $\frac{[\text{DMPSiH}_3][5]}{[\text{N}_2][4]}$; ΔG° values were calculated based on the experimental equilibrium constants. The results of these calculations, as well as the average values, are given in Table S3.

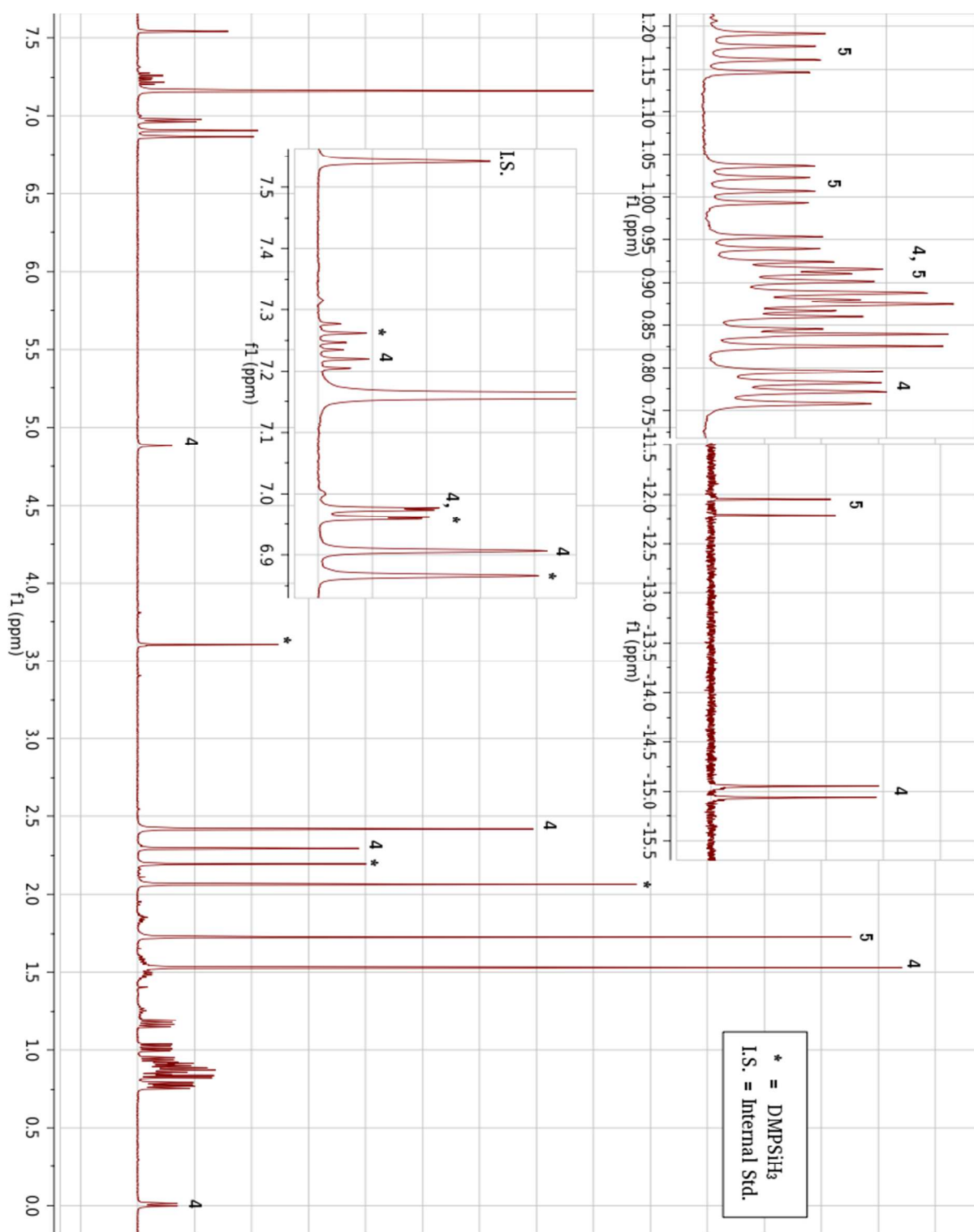


Figure S2: Sample spectrum of equilibrium mixture with peak assignments.

