Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Terminal Fe^I-N_2 and $Fe^{II}\cdots H$-C interactions supported by tris(phosphino)silyl ligands

*Neal P. Mankad, Matthew T. Whited, and Jonas C. Peters**

Experimental Section.

General Considerations. All manipulations were carried out using standard Schlenk or glovebox techniques under a dinitrogen atmosphere. Unless otherwise noted, solvents were deoxygenated and dried by thoroughly sparging with N_2 gas followed by passage through an activated alumina column. Non-halogenated solvents were tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran in order to confirm effective oxygen and moisture removal. All reagents were purchased from commercial vendors and used without further purification unless otherwise stated. 2-(diphenylphosphino)phenyl bromide,[1] 2-(diisopropylphosphino)phenyl bromide,[2] and mesityliron(II)[3] were prepared according to literature procedures. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., degassed, and dried over activated 3-Å molecular sieves prior to use.

X-ray Crystallography Procedures. X-ray diffraction studies were carried out at the Beckman Institute Crystallography Facility on a Brüker Smart 1000 CCD diffractometer and solved using SHELX v. 6.14. 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. Special refinement details used for the disordered solvent region in **3** and for the entire data set in **9** are specified in the comments sections of the cif files.

Spectroscopic measurements. Varian Mercury-300 and Inova-500 spectrometer was used to record ^1H, ^{13}C, ^{29}Si, and ^{31}P NMR spectra at ambient temperature unless otherwise indicated. ^1H and ^{13}C chemical

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[1] M. T. Whited, E. Rivard, J. C. Peters, *Chem. Commun.*, **2006**, 1613.

[2] a) R. Talay, D. Rehder, *Zeit. f. Natur, B: Anorg. Chem.*, **1981**, *36*, 451. b) M. Tamm, B. Dreβel, K. Baum, T. Lügger, T. Pape, *J. Organomet. Chem.*, **2003**, *677*, 1.

[3] A. Klose, E. Solari, R. Ferguson, C. Floriani, A. Chiesi-Villa, C. Rizzoli, *Organometallics*, **1993**, *12*, 2414.

shifts were referenced to the residual solvent peaks. ^{31}P chemical shifts were referenced to external phosphoric acid (δ = 0 ppm). ^{29}Si chemical shifts were referenced to external tetramethylsilane (δ = 0 ppm). Optical spectroscopy measurements were taken on a Cary 50 UV/Vis Spectrophotometer using a 1-cm quartz cell sealed with a Teflon stopper. X-band EPR spectra were obtained on a Bruker EMX spectrometer (controlled by Bruker Win EPR software v. 3.0) equipped with a rectangular cavity working in the TE_{102} mode and an Oxford continuous-flow helium cryostat (temperature range 3.6-300 K). Accurate EPR frequency values were provided by a frequency counter built into the microwave bridge. EPR spectra were simulated using the W95EPR program.[4]

Electrochemistry. Electrochemical measurements were carried out in a glovebox under a dinitrogen atmosphere in a one-compartment cell using a CH Instruments 600B electrochemical analyzer. A glassy carbon electrode was used as the working electrode and platinum wire was used as the auxillary electrode. The reference electrode was $Ag/AgNO_3$ in THF. The ferrocene couple Fc^+/Fc was used as an external reference. Solutions (THF) of electrolyte (0.3 M tetra-*n*-butylammonium hexafluorophosphate) and analyte were also prepared under an inert atmosphere.

Synthesis of tris(2-(diphenylphosphino)phenyl)silane ([SiP$^{Ph}_3$]H, 1). Under a dinitrogen atmosphere, 2-(diphenylphosphino)phenyl bromide (6.65 g, 19.5 mmol) was dissolved in diethyl ether (100 mL) and cooled to -78°C. *n*-Butyllithium (8.30 g of a 1.6 M solution in hexanes, 19.5 mmol) was added slowly, giving a light orange solution with a tan-colored precipitate. This mixture was allowed to warm gradually to room temperature and then stirred for 1 h, after which the volatiles were removed *in vacuo*. Toluene (100 mL) was added, and the cloudy orange solution was cooled back to -78°C. Trichlorosilane (0.660 mL, 6.54 mmol) was added in one portion, and the resulting mixture was warmed to room temperature gradually. After stirring for 0.5 h at room temperature, the reaction was heated in a sealed reaction bomb to 110°C for 15 h. The resulting yellow solution and white precipitate were cooled to room temperature and filtered through Celite, and the filtrate was concentrated to white solids. Petroleum ether (60 mL) was

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[4] F. Neese, *QCPE Bull.* **1995**, *15*, 5.

added and the resulting mixture was stirred vigorously for 20 min, at which point tan solids were collected on a sintered glass frit and washed with additional petroleum ether (2 x 10 mL) to afford $[SiP^{Ph}_3]H$ as a fine tan powder (4.59 g, 87%). ^1H NMR (C_6D_6, δ): 7.63 (dm, *J* = 1.5 and 6.3 Hz, 3H), 7.34 (ddm, *J* = 1.0, 3.9, and 7.8 Hz, 3H), 7.25-7.20 (m, 12H), 7.05 (td, *J* = 1.5 and 7.3 Hz, 6H), 7.02-6.95 (m, 19H). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 145.5 (d, *J* = 11.4 Hz), 144.3 (t, *J* = 4.0 Hz), 144.0 (t, *J* = 4.0 Hz), 138.8 (d, *J* = 14.6 Hz), 138.5 (d, *J* = 12.8 Hz), 134.7, 134.5 (d, *J* = 19.2 Hz), 130.4, 128.8, 128.6 (d, *J* = 17.3 Hz). $^{29}Si\{^1H\}$ NMR (C_6D_6, δ): -33.8 (q, $^3J_{Si\text{-}P}$ = 24.4 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): -10.4 (s). IR (KBr, cm^{-1}): 3044, 2170 (ν[Si-H]), 1580, 1478, 1429, 1109, 795. Anal. Calcd for $C_{54}H_{43}P_3Si$: C, 79.78; H, 5.33. Found: C, 79.39; H, 5.61.

Synthesis of tris(2-(diisopropylphosphino)phenyl)silane ($[SiP^{iPr}_3]H$, 2). (2-bromophenyl)diisopropylphosphine (4.1429 g, 15.164 mmol) was dissolved in 100 mL of diethyl ether and chilled to -78 °C, and *n*-butyllithium (1.60 M sol'n in hexanes, 9.50 mL, 15.2 mmol) was added dropwise, causing a darkening of the solution and gradual precipitation of solids. After 15 min, the slurry was brought to room temperature and stirred for 2 h, after which volatiles were removed *in vacuo* to yield a pale red powder. The powder was redissolved in toluene (80 mL), chilled to -35 °C, and trichlorosilane (511 μL, 5.06 mmol) was added in one portion, resulting in the immediate precipitation of white solids and lightening of the solution. The mixture was stirred at room temperature for 30 min, then at 90 °C for 15 h, and filtered through Celite to give a clear, light orange solution. Solvents were removed *in vacuo* to give an orange oil, and the addition of petroleum ether (20 mL) caused the precipitation of white solids. These were isolated on a frit and washed with petroleum ether (2 x 5 mL) to yield **2** as a white powder. Subsequent crops could be isolated by crystallization from concentrated petroleum ether solutions at -35 °C (0.5439 g, 18%). ^1H NMR (C_6D_6): δ 7.46 – 7.34 (m, 3H, Ar-*H*). 7.30 – 7.20 (m, 3H, Ar-*H*), 7.20 – 7.10 (td, *J* = 1.2 and 7.2 Hz, 3H, Ar-*H*), 7.02 – 6.92 (tt, *J* = 1.5 and 7.5 Hz, 3H, Ar-*H*), 2.05 – 1.85 (doublet of septets, $^2J_{HP}$ = 6.9 Hz, $^3J_{HH}$ = 3.0 Hz, 6H, $-CH(CH_3)_2$), 1.20 – 1.02 (m, 18H, $-CH(CH_3)_2$), 1.00 – 0.88 (m, 18H, $-CH(CH_3)_2$). ^{31}P NMR (C_6D_6): δ 1.7 (s). IR (THF, cm^{-1}) ν(Si-H): 2218. Anal. Calcd. for $C_{36}H_{55}P_3Si$: C, 71.02; H, 9.11. Found: C, 71.09; H, 9.38.

