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A Tertiary Carbon–Iron Bond as an $Fe^{I}Cl$ Synthon and the Reductive Alkylation of Diphosphine-Supported Iron(II) Chloride Complexes to Low-Valent Iron

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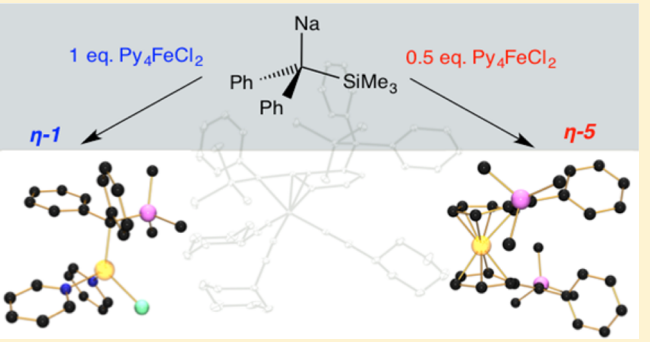
Supporting Information

ABSTRACT: Ligand-induced reduction of ferrous alkyl complexes via homolytic cleavage of the alkyl fragment was explored with simple chelating diphosphines. The reactivities of the sodium salts of diphenylmethane, phenyl(trimethylsilyl)methane, or diphenyl(trimethylsilyl)methane were explored in their reactivity with $(py)_4FeCl_2$. A series of monoalkylated salts of the type $(py)_2FeRCl$ were prepared and characterized from the addition of 1 equiv of the corresponding alkyl sodium species. These complexes are isostructural and have similar magnetic properties. The double alkylation of $(py)_4FeCl_2$ resulted in the formation of tetrahedral high-spin iron complexes with the sodium salts of diphenylmethane and phenyl(trimethylsilyl)methane that readily decomposed. A bis(cyclohexadienyl) sandwich complex was formed with the addition of 2 equiv of the tertiary alkyl species sodium diphenyl(trimethylsilyl)methane. The addition of chelating phosphines to $(py)_2FeRCl$ resulted in the overall transfer of Fe(I) chloride concurrent with loss of pyridine and alkyl radical. $(dmpe)_2FeCl$ was synthesized via addition of 1 equiv of sodium diphenyl(trimethylsilyl)methane, whereas the addition of 2 equiv of the sodium compound to $(dmpe)_2FeCl_2$ gave the reduced Fe(0) nitrogen complex $(dmpe)_2FeN_2$. These results demonstrate that iron–alkyl homolysis can be used to afford clean, low-valent iron complexes without the use of alkali metals.

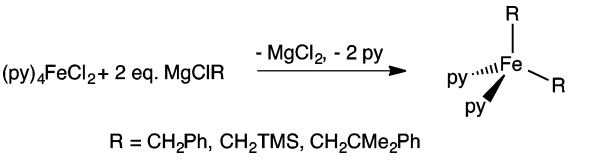


INTRODUCTION

Ferrocene stands as the prototypical organoiron complex, readily synthesized and persistent under ambient conditions.[1] The half-sandwich Fp derivatives (cyclopentadienyliron dicarbonyl) of the type Fp(X), where X is a one-electron donor, have also been extensively studied. These cyclopentadienyl-supported iron complexes owe their stability to strong field ligands, an electronically saturated 18-electron count at the metal center, and a saturated coordination sphere.[1a,2] Outside of cyclopentadienyl chemistry, iron alkyl compounds have remained relatively uncommon. Burgeoning recent interest in iron alkyl complexes can be traced to the discovery of base-metal-centered olefin polymerization catalysts of Brookhart and Gibson.[3] The original discovery showed that bis(imino)-pyridine chelates of iron dihalide, when combined with an excess of MAO (methyl aluminoxane), yielded ethylene polymerization catalysts that either produced linear high density polyethylene[4] or ethylene oligamers with a nearly ideal Schultz–Flory distribution.[3a,5] However, the nature of the catalytically competent species of the "activated" iron complex remained elusive and was a contentious topic for many years. In the case of bis(imino)pyridine-supported catalysis, initial reports supported by EPR and Mössbauer spectroscopy implicated a ferric (Fe(III)) complex as the active species under catalytic conditions.[6] Later studies described the synthesis and ethylene polymerization activity of bis(imino)-pyridine-supported ferrous (Fe(II)) monoalkyl cations, challenging the previous description of the active species.[7] This conflict in assignment of the active species has led researchers to investigate complexes with iron–alkyl σ bonds more actively in recent years.

While investigating methods of synthesizing bis(imino)-pyridine-supported iron dialkyl compounds, Cámpora and co-workers discovered the synthesis of an easily accessible iron dialkyl supported simply by two pyridine ligands (Scheme 1).[8] Reactions of the readily available tetrakis(pyridine)iron(II) chloride complex $(py)_4FeCl_2$ with 2 equiv of an alkyl Grignard give a practical source of "Fe-$(alkyl)_2$" when the corresponding

Scheme 1. First Reported Synthesis of Bis(pyridine)iron Dialkyl Complex



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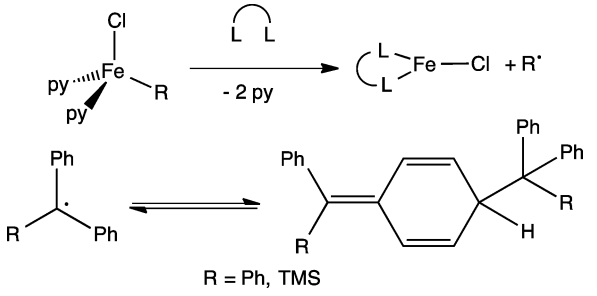
alkyl group is a neosilyl, neophyl, or benzyl group. An investigation by the Chirik group also led to the isolation of the monoalkyl monochloride derivatives $(py)_2Fe(R)Cl$, as well as obseration of the loss of a neopentyl fragment upon addition of bis(imino)pyridine chelate to either $(py)_2Fe(neopentyl)_2$ or $(py)_2Fe(neopentyl)(neosilyl)$, yielding an iron(I) species.[9] These results indicate that alkyl species of iron may provide good synthetic routes to low-valent iron centers, obviating the use of alkali metals or other aggressive reducing agents.