Table S1: Integrals used for determination of equilibrium species concentrations							
Compound	Internal Standard	3	3	3	3	3	3
Protons	3	4	2	12	6	6	3
Integral range (δ , ppm)	7.555 – 7.528	6.920 – 6.895	4.949 – 4.820	2.472 – 2.379	2.326 – 2.272	0.806 – 0.739	0.030 – 0.021
Compound	DMPSiH3	DMPSiH3	DMPSiH3	DMPSiH3	4	4	4
Protons	4	3	6	12	15	3	3
Integral range (δ , ppm)	6.882 – 6.851	3.821 – 3.367	2.241 – 2.175	2.102 – 2.027	1.777 – 1.693	1.200 – 1.138	1.048 – 0.984

Table S2: Average concentrations (mol/L) found by integration against internal standard								
Sample	[3] + [4]	[3]	stdev [3]	[4]	Stdev [4]	[DMPSiH3]	stdev [DMPSiH3]	[N2]
1	0.00738	0.00140	0.00016	0.00589	0.00048	0.00607	0.00032	0.00493
2	0.01272	0.00411	0.00036	0.00855	0.00029	0.00867	0.00061	0.00493
3	0.02517	0.01276	0.00075	0.01224	0.00044	0.01257	0.00065	0.00493

Table S3: Calculated equilibrium constants and ΔG°				
Sample	K	error in K	ΔG° (kcal/mol)	error in ΔG°
1	5.195	0.116	-0.958	-0.013
2	3.665	0.051	-0.755	-0.008
3	2.450	0.018	-0.521	-0.004
	Average K	error	Average ΔG°	error
	3.77	0.06	-0.745	0.008

Crystallographic Data Tables

Table S4: Crystal data and structure refinement for Compound 2

Identification code	Compound 2
Empirical formula	C ₃₄ H ₄₄ SiFe
Formula weight	504.29
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	8.3942(6)
b/Å	9.3342(7)
c/Å	18.0496(13)
$\alpha/^\circ$	93.8800(10)
$\beta/^\circ$	93.4510(10)
$\gamma/^\circ$	107.7960(10)
Volume/Å ³	1338.61(17)
Z	2
ρ_{calc} /mg/mm ³	1.251
m/mm ⁻¹	0.628
F(000)	500.0
2 Θ range for data collection	4.54 to 50.67°
Index ranges	-10 ≤ h ≤ 10, -11 ≤ k ≤ 11, -21 ≤ l ≤ 21
Reflections collected	20883
Independent reflections	4780[R(int) = 0.0215]
Data/restraints/parameters	4780/0/313
Goodness-of-fit on F ²	1.050
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0338, wR ₂ = 0.0904
Final R indexes [all data]	R ₁ = 0.0376, wR ₂ = 0.0934
Largest diff. peak/hole / e Å ⁻³	1.11/-0.31

Table S5: Crystal data and structure refinement for Compound 3.

Identification code	Compound 3
Empirical formula	C ₃₇ H ₄₄ SiFe
Formula weight	572.66
Temperature/K	99.99
Crystal system	triclinic
Space group	P-1
a/Å	8.7703(3)
b/Å	11.2002(3)
c/Å	17.3519(5)
$\alpha/^\circ$	95.5940(10)
$\beta/^\circ$	104.4630(10)
$\gamma/^\circ$	107.3250(10)
Volume/Å ³	1548.10(8)
Z	2
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.229
μ/mm^{-1}	0.549
F(000)	612.0
Radiation	MoK α ($\lambda = 0.71073$)
2 θ range for data collection/ $^\circ$	3.876 to 50.974
Index ranges	$-10 \leq h \leq 10$, $-11 \leq k \leq 13$, $-20 \leq l \leq 20$
Reflections collected	19556
Independent reflections	5699 [$R_{\text{int}} = 0.0331$, $R_{\text{sigma}} = 0.0339$]
Data/restraints/parameters	5699/0/371
Goodness-of-fit on F ²	1.062
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0427$, $wR_2 = 0.1043$
Final R indexes [all data]	$R_1 = 0.0511$, $wR_2 = 0.1163$
Largest diff. peak/hole / e Å ⁻³	0.81/-0.65