Synthesis of [SiP$^{Ph}_3$]Fe(Mes) (3). [SiP$^{Ph}_3$]H (3.06 g, 3.77 mmol) and mesityliron(II) (1.11 g, 3.77 mmol) were combined in benzene (40 mL) and heated to 65°C for 14 h. Volatiles were removed *in vacuo*, petroleum ether (100 mL) was added, and the mixture was stirred for 30 min. Filtration through Celite afforded a strawberry red filtrate that was concentrated to oily red solids. Benzene (15 mL) was added, and the clear red solution was lyophilized to give a fine red powder (1.70 g, 46%). Though this material was typically utilized without further purification, analytically pure material could be obtained by cooling a saturated petroleum ether solution to -30°C for 16 h. Crystals suitable for x-ray diffraction were obtained by diffusion of hexamethyldisiloxane vapors into a saturated petroleum ether solution at -30°C. ^{1}H NMR (C_6D_6, δ): 8.50 (d, *J* = 7.2 Hz, 6H), 7.6-6.8 (m, 29H), 6.7-6.5 (m, 18H), 5.33 (br, *ortho*-C$\underline{H}_3$), 1.84 (s, 3H, *para*-C$\underline{H}_3$), 0.58 (br, *ortho*-C$\underline{H}_3$). ^{1}H NMR (toluene-d_8, -60°C, δ): 8.48 (d, *J* = 7.2 Hz, 2H), 8.33 (d, *J* = 7.8 Hz, 1H), 7.6-6.9 (m, 29H), 6.8-6.6 (m, 15H), 6.52 (t, *J* = 7.5 Hz, 1H), 6.36 (t, *J* = 7.8 Hz, 2H), 4.60 (*ortho*-C$\underline{H}_3$), 1.88 (s, 3H, *para*-C$\underline{H}_3$), 1.10 (*ortho*-C$\underline{H}_3$), -0.24 (*ortho*-C$\underline{H}_3$). ^{13}C{^{1}H} NMR (C_6D_6, d): 157.4 (br), 150.0 (br), 139.5 (br), 134.7, 134.5 (d, *J* = 19.2 Hz), 132.7, 132.5, 131.7 (br), 130.9, 130.4, 128.9, 128.8, 127.3, 127.2, 104.9 (br, mesityl *ipso*-$\underline{C}$), 23.1 (s, *ortho*-$\underline{C}H_3$), 20.5 (s, *para*-$\underline{C}H_3$), 14.6 (s, *ortho*-$\underline{C}H_2$-H-Fe). ^{31}P{^{1}H} (C_6D_6, δ): 72.0 (br). ^{31}P{^{1}H} (toluene-d_8, -60°C, δ): 76.0 (t, 1P, $^2J_{PP}$ = 10.7 Hz), 73.3 (d, 2P, $^2J_{PP}$ = 10.7 Hz). UV-Vis (toluene, nm(M^{-1}cm^{-1})): 367(5000), 508(3800). IR (KBr, cm^{-1}): 3049, 2956, 2910, 1584, 1479, 1429, 1100, 838. Anal. Calcd for $C_{63}H_{53}FeP_3Si$: C, 76.67; H, 5.41. Found: C, 77.50; H, 5.37.

Synthesis of [SiP$^{Ph}_3$]FeCl (4). [SiP$^{Ph}_3$]Fe(Mes) (1.02 g, 1.03 mmol) was dissolved in diethyl ether (40 mL) and cooled to -78°C. Hydrogen chloride (1.0 mL of a 1.0 M solution in diethyl ether, 1.0 mmol) was added in one portion by syringe. The solution was allowed to warm to room temperature with stirring, resulting in gradual precipitation of an orange solid. After stirring the reaction at room temperature for 1.5 h, the orange solid was collected on a sintered glass frit and washed with additional portions of diethyl ether (2 x 10 mL), affording an analytically pure sample of [SiP$^{Ph}_3$]FeCl (0.555 g, 60%). Crystals suitable for x-ray diffraction were obtained by slow diffusion of petroleum ether vapors into a dichloromethane solution. ^{1}H NMR (C_6D_6, δ): 12.32, 7.61, 6.99, 4.67, 3.29, -2.09, -5.03. μ_{eff} (C_6D_6, Evans' method, 23°C): 2.9 μ_B. UV-Vis (toluene, nm($M^{-1}cm^{-1}$)): 426(4700), 479(5700). IR (KBr, cm^{-1}): 2363, 1482, 1433, 1103. Anal. Calcd for $C_{54}H_{42}ClFeP_3Si$: C, 71.81; H, 4.69. Found: C, 71.82; H, 4.41.

Alternative synthesis of 4. To a THF-suspension (30 mL) of **1** (1.43 g, 1.76 mmol) and $FeCl_2$ (0.224 g, 1.76 mmol) was added 1,4-dioxane (3 mL). The entire mixture was cooled to -78°C, and CH_3MgBr (1.17 mL of a 3.0 M solution in Et_2O, 3.51 mmol) was added by syringe with stirring. The solution was kept stirring at -78°C for 0.5 h, and then was stirred at room temperature for 12 h, resulting in a cloudy brown mixture. Volatiles were removed *in vacuo*. Diethyl ether (50 mL) was added and the mixture filtered through Celite. The resulting red filtrate was cooled to -78°C, and HCl (1.75 mL of a 1.0 M solution in Et_2O, 1.75 mmol) was added, forming a light orange precipitate. After stirring at room temperature for 0.5 h, this precipitate was collected on a sintered glass frit, washed with additional portions of diethyl ether, and dried. ^{1}H NMR confirmed the product's identity as **4**. Yield: 0.381 g, 24%.

Synthesis of [SiP$^{iPr}_3$]FeCl (5). To a stirring slurry of ferrous chloride (30.6 mg, 0.241 mmol) in THF (10 mL) was added a solution of H[SiP$^{iPr}_3$] (147.2 mg, 0.2418 mmol) in THF (5 mL), causing a color change to yellow. The resulting solution was chilled to -78 °C, and MeMgCl (3.0 M in THF, 81 μL, 0.24 mmol) was diluted in THF (1 mL) and added dropwise, causing an immediate darkening of the solution. The reaction was stirred at -78 °C for 1 h, then warmed to room temperature and stirred 3 h to give a dark orange solution. The solution was filtered through Celite and concentrated to an orange film *in vacuo*. The residues were extracted into benzene, filtered, lyophilized, and washed with petroleum ether (3 x 3 mL) to yield **5** as an orange powder (72.5 mg, 43%). Crystals suitable for X-ray diffraction were obtained by slow evaporation of benzene from a concentrated solution. ^{1}H NMR (C_6D_6): δ 6.3, 5.9, 5.4, 4.7, 3.7, 3.2, 2.5, 2.0, 1.4, 1.1, 0.9, 0.3, -2.5. UV-vis (THF) λ_{max}, nm (ε, M^{-1} cm^{-1}): 471 (990), 379 (2100). Evans Method (C_6D_6): 3.3 μ_B. Anal. Calcd. for $C_{36}H_{54}ClFeP_3Si$: C, 61.85; H, 7.79. Found: C, 62.34; H, 7.96.

Synthesis of [SiP$^{Ph}_3$]Fe(N_2) (6). Sodium (8.3 mg, 0.36 mmol) and mercury (0.714 g) were combined in THF (1 mL). Solid [SiP$^{Ph}_3$]FeCl (0.322 g, 0.357 mmol) was added, and the total volume was brought up to 15 mL. After vigorous stirring for 6 h at room temperature, a brown supernatant was decanted off the Na/Hg amalgam and concentrated *in vacuo* to brown solids. Benzene (10 mL) was added, and the resulting cloudy solution was filtered through Celite. The resulting red-orange filtrate was lyophilized, providing spectroscopically pure $[SiP^{Ph}_3]Fe(N_2)$ as a fluffy red-orange solid (0.278 g, 87%). Crystals suitable for x-ray diffraction were obtained by slow diffusion of petroleum ether vapors into a THF solution. ^1H NMR (C_6D_6, δ): 10.48, 7.98, 7.42, 6.17, 4.46, -1.6 – -2.1 (br), -1.86. μ_{eff} (C_6D_6, Evans' method, 23°C): 1.8 μ_B. UV-Vis (toluene, nm($M^{-1}cm^{-1}$)): 347(9400). IR (KBr, cm^{-1}): 3048, 2041 (ν_{NN}), 1578, 1477, 1432, 1096. Note: Though all solution data we have collected indicates the presence of **6** in pure form, the lability of the dinitrogen ligand complicated isolation of analytically pure solid samples. As a result, combustion analysis and Toepler pump analysis indicated low levels of nitrogen. To probe this instability, we note that after repeated lyophilization of **6** from benzene over several hours, a new paramagnetic species is observed as **6** decays. This unidentified paramagnetic species subsequently decomposes at temperatures as low as -30°C to cleanly generate $[SiP^{Ph}_3]H$ in benzene solution.

$[SiP^{iPr}_3]Fe(N_2)$ (7). A dark green solution of sodium naphthalide was prepared by stirring a colorless solution of naphthalene (8.6 mg, 0.067 mmol) in THF (3 mL) over excess sodium metal (8.0 mg, 0.35 mmol) for 3 h. The resulting naphthalide solution was filtered away from sodium and added dropwise to an orange solution of **5** (46.8 mg, 0.0669 mmol) in THF (5 mL), causing the color of the solution to change to dark orange over a period of several minutes. The reaction was allowed to proceed overnight, filtered, and volatiles removed *in vacuo* to give an orange-red film. The residues were extracted into benzene (5 mL), filtered and dried. The residues were triturated with petroleum ether (1 x 5 mL) to give a red powder that was washed with petroleum ether (2 x 3 mL) to yield spectroscopically pure **7** (10.5 mg, 23%). Crystals suitable for X-ray diffraction were obtained by slow evaporation of benzene from a concentrated solution. ^1H NMR (C_6D_6): δ 10.0, 5.9, 5.5, 4.8, 3.8, 3.3, 0.3. Evans Method (C_6D_6): 2.2 μ_B. IR (THF, cm^{-1}) $\nu(N_2)$: 2008. UV-vis (THF) λ_{max}, nm (ε, M^{-1} cm^{-1}): 468 (1800), 380 (3500).