Many groups have taken advantage of the utility of Cámpora's reagent to substitute a variety of chelates onto the iron center.[10] Reports of such reactivity have until now been limited to primary (1°) metallo-carbon centers, leaving the alkyl−iron bond intact. This report utilizes the methods of Cámpora to investigate the reaction of $(py)_4FeCl_2$ with bulkier alkyl sodium reagents of 2° and 3° carbon centers in order to obtain low-valent iron species. Tertiary carbon moieties such as triphenylmethyl and diphenyl(trimethylsilyl)methyl are particularly attractive as radical leaving groups because they are sterically demanding groups that form relatively stable radicals, qualities which may facilitate reduction via metal−alkyl bond cleavage. The formation of tertiary radicals may minimize possible side reactions,[11] and the reactions can be followed by observing the formation of the known Gomberg dimer like products of radical coupling (Scheme 2).[12]

Scheme 2. Proposed Reactivity of the Iron−Tertiary Alkyl Bond

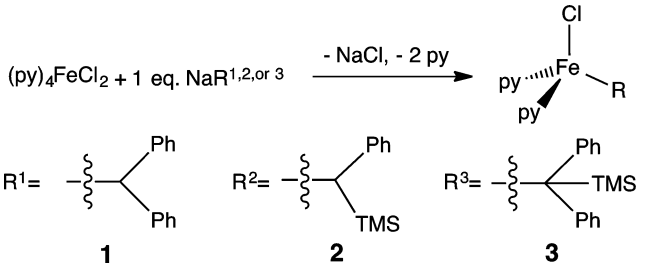


Low-valent, dinitrogen-bound iron centers continue to generate interest for the analogy drawn to the Haber−Bosch process. Herein we investigate the reactivity of 2° and 3° sodium alkyls with $(py)_4FeCl_2$ in order to explore the ability of $(py)_2Fe(R)Cl$ to act as an Fe(I) source upon chelation of bidentate phosphine ligands. Secondary and tertiary alkyls were investigated as the alkyl moiety to ensure dealkylation, with an emphasis placed on 3° carbon centers. The tertiary alkyl salt was also used in reactivity studies with iron complexes supported by the chelating diphosphine ligands dmpe (1,2-(dimethylphosphino)ethane) and dppene (*cis*-1,2-(diphenylphosphino)ethylene). The results from these investigations indicate that bulky alkyl groups prove useful in obtaining mono- or zerovalent iron complexes with concomitant loss of alkyl radical. Although the use of reductive alkylations at iron centers is known,[13] the isolation of an Fe(I) synthon is a useful development in low-valent iron chemistry.

RESULTS AND DISCUSSION

Alkylation of $(py_4)FeCl_2$ with 2° and 3° Carbon Alkyl Sodium Salts. Addition of 1 equiv of the sodium salt of diphenylmethane, phenyl(trimethylsilyl)methane, or diphenyl(trimethylsilyl)methane to $(py)_4FeCl_2$ resulted in the formation of the corresponding high-spin tetrahedral dipyridine iron alkyl chloride complexes $(py)_2FeRCl$ (**1**, R = Ph_2CH; **2**, R = Ph(TMS)CH; **3**, R = $Ph_2C(TMS)$; TMS = trimethylsilyl) (Scheme 3). These reactions were performed either in benzene

Scheme 3. Synthesis of Bis(pyridine)iron Chloro Alkyl Complexes from Sodium Alkyl Reagents



at room temperature or in cold (−35 °C) diethyl ether by the addition of the solid alkyl sodium salt with negligible difference in purity and yield. Isolation of **2** was performed by filtration through Celite and removal of the solvent. Purification by recrystallization from fluorobenzene layered with hexane at −35 °C gave **2** as dark orange-red crystals. **1** was worked up in the same fashion but decomposed upon attempted crystallization. Rinsing with hexane afforded **1** as a slightly impure solid. Both **1** and **2** quickly decomposed to insoluble material as solids at room temperature. Filtration of **3** through Celite followed by slow evaporation of solvent under reduced pressure gave a bright orange crystalline precipitate. Magnetic susceptibilities of **1**−**3** furnished magnetic moments of 4.82, 4.68, and 4.73 μ_B, respectively. These values are close to the spin-only value of four unpaired electrons (4.90 μ_B) expected for a high-spin iron(II) complex. The ^{1}H NMR spectra of **1**−**3** exhibited broad resonances over a 200 ppm range. These chemical shift ranges are in agreement with the monoalkyl chloride complexes reported by Chirik and co-workers.[9]

The solid-state structures of **2** and **3** were determined via single-crystal X-ray diffraction studies (Figure 1). Attempts to grow crystals of **1** suitable for X-ray diffraction were unsuccessful. Iron−carbon bond lengths for **2** and **3** were found to be 2.072 and 2.093 Å, respectively. These are comparable to the iron−carbon bond lengths reported by Cámpora for the dialkyl species $(py)_2Fe(neophyl)_2$, 2.091 and 2.090 Å, respectively, for the two neophyl groups.[8] The differences in steric demand of the 2° versus the 3° carbon centers do not lead to significant changes in the iron−alkyl bond lengths.

Addition of 2 equiv of either sodium diphenylmethane or sodium phenyl(trimethylsilyl)methane to $(py)_4FeCl_2$ in diethyl ether or benzene resulted in the formation of unstable paramagnetic iron complexes. ^{1}H NMR spectra obtained directly following synthesis confirm the formation of new species, with resonances distinct from those of **1** and **2**, respectively. At room temperature both complexes decomposed within hours to insoluble dark material concurrent with the formation of diphenylmethane or benzyltrimethylsilane, respectively. The initial products from this reaction are assigned as the dialkyl $(py)_2FeR_2$ complexes (**4**, R = Ph_2CH; **5**, R = Ph(TMS)CH) (Scheme 4). Attempts to further characterize these compounds were hindered by the facile decomposition of these materials. The addition of 2 equiv of sodium diphenyl(trimethylsilyl)methane to $(py)_4FeCl_2$ resulted in the formation

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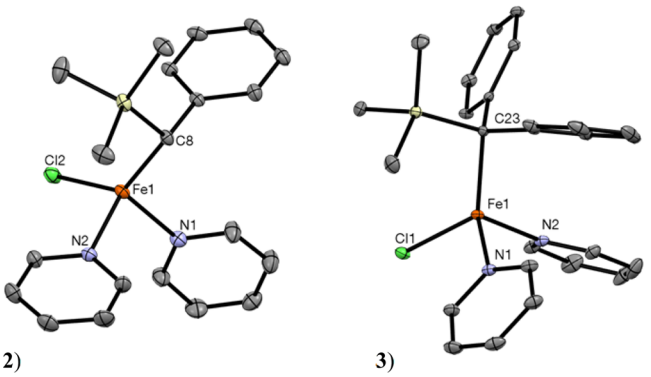
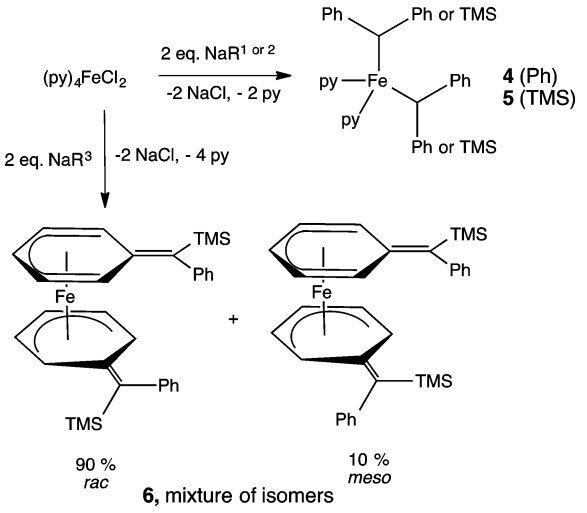


