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Supporting Information

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An η^3-H_2SiR_2 adduct of $[PhB(CH_2P^iPr_2)_3]Fe^{II}(H)$

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Experimental Section.

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General Considerations. All syntheses reported were carried out using standard glovebox and Schlenk techniques in the absence of water and dioxygen, unless otherwise noted. Benzene, petroleum ether, tetrahydrofuran, and toluene were degassed and dried by sparging with N_2 gas followed by passage through an activated alumina column. All solvents were stored over 3-Å molecular sieves. Deuterated benzene, and toluene were purchased from Cambridge Isotope Laboratories, Inc., degassed via repeated freeze-pump-thaw cycles, and dried over 3-Å molecular sieves. Solvents were frequently tested using a standard solution of sodium benzophenone ketyl in tetrahydrofuran to confirm the absence of oxygen and moisture. Complex **1**,[**] [PhBP$^{iPr}{}_3$]FeCl,[††] [PhBP$^{iPr}{}_3$]Fe(H)$_3$(PMe$_3$),[**] and PhSiD$_3$[‡‡] were prepared using literature methods. The generation of [PhBP$^{iPr}{}_3$]Fe-CD$_3$ (**1-*d*$_3$**) followed the same protocol reported for **1** using CD$_3$Li instead of CH$_3$Li. All other chemicals were purchased from Aldrich, Strem or Gelest and used without further purification. NMR spectra were recorded at ambient temperature unless otherwise stated on Varian Mercury 300 MHz, and Varian Inova 500 MHz instruments. ^{1}H and ^{13}C NMR chemical shifts were referenced to residual solvent. ^{31}P NMR chemical shifts were referenced to 85% H$_3$PO$_4$. ^{29}Si NMR was referenced to tetraethylsilane. IR spectra were recorded on a Bio-Rad Excalibur FTS 3000 spectrometer controlled by Win-IR Pro software. Elemental Analyses were performed by Desert Analytics, Tuscon, AZ. X-ray diffraction experiments were carried out by the Beckman Institute Crystallographic Facility on a Bruker Smart 1000 CCD diffractometer.

X-ray Crystallography Procedures. X-ray quality crystals were grown as indicated in the experimental procedures per individual complex. The crystals were mounted on a glass fiber with Paratone N oil. Structures were determined using direct methods with standard Fourier techniques using the Bruker AXS software package.

Electronic Structure Calculations. A hybrid density functional calculation and natural bond orbital (NBO) analysis was performed for [PhBP$^{iPr}{}_3$]Fe(H)(η^3-H$_2$SiPhMe) using the Jaguar package (version 5.0, release 20). The calculation employed B3LYP with LACVP** as the basis set. A geometry optimization was carried out starting from coordinates based on the solid state structure of [PhBP$^{iPr}{}_3$]Fe(H)(H$_2$SiPhMe) as the initial HF guess. No symmetry constraints were imposed and the

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[**] E. J. Daida, J. C. Peters, *Inorg. Chem.* **2004**, 7474.

[††] Betley, T. A.; Peters, J. C. *Inorg. Chem.* **2003**, *42*, 5074-5084.

[‡‡] Benkeser, R.A.; Landesman, H.; Foster, D.J. *J. Am. Chem. Soc.* **1952**, *74*, 648-650.

calculation was performed assuming a singlet ground electronic state. Geometry optimizations were also performed using a slightly perturbed starting structures in which the three hydrides were placed in symmetry equivalent positions (pseudo three-fold) at typical Fe-H distances but beyond bonding distance to the Si atom. This perturbed starting point provided the same minimized geometry as when the crystallographic coordinates were used as the initial guess. Natural atomic charges and bond orders obtained from the NBO calculation are summarized in Table A1 below.

NMR Simulation. NMR simulations were performed using gNMR V4.0.1 assuming three equivalent protons, each coupling to one *trans* phosphorus atom and two *cis* phosphorus atoms. A linewidth of 8.0 Hz achieved the most accurate simulation. Second order effects were taken into account by using a P-P coupling constant of 62 Hz.

