Electron-Deficient Iron Alkyl Complexes Supported by Diimine Ligand (Ph2CN)2C2H4: Evidence for Reversible Ethylene Binding

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Received July 17, 2008

Reaction of diimine ligands (Ph2CN)2C2H4 (n = 2, a; n = 3, b) with FeCl3 or FeBr3 results in formation of the corresponding high-spin ferrous complexes [(Ph2CN)2C2H4]FeX2 (1a, X = Cl; 2a, X = Br) and [(Ph2CN)2C2H4]FeCl2 (1b). Dialkyl [(Ph2CN)2C2H4]Fe(CH2SiMe3)2 (3a) was prepared by treatment of (py)2Fe(CH2SiMe3)2 with diimine ligand a. Addition of B(C6F5)3 to 3a at −30 °C resulted in Me6SiCH2 abstraction, affording [[(Ph2CN)2C2H4]Fe(CH2SiMe3)]2Me6SiCH2B(C6F5)3 (5a). 19F NMR spectroscopy revealed that this compound exists as a contact ion-pair in toluene solution. Compound 5a decomposes at room temperature in bromobenzene-d5 or toluene-d5, affording dication [{(Ph2CN)2C2H4}Fe(C6F5)]2 (6a); at elevated temperatures in toluene-d5 the formation of [[(Ph2CN)2C2H4]Fe(CH2SiMe3)C6F5] (7a) was observed as well. Neither ferrous chloride {(Ph2CN)2C2H4}FeCl2 activated with methylaluminoxane nor contact ion-pair 5a is active in the polymerization of ethylene. Instead we were able, for the first time, to observe reversible ethylene binding to a cationic iron alkyl complex.

Introduction

Ever since the initial publications by the groups of Brookhart1 and Gibson,2 in which they independently reported the use of pyridine-diimine complexes of iron as efficient catalysts for the polymerization of ethylene, many research groups have prepared related iron catalysts in order to tune catalyst performance, and with that the properties of the polymer obtained.3 Electron-deficient, cationic iron(II) alkyl complexes are often implied as the active species,4 although zerovalent5 and trivalent6 iron species have been proposed as well. It is known that treatment of PDI iron complexes with alkyl halides affords cationic iron alkyl complexes with nonconjugated diimine ligands (Ph2CN),7 and trivalent iron complex [(PDI)Fe(CH2SiMe3)2] with FeCl3 has been prepared as well.8 Electron-deficient, cationic iron alkyl complexes with pyridine- or pyridine-based ligands are known to be active in the polymerization of ethylene.5,8,9

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Results and Discussion

Synthesis of Iron Halide Complexes. Ferrous dichlorides \((\text{PhCN})_2\text{C}_2\text{H}_4\text{FeCl}_2\) (1a) and \((\text{PhCN})_2\text{C}_2\text{H}_4\text{FeCl}_2\) (1b) and dibromide \((\text{PhCN})_2\text{C}_2\text{H}_4\text{FeBr}_2\) (2a) were prepared by stirring THF suspensions of anhydrous FeCl2 or FeBr2 with the corresponding diimine ligands (Scheme 2). The compounds could be isolated in good yields (72–90%) by removal of the solvent and extraction with dichloromethane. After filtering the extracts over Celite compounds 1a and 2a were obtained as yellow (ligand a) or orange (ligand b) powders by evaporation of the solvent. The compounds have a high-spin ground state, similar to α-dimine complexes of this type.11 Both compounds 1a and 2a12 were studied by single-crystal X-ray diffraction (see Figure 1 for an ORTEP representation of 1a and Table 1 for pertinent bond distances and angles of both structures; the structure of 2a can be found in the Supporting Information).

Both compounds crystallize in the P21/c space group with two independent molecules in the asymmetric unit that have similar metrical parameters, and only one of each will be discussed here. The geometry around the iron center in complexes 1a and 2a can be best described as a distorted tetrahedron, with bond distances for the first (average Fe–N: 2.130(4) Å for 1a and 2.101(4) Å for 1c; average Fe–Cl: 2.2588(13) Å for 1a and 2.22222238(10) Å for 1c) and a larger bite angle (81.88(9)° for 1a) and 81.7(3)° for 1c). The geometry of 1a confirms its formulation, and an ORTEP representation is shown more pronounced shifts. One of these is shifted to low field (δ 57.5–177.3 ppm) and one to high field (δ −26.9 to −53.3 ppm). These are tentatively assigned to the o-CH and m-CH of the phenyl group that is directed toward the iron center. See Figure 2 for a representative 1H NMR spectrum.