Figure 1. Solid-state structures of **2** and **3**, presented with 50% probability ellipsoids. Solvent molecules and hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and bond angles (deg) for **2**: Fe(1)−C(1) = 2.073(2), Fe(1)−N(1) = 2.115(2), Fe(1)−N(2) = 2.117(2), Fe(1)−Cl(1) = 2.284(1); N(1)−Fe(1)−C(1) = 108.62(7), N(2)−Fe(1)−C(1) = 108.03(7), N(1)−Fe(1)−N(2) = 99.59(7), N(1)−Fe(1)−Cl(1) = 108.03(7), C(1)−Fe(1)−Cl(2) = 130.70(5). Selected bond lengths (Å) and bond angles (deg) for **3**: Fe(1)−C(1) = 2.093(2), Fe(1)−N(1) = 2.129(2), Fe(1)−N(2) = 2.129(2), Fe(1)−Cl(1) = 2.3058(1); N(1)−Fe(1)−C(1) = 114.17(8), N(2)−Fe(1)−C(1) = 112.95(8), N(1)−Fe(1)−N(2) = 100.50(8), N(1)−Fe(1)−Cl(1) = 102.08(6), C(1)−Fe(1)−Cl(2) = 123.67(7).

Scheme 4. Dialkylations of $(py)_4FeCl_2$ with Na-R^{1-3}



of the dark red-brown iron complex **6** (Scheme 4). ^{1}H NMR spectroscopy revealed **6** to be a mixture of isomers. The isomers of **6** are diamagnetic, each with a diagnostic pattern of resonances between 3.7 and 4.6 ppm (Figure 2), consisting of three triplets and two doublets, consistent with an η^5-cyclohexadienyl ligand. This region integrated against the trimethylsilyl fragment and aromatic region suggests an iron sandwich compound containing solely two diphenyl(trimethylsilyl)methane alkyl ligands, each with an η^5-cyclohexadienyl group coordinated to the iron center. This arrangement provides a ferrocene-like 18-electron compound. The added stability from the formation of a tetrasubstituted olefin allows for the 3° carbanion to undergo this hapticity shift from η^1 to η^5. The secondary carbon centers in compounds **4** and **5** remain η^1 and are more susceptible to degradation.

Of the two isomers of **6** formed in the reaction, we assign the major isomer as the C_2 (*rac*) isomer, since the bulky

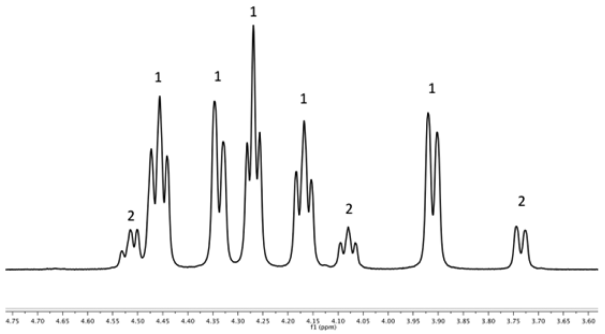


Figure 2. Resonances observed in the ^{1}H NMR spectrum between 3.7 and 4.6 ppm, showing the two isomers of **6**. The minor isomer is labeled 2, and two resonances are hidden under the resonances of isomer 1.

trimethylsilyl groups are anti to one another, and the minor product (10%) as the C_s (*meso*) isomer. A solid-state structure was obtained to unambiguously characterize the complex, the C_2 complex being the observed isomer in the solid state (Figure 3). Analogous bis(cyclohexadienyl)iron complexes have previously been reported from the reaction of either cyclohexadienyl or 6,6-dimethylcyclohexadienyl potassium and iron chloride in THF. *exo*-Methylene derivatives have classically been synthesized via deprotonation of alkyl-substituted η^6-aryl iron cations of mixed-sandwich cyclopentadienyl compounds.[14]

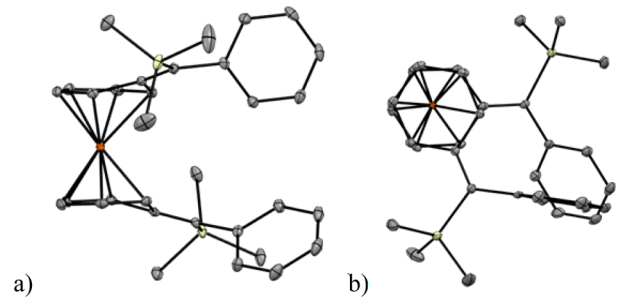


Figure 3. Side view (a) and top-down view (b) of the solid-state structure of **6** shown with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Attempts to disrupt the sandwich complex **6** and change the hapticity of one of the alkyl ligands from η^5 to η^1 were unsuccessful. The addition of the chelating phosphines dmpe (1,2-(dimethylphosphino)ethane) and dppene (*cis*-1,2-(diphenylphosphino)ethylene) resulted in no reaction, even with extended reaction times. Over the course of several days **6** showed slight decomposition (~10%) to colloidal iron and alkane with no formation of a new organometallic iron product. Heating the reaction mixture to 70 °C expedited the decomposition. The addition of either cyclohexyl or *tert*-butyl isocyanide did not yield a new product; however, the C_2 and C_s isomers reached a roughly 50:50 ratio following addition of the isocyanide, suggestive of a ligand-induced isomerization process (Supporting Information).

Given the hapticity shift of the tertiary alkyl upon double alkylation of iron to form **6**, we attempted to induce a hapticity shift using the monoalkylated iron complex **3**. Upon addition of cyclohexyl isocyanide to **3** in THF, the bright orange solution turned dark red-brown. ^{1}H NMR investigation of the reaction mixture indicated a large quantity of the dimerized alkyl radical 1-diphenyl(trimethylsilyl)methyl-4-(phenyl(trimethylsilyl)-

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methyl)benzene[12] and diphenyl(trimethylsilyl)methane, along with broad peaks indicating the presence of paramagnetic species. Crystallization of the hexane-soluble material produced both a colorless solid and a small quantity of an orange crystalline material. Single-crystal X-ray diffraction measurements of the orange crystalline material yielded a structure demonstrating the hapticity shift of the starting iron compound to form, in very low yield, the piano-stool tris(isocyanide) iron complex **11** (Figure 4). Attempts to increase the quantity and purity of **11** failed, as the complex displayed solubility properties similar to those of the free alkane.

