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Synthesis and Characterization of Pentaphosphino Zero-Valent Iron Complexes and Their Corresponding Iron(II)-Chloride and -Hydride Complexes

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A pentaphosphino iron(II)-chloride species [^{t}SiP$_3$(dmpm)FeCl][Cl] (**1-Cl**) (^{t}SiP$_3$ = ^{t}BuSi(CH$_2$PMe$_2$)$_3$, dmpm = Me$_2$PCH$_2$PMe$_2$) was prepared from [(^{t}SiP$_3$Fe)$_2$(μ-Cl)$_3$][Cl] and dmpm. This species was reduced to give the corresponding iron(0) complex, ^{t}SiP$_3$(dmpm)Fe (**3**), in near quantitative yield. Analogous complexes [SiP$_3$(dmpe)FeCl][Cl] (**2-Cl**) and SiP$_3$(dmpe)Fe (**4**) (SiP$_3$ = MeSi(CH$_2$PMe$_2$)$_3$, dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$) were prepared in the same manner as **1** and **3** but with lower yields because of competitive ligand rearrangement reactions that gave byproduct of *trans*-(dmpe)$_2$FeCl$_2$ and (dmpe)$_5$Fe$_2$ (**5**). [^{t}SiP$_3$(dmpm)FeH][A] (**6**) was prepared from the reaction of **3** with weak acids (HA), and the pK_a of **6** was established to be approximately 25. Attempts to prepare pentaphosphino-iron(0) complexes of the form SiP$_3$(PR$_3$)$_2$Fe using PPh$_3$ and PMe$_3$ resulted in cyclometalated products, SiP$_3$FeH((o-C$_6$H$_4$)PPh$_2$) (**7**) and SiP$_3$FeH(CH$_2$PMe$_2$) (**8**). Synthesis and characterization of these complexes, including crystal structures of **1**−**5**, are reported.

Introduction

Iron(0) complexes have been employed in bond activation processes of C−H,[1−9] C−S[4,6,10] and to a lesser extent, C−X[11−13] bonds (X = halogen). To the best of our knowledge, no studies of well-defined iron(0) complexes reacting with chlorinated ethylenes have been conducted despite increasing interest in the groundwater remediation reaction that occurs in permeable reactive barriers[14,15] between bulk iron(0) and ubiquitous chlorinated solvents.[16,17] We have a strong interest in studying dechlorination reactions through the use of model complexes,[18] thus motivating the work presented here on the development of a model for iron(0).

Iron-phosphine complexes are promising for modeling the reactions of iron(0) with chlorinated hydrocarbons. As opposed to carbonyl and arene ligands, with which one can argue about the oxidation state of the metal center, phosphine ligands have the ability to stabilize low oxidation states of iron without significant back-bonding. 18-Electron pentaphosphino iron(0) complexes with dissociable ligands, or ligand arms, represent relatively stable precursor complexes with access to the reactive 16-electron, coordinatively unsaturated intermediate species responsible for activation of inert C−H bonds, including the C−H bond of methane.[8]

In this work, we present the synthesis and characterization of a pentaphosphino zero-valent iron complex, ^{t}SiP$_3$(dmpm)Fe (^{t}SiP$_3$ = ^{t}BuSi(CH$_2$PMe$_2$)$_3$, dmpm = Me$_2$PCH$_2$PMe$_2$) (**3**), and a new synthetic route to a similar iron(0) complex previously reported, SiP$_3$(dmpe)Fe (SiP$_3$ = MeSi(CH$_2$PMe$_2$)$_3$, dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$) (**4**). Preparation and characterization of corresponding phosphinoiron-chloride and -hydride complexes are presented as well, as they are probable products and intermediates in dechlorination reactions. We also touch on the propensity of the SiP$_3$Fe^0 moiety to cyclometallate with available C−H donors of monodentate phosphines in the

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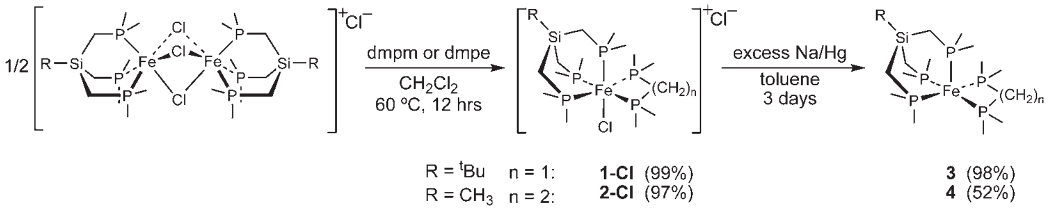

Figure 1. Synthetic route to complexes **1**−**4**. Percent yields are given in parentheses.

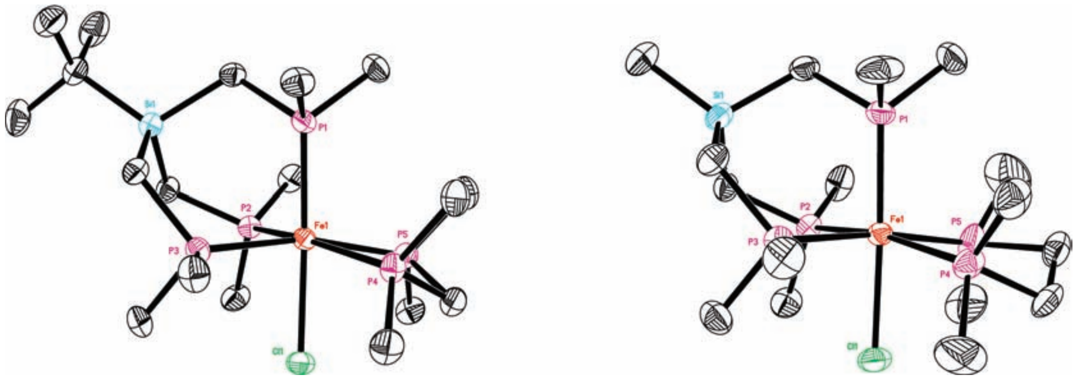

Figure 2. ORTEP diagrams of **1-BPh$_4$**, [^{t}SiP$_3$(dmpm)FeCl][BPh$_4$] (left), and **2-Cl**, [SiP$_3$(dmpe)FeCl][Cl] (right), with the thermal ellipsoids drawn at 50% probability level. The outer sphere anions were removed from both diagrams for clarity. The disorder of the dmpe ligand in **2-Cl** is not shown.

preparation and spectroscopic characterization of SiP$_3$FeH((*o*-C$_6$H$_4$)PPh$_2$) (**7**) and SiP$_3$FeH(CH$_2$PMe$_2$) (**8**).

Results and Discussion

Iron(II)-Chloride Complexes. Two pentaphosphino iron(0) complexes, ^{t}SiP$_3$(dmpm)Fe, **3**, and SiP$_3$(dmpe)Fe, **4**, were prepared through a two-step synthesis in which the iron(II)-chloride intermediates were isolated and characterized (Figure 1). Attempts to perform the reaction in a single step according to a procedure similar to that described by Boncella[19,20] through the reduction of the chloroiron-dimer in the presence of the desired ligand gave lower yields when compared to our two-step synthesis. Howarth and Wong previously reported the preparation of **4** through a different synthetic route starting with (η-C$_6$H$_6$)(PMe$_3$)$_2$Fe.[21] However, because the preparation of (η-C$_6$H$_6$)(PMe$_3$)$_2$Fe is demanding, we have found the synthetic method presented here, from readily available reactants, to be a more facile route.