Synthesis of Neutral Iron Alkyl Complexes. Treatment of 1a or 2a with 2 equiv of LiCH2SiMe3 in benzene-d6 solution resulted in a color change from yellow to brownish-red.13 1H NMR spectroscopy of the reaction mixture revealed the number of signals expected for a C2v symmetric dialkyl complex \((\text{PhCN})_2\text{C}_2\text{H}_4\text{Fe}(\text{CH}_2\text{SiMe}_3)_2\) (3a), taking into account that the protons for the methylene groups that are directly bound to the paramagnetic iron center are usually not observed.7,11 Performing these reactions on a preparative scale did not allow the clean formation of dialkyl complex 3a. One explanation may be that alkylation reactions of iron halides with imine-based ligands can be susceptible to a number of side reactions, such as reduction of the iron center7a,14 and alkylation of the ligand.7b Compound 3a, however, could be obtained in good yield (70%) by treatment of the iron-dialkyl reagent (py)Fe(CH2SiMe3)12c with 1 equiv of the ligand. When the reaction was performed on an NMR tube scale and the volatiles of the reaction mixture were transferred into a tube with a known amount of ferrocene internal standard, it was found (by integration) that only 1 equiv of pyridine was released during the reaction, suggesting the formation of the monopyridine adduct \((\text{PhCN})_2\text{C}_2\text{H}_4\text{Fe}(\text{CH}_2\text{SiMe}_3)_2\) (py) (3a·py). In the initial reaction mixture no free pyridine was observed, suggesting a fast (on the NMR time scale) exchange between free and bound pyridine. Recrystallization of 3a·py from pentane at −30 °C afforded single crystals of the pyridine-free compound \((\text{PhCN})_2\text{C}_2\text{H}_4\text{Fe}(\text{CH}_2\text{SiMe}_3)_2\) (3a).

As expected, iron dialkyl 3a has a high-spin ground state \((\Delta_{ls} = 4.9 \mu_B)\).

Treatment of 1b with LiCH2SiMe3 in benzene-d6 in an NMR tube resulted in a reddish-brown, intractable mixture of products. Furthermore, dissolving (py)Fe(CH2SiMe3)2 and the C2-bridged diimine ligand b in benzene-d6 did not result in formation of the corresponding dialkyl complex (3b). Instead, a mixture of the starting materials was observed by 1H NMR spectroscopy, even after shaking the NMR tube for 3 days at room temperature.

Synthesis of Cationic Iron Alkyl Complexes. THF-solvated cation \([\text{(PhCN})_2\text{C}_2\text{H}_4\text{Fe}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})][\text{BPh}_4]\) (4a) was prepared in reasonable yield (53%) by reaction of a 1:1 mixture of dialkyl 3a and Brønsted acid [PhNMe2H][BPh4] in THF. The compound was isolated as yellow crystals by diffusion of pentane into a THF solution of the compound. X-ray analysis confirms its formulation, and an ORTEP representation is depicted in Figure 3 (see Table 1 for pertinent bond distances and angles). The geometry of the compound is similar to the other ferrous complexes described in this study, with slightly

(12) A small amount of crystals of compound 2a was obtained during the decomposition of compound 5a in bromobenzene-d5. These crystals were used for a single-crystal X-ray analysis.


Figure 1. ORTEP representations at the 30% probability level of 1a and 3a. Hydrogen atoms are omitted for clarity.

Table 1. Pertinent Bond Distances and Angles for 1a, 2a, 3a, 4a, 6a, and 7a

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<td>2.073(6)</td>
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<td>2.374(2)</td>
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<td>137.06(12)</td>
<td>83.5(2)</td>
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*Fe and N(1) for 3a and 7a. †Fe and N(2) for 3a and 7a. ‡X = Cl11 (1a); Br11 (2a); C(29) (3a); O(11) (4a); N(13) (6a); C(29) (7a). §Y = Cl12 (1a); Br12 (2a); C(29) (3a); C(129) (4a); N(14) (6a); C(35) (7a). ‖C(1) for 3a and 7a; C(17) for 6a. ‡C(16) for 3a and 7a; C(122) for 6a.

contraction of metal–ligand bond distances, a result of the increased electron deficiency of the metal center.