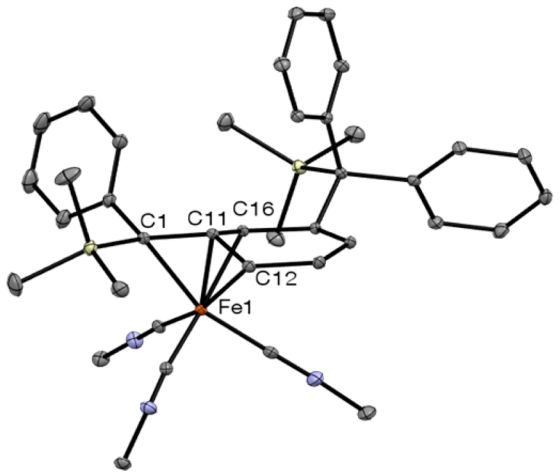
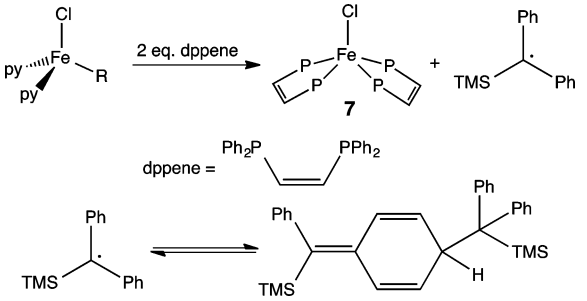


Figure 4. Complex **11** shown with 50% probability ellipsoids. Cyclohexyl groups of the isocyanide ligands and hydrogen atoms are omitted for clarity.

Complex **11** bears a dimerized diphenyl(trimethylsilyl)methane, although the dimerization occurs at the meta position of the aryl ring rather than at the typical para position. The iron coordinates in an η^4 fashion to the aryl/*exo*-methylene group of the alkyl, but due to the meta carbon dimerization, the aryl group bears a diradical, making this moiety a four-electron donor, giving the iron an 18-electron configuration. Similar 18-electron iron piano-stool complexes bearing carbonyl and trimethylenemethane ligands have been known for some time and represent a seminal example of how a metal center can stabilize a very reactive organic species through complex formation.[15] This is the first example to our knowledge of a carbonyl-free derivative. Angles and bond distances, as well as simplified representations of the four-atom, four-electron alkyl ligand can be found in the Supporting Information.

The reductive dealkylation of **3** was pursued using chelating diphosphines to induce homolysis of the iron−alkyl bond. The addition of 1 equiv of dppene resulted in the formation of 1/2 equiv of $(dppene)_2FeCl$ (**7**), with starting material composing the remaining iron. Complete conversion to $(dppene)_2FeCl$ could be achieved by adding 2 equiv of dppene to **3**, yielding **7** and a tertiary radical (Scheme 5). Formation of $(dppene)_2FeCl$ arises from loss of the alkyl fragment, most likely as a tertiary carbon radical. Diphenyl(trimethylsilyl)methane and the radical dimerization product are observed by ^1H NMR spectroscopy. Broad resonances of $(dppene)_2FeCl$ compose the remainder of the spectrum. Performing the reaction in toluene-d_8 did not yield deuterium incorporation into the alkane. We are not certain of the source of the protons but feel that small quantities of adventitious water on the glassware or in the

Scheme 5. Addition of dppene to 3 Results in the Formation of 7 and a Tertiary Radical



solvent are responsible for the amount of diphenyl(trimethylsilyl)methane observed. Verification of the formation of $(dppene)_2FeCl$ was achieved by comparison to an independently prepared sample made via reduction of $(dppene)_2FeCl_2$ with 1 equiv of sodium metal. Compound **7** could also be synthesized by the comproportionation of $(dppene)_2FeCl_2$ with $(dppene)_2Fe(N_2)$ (**8**). Compound **8** was synthesized by reducing $(dppene)_2FeCl_2$ with 2 equiv of sodium in THF under N_2 with naphthalene as a catalyst.

Despite continuing interest in low-valent diphosphine-supported iron compounds, the dppene-supported iron(I) chloride and the iron(0) dinitrogen complex have yet to be reported in the literature, although a very similar iron(I) monochloride compound has previously been reported.[16] Magnetic susceptibility measurements of **7** using the Evans method yielded an effective magnetic moment of 2.1 μ_B, slightly higher than the spin-only value expected for a low-spin iron(I) compound. The structure of $(dppene)_2FeCl$ was unambiguously assigned by single-crystal X-ray diffraction. The solid-state structure of **7** shows a distorted-trigonal-bipyramidal structure, with the equatorial plane containing the chlorine ligand. The solid-state structure of **8** was also obtained and shows further distortion from an ideal TBP geometry, with the equatorial P(2)−Fe(1)−P(4) angle increasing to over 30°. Further discussion, distances, and angles regarding the solid-state structures of both **7** and **8** are given (Supporting Information) along with the corresponding solid-state structures (Figure 5). Complex **8** proved difficult to isolate, as it was prone to decomposition and displayed solubility characteristics similar to those of free dppene. Attempts to crystallize **8** from the mother liquor or recrystallize isolated material yielded a light brown powder that did not display the characteristic N_2 stretch in the IR spectra. Only once did a crystallization of the mother liquor yield dark red crystals suitable for X-ray diffraction (Supporting Information). A comparison of N_2 stretches of analogous bis(dichelating)phosphine iron(0) complexes is given (Table 1), yielding a metric that illustrates a trend in the relative electron-donating power of the supporting phosphine ligands.

The results from the investigation with dppene, specifically the difficulty in isolating the Fe(0) dinitrogen adduct, led us to examine the reactivity with dmpe-supported iron. The addition of 2 equiv of dmpe to **3** under the same conditions as were employed with dppene resulted in the formation of $(dmpe)_2FeCl_2$ along with a dark uncharacterized precipitate. This differing reactivity with dmpe moved us to investigate the reactivity of sodium diphenyl(trimethylsilyl)methane with $(dmpe)_2FeCl_2$ in order to obtain tractable, low-valent iron compounds. In addition, if the bulky diphenyl(trimethylsilyl)methane can bind to the metal center, it would more likely