Table S6: Crystal data and structure refinement for Compound 4

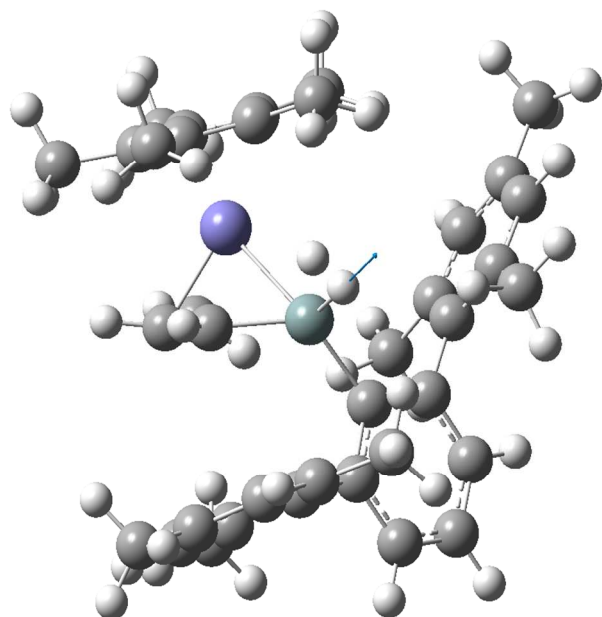
Identification code	Compound 4
Empirical formula	C ₄₄ HSiP ₂ Fe
Formula weight	646.23
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	8.8981(5)
b/Å	11.8359(7)
c/Å	18.8372(12)
$\alpha/^\circ$	72.175(3)
$\beta/^\circ$	82.686(3)
$\gamma/^\circ$	76.623(3)
Volume/Å ³	1833.98(19)
Z	2
ρ_{calc} /mg/mm ³	1.170
m/mm ⁻¹	0.525
F(000)	640.0
2 θ range for data collection	2.276 to 51.036°
Index ranges	-10 ≤ h ≤ 10, -13 ≤ k ≤ 14, 0 ≤ l ≤ 22
Reflections collected	6707
Independent reflections	6707[R(int) = ?]
Data/restraints/parameters	6707/0/427
Goodness-of-fit on F ²	1.020
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0556, wR ₂ = 0.1282
Final R indexes [all data]	R ₁ = 0.0948, wR ₂ = 0.1415
Largest diff. peak/hole / e Å ⁻³	0.49/-0.44

Table S7: Crystal data and structure refinement for Compound 5

Identification code	Compound 5
Empirical formula	C ₁₇ H ₃₃ N ₂ PFe
Formula weight	352.27
Temperature/K	100.0
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	8.7299(4)
b/Å	9.9984(5)
c/Å	21.5918(11)
α /°	90
β /°	91.279(2)
γ /°	90
Volume/Å ³	1884.17(16)
Z	4
ρ_{calc} /g/cm ³	1.242
μ /mm ⁻¹	0.882
F(000)	760.0
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/°	3.774 to 50.978
Index ranges	-10 \leq h \leq 10, -12 \leq k \leq 12, -26 \leq l \leq 26
Reflections collected	44790
Independent reflections	3481 [R_{int} = 0.0488, R_{sigma} = 0.0241]
Data/restraints/parameters	3481/0/204
Goodness-of-fit on F ²	1.016
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0991, wR_2 = 0.3217
Final R indexes [all data]	R_1 = 0.1017, wR_2 = 0.3231
Largest diff. peak/hole / e Å ⁻³	1.64/-1.31