Synthesis of $\{[SiP^{Ph}_3]Fe(N_2)\}\{Na(12\text{-crown-}4)_2\}$ (8). Sodium (2.3 mg, 0.10 mmol) and mercury (0.552 g) were combined in THF (1 mL). A THF solution (8 mL) of $[SiP^{Ph}_3]Fe(N_2)$ (73.5 mg, 0.0821 mmol) and then 12-crown-4 (40.0 mL, 0.247 mmol) were added, resulting in a red-purple solution. The reaction was stirred vigorously for 6.5 h, then the deep purple supernatant was decanted off the Na/Ha amalgam, filtered through Celite, and concentrated *in vacuo* to purple solids. The residue was triturated with diethyl ether (10 mL), and a purple microcrystalline solid was collected on a sintered glass frit. Additional diethyl ether washes (2 x 10 mL) yielded analytically pure $\{[SiP^{Ph}_3]Fe(N_2)\}\{Na(12\text{-crown-}4)_2\}$ (63.5 mg, 71%). ^{1}H NMR (THF-d_8, δ): 8.22 (d, J = 10.5 Hz, 3H), 7.4-6.4 (m, 39H), 3.55 (s, 32H, 12-crown-4). ^{31}P{^{1}H} NMR (THF-d_8, d): 84.3 (s). UV-Vis (THF, nm($M^{-1}cm^{-1}$)): 415(6100), 460(6300). IR (KBr, cm^{-1}): 3042, 2963, 2911, 2866, 1967 (ν_{NN}), 1578, 1476, 1431, 1364, 1289, 1244, 1134, 1096, 1023, 916. Anal. Calcd for $C_{70}H_{74}FeN_2O_8P_3Si$: C, 66.14; H, 5.87; N, 2.20. Found: C, 66.35; H, 5.85; N, 1.77.

Synthesis of $\{[SiP^{Ph}_3]Fe(thf)\}\{BAr^F_4\}$ (9). A THF solution (1 mL) of $[FeCp_2][BAr^F_4]$ (48.6 mg, 0.0463 mmol) was added slowly to a stirring THF solution (2 mL) of **6** (42.2 mg, 0.0471 mmol) at room temperature. After stirring for 2 h, the volatiles were removed and **9** was recrystallized from Et_2O/petroleum ether (-30°C). Yield: 54.5 mg (65%). ^{1}H NMR (10:1 C_6D_6/THF-d_8, δ): 8.22, 7.63, 7.09, 6.99, 3.32, 0.82. μ_{eff} (10:1 C_6D_6/THF-d_8, Evans' method, 23°C): 5.6 μ_B. ^{19}F NMR (10:1 C_6D_6/THF-d_8, δ): -60 (s). IR (KBr, cm^{-1}): 3055, 2961, 1611, 1439, 1356, 1280, 1125, 867, 839. Anal. Calcd for $C_{90}H_{62}BF_{24}FeOP_3Si$: C, 59.95; H, 3.47; N, 0.00. Found: C, 55.28; H, 3.72; N, <0.05. Note: Satisfactory combustion analysis for this complex was not obtained, possibly due to lability of the thf ligand. However, an analogous preparation was used to access $\{[SiP^{Ph}_3]Fe(thf)\}\{BPh_4\}$, whose x-ray quality crystals were grown by diffusion of Et_2O vapors into a THF solution. See main text, ref 15.

Synthesis of $[SiP^{Ph}_3]Fe(CO)$ (10). Sodium (4.2 mg, 0.18 mmol) and mercury (0.982 g) were combined in THF (1 mL). Solid $[SiP^{Ph}_3]FeCl$ (0.153 g, 0.169 mmol) was added, and the total volume was brought up to 5 mL. After vigorous stirring for 3.5 h at room temperature, a brown supernatant was decanted off the Na/Hg amalgam and concentrated *in vacuo* to brown solids. Benzene (10 mL) was added, and the resulting cloudy solution was filtered through Celite into a resealable Schlenk tube. The resulting red-orange filtrate was frozen, evacuated, and backfilled with CO (1 atm). After stirring at room temperature for 1 h, the solution was filtered through Celite and concentrated to brown solids. Trituration with petroleum ether (10 mL) provided a brown powder that was collected on a sintered glass frit and washed with additional portions of petroleum ether, providing [SiP$^{Ph}{}_3$]Fe(CO) (0.062 g, 41%). ^{1}H NMR (C_6D_6, δ): 10.37, 7.62, 7.01, 6.15, 5.29, -1.02, -1.52. μ_{eff} (C_6D_6, Evans' method, 23°C): 2.1 μ_B. UV-Vis (toluene, nm($M^{-1}cm^{-1}$)): 335(2400), 411(1600). IR (C_6H_6, cm^{-1}): 1881 (ν_{CO}). Anal. Calcd for $C_{55}H_{42}FeOP_3Si$: C, 73.75; H, 4.73; N, 0,00. Found: C, 73.22; H, 4.68; N, 0.28.

Reaction of 6 and 7 with acids. [SiP$^R{}_3$]FeN_2 (approx 10 mg), and in some cases a sacrificial Cr(II) reagent (10 equiv per Fe), were dissolved in THF (3 mL) in a 2-neck 25-mL round-bottom flask and sealed with septa. An ethereal solution of the acid (10 equiv per Fe) was added via syringe, and the resulting solution was stirred overnight under septum seal. Volatiles were then vacuum-transferred onto a frozen HCl solution (5 mL, 1.0 M in Et_2O). A solution of NaO^{t}Bu (>15 equiv) in THF (5 mL) was then added to the source flask via syringe through the second neck, and the mixture was stirred vigorously for 30 min. The volatiles were again vacuum-transferred into the same receiving flask. The combined distillates were concentrated to white solids by rotary evaporation and analyzed by ^{1}H NMR (DMSO-d_6) with mesitylene added as an internal integration standard. [N_2H_6]Cl_2 was detected[5] in modest yields based on ^{1}H NMR integration. The results of these experiments are summarized in Table A1.

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[5] Identical spectra were obtained by exposing hydrazine (anhydrous, Aldrich) to a large excess of HCl (1.0 M in Et_2O), followed by concentration and dissolution in DMSO-d_6.

Table A1. Summary of protolytic hydrazine formation experiments.

Phosphine substituent	H^+	e^-	Solvent	Yield of N_2H_4 per Fe
Ph	HCl	None	THF	7%
Ph	HBF_4	None	THF	17%
Ph	HBF_4	$CrCl_2$	THF	47%
Ph	HBF_4	$CrCp^*_2$	THF	42%
Ph	HBF_4	$CrCp^*_2$	THF, 0°C	28%
Ph	HBF_4	$CrCp^*_2$	THF, add H^+ dropwise	23%
Ph	HBF_4	$CrCp^*_2$	Et_2O	15%
Ph	HBF_4	$CrCp^*_2$	C_6H_6	<5%
Ph	$[LutH]BPh_4$	$CrCp^*_2$	THF	0%
Ph	$[LutH]BPh_4$	$CrCp^*_2$	C_6H_6	0%
iPr	HBF_4	$CrCp^*_2$	THF	9%
iPr	$[HNiPr_2Et]BPh_4$	$CrCp^*_2$	THF	13%
iPr	$[HNiPr_2Et]BPh_4$	$CrCp^*_2$	C_6H_6	0%
iPr	$[LutH]BPh_4$	$CrCp^*_2$	C_6H_6	0%

Lut = 2,6-lutidine, Cp* = pentamethylcyclopentadienyl

Figure A1. Cyclic voltammograms of a) [SiP$^{iPr}_3$]FeCl (**5**) and b) [SiP$^{Ph}_3$]FeCl (**4**). Potential scale is vs FeCp$_2^+$/FeCp$_2$.