Compound **1-Cl**, [^{t}SiP$_3$(dmpm)FeCl][Cl], was prepared quantitatively from the reaction of [(^{t}SiP$_3$Fe)$_2$(μ-Cl)$_3$][Cl] with dmpm at 60 °C and was isolated as a dark pink solid that is relatively stable in air and thermally stable to at least 110 °C. Metathesis of the Cl$^-$ for BPh$_4$$^-$ in the reaction of **1-Cl** with NaBPh$_4$ to give **1-BPh$_4$** was carried out to aid in characterization. Compound **1-Cl** was characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and electrospray ionization high-resolution mass spectrometry (ESI-HRMS) and **1-BPh$_4$** by X-ray crystallography and cyclic voltammetry (CV).

Characteristic NMR resonances of **1-Cl** include the highly resolved diastereotopic protons of the dmpm-methylene unit (^{1}H δ ppm 2.8, 3.5) as well as three complexly coupled peaks in the ^{31}P{^{1}H} NMR spectrum with an integrated intensity peak ratio of 1:2:2 and patterns consistent with an AA′BB′C spin system. No differences between **1-Cl** and **1-BPh$_4$** were observed in the NMR spectra. The elemental composition of **1** (537.1 *m*/*z*) was confirmed via ESI-HRMS using a poly(ethylene glycol) exact mass internal standard.

Crystals of **1-BPh$_4$** suitable for X-ray diffraction were obtained from slow evaporation of acetonitrile at ambient temperature. The structure determination confirmed a distorted octahedral geometry about iron because of the small (< 90°) chelate angle of dmpm (Figure 2). A slightly elongated Fe−Cl bond length in **1-BPh$_4$** (0.2 to 0.7 Å) compared to other P$_5$FeCl$^+$ complexes, [P(CH$_2$CH$_2$-PMe$_2$)$_3$PPh$_3$FeCl][BPh$_4$][22] and [(PF$_2$Ph)$_5$FeCl][FeCl$_4$],[23] suggests an enhanced electron donating ability from the alkyl phosphines of the dmpm and ^{t}SiP$_3$ ligands. Select crystallographic parameters, bond lengths, and angles are presented in Tables 1 and 2.

The electrochemical behavior of **1-BPh$_4$** (0.5 mM) was evaluated by CV using a glassy carbon working electrode at room temperature in *N*,*N*-dimethylformamide (DMF). The collected CV data showed a reversible one-electron Fe^{3+}/Fe^{2+} couple at +0.58 V (versus Ag$^+$/AgCl) and an irreversible two-electron Fe^{2+}/Fe^0 peak at a potential of −1.64 V. A small anodic peak that is related to the irreversible peak was also observed at 0.31 V, although only after reduction (Figure 3). The electrochemically generated iron(0) species (**3**) has independently been found to react with any solvent that was suitable for CV

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Table 1. X-ray Crystallographic Data for Complexes **1**−**5**

	1-BPh$_4$	**2-Cl**	**3**	**4**	**5**
empirical formula	$C_{42}H_{67}BClFeP_5Si$	$C_{16}H_{43}Cl_2FeP_5Si$	$C_{18}H_{47}FeP_5Si$	$C_{16}H_{43}FeP_5Si$	$C_{15}H_{40}FeP_5$
fw, g mol^{-1}	857.01	545.19	502.35	474.29	430.17
color/habit	red/block	pink/block	red/plate	red/block	orange/plate
crystal system	orthorhombic	monoclinic	triclinic	orthorhombic	triclinic
space group	$P2_12_12_1$	$C2/c$	$P\bar{1}$	$Pna2_1$	$P\bar{1}$
a, Å	12.058(2)	33.776(2)	13.515(1)	17.790(9)	9.075(1)
b, Å	12.668(2)	9.5076(7)	14.039(1)	14.919(7)	9.224(1)
c, Å	29.658(6)	18.121(1)	15.150(2)	9.317(4)	15.328(2)
α, degrees	90	90	76.833(2)	90	101.020(2)
β, degrees	90	115.254(1)	77.260(2)	90	98.323(2)
γ, degrees	90	90	87.623(2)	90	113.373(2)
V, Å^3	4530(1)	5262.9(6)	2729.9(5)	2473(2)	1120.9(2)
Z	4	8	4	4	2
D_{calc}, g cm^{-3}	1.257	1.376	1.222	1.274	1.278
F(000)	1824	2304	1080	1016	462
reflns collect	53740	30228	23515	28300	12929
ind. reflns	10386	6043	11448	5651	4986
R$_1$, wR$_2$ ($I > 2\sigma(I)$)	0.0426, 0.0890	0.0314, 0.0680	0.0343, 0.0849	0.0339, 0.0620	0.0298, 0.0696
R$_1$, wR$_2$, all data	0.0537, 0.0927	0.0429, 0.0721	0.0448, 0.0926	0.0432, 0.0645	00447, 0.756
GOF	1.054	1.033	1.026	1.027	1.091

Table 2. Selected Bond Lengths (Å) and Angles (deg) of Complexes **1**−**5**

bond/angle	**1-BPh$_4$**	**2-Cl**	**3**	**4**	**5**
Fe−P1	2.2309(9)Å	2.2550(6)Å	2.1453(7)Å	2.159(1)Å	2.1736(6)Å
Fe−P2	2.2706(9)Å	2.2889(6)Å	2.1564(6)Å	2.198(1)Å	2.1580(6)Å
Fe−P3	2.2496(9)Å	2.2982(5)Å	2.1624(7)Å	2.179(1)Å	2.1655(6)Å
Fe−P4	2.3029(9)Å	2.2962(6)Å	2.1826(7)Å	2.1954(9)Å	2.1625(6)Å
Fe−P5	2.3063(9)Å	2.3059(6)Å	2.1798(7)Å	2.1751(9)Å	2.1811(6)Å
Fe−Cl	2.3749(9)Å	2.3800(5)Å			
P4−Fe−P5	72.61(3)°	83.58(2)°	72.66(3)°	82.35(4)°	82.14(2)°
P3−Fe−P5	166.40(3)°	172.58(2)°	149.83(3)°	140.67(4)°	154.23(3)°
P2−Fe−P4	164.44(3)°	169.28(2)°	154.08(3)°	166.28(4)°	151.12(3)°
P1−Fe−Cl	174.35(3)°	176.36(2)°			

analysis, including DMF; this reactivity may explain the irreversibility of the peak associated with the iron(0) species, and the related anodic peak can then be attributed to an oxidative process of the resulting product. While both Fe^{2+}/Fe^{+} and Fe^{4+}/Fe^{3+} couples have previously been reported with phosphine-stabilized iron(II) complexes, neither were observed electrochemically with **1-BPh$_4$**.[24,25]