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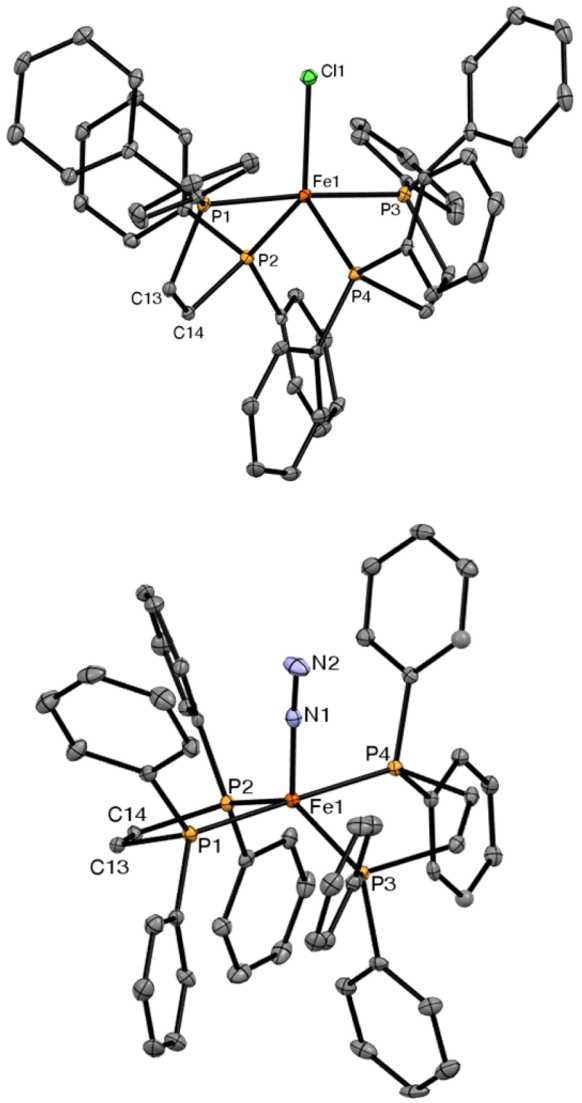

Figure 5. Solid-state structures of **7** (a) and **8** (b) shown with 50% probability ellipsoids. Hydrogen atoms and solvent molecules are omitted for clarity.

Table 1. Comparison of the N_2 Stretches of Zerovalent Bis(diphosphine) Iron Complexes

complex	N_2 stretch (cm^{-1})	d(N–N) (Å)
$dppe_2Fe(N_2)$[a]	2068	
$(dppene)_2Fe(N_2)$[b]	2021	1.125(5)
$(dmpe)_2Fe(N_2)$[b]	1976	1.133(7)
$(DMeOPrPE)_2Fe(N_2)$[c]	1966	
$depe_2Fe(N_2)$[d]	1955	1.139(13)

[a]Generated in situ; ref 18. [b]This work. [c]Reference 21a. [d]Reference 22.

coordinate to the sterically less demanding complex supported with dmpe rather than the more sterically crowded dppene-supported complex. The addition of 1 equiv of the tertiary sodium salt in diethyl ether at −30 °C resulted in the formation of a green powder that was tentatively assigned as the iron(I) monochloride complex $(dmpe)_2FeCl$ (**9**). Attempts to purify or analyze this green substance resulted in the isolation of either $(dmpe)_2FeCl_2$ or the zerovalent dinitrogen adduct $(dmpe)_2Fe(N_2)$, leading us to believe that the isolated green powder was a mixture of the two iron complexes.

The addition of 2 equiv of sodium diphenyl(trimethylsilyl)methane to $(dmpe)_2FeCl_2$ under the same conditions resulted in the formation of $(dmpe)_2Fe(N_2)$ in good yields. Spectroscopic characterization was consistent with previously reported $(dmpe)_2Fe(N_2)$.[17] $(dmpe)_2Fe(N_2)$ was proposed to be monomeric and IR spectroscopy in a benzene solution showed that it exhibits an N_2 stretch of 1976 cm^{-1}. However, when $(dmpe)_2FeN_2$ was crystallized from diethyl ether or hexane, it was determined to be the N_2 bridging diiron complex $((dmpe)_2Fe)_2(\mu\text{-}N_2)$ (**10**) (Supporting Information). A KBr pellet of crystallized **10** showed only negligible absorption at 1976 cm^{-1}, but a Raman spectrum of crystallized **10** yielded an intense Raman stretch at 1942 cm^{-1}. The solid-state structure was obtained, and despite significant twinning and enantiomeric disorder, a good model of **10** was found and reasonable structural parameters were obtained. The N_2 bond length of 1.133(7) Å is indicative of a nonreduced N_2 ligand.

A recent report by Field made use of zerovalent $(dmpe)_2Fe(N_2)$ as a means of producing ammonia from dinitrogen bound to an iron center, furthering the results of previous studies that also describe the formation of ammonia from dinitrogen complexes of zerovalent iron.[19] The report by Field rigorously excludes functionalization of the nitrogen ligand of $(dmpe)_2Fe(N_2)$ by protonation with HCl or triflic acid. Rather, a mechanism invoking dinitrogen activation via a strong electrophile (TMS-triflate), followed by addition of triflic acid, leads to the formation of ammonium salt. These results clarify earlier reports by Leigh where ammonium formation was observed upon the addition of acids to $(dmpe)_2Fe(N_2)$.[20] Reports by Tyler also indicate that ammonium is formed upon the addition of acids to $(DMeOPrPE)_2Fe(N_2)$ (DMeOPrPE = 1,2-[bis(dimethoxypropyl)phosphino]ethane).[21] In contrast with this work, similar investigations by Komiya using $depe_2Fe(N_2)$ did not yield formation of ammonia.[22] As the interest in nitrogen fixation with reduced iron centers continues, we feel that the solid-state structure may add to the discussion of the mechanism by introducing the possibility of the sterically accessible dmpe-supported iron of forming bimetallic complexes during the functionalization of dinitrogen, similar to what Tyler et al. have observed in their system.[20] Mechanistic investigations invoking a bimetallic pathway for N_2 activation with $(dmpe)_2Fe(N_2)$ have yet to be experimentally excluded.

SUMMARY/CONCLUSION

We have shown that bulkier 2° and 3° carbon centers can be added to an iron center analogously to the reaction pioneered by Cámpora using $(py)_4FeCl_2$ with the use of sodium alkylating reagents. The monoalkyl products of both 2° and 3° sodium alkyl reagents were successfully isolated and characterized. A ferrocene-like sandwich structure was obtained upon addition of 2 equiv of sodium diphenyl(trimethylsilyl)methane to $(py)_4FeCl_2$. This set of results confirms the potential for ambidentate coordination of diphenyl(trimethylsilyl)methide to a metal center. The double alkylations with the secondary alkyl salts resulted in the formation of presumed tetrahedral bis(pyridine)iron dialkyl complexes that readily decomposed over the course of hours. A hapticity shift from η^1 to η^4 occurred upon the addition of an alkyl isocyanide to **3**, resulting in the formation of the trimethylenemethane-like 18-electron complex **11**.