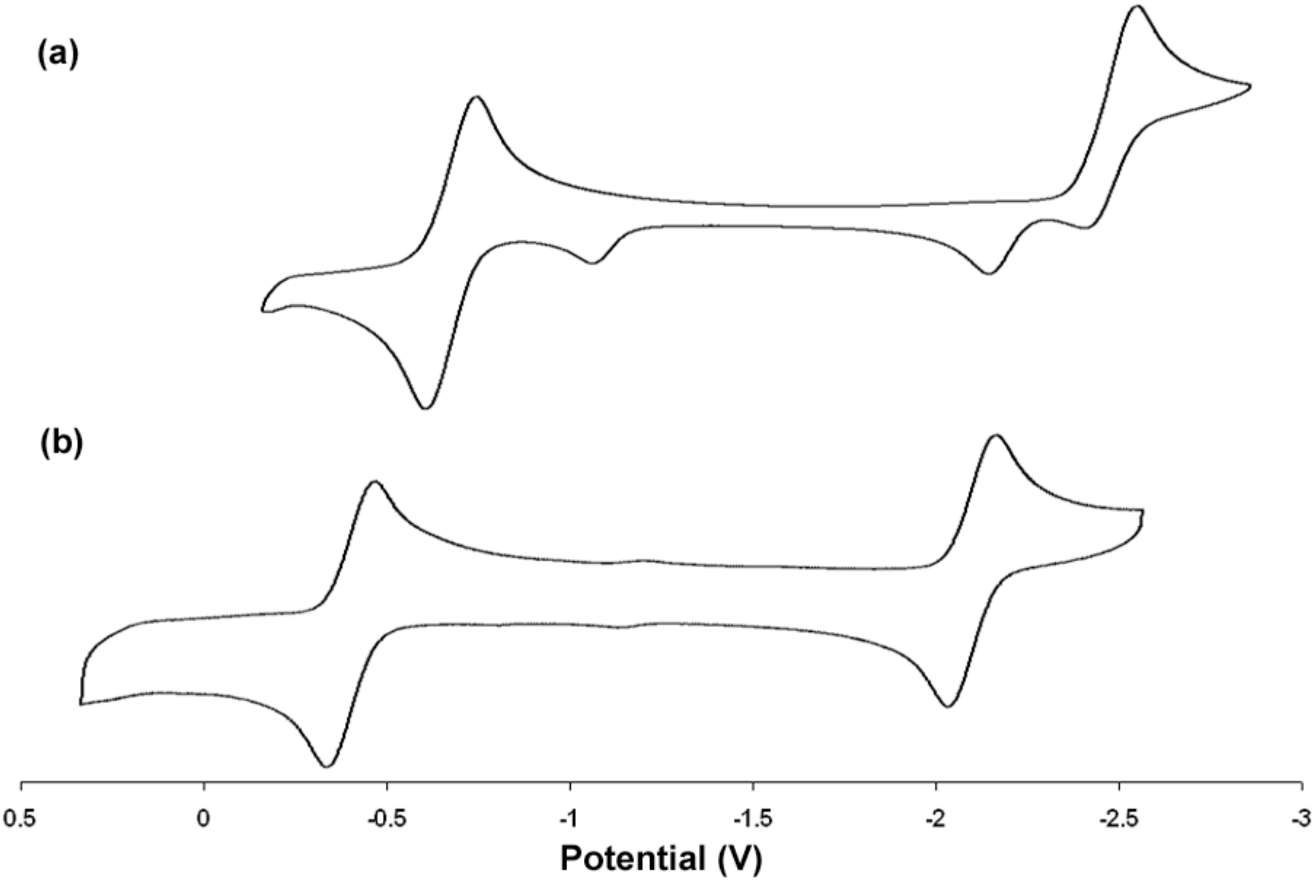


Figure A2. Cyclic voltammograms of $[SiP^{Ph}_3]FeN_2$ (**6**, *top*) and $[SiP^{iPr}_3]FeN_2$ (**7**, *bottom*).

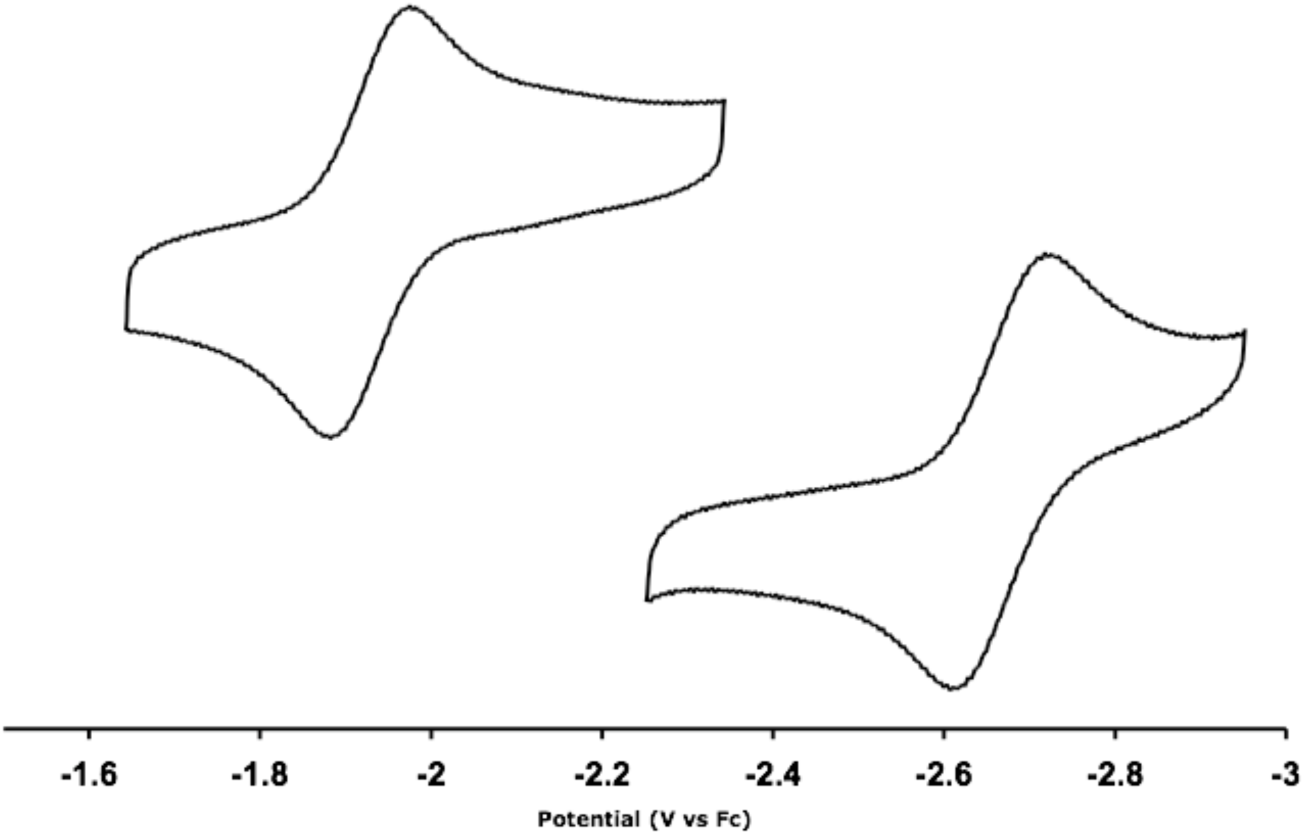
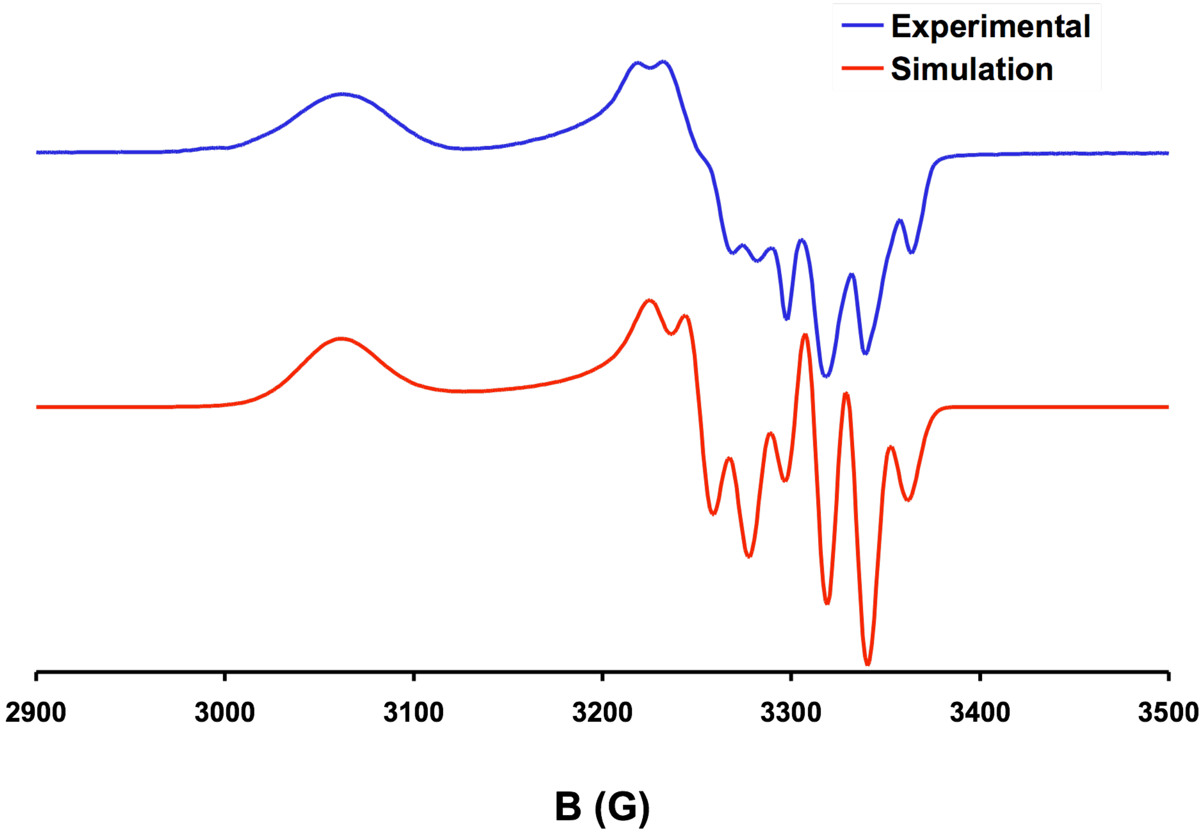


Figure A3: X-band EPR spectrum of $[\mathrm{SiP^{Ph}}_3]\mathrm{FeN_2}$ (**6**) (*blue*) and simulation (*red*) in a 2-methyltetrahydrofuran glass at 4 K.