A base-free iron alkyl complex (5a) was prepared by addition of a cold (−30 °C) toluene-d6 solution of B(C6F5)3 to a cooled solution of 3a in toluene-d6. This resulted in a color change from purple to yellow. After replacing the solvent with THF-d6, a species was observed with a similar 1H NMR spectrum to that of 4a′, suggesting the initial formation of ion-pair \( [(\text{PhCN})_2C_6H_5Fe(CH_2SiMe_3)]\)\([\text{Me}_2\text{SiCH}_2B\text{C}_6\text{F}_3] \) (5a, Scheme 3). The ESI-MS of a solution of 4a in THF revealed a peak at \( m/z = 603.3 \) and 531.1 g/mol (calcd for the cation of 4a, 603.3; for the cation of 5a, 531.2) in the positive-ion spectrum and at \( m/z = 599.1 \) (calcd for \([\text{Me}_2\text{SiCH}_2B\text{C}_6\text{F}_3]\), 599.1) in the negative-ion spectrum. Hence, similar to the \( \alpha \)-dimine case, the coordination sphere of the iron center in 3a is sufficiently open to allow abstraction of a \( \text{Me}_2\text{SiCH}_2\) group,11 and there is no indication for \( \text{Me}_2\text{SiCH}_2\)-methyl group abstraction.11 It should be noted that, in the case of the \( \alpha \)-dimine complex, the iron alkyl cation \( [(2,6-i-\text{Pr}_2\text{C}_6\text{H}_4\text{N})(\text{C}_2\text{Me}_3)]\)\([\text{Fe}(\text{CH}_2\text{SiMe}_3)] \) could not be observed. Instead, \( [(2,6-i-\text{Pr}_2\text{C}_6\text{H}_4\text{N})_2\text{Fe}(\text{CH}_2\text{SiMe}_3)] \) was obtained, the result of a fast \( \text{C}_2\text{F}_4 \) transfer in the initially generated ion-pair (vide infra).11

The 19F NMR spectrum of 5a in toluene-d8 (at a concentration of 30.2 mM) revealed three resonances at \( \delta = -98.5 \) (m-F), -118.1 (o-F), and -152.3 (p-F) ppm for the pentafluorophenyl groups, indicative of a coordinated borate anion.15,16 Interestingly, the chemical shifts are sensitive to the concentration of the ion-pair, with the signals shifting to lower field upon dilution (Figure 4). In general a concentration dependency could suggest the presence of an equilibrium between a solvent-separated and a contact ion-pair, though in that case a shift in the opposite direction is expected. The concentration dependency observed here may be the result of the formation of higher aggregates at higher concentrations, which will in turn affect the strength of the ion-pairing.17 Addition of a drop of THF to a diluted toluene solution of 5a (9.19 mM) results in a shift of the three fluorine resonances to \( \delta = -124.8 \) (o-F), 162.2 (m-F), and 162.5 (p-F) ppm. This suggests that there is still an interaction between the ions in THF adduct 4a in toluene, although this interaction is much weaker compared to that in the contact ion-pair 5a. When dissolving compound 5a in THF-d8, resonances are observed at \( \delta = -129.7 \) (o-F), -164.7 (p-F), and -166.8 (m-F) ppm, as expected for a noncoordinating anion.18

During the synthesis of the contact ion-pair (5a) at room temperature in toluene-d8 or bromobenzene-d8, a secondary iron species (6a) was observed as well. In bromobenzene-d8 species 6a was observed exclusively after standing for 24 h at room temperature. The compound was characterized as \( [(\text{PhCN})_2\text{-}(\text{C}_6\text{H}_4\text{N})_2\text{Fe}]\)\([\text{Me}_2\text{SiCH}_2B\text{C}_6\text{F}_3] \) (6a) by single-crystal X-ray analysis (see Figure 3 for an ORTEP representation and Table 1 for selected bond distances and angles).19 Iron dication 6a can be prepared purposely by treating dialkyl complex 3a with...
2 equiv of B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} in the presence of an additional equivalent of the ligand in toluene solution (Scheme 3). A closer inspection of the structure of 6a reveals that, in contrast to the other structures described in this paper, the iron center no longer adopts a distorted tetrahedral geometry. Instead its geometry is in between tetrahedral and square planar, with an angle between the N(11)-Fe(1)-N(12) and N(13)-Fe(1)-N(14) planes of 48.8(3)°. A similar ligand redistribution reaction was observed in the neutral ferrous amidinate complex [FeCl\textsubscript{2}]{\mu-(2,6-i-Pr\textsubscript{2}C\textsubscript{6}H\textsubscript{3}NC}{Ph}NC\textsubscript{2}H\textsubscript{4}NMe\textsubscript{2}}\textsubscript{15c} and in the attempted synthesis of a cationic amidinate complexes of the type [{PhCN}{\textsubscript{2}C\textsubscript{6}H\textsubscript{3}}Fe(CH\textsubscript{2}SiMe\textsubscript{3})\textsubscript{2}]\textsuperscript{+}\textsubscript{\textsubscript{20}}. The fate of the side product in the disproportionation reaction observed here is as yet unknown, though analysis of the reaction mixture by GC-MS reveals the formation of (Me\textsubscript{3}SiCH\textsubscript{2})\textsubscript{2}, suggesting concomitant formation of [Fe(CH\textsubscript{2}SiMe\textsubscript{3})\textsubscript{2}].