Compound **2-Cl**, [SiP$_3$(dmpe)FeCl][Cl], was synthesized in 97% yield from the reaction of [(SiP$_3$Fe)$_2$(μ-Cl)$_3$][Cl] with dmpe and characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, ESI-HRMS, and X-ray crystallography. Room temperature ^{31}P{^{1}H} NMR spectra of this compound showed three highly coupled peaks in a pattern consistent with an AA′BB′C spin system of integrated intensity ratio 2:1:2. A simulation of the spectrum using Varian software confirmed this spin system and allowed for determination of the distinguishable P−P coupling constants (Figure 4). The sign and magnitude of the calculated constants follow the trends expected for two-bond phosphorus−phosphorus coupling across a metal center.[26]

ESI-HRMS was used to verify the elemental composition of **2** with poly(ethylene glycol) internal standard. A signal for [SiP$_3$(dmpe)FeCl]$^+$ was observed at 509.0 *m*/*z* with an isotope pattern consistent with an iron and chlorine containing species. The molecular structure of **2-Cl** was determined by X-ray crystallography with crystals grown from CH_2Cl_2 at room temperature. Disorder in the dmpe ligand required modeling of the methylene moieties over two positions. Structural features similar to those discussed for **1-BPh$_4$** were also observed for **2-Cl**, including a distorted octahedral geometry and a longer Fe−Cl bond than previously observed for complexes with a phosphorus atom *trans* to the chloride. See Figure 2 for the Oak Ridge thermal ellipsoid plot (ORTEP) diagram of **2-Cl** and Tables 1 and 2 for crystal and structural data of interest.

Iron(0) Complexes. Compound **3**, ^{t}SiP$_3$(dmpm)Fe, was prepared in 98% yield from the reduction of **1-Cl** with sodium amalgam at room temperature. The isolated oily product readily decomposed upon exposure to trace oxygen but was thermally stable to at least 100 °C in toluene. Compound **3** was characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, electron-impact high-resolution mass spectra (EI-HRMS) and X-ray crystallography. The reduction potential characterization of **3** was determined from CV on **1-BPh$_4$** (Figure 3).

EI-HRMS of **3** resulted in a signal with an isotope pattern consistent with an iron-containing complex at 502.1 *m*/*z* and the elemental composition was confirmed with perfluorokerosene internal standard. The ambient temperature ^{31}P{^{1}H} NMR of **3** showed two resonances, a quartet and a triplet for the dmpm and ^{t}SiP$_3$ phosphorus nuclei, respectively, that are consistent with fluxional

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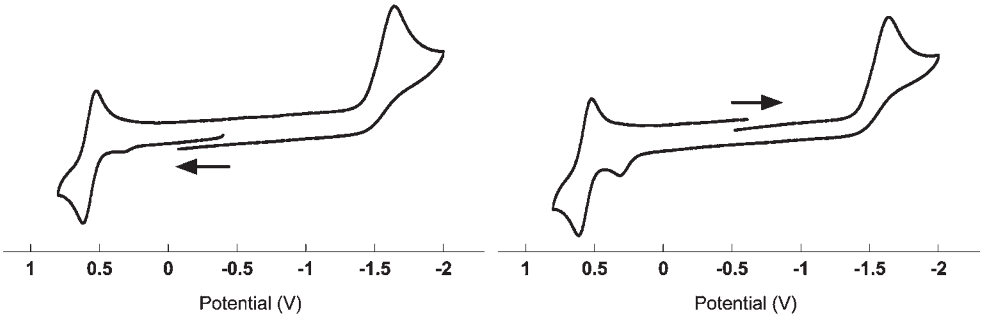

Figure 3. Cyclic voltammograms of complex **1-BPh$_4$** (0.5 mM in DMF) recorded at a glassy carbon electrode and referenced to Ag$^+$/AgCl (sweep rate: 100 mV/s, supporting electrolyte: 0.1 M TBAPF$_6$). The anodic (left) and cathodic (right) directional traces are shown.

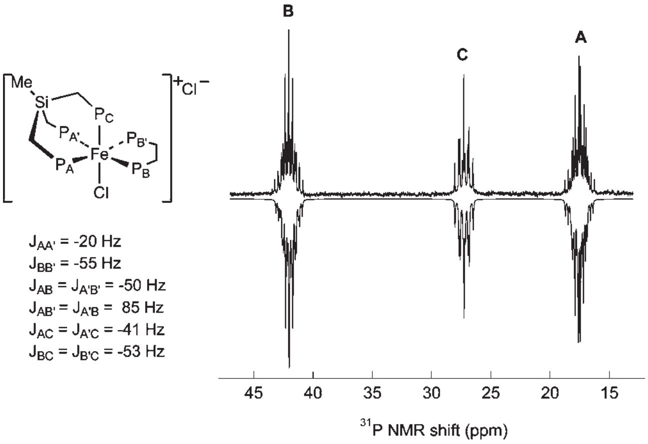

Figure 4. ^{31}P{^{1}H} NMR simulation of **2-Cl**. The experimental spectrum is shown on top and the simulated spectrum using an AA′BB′C spin system on the bottom. The coupling constants were determined from the simulation.

behavior on the NMR time scale. No decoalescence of the resonances was detectable at temperatures down to -85 °C.

The X-ray structure of **3** exhibits a slight distortion from square pyramidal about the iron center with $\tau = 0.07$ (on a τ scale from 0 to 1, with 0 and 1 corresponding to idealized square pyramidal and trigonal bipyramidal geometries, respectively[27]). This is consistent with other five coordinate phosphine-ligated complexes containing small bite angle diphosphines (e.g., dmpm and dmpe) that have previously been observed to favor a square pyramidal geometry over trigonal bipyramidal.[28−30] The vacant site created by the square pyramidal geometry is desirable for a model of bulk iron, as it gives an open reactive site similar to an iron surface.

Compound **4**, SiP$_3$(dmpe)Fe, was synthesized in 52% yield from the reduction of **2-Cl** using sodium amalgam in toluene and characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, EI-HRMS, and X-ray crystallography. During the preparation of **4**, ligand rearrangement reactions involving loss of SiP$_3$ produced previously reported byproducts *trans*-(dmpe)$_2$FeCl$_2$[31] and (dmpe)$_5$Fe$_2$[32] (**5**). Both contaminants could be removed through recrystallization to give a pure solution of **4**. It was also possible to structurally characterize one of the impurities, pentaphosphino-iron(0) dimer, (dmpe)$_5$Fe$_2$ (**5**) ($\tau = 0.05$, see Figure 6 and Tables 1 and 2 for structural information).