Simulation parameters:
$\nu = 9.3743$ GHz
$g_1 = 2.013$, $g_2 = 2.051$, $g_3 = 2.187$
For 3 equivalent P atoms: $A_1 = 58$ G, $A_2 = 55$ G, $A_3 = 5.8$ G
Linewidths: $W_1 = 8.0$ G, $W_2 = 9.5$ G, $W_3 = 26.0$ G

Figure A4. Fully labelled diagram of [SiP$^{Ph}{}_3$]FeMes (**3**) and co-crystallized hydrocarbon solvent molecules.

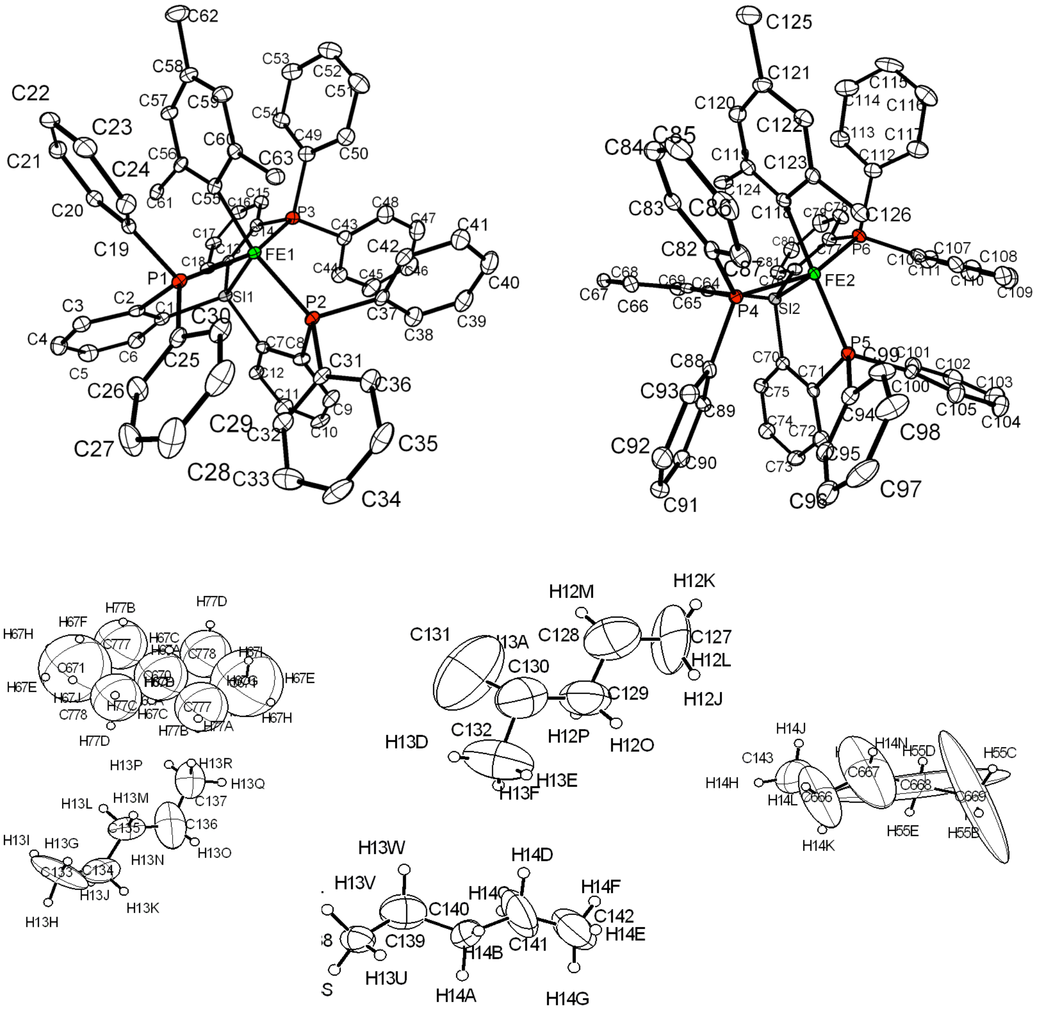


Table A2 Crystal data and structure refinement for **3**.

Identification code	npm54	
Empirical formula	$C_{149.5}H_{162}Fe_2P_6Si_2$	
Formula weight	2312.49	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.966(5) Å	α = 101.547(16)°
	b = 21.469(12) Å	β = 93.092(18)°
	c = 27.269(13) Å	γ = 100.968(10)°
Volume	6147(5) Å^3	
Z	2	
Density (calculated)	1.249 Mg/m^3	
Absorption coefficient	0.387 mm^{-1}	
F(000)	2458	
Crystal size	.37 x .35 x .13 mm^3	
Theta range for data collection	1.37 to 35.99°.	
Index ranges	$-14 \leq h \leq 16$, $-35 \leq k \leq 27$, $-33 \leq l \leq 42$	
Reflections collected	69138	
Independent reflections	33909 [R(int) = 0.0738]	
Completeness to theta = 35.99°	58.2 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	33909 / 10 / 1442	
Goodness-of-fit on F^2	0.952	
Final R indices [I>2sigma(I)]	R1 = 0.0656, wR2 = 0.1590	
R indices (all data)	R1 = 0.1357, wR2 = 0.1894	
Largest diff. peak and hole	1.213 and -0.662 e.Å^{-3}	

Figure A5. Fully labelled diagram of $[\mathrm{SiP^{Ph}}_3]$FeCl (**4**) and a co-crystallized CH_2Cl_2 molecule.

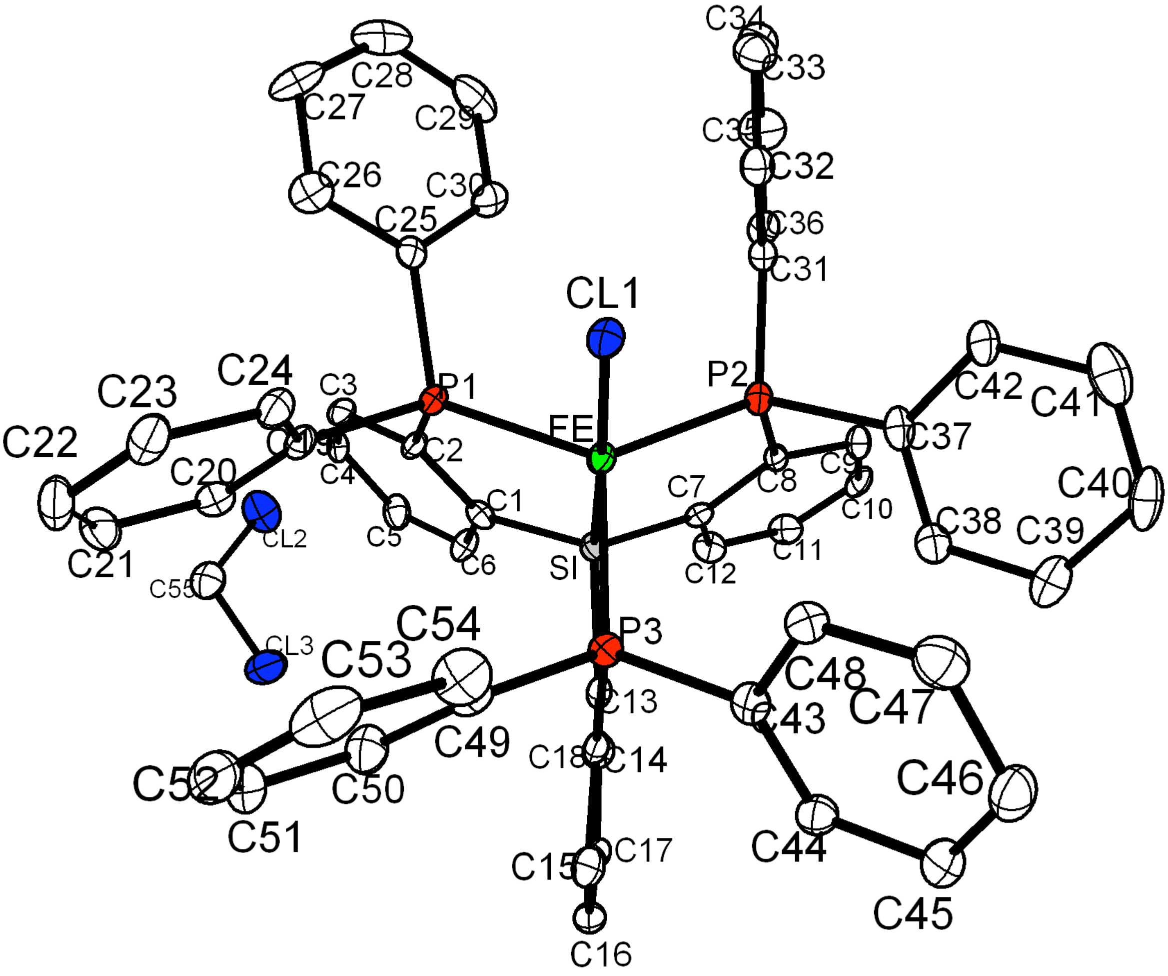


Table A3. Crystal data and structure refinement for **4**.