The addition of 2 equiv of dppene to **3** resulted in the formation of $(dppene)_2FeCl$ concurrent with the formation of

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the dimerized radical of the alkyl ligand. This overall transfer of "Fe−Cl" highlights the utility of simple iron alkyl structural types as monovalent iron precursors. Thus, **3** behaves as an isolable iron(I) synthon. Studies on the transfer of the iron(I) moiety are ongoing with a variety of ligand architectures. Furthermore, the reactivity of 2 equiv of the sodium salt with $(dmpe)_2FeCl_2$ resulted in the formation of the known complex $(dmpe)_2Fe(N_2)$. A solid-state structure revealed the bimetallic nature of the molecule that crystallized as $((dmpe)_2Fe)_2(\mu\text{-}N_2)$. Thus, NaR^3 can also be used as a reductive alkylation agent as well as in formation of the iron(I) synthon **3**.

EXPERIMENTAL SECTION

General Considerations. All air- and moisture-sensitive manipulations were carried out using standard vacuum line Schlenk techniques or in an MBraun drybox containing a purified nitrogen atmosphere. THF, diethyl ether, toluene, and *n*-hexane were dried over molecular sieves and shaved sodium before use. Pyridine was dried with molecular sieves and passed through neutral alumina before use. THF-d_8, DMSO-d_6, $CDCl_3$, and C_6D_6 were purchased from Cambridge Isotope Laboratories and dried over 4 Å molecular sieves. The chemicals dppene, dmpe, $FeCl_2$, diphenylmethane, benzyltrimethylsilane, sodium *tert*-butoxide, and *n*-butyllithium were purchased from Fisher Scientific and were used as received. The compounds $(py)_4FeCl_2$,[23] $(dppene)_2FeCl_2$,[24] $(dmpe)_2FeCl_2$,[25] Ph_2TMSCH,[26] $Ph_2TMSCNa$,[26] Ph_2CHNa,[27] and $PhTMSCHNa$[26] were synthesized according to published procedures.

^1H NMR, ^{13}C NMR, and ^{31}P NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer operating at 400.132, 100.627, and 161.978 MHz, respectively. All ^1H and ^{13}C NMR chemical shifts are reported relative to $SiMe_4$ using the ^1H (residual in the deuterated solvents) and ^{13}C chemical shifts of the solvent as a secondary standard. Paramagnetically shifted peaks are listed with the peak width at half-height (Hz). Infrared spectra were collected on a Thermo Scientific Nicolet iS10 spectrometer equipped with a Smart Omni transmission tool for the collection. Raman micro spectrometric measurements were collected using a DXRxi Raman Imaging Microscope. A 532 nm laser was focused on the sample using a 10× objective providing a spot size of 7 um. A spectral collection consisted of 100 scans at 0.2 s exposures to the laser operating at 0.1 mW.

Single crystals suitable for X-ray diffraction were coated with n-Paratone (dried under reduced pressure overnight at 100 °C) oil in a drybox, placed on a nylon loop, and then transferred to the goniometer head of a Bruker X8 APEX 2 diffractometer equipped with a molybdenum X-ray tube (λ = 0.71073 Å) or to a Bruker D8 Quest instrument equipped with a molybdenum X-ray tube (λ = 0.71073 Å).[28] A hemisphere routine was used for data collection and determination of lattice constants. The space group was identified, and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS.[29] The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures.[30] Complex **10** was solved using both SHELX (heavy atoms and disorder) and OLEX2 (hydrogen atoms).[31]

Synthesis of $Ph_2TMSCNa$ (Na-R^3). In a 250 mL round-bottom flask in an inert atmosphere drybox were placed 7.5 g (31.19 mmol) of diphenyl(trimethylsilyl)methane and 150 mL of hexane to dissolve the white solid. With stirring, finely powdered sodium *tert*-butoxide (3.00 g, 31.20 mmol) was added and the mixture stirred for 30 min. *n*-Butyllithium (1.6 M; 22 mL, 1.1 equiv) in hexanes was added to the fine slurry, which began slowly to turn red. The reaction mixture was stirred overnight, after which time a red-orange precipitate had formed. The precipitate was collected on a glass frit and washed with 3 × 50 mL of hexane. Volatiles were removed under reduced pressure, yielding 7.20 g (88%) of Na-R^3 that was spectroscopically identical with a previously reported sample.[25] X-ray-quality single crystals of the THF adduct of Na-R^3 were grown from a concentrated THF solution layered at −30 °C with *n*-hexane.

Synthesis of Chloro(diphenylmethyl)iron Bis(pyridine) (1). $(py)_4FeCl_2$ (1.00 g, 2.256 mmol) was placed in a 100 mL round-bottom flask along with 50 mL of diethyl ether and cooled to −30 °C. To this cooled, stirred slurry (0.600 g, 2.275 mmol) was added $NaCHPh_2$ at once, the reaction mixture was warmed to reach room temperature, stirred for an additional 1 h, and then filtered through Celite, and the volatiles were removed. The residue was washed with hexane, dried, and collected to yield 0.320 g (34%) of a gummy brown-orange material identified as **1**. Attempts to purify **1** by recrystallization resulted in decomposition into a dark, insoluble pyrophoric material. Attempts to obtain elemental analysis data on **1** resulted in unsuccessful values, most likely due to the facile decomposition of the material.

Analysis for $C_{23}H_{21}ClFeN_2Si$: ^1H NMR (C_6D_6) δ −54.04 (411 Hz), −34.16 (1027 Hz), 1.79 (45 Hz), 10.33 (126 Hz), 17.39 (488 Hz), 25.85 (173 Hz), 38.88 (191 Hz); μ_{eff} (Evans, C_6D_6, 19 °C, μ_B) 4.82.

Synthesis of Chloro(phenyltrimethylsilylmethyl)iron Bis(pyridine) (2). In a 100 mL round-bottom flask, 1.00 g (2.256 mmol) of $(py)_4FeCl_2$ was added to 50 mL of diethyl ether and cooled to −30 °C. To the stirred iron slurry was added 2.256 mmol of Na(CH(TMS)Ph) over 5 min in 10 portions. The reaction mixture was stirred for 1 h and then filtered through Celite, and the volatiles of the mother liquor were removed. The residue was taken up in benzene, layered with 3 volume equiv of hexane, and cooled to −30 °C. Crystalline material formed, but the crystals would dissolve in residual solvent when they were warmed to room temperature. The crystals also slowly dissolved in n-Paratone oil. Removal of the mother liquor followed by removal of volatiles yielded 0.220 g (23%) of a sticky dark orange material identified as **2**. Single crystals were grown from a concentrated benzene/hexane solution (~1/3) at −30 °C and melted/dissolved upon warming. Attempts to obtain elemental analysis data on **2** resulted in unsuccessful values, most likely due to the facile decomposition of the material. Analysis for $C_{20}H_{25}ClFeN_2Si$: ^1H NMR (C_6D_6) δ −54.04 (411 Hz), −34.16 (1027 Hz), 1.79 (45 Hz), 10.33 (126 Hz), 17.39 (488 Hz), 25.85 (173 Hz), 38.88 (191 Hz); μ_{eff} (Evans, C_6D_6, 19 °C, μ_B) 4.68. The lack of elemental analysis data is a consequence of the oily nature of the material. The ^1H spectrum shows very little impurity.