The elemental composition of **4** (474.1 *m*/*z*) was confirmed by EI-HRMS with perflourokerosene internal standard. X-ray characterization of **4** demonstrates an intermediate distortion between square pyramidal and trigonal bipyramidal geometries with a τ value of 0.43 (Figure 5). The larger bite angle of dmpe and the flexibility acquired with an extra methylene unit account for the enhanced distortion when compared to **3**. See Tables 1 and 2 for crystal data and structural metrics.

dmpe vs dmpm. Through the synthesis of two analogous Fe(0) complexes, **3** and **4**, it was found that the dmpm-containing complex (**3**) had enhanced stability over the dmpe-containing complex (**4**) as evidenced by the lack of byproduct formation and near quantitative yields. Of the slight structural differences in these complexes, the change from SiP$_3$ to ^{t}SiP$_3$ has been found to enhance solubility and crystallinity[33] but was not expected to create the stability divergences observed. Instead, the choice of bidentate ligand (dmpe or dmpm) is suggested to account for the difference by influencing the binding ability of the tripodal ligand because the byproduct identified in the preparation of **4**, *trans*-Fe(dmpe)$_2$Cl$_2$ and (dmpe)$_5$Fe$_2$ (**5**), require the dissociation of the tripodal ligand, yet these types of products are not observed in the preparation of dmpm-containing **3**. The more strained bite angle of dmpm (72.66°) results in a diminished *trans*-effect, allowing for the tripodal ligand to bind more tightly than when dmpe (82.35°) is used. This hypothesis is supported by X-ray crystallographic data in which the ^{t}SiP$_3$Fe−P bonds *trans* to dmpm are on average 0.025 Å shorter in **3** than the identical bonds in **4**. The Fe−P bond lengths of the bidentate ligand in **3** and **4** remain constant near 2.18 Å in both complexes, a length comparable to other iron(0) complexes with phosphine ligands.[34−36] The same trends in bond lengths were also observed in the precursor Fe(II)-Cl complexes where the

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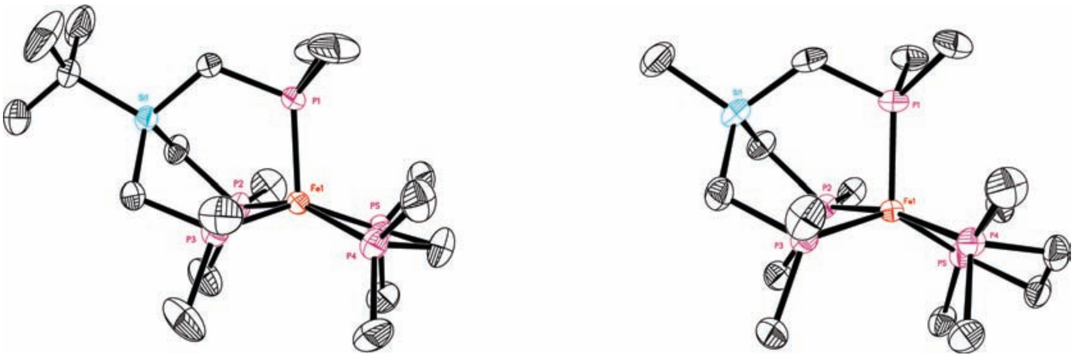


Figure 5. ORTEP diagrams of **3**, ^{t}SiP$_3$(dmpm)Fe (left), and **4**, SiP$_3$(dmpe)Fe (right), with the thermal ellipsoids drawn at 50% probability level. One molecule of **3** in the asymmetric unit and the disorder of the methylene units on ^{t}SiP$_3$ were removed for clarity.

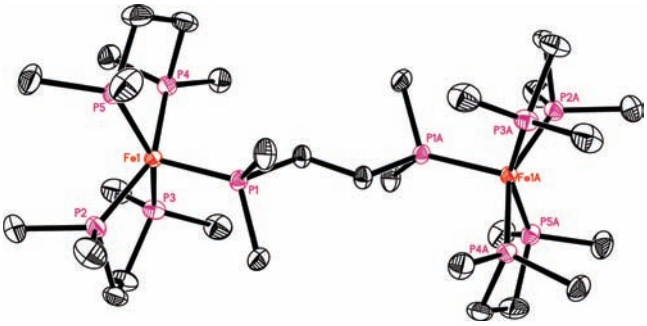


Figure 6. ORTEP diagram of **5**, (dmpe)$_5$Fe$_2$, with the thermal ellipsoids drawn at 50% probability level.

Fe$-$P bonds in the tripodal ligand of **1-BPh$_4$** are 0.034 Å shorter than in **2-Cl**.

Further support for the more tightly bound tripodal ligand in dmpm-containing complexes comes from the analysis of ^{31}P{^{1}H} NMR spectra of **3** and **^{t}SiP$_3$-4** (^{t}SiP$_3$(dmpe)Fe, the analogous ^{t}SiP$_3$ version of **4**, see Supporting Information for synthesis and full NMR characterization of this complex). A 6 ppm downfield shift of the ^{t}SiP$_3$ ligand (16.4 to 22.5 ppm, δ of free ^{t}SiP$_3$: -54.21 ppm) is observed from the dmpe complex to the dmpm complex (Figure 7). The J_{PP} coupling constants also increased from 11.7 Hz (**^{t}SiP$_3$-4**) to 17.5 Hz (**3**). A similar comparison between other dmpm- and dmpe-containing species, [(MeC(CH$_2$PMe$_2$)$_3$)(dmpm/dmpe)MCl]$^{2+}$ (M = Rh, Co), revealed the same trends in bond length decrease and downfield ^{31}P NMR shift of the tripodal ligand with the replacement of dmpe with dmpm.[37]

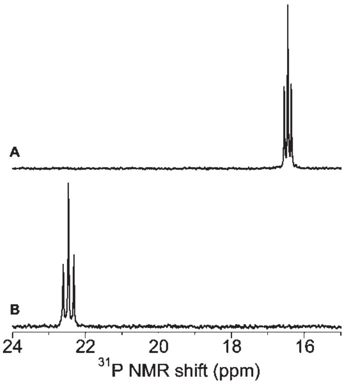
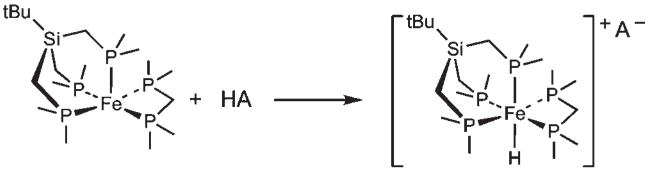


Figure 7. ^{31}P{^{1}H} NMR comparison of the ^{t}SiP$_3$ resonance from **^{t}SiP$_3$-4** (**A**) and **3** (**B**) in C$_6$D$_6$.



3 **6**

Figure 8. [^{t}SiP$_3$(dmpm)FeH][A], **6**, is observed from the reaction of **3** with weak acids (HA, p$K_a \leq 25$). The isolated form was prepared with HA = NH$_4$PF$_6$.

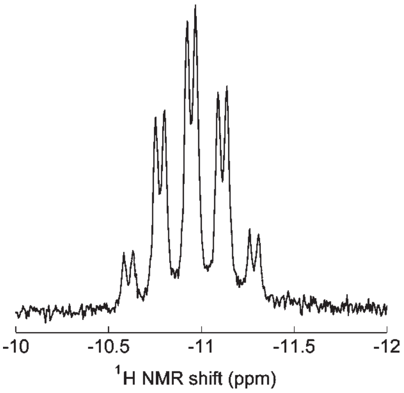


Figure 9. Characteristic iron-hydride peak of **6** observed in the ^{1}H NMR spectrum (CD$_3$CN, J_{HP} = 13, 51 Hz).