Computational Details: All calculations were performed using the Gaussian09 suite of programs.⁶ Frequency calculations on **3** were performed using the B3LYP functional.⁷ The 6-31G basis set⁸ modified with diffuse functions (++)⁹ and polarization functions (d,p)¹⁰ was employed for both optimization and frequency calculations. The geometry was optimized starting from the solid state structure of **3** at the same level of theory; the optimized geometry is available as a separate .xyz file.

2219 cm⁻¹:



1400 cm⁻¹:

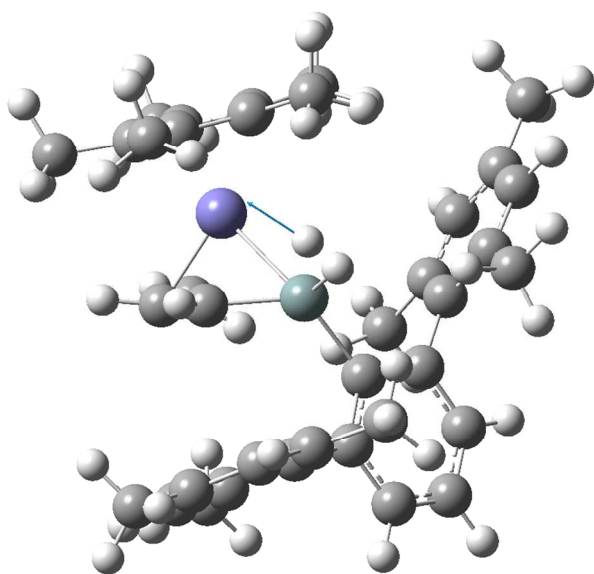


Figure S3: Vibrational modes of interest in **3**.

References:

- (1) Threlkel, R. S.; Bercaw, J. E.; Seidler, P. F.; Stryker, J. M.; Bergman, R. G. *Organic Syntheses* **1987**, 65 .
- (2) Betley, T. A.; Peters, J. C. *Inorganic Chemistry* **2003**, 42, 5074-5084.
- (3) Simons, R. S.; Haubrich, S. T.; Mork, B. V.; Niemeyer, M.; Power, P. P. *Main Group Chem.* **1998**, 2, 275-283.
- (4) Tran, N. T.; Min, T.; Franz, A. K. *Chemistry: A European Journal* **2011**, 17, 98979900.
- (5) Battino, R.; Rettich, T.R.; and Tominga, T. *J. Phys. Chem. Ref. Data.* **1984**, 13, 563-600.
- (6) Gaussian 09, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Oth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.
- (7) (a) Becke, A.D. *J. Chem. Phys.* **1993**, 98,5648-5652. (b) Lee, C.; Yang, W.; Parr, R.G. *Phys. Rev. B* **1988**, 37, 785-789. (c) Vosko, S.H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, 58, 1200-1211.

- (d) Stephens, P.J.; Devlin, F.J.; Chabalowski, C.F.; Frisch, M.J. *J. Phys. Chem.* **1994**, *98*, 11623-11627
- (8) (a) Rassolov, V. A.; Ratner, M. A.; Pople, J. A.; Redfern, P. C.; Curtiss, L. A. *J. Comp. Chem.*, 2001, **22**, 976-984. (b) Rassolov, V. A.; Pople, J. A.; Ratner, M. A.; Windus, T. L.; *J. Chem. Phys.*, **1998**, *109*, 1223-1229.
- (9) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comp. Chem.*, **1983**, *4*, 294-301.
- (10) (a) Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. *J. Chem. Phys.*, **1988**, *89*, 2193-2218. (b) Petersson, G. A.; Al-Laham, M. A. *J. Chem. Phys.*, 1991, **94**, 6081-6090.