Thermolysis of 5a in toluene (2 days, 50 °C) resulted in formation of a mixture of compound 6a, which precipitates as a yellow solid, and a new iron species, [{Ph\textsubscript{2}CN}{\textsubscript{2}C\textsubscript{6}H\textsubscript{3}}Fe(CH\textsubscript{2}SiMe\textsubscript{3})\textsubscript{2}]\textsubscript{7a}. Compound 7a is highly soluble in aromatic and aliphatic solvents and could be isolated by

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(19) Single crystals were also obtained from a thermolysis experiment (50 °C) of 5a in toluene. This afforded a similar structure, but with cyclohexane rather than bromobenzene cocrystallized in the lattice. The cif file of the crystals structure determination can be found in the Supporting Information.
spectroscopy, however, revealed that compound 1 equiv of ethylene to a 30.2 mM toluene-unreactive toward the olefin (Scheme 4). After the addition of 4.2, 6.4, 9.5, and 13 equiv of ethylene in toluene-Rrophenyl group. Again, a comparison of bond distances to the metal center imparted by the electron-withdrawing pentafluorophenyl group attached to the iron center. One signal, presumably the α-F resonance, could not be observed.

**Reactivity toward Ethylene.** Well-defined iron alkyl cation 5a was treated with ethylene, but no polymerization of the olefin was observed. Likewise, treatment of ferrous chloride 1a with MAO (MAO = methylaluminoxane) in toluene in the presence of ethylene (5 bar, 30 min) did not result in ethylene uptake, and no formation of a substantial amount of polyethylene was observed. Following the reaction of 5a with ethylene by NMR spectroscopy, however, revealed that compound 5a is not unreactive toward the olefin (Scheme 4). After the addition of 1 equiv of ethylene to a 30.2 mM toluene-δd solution of 5a, the 1H NMR spectrum of the reaction mixture reveals a broad signal at 14.5 ppm (Δν1/2 = 306 Hz) for the olefin (Figure 5). This suggests formation of an ethylene adduct, in which the coordinated molecule of ethylene is in fast exchange, relative to the NMR time scale, with free ethylene in solution. As expected, the signal shifts upfield upon increasing the ethylene concentration. The 19F NMR spectrum of the reaction mixture corroborates such an equilibrium, as an increase of the ethylene pressure results in an upfield shift of the fluorine resonances toward the values expected for a ligand-separated ion-pair (Figure 5). Unfortunately, during the course of the reaction the formation of a yellowish-brown oil was observed, frustrating quantification of the equilibria involved. The yellowish oil was identified as [(Ph2CN)2(C2H4)2]Fe[Me3SiCH2B(C6F5)3].

**Conclusions**

Diimines (Ph2CN)2C2H5 (n = 2, 3) are suitable ligands for the stabilization of electron-deficient iron complexes, and in case of the ligand with the C₂ bridge, both neutral and cationic iron alkyl complexes were prepared. Ligand binding is more labile compared to the α-diimine ligand framework, as the cationic ironalkylcomplex[[[(Ph2CN)2C2H4]Fe(Ph2SiMe2)]Me3SiCH2B-(C6F5)3] rearranges to dication [((Ph2CN)2C2H4)2Fe]2⁺, the result of a ligand redistribution reaction. In toluene, at 50 °C a secondary thermolysis product was observed as well, which was identified as [((Ph2CN)2C2H4)Fe(Ph2SiMe3)C2Fs]. Whereas we were able, for the first time, to observe an ethylene adduct of an iron alkyl cation, the compound is not an active catalyst for the polymerization of olefins. This suggests that the barrier for ethylene insertion is the determining factor in this system. Unfortunately, a comparison with the α-diimine system is not possible, as in that case pentafluorophenyl abstraction from the borate anion is instantaneous and an iron alkyl cation cannot be observed.