Iron(II)-Hydride Complexes. The preparation of iron(II)-hydride complexes, [^{t}SiP$_3$(dmpm)FeH][A] (**6**), was achieved through reaction of **3** with weak acids (HA) in toluene or C$_6$D$_6$ at room temperature (Figure 8). Characterization of **6**, including ^{1}H and ^{31}P NMR, IR, and ESI-HRMS, was performed on the iron-hydride complex isolated from reaction of **3** with ammonium hexafluorophosphate (NH$_4$PF$_6$) according to the procedure described by Howarth and Wong.[21] ^{1}H NMR spectroscopy reveals a characteristic quintet of doublets hydride resonance (δ ppm -11.3, C$_6$D$_6$, -10.9, CD$_3$CN) that collapses to a singlet in the ^{1}H{^{31}P} spectrum (Figure 9). A

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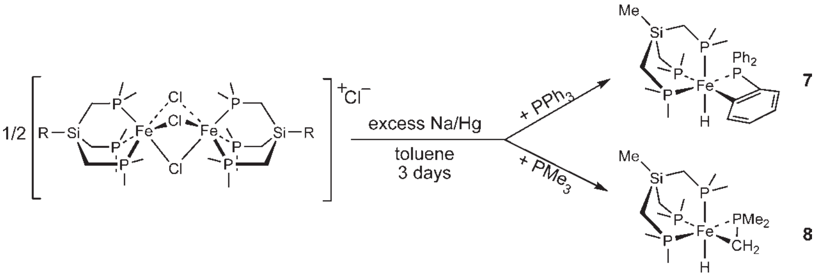

Figure 10. Preparation of the cyclometalated complexes **7**, SiP$_3$FeH((*o*-C$_6$H$_4$)PPh$_2$), and **8**, SiP$_3$FeH(CH$_2$PMe$_2$).

similar hydride peak for the analogous complex [SiP$_3$(dmpe)FeH][PF$_6$] prepared from the reaction of **4** with NH$_4$PF$_6$ has also been reported.[21] An upfield shift from the corresponding chloride complex is observed in the ^{31}P{^{1}H} NMR resonance for the phosphorus *trans* to the hydride, consistent with a hydride complex. IR spectroscopy also revealed an absorbance attributed to an Fe−H stretch at 1831 cm^{-1}, similar to that reported for the pentaphosphino-iron hydride complex, [(dmpm)$_3$FeH][BF$_4$].[30] A signal at 503.1 *m*/*z* in the ESI-HRMS corresponding to [^{t}SiP$_3$(dmpm)FeH]$^+$ was observed and matched the exact mass within 2 ppm.

The reactivity of **3** with weak acids demonstrated the basic nature of the iron(0) complex. This characteristic may be attributed to the strong electron donating ability of **3** as quantified by the negative reduction potential (−1.64 V). To quantify the basicity of **3**, the pK_a of the conjugate acid, **6**, was determined. Titration or equilibrium experiments could not be used to establish the pK_a because a non-reactive solvent in which both **3** and **6** were completely soluble was not found.

Instead, to estimate the pK_a a series of increasingly weaker acids were reacted in 1:1 ratios (21 mM) with **3** in C$_6$D$_6$. The reactions were analyzed by ^{1}H NMR spectroscopy within 10 min of mixing. If no hydride resonance was observed, the reactions were kept at room temperature and reanalyzed after 24 h. In the event of precipitate formation, reaction mixtures were concentrated to a solid and redissolved in CD$_3$CN for NMR analysis. It should be noted that some of these hydride-anion complexes were not stable and went on to form other products; however, any evidence of hydride formation was deemed a deprotonation by **3**. The following acids were used, with their aqueous pK_a values given in parentheses: NH$_4$PF$_6$ (9.3[38]), BHT (> 10, the pK_a of phenol[39]), diethyl malonate (13.3[40]), methanol (15.2[41]), *tert*-butyl alcohol (16.5[41]), indene (19.0[42]), fluorene (22.7[42]), ethyl acetate (24.5[40]), acetonitrile (25[40]) and triphenylmethane (31.5[42]). For all acids with pK_a ≤ 23, the hydride resonance indicative of **6** was observed upon initial analysis. A small hydride peak was observed with ethyl acetate and acetonitrile after 24 h, and no reaction was observed with triphenylmethane. On the basis of these observations, the pK_a of **6** is estimated to be approximately 25.

Cyclometalated Complexes. Attempts were made to prepare additional pentaphosphino iron(0) complexes of the type SiP$_3$(PR$_3$)$_2$Fe, similar to those reported by Karsch,[43,44] using a modification of the method described by Boncella.[19] In each case cyclometalation of the monodentate phosphine was observed. Complexes SiP$_3$FeH((*o*-C$_6$H$_4$)PPh$_2$) (**7**) and SiP$_3$FeH(CH$_2$PMe$_2$) (**8**) were prepared by reduction of [(SiP$_3$Fe)$_2$(μ-Cl)$_3$][Cl] in toluene with excess sodium amalgam in the presence of PPh$_3$ or PMe$_3$, respectively (Figure 10). These complexes were characterized by ^{1}H and ^{31}P NMR spectroscopy. A highly coupled ^{1}H resonance (δ ppm −7.01, **7**, and −12.90, **8**) corresponding to an iron-hydride in addition to an upfield shifted resonance in the ^{31}P{^{1}H} NMR (δ ppm 10.06, **7**, and −17.36, **8**) are consistent with a phosphorus atom *trans* to a hydride. The cyclometalated products were found to be quite stable to thermolysis, with **7** showing no decomposition up to 100 °C in C$_6$D$_6$.

Others have also observed these types of metallocycles formed through intramolecular C−H activation of available alkyl groups by coordinatively unsaturated iron(0) species.[45−49] A three-membered metallocyclic ring with PMe$_3$, similar to **8**, has also been observed in other iron and ruthenium complexes.[50,51] The reaction depicted in Figure 10 is presumed to go through an unsaturated intermediate that is responsible for the metallocycle products.[49]

Conclusions

A new phosphine-ligated iron(0) complex, ^{t}SiP$_3$(dmpm)Fe, was prepared from the reduction of [^{t}SiP$_3$(dmpm)FeCl][Cl]. It was shown that the identity of the bidentate ligand is important to the stability of this type of complex, as the analogous dmpe-containing species was prone to rearrangement reactions during synthesis. Similarly, monodentate ligands paired with SiP$_3$ were not suitable for preparation of iron(0) complexes as cyclometalation occurred. ^{t}SiP$_3$(dmpm)Fe exhibits square pyramidal geometry (τ = 0.07), is strongly

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reducing (−1.64 V), and basic in nature with the ability to deprotonate weak acids with a p$K_a \leq 25$. These characteristics of ^{t}SiP$_3$(dmpm)Fe, in addition to the capability of preparing the related hydride and chloride species, are promising for the use of this complex in the study of Fe(0)-mediated dechlorination reactions. Reactivity studies of ^{t}SiP$_3$(dmpm)Fe with C−Cl bonds will be reported in due course.