Identification code	npm53	
Empirical formula	$C_{55}H_{44}Cl_2FeP_3Si$	
Formula weight	952.65	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.1583(15) Å	α = 87.973(2)°
	b = 13.2714(18) Å	β = 84.822(2)°
	c = 15.689(2) Å	γ = 86.423(2)°
Volume	2308.3(5) Å^3	
Z	2	
Density (calculated)	1.371 Mg/m^3	
Absorption coefficient	0.610 mm^{-1}	
F(000)	986	
Crystal size	.18 x .067 x .041 mm^3	
Theta range for data collection	1.54 to 26.05°.	
Index ranges	$-13 \le h \le 13, -15 \le k \le 15, -11 \le l \le 18$	
Reflections collected	13098	
Independent reflections	7641 [R(int) = 0.0671]	
Completeness to theta = 26.05°	83.8 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7641 / 0 / 569	
Goodness-of-fit on F^2	0.956	
Final R indices [I>2sigma(I)]	R1 = 0.0504, wR2 = 0.0786	
R indices (all data)	R1 = 0.0975, wR2 = 0.0886	
Largest diff. peak and hole	0.587 and -0.466 e.Å^{-3}	

Figure A6. Fully-labelled diagram of (κ^2-[SiP$^{iPr}{}_3$]H)FeCl$_2$. The Si-H hydrogen atom (H1) was located on the difference map and refined as an isotropic atom.

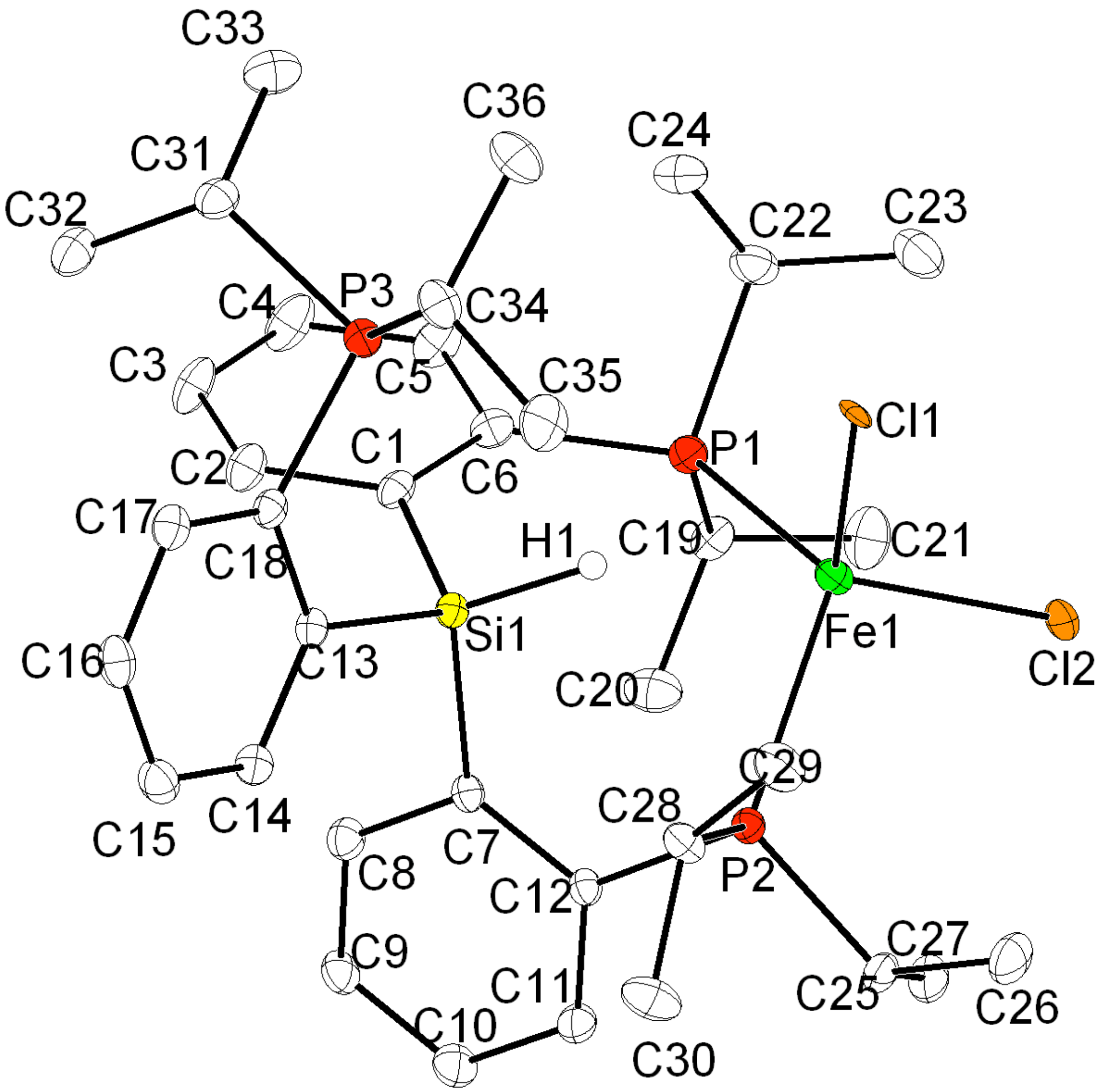


Table A4. Crystal data and structure refinement for (κ^2-[SiP$^{iPr}{}_3$]H)FeCl$_2$.

Identification code	mtw47	
Empirical formula	$C_{36}H_{55}Cl_2FeP_3Si$	
Formula weight	735.55	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 13.0548(19) Å	α = 90°
	b = 13.718(3) Å	β = 104.102(11)°
	c = 22.356(6) Å	γ = 90°
Volume	3883.0(13) Å^3	
Z	4	
Density (calculated)	1.258 Mg/m^3	
Absorption coefficient	0.704 mm^{-1}	
F(000)	1560	
Crystal size	0.34 x 0.29 x 0.19 mm^3	
Theta range for data collection	1.88 to 35.37°.	
Index ranges	$-20 \le h \le 17$, $-22 \le k \le 21$, $-35 \le l \le 33$	
Reflections collected	62610	
Independent reflections	15058 [R(int) = 0.0954]	
Completeness to theta = 35.37°	85.6 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15058 / 0 / 404	
Goodness-of-fit on F^2	1.091	
Final R indices [I>2sigma(I)]	R1 = 0.0688, wR2 = 0.2048	
R indices (all data)	R1 = 0.1255, wR2 = 0.2406	
Largest diff. peak and hole	3.615 and -0.796 e.Å^{-3}	

Figure A7. Fully-labelled diagram of [SiP$^{iPr}{}_3$]FeCl (**5**) and a co-crystallized benzene molecule.