(2,4,6-trimethylphenyl)silane ($MesSiH_3$). Neat $SiCl_3H$ (3.72 mL, 36.9 mmol) was dissolved in Et_2O (250 mL). To this stirring solution was added 2,4,6-trimethylphenylmagnesium bromide (36.9 mL, 1.0M in Et_2O, 36.9 mmol) over 30 minutes at room temperature, resulting in the precipitation of white solids. The mixture was stirred for 6 hours at room temperature. The solution was cooled to -35 °C and stirred while $LiAlH_4$ (4.19 g, 111 mmol) was added in small portions over the course of 1 hour. The mixture was allowed to warm to room temperature and stirred for 12 hours, then filtered through Celite to remove salts. The filtrate was slowly poured over ice (50 g). The E_2O layer was separated, washed with water (2 x 20 mL), dried over Mg_2SO_4, and volatiles were removed in vacuo. Distillation (45 °C, full vacuum) provided the product as a clear liquid (3.5 g, 63%). The NMR spectroscopic data was identical to that reported previously for this silane.[§§]

$[PhB(CH_2P^iPr_2)_3]Fe(H)(h^3\text{-}SiH_2MePh)$ (2). Solid **1** (0.0828 g, 0.150 mmol) was dissolved in C_6H_6 (3 mL). To this solution was added neat $PhSiH_3$ (18.5 µL, 0.150 mmol). The resulting solution

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[§§] Minge, O.; Nogai, S.; Schmidbaur, H. *Z. Naturforsch*. **2004**, 153-160.

immediately became deep red in color. After stirring for 30 minutes at room temperature, the volatiles were removed in vacuo. The red solids were redissolved in minimal Et_2O (1 mL) and cooled to -35 ^oC for 12 hours. The resulting red crystals were dried in vacuo to yield analytically pure product (0.0641, 65%). ^1H NMR (300 MHz, C_6D_6): δ 8.05 (m, 2H, *o*-PhB), 7.97 (m, 2H, *o*-PhSi), 7.62 (m, 2H, *m*-PhB), 7.35 (m, 2H, *m*-PhSi), 7.24 (m, 2H, *p*-PhSi, PhB), 1.72 (m, 6H, C*H*(CH_3)$_2$), 1.16 (m, 36H, CH(C*H*$_3$)$_2$), 1.03 (m, 3H, SiMe), 0.94 (m, 6H, CH_2), -13.45 (m, 3H, Si/Fe-H, $^1J_{Si\text{-}H}$ = 68 Hz). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ 76.2. $^{29}Si\{^1H\}$ NMR (99.3 MHz, C_6D_6): δ 161.6. $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ 159(br), 152 (br), 134.9, 132.4, 131.4, 127.8, 126.1, 124.0, 33.3, 23.2, 20.1, 16.6. UV-Vis (C_6H_6) ?$_{max}$, nm (e, $M^{-1}cm^{-1}$): 500 (sh). IR (KBr/C_6H_6): ?(Fe-H) 2034 cm^{-1}. Anal. Calcd. for $C_{34}H_{64}BFeP_3Si$: C, 61.82; H, 9.77. Found: C, 61.51; H, 9.49. Complex **2-*d*$_3$** was prepared analogously to **2** using **1-*d*$_3$** and provided consistent NMR data. IR (C_6H_6): ?(Fe-D) 1445 cm^{-1} (calcd: 1440 cm^{-1}).

[PhB($CH_2P^iPr_2$)$_3$]Fe(H)(h^3-H_2SiMesMe) (3). Solid **1** (0.0275 g, 0.0498 mmol) was dissolved in C_6H_6 and to this solution was added MesSiH_3 (10 µL, 0.0747 mmol). The resulting mixture was stirred for one hour and the solution gradually became bright red. Volatiles were removed in vacuo and the resulting solids were washed with petroleum ether (2 x 3 mL). The solids were then dissolved in minimal Et_2O (0.5 mL) and cooled to -35 °C over 12 hours to yield spectroscopically pure, X-ray quality crystals (0.0301 g, 86.0 %). ^1H NMR (300 MHz, toluene-*d*$_8$): δ 7.94 (m, 2H, *o*-PhB), 7.52 (m, 2H, *m*-PhSi), 7.27 (m, 1H, *p*-PhB), 6.62 (s, 2H, *m*-Mes), 2.45 (s, 6H, *o*-MesCH_3), 2.10 (s, 3H, *p*-MesCH_3), 1.66 (m, 6H, C*H*(CH_3)$_2$), 1.39 (s, 3H, Si-Me), 1.15 (m, 36H, CH(C*H*$_3$)$_2$), 0.85 (m, 6H, CH_2), -13.40 (m, 3H, $^1J_{Si\text{-}H}$ = 70 Hz). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ 79.5 (s). $^{29}Si\{^1H\}$ NMR (99.32 MHz, toluene-*d*$_8$): 160.4 (q, $^2J_{Si\text{-}P}$ = 59 Hz). Anal. Calcd. for $C_{37}H_{70}BFeP_3Si$: C, 63.25; H, 10.04. Found: C, 63.25; H, 9.66.