Experimental Section

General Considerations. All experiments were conducted under anhydrous and anaerobic (dinitrogen) conditions using a glovebox or Schlenk line. Chemicals were purchased from chemical suppliers and used as received unless noted. Toluene, diethyl ether, hexanes, pentane, and petroleum ether were distilled from sodium metal. Dichloromethane, acetonitrile, d_6-benzene, d_3-acetonitrile, and d_1-chloroform were dried over calcium hydride and distilled. Tetrahydrofuran was distilled from sodium-benzophenone ketyl, *N*,*N*-dimethylformamide was distilled under reduced pressure from calcium sulfate, and mercury was degassed prior to use. Small volumes of methanol, *tert*-butyl alcohol, indene, and ethyl acetate were degassed and stored over 4 Å molecular sieves. Tris(dimethylphosphinomethyl)-methylsilane (SiP$_3$)[52] and [(SiP$_3$Fe)$_2$(μ-Cl)$_3$][Cl][19] were prepared according to literature procedures.

^{1}H nuclear magnetic resonance (NMR) spectra were obtained on Varian Inova 300 MHz and Varian Unity Plus 400 MHz instruments. ^{13}C{^{1}H} NMR and ^{31}P{^{1}H} NMR spectra were obtained at 75 MHz and 121, respectively. ^{1}H and ^{13}C NMR spectra were referenced to the residual solvent peak while ^{31}P spectra were referenced to external 85% H$_3$PO$_4$. ESI-HRMS, in positive polarity, were collected on a Bruker II BioTOF mass spectrometer. A Finnigan MAT 95 double-focusing mass spectrometer with BE-geometry was used to collect EI-HRMS with sample introduction using a solids probe. Infrared (IR) spectra were collected with a Midac M series spectrometer.

Electrochemistry. CV experiments were performed with a BAS 100B electrochemical analyzer consisting of a Pt auxiliary electrode, a glassy carbon working electrode (A = 0.07 cm^{-1}), and a Ag$^+$/AgCl reference electrode containing 1.0 M KCl. The three-compartment cell was filled with dry DMF containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as the supporting electrolyte. The 5 mL working compartment, separated from the reference compartment by a modified Luggin capillary, was bubbled with argon prior to all experiments to deoxygenate the solution. Background cyclic voltammograms of the electrolyte solution were recorded prior to addition of the sample. Potentials were reported versus Ag$^+$/AgCl without correction for the junction potential. The E$^{o\prime}$ value for the ferrocenium/ferrocene couple under the stated conditions was +0.42 V. A scan rate of 100 mV/s and sample concentration of 0.5 mM were used.

X-ray Crystallography. Crystal structures of **1-BPh$_4$**, **2-Cl**, **3**, **4**, and **5** were collected using a Siemens or Bruker SMART Platform CCD diffractometer at 173(2) K using a graphite monochromator and Mo Kα radiation. Structures were solved using SHELXS-97[53] or SIR-97[54] and refined with SHELXL-97.[53] Crystallographic data for these complexes are given in Table 1.

Complexes **1-BPh$_4$** and **4** were each modeled as a racemic twin using a SHELXL TWIN command as 29.7% and 18.6% of the opposite enantiomer, respectively. Complex **2-Cl** showed disorder in the dmpe-CH$_2$ moieties and was modeled over two positions (52.5:47.5).

Complex **3** displayed a twisting disorder about the ^{t}SiP$_3$ ligand requiring the CH$_2$ components to be modeled over two positions (73:27 and 87:13 for the two asymmetric units, respectively). A warning for close atom contact between a PMe$_2$ hydrogen and a CH$_2$ hydrogen, both on ^{t}SiP$_3$, exists in checkCIF/PLATON for **3**. The methyl group could not be modeled over two positions, so the hydrogen close atom contact, insignificant to reactivity and structural features of interest, remains as an artifact of the disorder.

^{t}BuSi(CH$_2$PMe$_2$)$_3$ (^{t}SiP$_3$). Procedures for the preparation of tris(dimethylphosphinomethyl)-tertbutylsilane (or "trimpsi") have previously been published.[55,56] The procedure used for the synthesis of SiP$_3$ ligand was employed for the preparation of ^{t}SiP$_3$.[54] In brief, ^{t}BuSiCl$_3$ (12.4 g, 64.7 mmol) dissolved in 100 mL of Et$_2$O was added to the highly pyrophoric solid LiCH$_2$PMe$_2$[57] (18.0 g, 219 mmol) at −78 °C as described. The final colorless oil was passed through a silica column and dried in vacuo before collection. The oil was distilled at 140 °C under active vacuum (5.27 g, 16.9 mmol, 26.2% yield). Product decomposition was observed above 150 °C. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ 0.81 (br s, 6H, CH$_2$-^{t}SiP$_3$); 1.01 (br s, 18H, PMe$_2$); 1.16 (s, 9H, ^{t}Bu-Si). ^{31}P{^{1}H} (121 MHz, C$_6$D$_6$, 25 °C): δ −54.21 (s, ^{t}SiP$_3$).

[(^{t}SiP$_3$Fe)$_2$(μ-Cl)$_3$][Cl]. The procedure described by Boncella[19] was employed to synthesize the ^{t}SiP$_3$-analogue of [(SiP$_3$Fe)$_2$(μ-Cl)$_3$][Cl]) (>95% yield). ^{1}H NMR (300 MHz, CD$_3$CN, 25 °C): δ ppm 0.63 (m, 12H, CH$_2$-^{t}SiP$_3$); 0.80 (s, 18H, ^{t}Bu-Si); 1.53 (m, 36H, Me-^{t}SiP$_3$). ^{31}P{^{1}H} NMR (121 MHz, CD$_3$CN, 25 °C): δ ppm 44.15 (s, ^{t}SiP$_3$).

[^{t}SiP$_3$(dmpm)FeCl][X] (1-Cl, 1-BPh$_4$). [(^{t}SiP$_3$Fe)$_2$(μ-Cl)$_3$][Cl] (0.698 g, 0.798 mmol) was combined with bis(dimethylphophino)methane (dmpm) (275 μL, 1.74 mmol) in CH$_2$Cl$_2$ (40 mL) and placed into a 100 mL sealed reaction flask. The reaction was heated to 60 °C overnight. The reaction solution was filtered, concentrated to a solid, washed with CH$_2$Cl$_2$ (20 mL), and filtered again. The filtrate was concentrated to yield a clean dark pink solid (0.917 g, 1.59 mmol, 99% yield). The anion was exchanged from Cl$^-$ to BPh$_4^-$ by adding 1 equiv of NaBPh$_4$ to a solution of [^{t}SiP$_3$(dmpm)FeCl][Cl] in acetonitrile. The solution was filtered and concentrated to a solid. X-ray quality crystals were obtained from slow evaporation in acetonitrile at ambient temperature. ^{1}H NMR (300 MHz, CD$_3$CN, 25 °C): δ ppm 0.72 (d, J_{HP} = 2.3 Hz, 2H, CH$_2$-^{t}SiP$_3$); 0.91 (s, 9H, ^{t}Bu-Si); 1.0 (m, 4H, CH$_2$-^{t}SiP$_3$); 1.41 (d, J_{HP} = 5.1 Hz, 6H, Me-^{t}SiP$_3$); 1.49 (m, 12H, Me-^{t}SiP$_3$); 1.56 (m, 6H, Me-dmpm); 1.67 (m, 6H, Me-dmpm); 2.84 (q, J_{HP} = 11.2 Hz, 1H, CH$_2$-dmpm); 3.58 (q, J_{HP} = 12.8 Hz, 1H, CH$_2$-dmpm). ^{13}C{^{1}H} NMR (75 MHz, CD$_3$CN, 25 °C): δ ppm 5.04 (s, 2C, CH$_2$-^{t}SiP$_3$); 9.02 (m, 1C, C−Si); 9.97 (m, 1C, CH$_2$-^{t}SiP$_3$); 12.31 (t, J_{CP} = 14 Hz, 2C, PMe$_2$); 15.00 (t, J_{CP} = 13 Hz, 2C, PMe$_2$); 21.25 (m, 2C, PMe$_2$); 27.72 (br s, 5C, (CH$_3$)$_3$C−Si, PMe$_2$); 27.17 (d, J_{CP} = 23 Hz, 2C, PMe$_2$); 41.04 (t, J_{CP} = 25 Hz, 1C, CH$_2$-dmpe). ^{31}P{^{1}H} NMR (121 MHz, CD$_3$CN, 25 °C): δ ppm −10.23 (m, 2P, dmpm); 25.05 (m, 2P, ^{t}SiP$_3$); 35.27 (tt, J_{PP} = 43, 56 Hz, 1P, ^{t}SiP$_3$). ESI-HRMS-TOF (m/z): [M − Cl]$^+$ calcd for C$_{18}$H$_{47}$ClFeP$_5$Si, 537.1173; found, 537.1197.