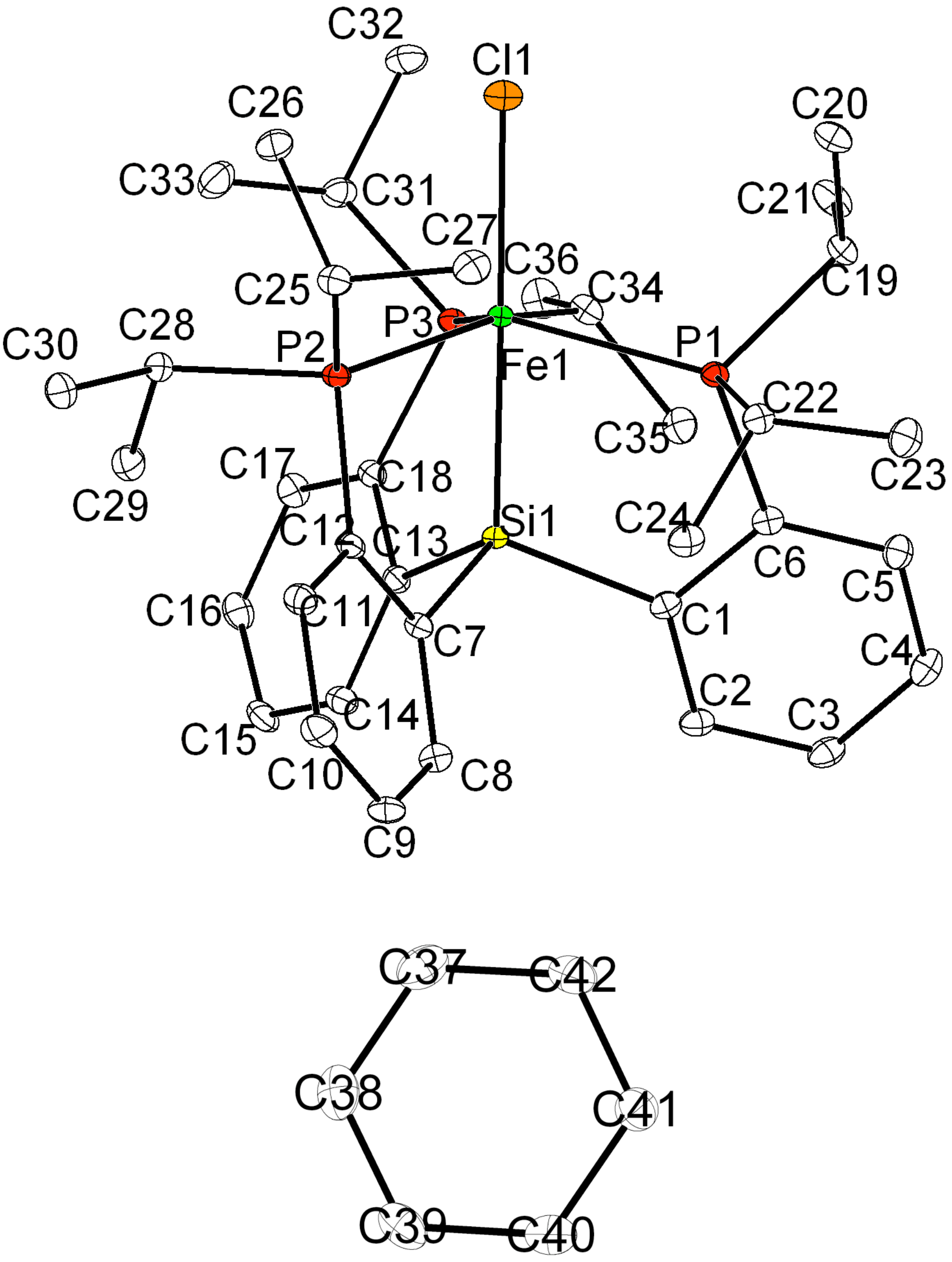


Table A5. Crystal data and structure refinement for **5**.

Identification code	mtw53	
Empirical formula	$C_{42}H_{60}ClFeP_3Si$	
Formula weight	777.20	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 12.913(4) Å	α = 90°
	b = 15.513(4) Å	β = 92.33(3)°
	c = 20.296(8) Å	γ = 90°
Volume	4062(2) $Å^3$	
Z	4	
Density (calculated)	1.271 Mg/m^3	
Absorption coefficient	0.613 mm^{-1}	
F(000)	1656	
Crystal size	0.37 x 0.26 x 0.21 mm^3	
Theta range for data collection	1.58 to 38.63°.	
Index ranges	$-22 \le h \le 22$, $-27 \le k \le 27$, $-34 \le l \le 34$	
Reflections collected	77474	
Independent reflections	20057 [R(int) = 0.0936]	
Completeness to theta = 38.63°	86.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	20057 / 0 / 445	
Goodness-of-fit on F^2	1.367	
Final R indices [I>2sigma(I)]	R1 = 0.0510, wR2 = 0.0872	
R indices (all data)	R1 = 0.1009, wR2 = 0.0956	
Largest diff. peak and hole	1.302 and -0.731 e.$Å^{-3}$	

Figure A8. Fully-labelled diagram of [SiP$^{Ph}_{3}$]FeN$_2$ (**6**).

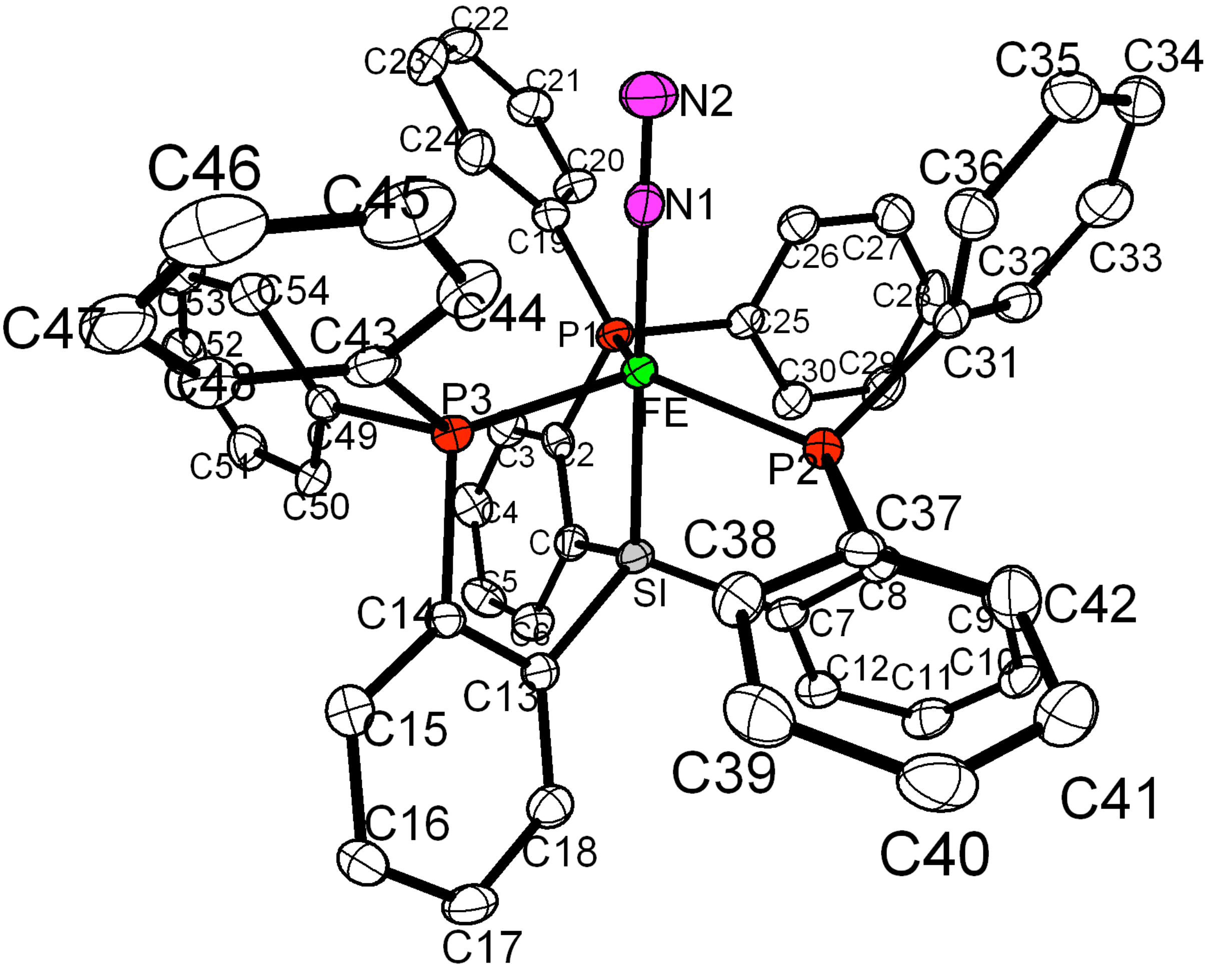


Table A6. Crystal data and structure refinement for **6**.

Identification code	npm56	
Empirical formula	$C_{54}H_{42}FeN_2P_3Si$	
Formula weight	895.75	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 12.7101(9) Å	α = 90°
	b = 17.4799(12) Å	β = 99.0290(10)°
	c = 19.7248(14) Å	γ = 90°
Volume	4328.0(5) Å ^{3}	
Z	4	
Density (calculated)	1.375 Mg/m^3	
Absorption coefficient	0.528 mm^{-1}	
F(000)	1860	
Crystal size	.18 x .16 x .14 mm^3	
Theta range for data collection	1.57 to 28.45∞.	
Index ranges	$-16 \leq h \leq 16$, $-22 \leq k \leq 23$, $-26 \leq l \leq 24$	
Reflections collected	34641	
Independent reflections	9873 [R(int) = 0.0732]	
Completeness to theta = 28.45∞	90.6 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9873 / 0 / 550	
Goodness-of-fit on F^2	1.343	
Final R indices [I>2sigma(I)]	R1 = 0.0481, wR2 = 0.0745	
R indices (all data)	R1 = 0.0882, wR2 = 0.0796	
Largest diff. peak and hole	0.954 and -0.577 e. Å $^{-3}$	

Figure A9. Fully-labelled diagram of $[SiP^{iPr}{}_3]FeN_2$ (**7**) and a co-crystallized benzene molecule. Atoms N1, N2, and Cl2 were treated as isotropic atoms; all other atoms were refined anisotropically. The occupancies of N1 and N2 refined to approx 0.97, while the occupancy of Cl2 refined to approx 0.03.