[PhB(CH$_2$P^{i}Pr$_2$)$_3$]Fe(D)(h^3**-D$_2$SiMePh) (2-*d*$_3$).** Complex **2-*d*$_3$** was prepared analogously to **2** using PhSiD$_3$. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 8.04 (m, 2H, *o*-PhB), 7.98 (m, 2H, *o*-PhSi), 7.61(m, 2H, *m*-PhB), 7.32 (m, 2H, *m*-PhSi), 7.25 (m, 2H, *p*-PhSi, PhB), 1.72 (m, 6H, C*H*(CH$_3$)$_2$), 1.17 (m, 36H, CH(C*H*$_3$)$_2$), 1.03 (s, 3H, Me), 0.95 (m, 6H, CH$_2$). ^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$): δ 79.2. IR (C$_6$H$_6$): ? = 1445 cm^{-1} (Fe-D) (calculated ? = 1440 cm^{-1}).

[PhB(CH$_2$P^{i}Pr$_2$)$_3$]Fe(H)(H$_2$SiCD$_3$Ph) (2-CD$_3$). Complex **2-CD$_3$** was prepared analogously to **2** using **1-d$_3$.** ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 8.05 (m, 2H, *o*-PhB), 7.94 (m, 2H, *o*-PhSi), 7.48 (m, 2H, *m*-PhB), 7.31 (m, 2H, *m*-PhSi), 7.22 (m, 2H, *p*-PhSi, PhB), 1.74 (m, 6H, C*H*(CH$_3$)$_2$), 1.18 (m, 36H, CH(C*H*$_3$)$_2$), 0.89 (m, 6H, CH$_2$), -13.42 (m, 3H, Fe-H). ^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$): δ 76.2.

Figure A1. Variable temperature ^{1}H NMR (20°C to -70°C, 300 MHz, toluene-d_8) of the hydride signal of [PhBP$^{iPr}{}_3$]Fe(H)(η^3-H_2SiPhMe) (**2**).

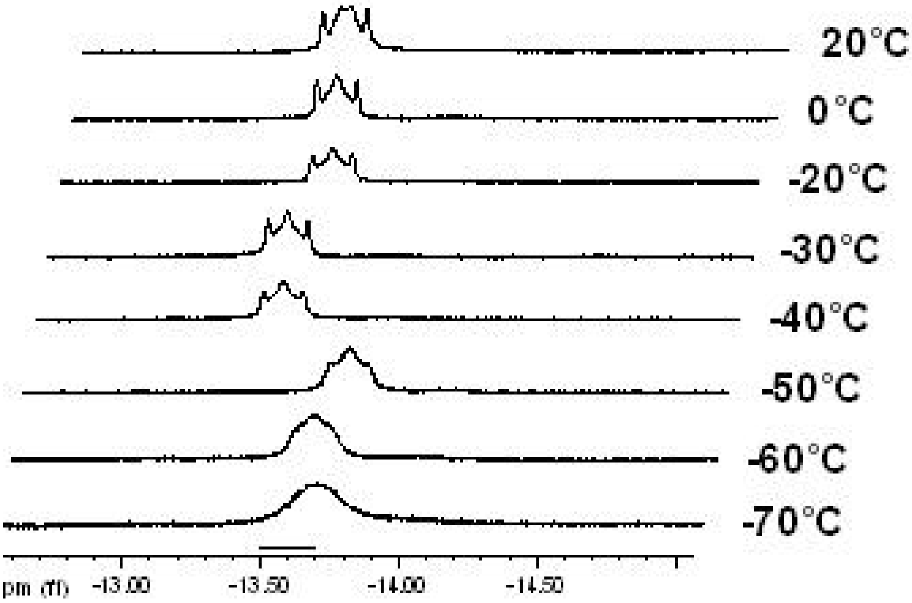


Figure A2. ^{29}Si / ^{1}H HMQC data recorded for complex **2** (0 °C, 99 MHz / 500 MHz, toluene-d_8).