Synthesis of Chloro(diphenyltrimethylsilylmethyl)iron Bis(pyridine) (3). $(py)_4FeCl_2$ (1.00 g, 2.256 mmol) was placed in a 100 mL round-bottom flask along with 50 mL of diethyl ether and cooled to −30 °C. To this cooled, stirred solution (0.600 g, 2.275 mmol) was added $NaCPh_2TMS$ at once, and the reaction mixture was warmed to room temperature and stirred for an additional 1 h. The initially pale yellow slurry turned orange over the course of the reaction. The reaction mixture was filtered over Celite and the solution concentrated to roughly 10 mL, at which time a bright orange precipitate began to form. The mother liquor was transferred to a vial and cooled to −30 °C while the orange precipitate was dried and collected. Following the cooling of the mother liquor, additional orange precipitate formed and was isolated. The total combined yield of the bright orange powder, identified as $(py)_2FeCl(CPh_2TMS)$ (**3**), was 0.85 g (92%). Compound **3** could be stored at −30 °C for several weeks with minimal degradation but at room temperature decomposed slowly over the course of several days. Anal. Calcd for $C_{26}H_{29}ClFeN_2Si$: C, 63.87; H, 5.98; N, 5.73. Found: C, 62.80; H, 5.83; N, 5.20. ^1H NMR (C_6D_6): δ −54.04 (411 Hz), −34.16 (1027 Hz), 1.79 (45 Hz), 10.33 (126 Hz), 17.39 (488 Hz), 25.85 (173 Hz), 38.88 (191 Hz). μ_{eff} (Evans, C_6D_6, 19 °C, μ_B): 4.73. The elemental analysis results consistently returned low for carbon. The ^1H spectrum is shown in the Supporting Information, and very little impurity was found.

Synthesis of Bis(*exo*-(1,1-trimethylsilylphenylmethylene)-η^5-cyclohexadienyl)iron (6). $(py)_4FeCl_2$ (1.00 g, 2.256 mmol) was placed in a 50 mL round-bottom flask along with 30 mL of diethyl ether and cooled to −30 °C. To this stirred slurry was added $NaCPh_2TMS$ (1.195 g, 4.550 mmol) at once, and the reaction mixture was warmed to room temperature and stirred for an additional 1 h. The initially pale yellow slurry turned burgundy and then orange-brown over the course of the reaction. The reaction mixture was filtered over Celite and the solution concentrated to roughly 10 mL.

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The reaction solution was then placed in a vial, cooled to −30 °C, and layered with hexane, and the brown solid (1.05 g, 87%) that formed was collected and dried under reduced pressure. Anal. Calcd $C_{32}H_{38}FeSi_2$: C, 71.89; H, 7.16. Found: C, 72.16; H, 7.21. ^{1}H NMR (C_6D_6): *rac* isomer, δ 0.22 (s, 9H, Si(CH_3)$_3$), 3.92 (dd, J = 7.1, 2.1 Hz, 1H), 4.17 (dd, J = 6.9, 5.2 Hz, 1H), 4.26 (t, J = 5.2, 1H), 4.34 (dd, J = 7.1, 2.1 Hz, 1H), 4.45 (dd, J = 6.9, 5.2 Hz, 1H), 7.11−7.02 (m, 3H), 7.26 (t, J = 7.5 Hz, 2H); *meso* isomer, δ 0.15 (s, 9H, Si(CH_3)$_3$), 3.73 (d, J = 7.0 Hz, 1H), 4.08 (t, J = 6.3 Hz, 1H), 4.51 (t, J = 6.3 Hz, 1H) 7.30−7.38 (m, 2H). The remaining three resonances are located under the resonances of the *rac* isomer. ^{13}C{^{1}H} NMR (C_6D_6): *rac* isomer, δ 1.2, 63.3, 63.4, 71.5, 84.4, 84.9, 109.1, 125.0, 128.9, 130.4, 137.1, 145.3; *meso* isomer, δ 1.0, 65.9, 67.5, 71.2, 83.6, 86.3, 130.3, 137.2. Four resonances were not located.

Reaction of (py)$_4$FeCl$_2$ with 2 equiv of Sodium Diphenylmethane (4). (py)$_4$FeCl$_2$ (1.00 g, 2.256 mmol) was placed in a 50 mL round-bottom flask along with 30 mL of diethyl ether and cooled to −30 °C. To this stirred slurry was added NaCHPh$_2$ (1.195 g, 4.550 mmol) at once, and the reaction mixture was warmed to room temperature and stirred for an additional 1 h. The initially pale yellow slurry turned burgundy and then dark brown over the course of the reaction. The reaction solution was filtered over Celite, and volatiles were removed. Attempts to recrystallize **4** resulted in an insoluble dark precipitate and pale yellow mother liquor.

Reaction of (py)$_4$FeCl$_2$ with 2 equiv of Sodium (Phenyltrimethylsilyl)methane (5). (py)$_4$FeCl$_2$ (1.00 g, 2.256 mmol) was added to a 50 mL round-bottom flask along with 30 mL of diethyl ether and cooled to −30 °C. To this stirred slurry was added NaCHPh(TMS) (1.195 g, 4.550 mmol) at once, and the reaction mixture was warmed to room temperature and stirred for an additional 1 h. The initially pale yellow slurry turned red over the course of the reaction.

Synthesis of (dppene)$_2$FeCl (7). (dppene)$_2$FeCl$_2$ (0.250 g, 0.272 mmol) and 10 mL of THF were combined in a 20 mL scintillation vial with a stir bar. This reaction slurry was cooled to −30 °C and, with stirring, NaCPh$_2$TMS (0.075 g, 0.275 mmol) was added at once and the reaction mixture was warmed to room temperature and stirred for an additional 1 h. Volatiles were then removed under reduced pressure, and the residue was taken up in benzene and filtered through Celite. The reaction solution was then diluted with 2 volume equiv (~10 mL) of hexane, and the mixture was cooled to −30 °C. The dark powder that formed was collected on a glass frit, rinsed with hexane, and dried under reduced pressure to yield 0.195 g (87%) g of dark crystals identified as (dppene)$_2$FeCl. Single crystals suitable for X-ray diffraction were grown from slow diffusion of hexane into a fluorobenzene solution of **7** at room temperature. Anal. Calcd for $C_{52}H_{44}ClFeP_4$: C, 70.64; H, 5.02. Found: C, 71.59; H, 5.32%. ^{1}H NMR (C_6D_6): δ 8.56 (br s, 934 Hz), 6.65 (br s, 124 Hz), 5.11 (br s, 124 Hz). μ_{eff} (Evans, C_6D_6, 19 °C, μ_B): 2.11. The elemental analysis results were consistently high in carbon by ~1%. No free dppene was observed in the ^{31}P spectrum. We attribute the high value to residual solvent, although the complex was triturated with pentane and dried for several hours.