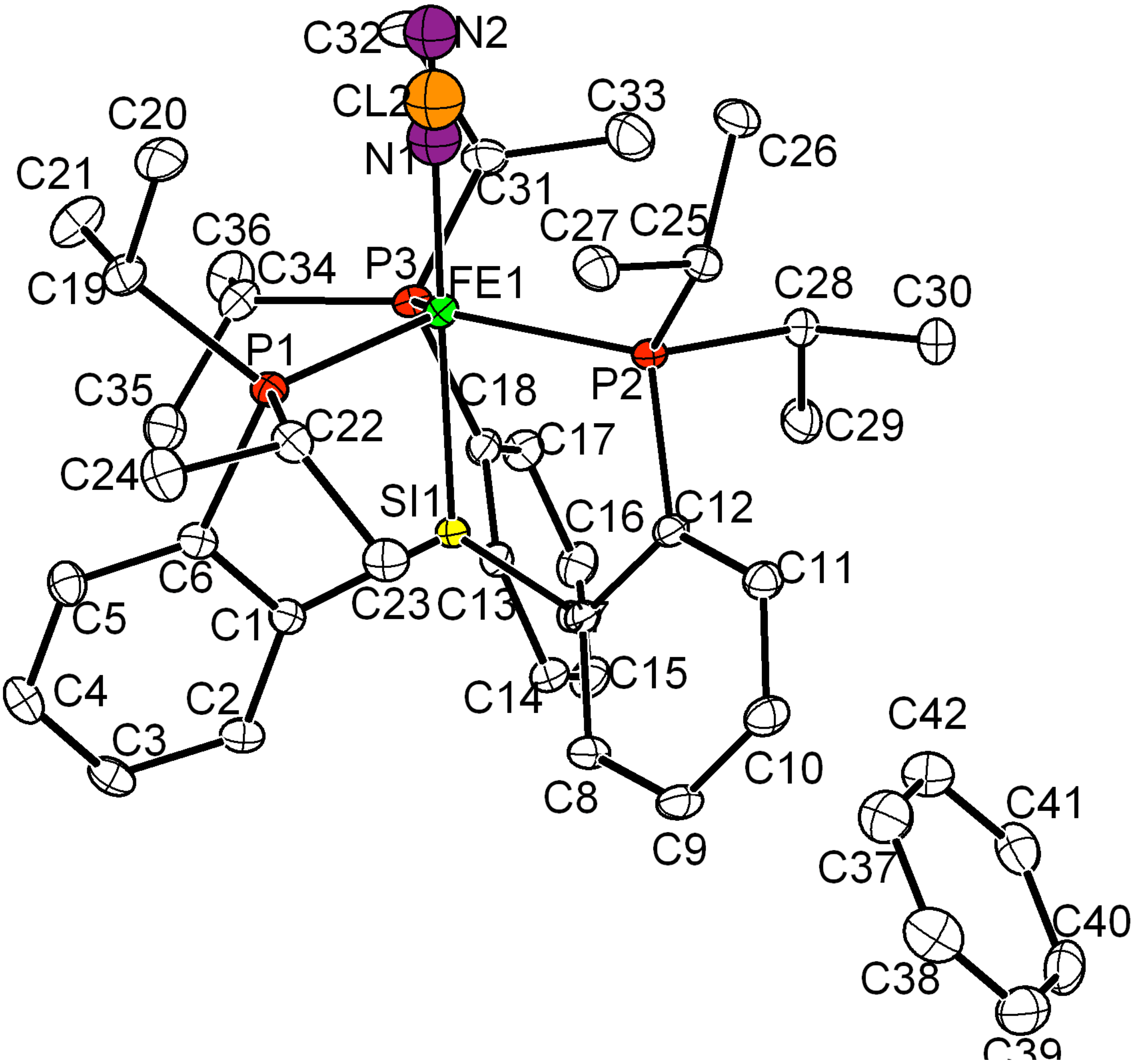


Table A7. Crystal data and structure refinement for **7**.

Identification code	mtw60	
Empirical formula	$C_{42}H_{60}Cl_{0.03}FeN_{1.94}P_3Si$	
Formula weight	765.45	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 12.759(2) Å	α = 90°.
	b = 15.4865(19) Å	β = 92.006(16)°.
	c = 20.561(4) Å	γ = 90°.
Volume	4060.1(11) $Å^3$	
Z	4	
Density (calculated)	1.317 Mg/m^3	
Absorption coefficient	0.617 mm^{-1}	
F(000)	1712	
Crystal size	0.35 x 0.33 x 0.17 mm^3	
Theta range for data collection	1.60 to 40.85°.	
Index ranges	$-22 \le h \le 23$, $-28 \le k \le 25$, $-37 \le l \le 35$	
Reflections collected	79596	
Independent reflections	24271 [R(int) = 0.0828]	
Completeness to theta = 40.85°	91.5 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	24271 / 0 / 452	
Goodness-of-fit on F^2	1.431	
Final R indices [I>2sigma(I)]	R1 = 0.0512, wR2 = 0.0892	
R indices (all data)	R1 = 0.0993, wR2 = 0.0966	
Largest diff. peak and hole	1.409 and -0.750 $e.Å^{-3}$	

Figure A10. Fully labelled diagram of **9**. Atoms O5, C200, and C201 have 50% occupancy.

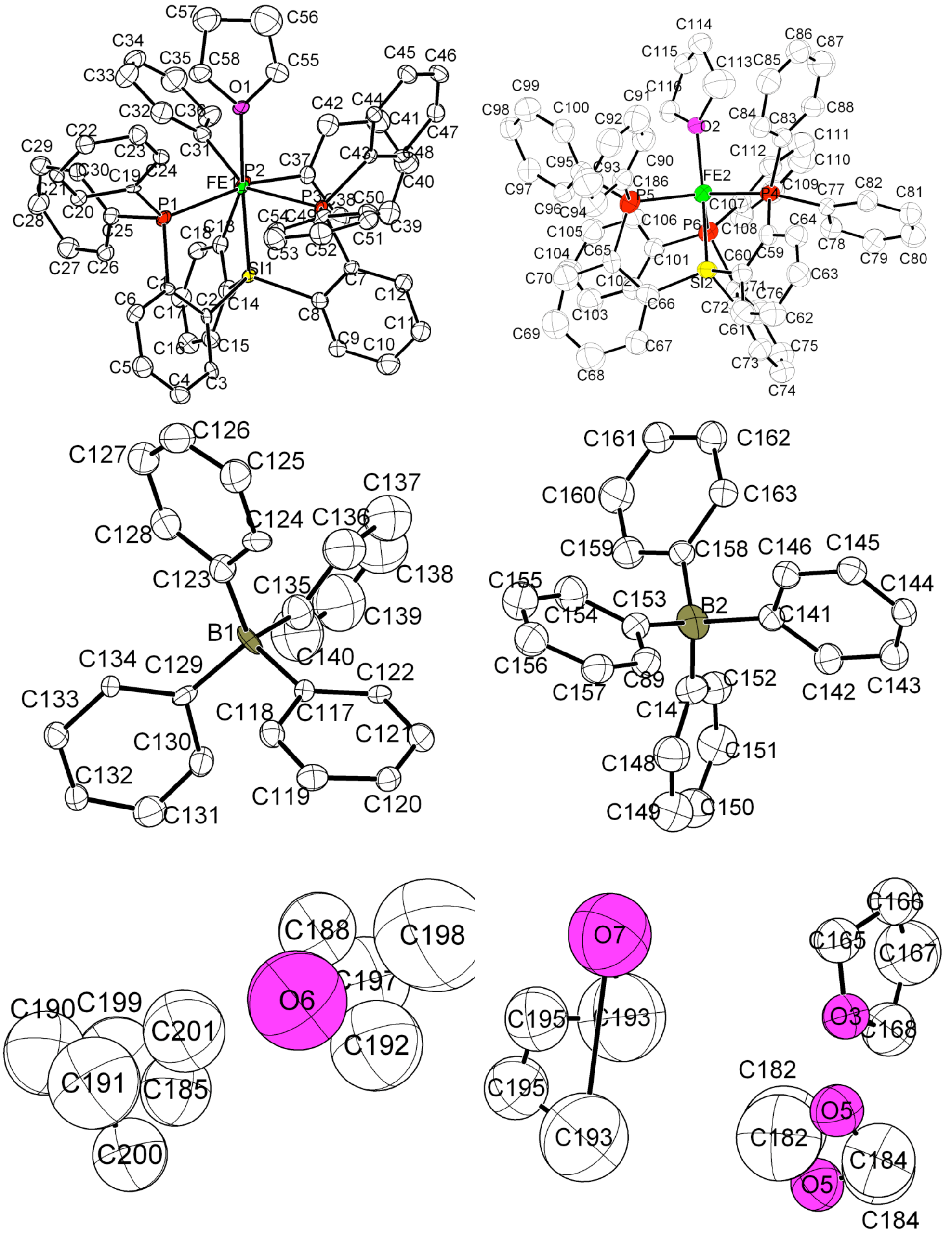


Table A8. Crystal data and structure refinement for **9**.

Identification code	npm61	
Empirical formula	$C_{300}H_{182}B_2Fe_2O_9P_6Si_2$	
Formula weight	4305.78	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 79.786(5) Å	α = 90°.
	b = 15.5571(9) Å	β = 99.316(2)°.
	c = 23.7631(14) Å	γ = 90°.
Volume	29107(3) $Å^3$	
Z	20	
Density (calculated)	4.913 Mg/m^3	
Absorption coefficient	0.957 mm^{-1}	
F(000)	44680	
Crystal size	0.30 x 0.24 x 0.06 mm^3	
Theta range for data collection	1.52 to 21.85°.	
Index ranges	$-78 \leq h \leq 83$, $-16 \leq k \leq 15$, $-23 \leq l \leq 23$	
Reflections collected	62552	
Independent reflections	14763 [R(int) = 0.1781]	
Completeness to theta = 21.85°	84.2 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14763 / 1128 / 1802	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2sigma(I)]	R1 = 0.1128, wR2 = 0.2673	
R indices (all data)	R1 = 0.2064, wR2 = 0.3108	
Largest diff. peak and hole	0.987 and -0.636 e.$Å^{-3}$	