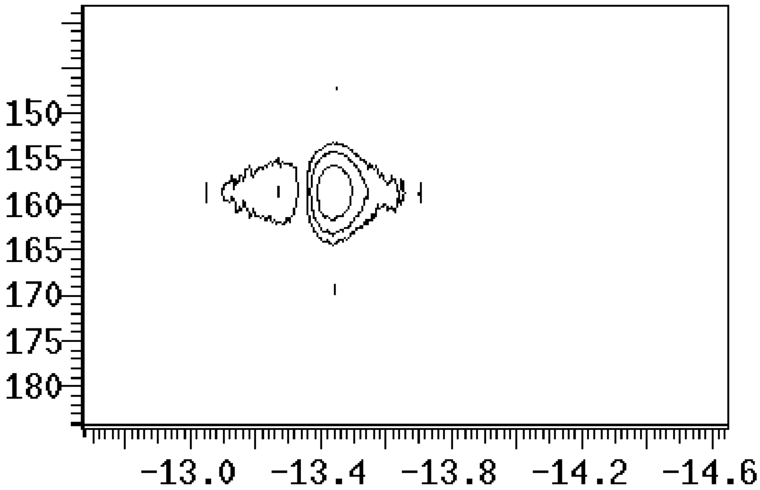


Figure A3: ^{1}H NMR spectra of (A) **2**, (B) **2-CD$_3$**, and (C) **2-d$_3$,** illustrating the disappearance of diagnostic peaks upon deuterium labeling. Resonances attributable to residual solvent (THF) are labeled “s”. Spectra were recorded in C_6D_6 on a 300 MHz instrument at ambient temperature.

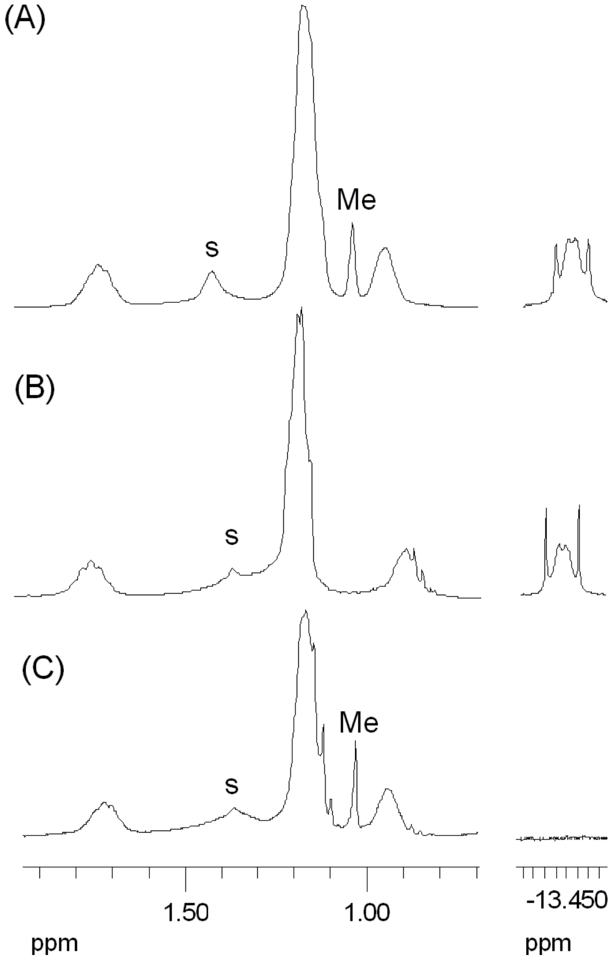


Figure A4. ^{29}Si/^{1}H HMQC data recorded for complex **3** (0°C, 99 MHz / 500 MHz, toluene-d_8).

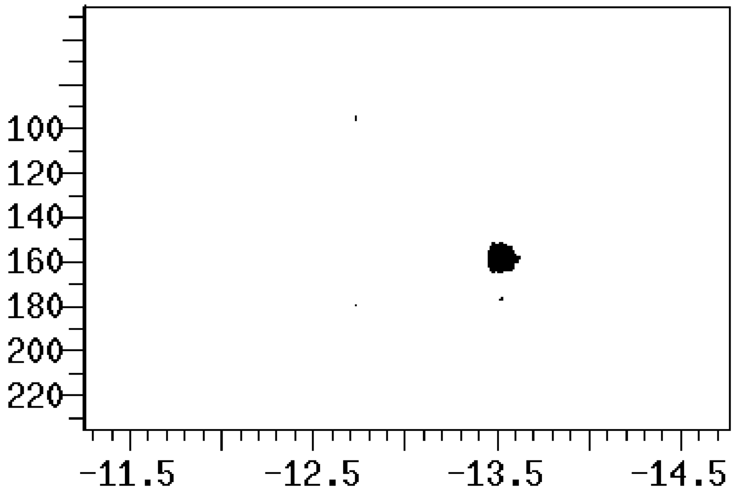
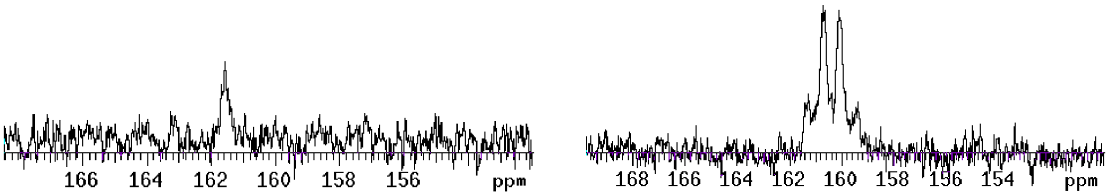