Alternate (a) Synthesis of 7. (py)$_2$FeCl(CPh$_2$TMS) (0.100 g, 0.204 mmol) was dissolved in 5 mL of benzene in a 20 mL scintillation vial. In a separate vial, dppene (0.165 g, 0.410 mmol) was dissolved in benzene and was subsequently added dropwise to the stirred solution of (py)$_2$FeCl(CPh$_2$TMS). The reaction mixture immediately became dark brown. Slight vacuum was applied until 5 mL of solvent remained, at which time the solution was layered with hexane and was allowed to sit undisturbed for 12 h. Large dark crystals formed overnight. These were collected on a sintered-glass frit and were spectroscopically identical with previously characterized samples of (dppene)$_2$FeCl. Crystals suitable for single-crystal X-ray diffraction were grown in the same fashion.

Alternative (b) Synthesis of 7. Sodium metal (0.012 g, 0.522 mmol) was smeared on the bottom of a 50 mL round-bottom flask. (dppene)$_2$FeCl$_2$ (0.480 g, 0.522 mmol) and 0.005 g of naphthalene were added as powders on top of the sodium. A 20 mL portion of THF was then added to the stirred solids. The reaction mixture was stirred until the sodium was consumed. Volatiles were then removed under reduced pressure, and the residue was taken up in diethyl ether and filtered through Celite. Volatiles were removed, and the brown solid was mobilized with hexane, collected on a glass frit, rinsed with hexane, and dried under reduced pressure to yield 0.335 g (73%) of a dark brown powder identified as (dppene)$_2$FeCl.

Attempted Synthesis of (dmpe)$_2$FeCl (9). (dmpe)$_2$FeCl$_2$ (0.250 g, 0.585 mmol) and 10 mL of diethyl ether were combined in a 20 mL scintillation vial with a stir bar. This reaction slurry was cooled to −30 °C and, with stirring, NaCPh$_2$TMS (0.155 g, 0.589 mmol) was added at once and the reaction mixture was warmed to room temperature and stirred for an additional 1 h. The reaction mixture was filtered through Celite, and volatiles were removed. The residue was then taken up in ether and layered with hexane and the mixture was cooled to −30 °C. The dark green powder that formed was collected on a glass frit, rinsed with hexane, and dried under reduced pressure to yield 0.190 g (83%) of a green-brown powder that was tentatively ascribed as (dmpe)$_2$FeCl. Attempts to purify this complex resulted in the formation of **8** and (dmpe)$_2$FeCl$_2$ and other unidentified decomposition products. ^{1}H NMR and ^{31}P NMR spectra obtained showed the presence of (dmpe)$_2$FeCl$_2$ and **8**.

Synthesis and Attempted Purification of (dppene)$_2$FeN$_2$ (8). Sodium metal (0.025 g, 0.525 mmol) was thinly spread on the bottom of a 50 mL round-bottom flask. (dppene)$_2$FeCl$_2$ (0.480 g, 0.522 mmol) and 0.010 g of naphthalene were added as powders on top of the sodium. A 20 mL portion of THF was then added to the stirred solids. The reaction mixture was stirred until the sodium was consumed. Volatiles were then removed under reduced pressure, and the residue was taken up in diethyl ether and filtered through Celite. Volatiles were removed, and the brown solid was dissolved in a minimum amount of diethyl ether and cooled to −30 °C. Dark crystals formed that were isolated by decanting the mother liquor and drying under reduced pressure to yield 0.167 g (36%) of a dark brown crystalline material identified as (dppene)$_2$Fe(N$_2$). This material was consistently contaminated with large quantities of the free dppene, and attempts to recrystallize the crude material furnished amore impure compound. Anal. Calcd for $C_{52}H_{44}FeN_2P_4$: C, 70.64; H, 5.06; N, 3.20. Found: C, 59.99; H, 4.64; N, 0.27. ^{31}P NMR (THF): δ 19.22 (d, $J_{P,P}$ = 64 Hz), 19.44 (d, $J_{P,P}$ = 64 Hz). IR (KBr): 2021 cm^{-1}. The elemental analysis was obtained even though it was known that the complex was unstable to search for remaining nitrogen content.

Synthesis of ((dmpe)$_2$Fe)$_2$(μ-N$_2$) (10). (dmpe)$_2$FeCl$_2$ (0.125 g, 0.272 mmol) and 10 mL of THF were combined in a 20 mL scintillation vial with a stir bar. This reaction slurry was cooled to −30 °C and, with stirring, NaCPh$_2$TMS (0.158 g, 0.550 mmol) was added at once and the reaction mixture was warmed to room temperature and stirred for an additional 1 h. Volatiles were then removed under reduced pressure, and the residue was taken up in benzene and filtered through Celite. Volatiles were removed, and the residue was taken up in a minimal amount of hexane and the mixture cooled to −30 °C. The red crystals that formed were collected on a glass frit and dried under reduced pressure to yield 0.085 g (78%) g of a deep red powder was consistent with a previously reported sample of ((dmpe)$_2$Fe)$_2$(μ-N$_2$). Crystals suitable for single-crystal X-ray diffraction were grown in the same fashion.

Observation of R^{3}Fe(CNCy)$_3$ (11). (py)$_2$FeCl(CPh$_2$TMS) (0.100 g, 0.204 mmol) was dissolved in 5 mL of diethyl ether in a 20 mL scintillation vial. This reaction slurry was cooled to −30 °C and, with stirring, cyclohexyl isocyanide (0.045 g, 0.410 mmol) was added at once and the reaction mixture was warmed to room temperature and stirred for an additional 1 h. The reaction solution was filtered over Celite and cooled to −30 °C. The formed solid material was contaminated with diphenyl(trimethylsilyl)methane and the dimer of the diphenyl(trimethylsilyl)methane radical. Crystals suitable for single-crystal X-ray diffraction were grown from hexane and were physically cleaned of free organic material before mounting. Due to the small quantity of crystals formed and the difficulty in purification (Supporting Information), determination of the yield for **11** and further characterization were not attempted.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00108.

Crystallographic details and spectra and notes pertaining to certain compounds presented in this paper (PDF)

X-ray crystallographic details compounds **2**, **3**, **6**−**8**, **10**, **11**, and $(THF)_3Na\text{-}R^3$ (CIF)

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Notes

The authors declare no competing financial interest.

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