[SiP$_3$(dmpe)FeCl][Cl] (2-Cl). This complex was prepared as described above for **1-Cl**, using [(SiP$_3$Fe)$_2$(μ-Cl)$_3$][Cl] (0.240 g, 0.31 mmol) and dmpe (100 μL, 0.60 mmol) in CH$_2$Cl$_2$ (20 mL) to

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give a pink solid (0.320 g, 0.587 mmol, 97% yield). ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ ppm −0.35 (s, 3H, Me-Si); 0.88 (d, J_{HP} = 12 Hz, 2H, CH$_2$−SiP$_3$); 1.14 (m, 4H, CH$_2$−SiP$_3$); 1.44 (d, J_{HP} = 7.2 Hz, 6H, Me-SiP$_3$); 1.52 (d, J_{HP} = 7.5 Hz, 6H, Me-SiP$_3$); 1.58 (d, J_{HP} = 6.0 Hz, 6H, Me-SiP$_3$); 1.69 (d, J_{HP} = 5.4 Hz, 6H, Me-dmpe); 1.74 (m, 6H, Me-dmpe); 2.06 (m, 4H, CH$_2$-dmpe). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 25 °C): δ ppm −0.98 (s, 1C, Me-Si); 14.54 (s, 1C, CH$_2$−SiP$_3$); 15.50 (t, J_{CP} = 13.7 Hz, 2C, CH$_2$−SiP$_3$); 17.34 (s, 2C, PMe$_2$); 19.54 (t, J_{CP} = 13.2 Hz, 2C, PMe$_2$); 21.33 (t, J_{CP} = 8.6 Hz, 2C, PMe$_2$); 25.44 (m, 2C, PMe$_2$); 28.72 (d, J_{CP} = 21 Hz, 2C, PMe$_2$); 30.82 (t, J_{CP} = 19.4 Hz, 2C, CH$_2$-dmpe). ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$, 25 °C): δ ppm 17.46 (m, see Results for coupling constants, 2P, SiP$_3$); 27.33 (tt, J_{PP} = −53, −41 Hz, 1P, SiP$_3$); 41.98 (m, see Results for coupling constants, 2P, dmpe). ESI-HRMS-TOF (*m*/*z*): [M − Cl]$^+$ calcd for C$_{16}$H$_{43}$ClFeP$_5$Si, 509.0855; found, 509.0858.

^{t}SiP$_3$(dmpm)Fe (3). To a suspension of **1-Cl** (0.456 g, 0.795 mmol) in toluene (50 mL) in a 100 mL round-bottom flask were added an excess of sodium metal and a drop of metallic mercury. The reaction was allowed to stir for 3 days, until the solution was dark red-brown in color. The solution was concentrated to a solid, extracted with hexanes, filtered (2×), and the solvent removed in vacuo to a yield a pure red solid (0.393 g, 0.782 mmol, 98% yield). X-ray quality crystals were obtained from toluene at −40 °C. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ ppm 0.65 (m, 6H, CH$_2$-^{t}SiP$_3$); 0.88 (s, 9H, ^{t}Bu-Si); 1.46 (t, J_{HP} = 3.9 Hz, 12H, Me-dmpm); 1.49 (br s, 18H, Me-^{t}SiP$_3$); 2.88 (t, J_{HP} = 10.5 Hz, 2H, CH$_2$-dmpm). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$, 25 °C): δ ppm 15.51 (br s, 3C, CH$_2$-^{t}SiP$_3$); 26.69 (m, 1C, C−Si); 27.09 (s, 4C, PMe$_2$); 29.98 (m, 3C, (*C*H$_3$)$_3$C−Si); 32.75 (m, 6C, PMe$_2$); 52.07 (m, 1C, CH$_2$-dmpm). ^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$, 25 °C): δ ppm −21.01 (q, J_{PP} = 17.5 Hz, 2P, dmpm); 22.46 (t, J_{PP} = 17.5 Hz, 3P, ^{t}SiP$_3$). EI-HRMS (70 eV) *m*/*z*: M$^+$ calcd for C$_{18}$H$_{47}$FeP$_5$Si, 502.1485; found, 502.1509.

SiP$_3$(dmpe)Fe (4). Complex **4** was prepared according to the method described for **3** except utilizing **2** (0.14 g, 0.26 mmol) in toluene (20 mL). Recrystallization in toluene produced crystals of the contaminant, (dmpe)$_5$Fe$_2$ (**5**), and a clean supernatant containing the desired material (0.065 g, 0.14 mmol, 52% yield). Red X-ray quality crystals of SiP$_3$(dmpe)Fe were isolated from toluene at −35 °C. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ ppm 0.07 (s, 3H, Me-Si); 0.72 (m, 6H, CH$_2$−SiP$_3$); 1.39 (pseudo t, "J_{HP}" = 3 Hz, 12H, Me-dmpe); 1.44 (br s, 18H, Me-SiP$_3$); 1.51 (m, 4H, CH$_2$-dmpe). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$, 25 °C): δ ppm 0.60 (pseudo q, "J_{CP}" = 6 Hz, 1C, Me-Si); 24.98 (s, 3C, CH$_2$−SiP$_3$); 28.37 (m, 2C, PMe$_2$); 30.18 (t, J_{CP} = 27 Hz, 2C, PMe$_2$); 32.82 (m, 6C, PMe$_2$); 36.31 (td, J_{CP} = 26, 3.5 Hz, 2C, CH$_2$-dmpe). ^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$, 25 °C): δ ppm 15.8 (t, J_{PP} = 11.6 Hz, 3P, SiP$_3$); 58.4 (q, J_{PP} = 11.6 Hz, 2P, dmpe). EI-HRMS (70 eV) *m*/*z*: M$^+$ calcd for C$_{16}$H$_{43}$FeP$_5$Si, 474.1172; found, 474.1200.