Figure A5. ^{29}Si NMR of **2** and **3,** illustrating the difference in their respective line shapes. $^{2}J_{Si\text{-}P}$ = 61 Hz for **3**.



2

3

Table A1. Natural atomic charges and bond orders from NBO analysis of **2**.

Atomic Charges		Bond Orders	
Fe	-0.37	Fe-H2	0.65
Si	1.38	Si-H1	0.80
H2	-0.13	Si-H3	0.83
H1	-0.13		
H3	-0.14		

Figure A6. Fully labeled diagram of $[PhBP^{iPr}_3]Fe(H)(\eta^3\text{-}H_2SiPhMe)$ (**2**).

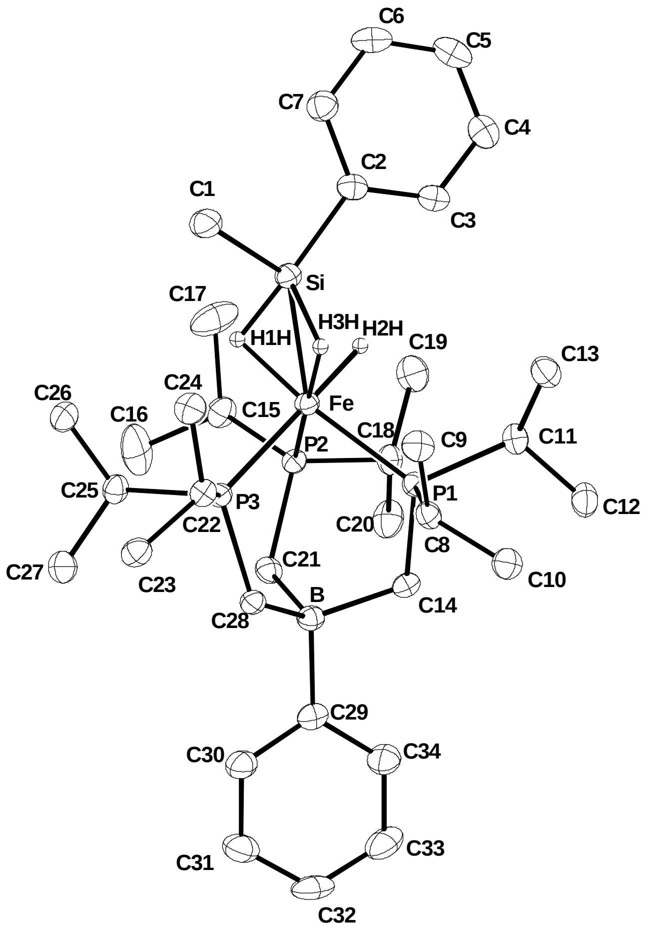


Table A2. Crystal data and structure refinement for **2**.

Identification code	cmt27	
Empirical formula	$C_{34}H_{64}BFeP_3Si$	
Formula weight	660.51	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.3852(12) Å	a= 95.172(2)°.
	b = 12.0036(13) Å	ß= 107.352(2)°.
	c = 16.1029(17) Å	? = 95.805(2)°.
Volume	2072.9(4) Å^3	
Z	2	
Density (calculated)	1.058 Mg/m^3	
F(000)	716	
Crystal size	0.28 x 0.30 x 0.31 mm^3	
? range for data collection	1.34 to 23.31°	
Index ranges	-12 = h = 12, -13 = k = 13, -17 = l = 17	
Reflections collected	27602	
Independent reflections	5992 [R(int) = 0.0554]	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5992 / 0 / 374	
Goodness-of-fit on F^2	1.068	
Final R indices [I>2σ(I)]	R1 = 0.0309, wR2 = 0.0816	
R indices (all data)	R1 = 0.0360, wR2 = 0.0841	
Largest diff. peak and hole	0.365 and -0.199 e.Å^{-3}	

Figure A7. Fully labeled diagram of [PhBP$^{iPr}{}_3$]Fe(H)(η^3-H$_2$SiMesMe) (**3**).