(dmpe)$_5$Fe$_2$ (5). This previously characterized complex[32] was isolated as a byproduct in the preparation of **4**. X-ray quality crystals were obtained from toluene. See preparation of **4** above. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ ppm 1.03 (d, J_{HP} = 3 Hz, 12H, Me-dmpe); 1.28 (br s, 24H, Me-dmpe); 1.54 (m, 4H, CH$_2$-dmpe); 1.57 (br s, 24H, Me-dmpe); 1.75 (m, 16H, CH$_2$-dmpe). ^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$, 25 °C): δ ppm 8.39 (t, J_{PP} = 9.4 Hz, 2P, bridging dmpe); 61.44 (d, J_{PP} = 9.4 Hz, 4P).

[^{t}SiP$_3$(dmpm)FeH][PF$_6$] (6). Prepared according the procedure described by Howarth[21] for the preparation of [SiP$_3$(dmpe)-FeH][PF$_6$] using **3** and NH$_4$PF$_6$ to give a orange solid (0.062 g, 0.123 mmol, 82% yield). ^{1}H NMR (300 MHz, CD$_3$CN, 25 °C): δ ppm −10.93 (dtt, J_{HP} = 13, 51, 51 Hz, 1H, Fe−H); 0.75 (d, J_{HP} = 3.3 Hz, 2H, CH$_2$-^{t}SiP$_3$); 0.86 (s, 9H, ^{t}Bu-Si); 0.88 (m, 4H, CH$_2$-^{t}SiP$_3$); 1.33 (m, 6H, Me-^{t}SiP$_3$); 1.47 (t, J_{HP} = 3.7 Hz, 6H, Me-dmpm), 1.57−1.64 (18H, overlapping m, Me-^{t}SiP$_3$, Me-dmpm); 3.04 (m, 2H, CH$_2$-dmpm). ^{31}P{^{1}H} NMR (121 MHz, CD$_3$CN, 25 °C): δ ppm −0.5 (m, 2P, dmpm); 20.7 (tt, J_{PP} = 33, 39 Hz, 1P, ^{t}SiP$_3$); 33.7 (m, 2P, ^{t}SiP$_3$). ESI-HRMS-TOF (*m*/*z*): [M − PF$_6$]$^+$ calcd for C$_{18}$H$_{48}$FeP$_5$Si, 503.1563; found, 503.1555. IR (Nujol mull, cm^{-1}) 1831, Fe−H stretch.

SiP$_3$FeH((*o*-C$_6$H$_4$)PPh$_2$) (7). To a solution of [(SiP$_3$Fe)$_2$(μ-Cl)$_3$][Cl] (0.34 g, 0.44 mmol) and PPh$_3$ (0.30 g, 1.13 mmol) in toluene (20 mL) in a 30 mL sealed flask were added an excess of sodium and a drop of metallic mercury. The solution was sonicated for 10 min and then stirred 4 days until red-brown in color. The reaction solution was filtered and washed with petroleum ether (20 mL). The filtrate was then concentrated to a solid. The solid was extracted into pentane, the resultant solution filtered, and the filtrate concentrated to approximately 4 mL. This solution was placed in the freezer (−35 °C) overnight yielding a brown solid (0.14 g, 0.24 mmol, 27% yield). ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ ppm −7.01 (dddd, J_{HP} = 27, 51, 51, 63 Hz, 1H, Fe−H); −0.07 (s, 3H, Me-Si); 0.20 (dd, J_{HP} = 6.9, 13.2 Hz, 1H, CH$_2$−SiP$_3$); 0.27 (m, 1H, CH$_2$−SiP$_3$); 0.36−0.52 (overlapping m, 3H, CH$_2$−SiP$_3$); 0.67 (dd, J_{HP} = 7.8, 14.4 Hz, 1H, CH$_2$−SiP$_3$); 1.18 (d, J_{HP} = 4.8 Hz, 3H, Me-SiP$_3$); 1.34 (d, J_{HP} = 6.0 Hz, 3H, Me-SiP$_3$); 1.52 (d, J_{HP} = 6.0 Hz, 3H, Me-SiP$_3$); 1.65 (d, J_{HP} = 7.5 Hz, 3H, Me-SiP$_3$); 6.60 (dd, J_{HP} = 6.6, 11.4 Hz, 1H, C$_6$H$_4$); 6.86 (t, J_{HP} = 6.6 Hz, 1H, C$_6$H$_4$); 7.0−7.7 (overlapping m, 8H, PPh$_2$); 7.66 (t, J_{HP} = 6.3 Hz, 2H, PPh$_2$); 8.53 (t, J_{HP} = 8.1 Hz, 2H, PPh$_2$). ^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$, 25 °C): δ ppm 10.1 (m, 1P, PMe$_2$); 22.6 (m, 1P, PPh$_2$); 31.87 (m, 1P, PMe$_2$); 41.6 (m, 1P, PMe$_2$).

SiP$_3$FeH(CH$_2$PMe$_2$) (8). To a solution of [(SiP$_3$Fe)$_2$(μ-Cl)$_3$]-[Cl] (0.33 g, 0.42 mmol) in toluene (40 mL) in a 100 mL sealed flask were added an excess of sodium and a drop of mercury. Under a flow of N$_2$, PMe$_3$ (100 μL, 97 mmol) was added and the flask sealed. The reaction was stirred for 3 days until green-brown in color, concentrated to a solid, and extracted into hexanes. The resultant solution was filtered, and the filtrate concentrated to a solid. The solid was extracted into pentane and placed in the freezer (−35 °C). Attempts to purify the product through crystallization were unsuccessful. The ^{31}P{^{1}H} NMR spectrum was consistent with **8** as the major product. An internal standard (diethylphenylphosphine) was used to estimate the percent conversion to **8** as 37%. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ ppm −12.78 (dq, J_{HP} = 26, 60 Hz, 1H, Fe−H); −0.98 (m, 1H, PCH$_2$−Fe); −0.42 (m, 1H, PCH$_2$−Fe); 0.04 (s, 3H, Me-Si); 0.51 (m, 4H, CH$_2$−SiP$_3$); 0.61 (m, 2H, CH$_2$−SiP$_3$); 1.15 (d, J_{HP} = 5.4 Hz, 3H, PMe$_2$); 1.19 (d, J_{HP} = 5.1 Hz, 3H, PMe$_2$); 1.42 (m, 12H, Me-SiP$_3$); 1.54 (m, 6H, Me-SiP$_3$). ^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$, 25 °C): δ ppm −17.36 (m, 1P, PMe$_2$); 27.5 (m, 1P, SiP$_3$−PMe$_2$); 37.6 (m, 1P, SiP$_3$−PMe$_2$); 43.8 (m, 1P, SiP$_3$−PMe$_2$).

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Supporting Information Available: Synthesis and NMR characterization of complexes **^{t}SiP$_3$-2** and **^{t}SiP$_3$-4**, ORTEP diagrams (showing disorder with methyl groups removed) for complexes **1**−**5** and CIF files for complexes **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.