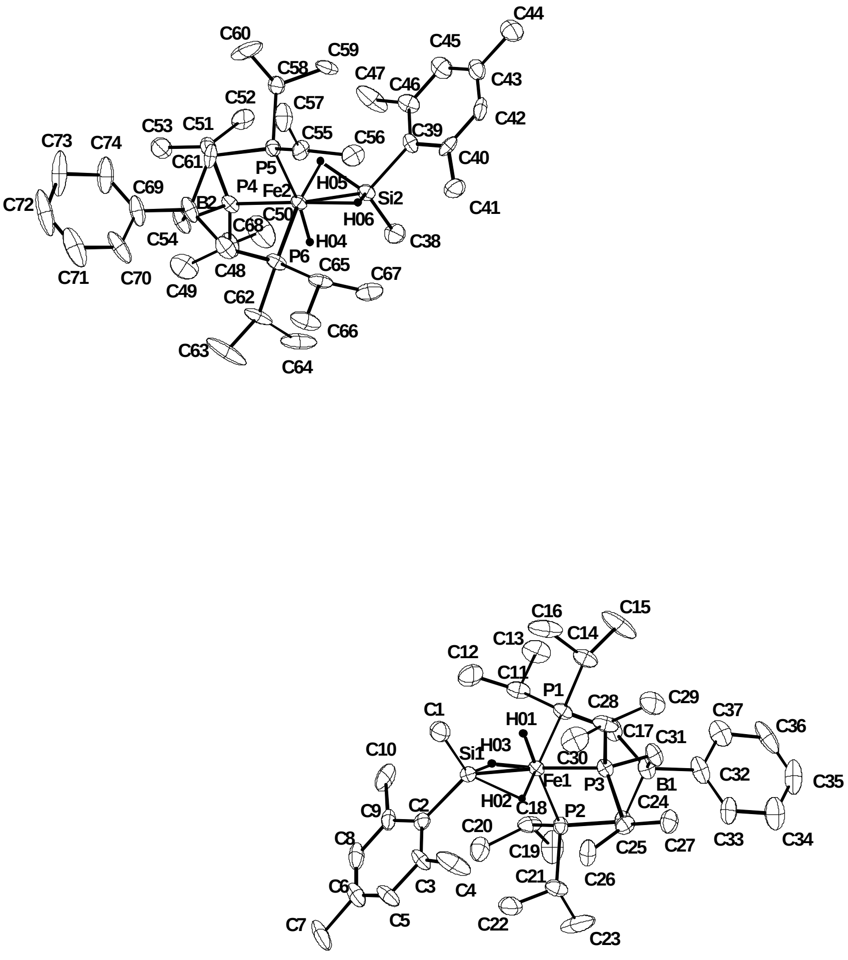


Table A3. Crystal data and structure refinement for **3**.

Identification code	cmt35	
Empirical formula	$C_{37}H_{70}BFeP_3Si$	
Formula weight	702.59	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 18.1126(13) Å	α= 90°.
	b = 20.3251(14) Å	β= 90°.
	c = 21.6417(16) Å	γ = 90°.
Volume	7967.2(10) $Å^3$	
Z	8	
Density (calculated)	1.171 Mg/m^3	
Absorption coefficient	0.553 mm^{-1}	
F(000)	3056	
Crystal size	0.26 x 0.28 x 0.35 mm^3	
Theta range for data collection	1.47 to 31.51°.	
Index ranges	-22 = h = 22, -29 = k = 28, -28 = l = 31	
Reflections collected	86425	
Independent reflections	22950 [R(int) = 0.0798]	
Completeness to theta = 31.51°	89.5 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	22950 / 0 / 826	
Goodness-of-fit on F^2	1.677	
Final R indices [I>2s (I)]	R1 = 0.0609, wR2 = 0.0920	
R indices (all data)	R1 = 0.1024, wR2 = 0.0988	
Absolute structure parameter	0.49(2)	
Largest diff. peak and hole	1.439 and -1.209 e.$Å^{-3}$	