**Figure 5.** From top to bottom: 19F NMR (left) and 1H NMR (right) spectra of the reaction mixture containing compound 5a and 1.1, 2.1, 4.2, 6.4, 9.5, and 13 equiv of ethylene in toluene-δd, respectively.
Experimental Section

General Considerations. All manipulations of air- and moisture-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk and vacuum line techniques or in an MBraun glovebox. Solvents (THF, pentane, toluene) were dried by percolation under a nitrogen atmosphere over columns of alumina, molecular sieves, and supported copper oxygen scavenger (BASF R3-11) or by distillation from Na/K alloy (cyclohexane, benzene-

\(d_6\), THF-\(d_6\), or CaH2 (chloroform-\(d\), bromobenzene-\(d_6\), dichlo-romethane). Reagents were purchased from commercial providers and used without purification unless stated otherwise. Anhydrous FeCl3, (Ph3CN)2C6H4, (py2)2Fe(CH3SiMe3)2, LiCH3SiMe3,23 [PhNMMe2][BPh4]24 and B(C6F5)325 were prepared following literature procedures. NMR spectra were recorded on Varian Inova 500, Varian Gemini VXR 400, Varian VXR 300, and Varian Gemini 200 instruments.1'H chemical shifts are referenced to residual protons in deuterated solvents and are reported relative to 500, Varian Gemini VXR 400, Varian VXR 300, and Varian Gemini 200 instruments.1'H chemical shifts are referenced to residual protons in deuterated solvents and are reported relative to tetramethylsilane;1'H chemical shifts are reported relative to \(\alpha,\alpha,\alpha\)-trifluorotoluene (\(\delta = -65\) ppm), used as an external reference. For paramagnetic molecules, the chemical shifts are followed by the peak width at half-height in hertz, followed by integration value to 200 ms. Magnetic moments are determined by the Evans method.26 Elemental analyses were performed by the Microanalytical Department at the University of Groningen. Reported values are the averages of two independent determinations. The electrosporption ionization mass spectrometry (ESI-MS) experiments were conducted on an API III (PE SCIEX) triple quadrupole MS system with an IonSpray (pneumatically assisted electrospray) source equipped with a gas curtain, which is contained in a different angular settings (SADABS),27 Lorentz and polarization effects, scale variation, decay, and multi-scan absorption correction (\(\delta = 26.9\) ppm). Anal. Calcd for LiCH3SiMe3: C, 58.66; H, 4.60; N, 4.56. Found: C, 58.52; H, 4.70; N, 4.54. Found: C, 58.42; H, 4.49; N, 4.42. Generalization of \((\text{Ph}_2\text{CN})_2\text{C}_6\text{H}_4\) \(\text{FeCl}_2\) (1a). THF (20 mL) was added to a mixture of a (1.55 g; 3.99 mmol) and FeCl3 (0.514 g; 4.06 mmol). The resulting suspension was stirred overnight. The solvent was removed in vacuo and a yellow powder was obtained. The compound was extracted using dichloromethane. The extractions were filtered through a pad of Celite, affording a yellow solution. The solvent was removed in vacuo, affording 1.85 g (3.59 mmol, 90%) of the title compound as a yellow solid. Lagging a dichloromethane solution of the solid with pentane resulted in crystals suitable for X-ray analysis.1'H NMR (CDCl3, RT): \(\delta = 69.6\) (4H, 579 Hz), 13.1 (4H, 24 Hz), 5.3 (4H, 73 Hz), 2.9 (2H, 23 Hz), 1.8 (4H, 66 Hz), –0.5 (2H, 34 Hz), –26.9 (4H, 601 Hz). Anal. Calcd for C19H24Fe2Cl2: C, 65.27; H, 4.70; N, 5.44. Found: C, 64.64; H, 4.67; N, 5.25. \(\mu_{\text{eff}} = 5.3\) \(\mu_0\).

\((\text{Ph}_2\text{CN})_2\text{C}_6\text{H}_4\) \(\text{FeCl}_2\) (1b). Compound 1b was prepared analogous to 1a, by treating b (1.47 g; 3.79 mmol) with FeCl3 (0.480 g; 3.78 mmol) in THF (20 mL). This afforded 1.51 g (2.85 mmol; 75%) of 1b.1'H NMR (CDCl3, RT): \(\delta = 126.0\) (4H, 916 Hz), 35.6 (4H, 1009 Hz), 10.4 (4H, 35 Hz), 9.5 (2H, 51 Hz), 7.2 (4H, 44 Hz), 4.8 (2H, 32 Hz), 3.9 (2H, 411 Hz), –0.1 (4H, 98 Hz). A sample for analysis was recrystallized from CHCl3/cyclohexane. Anal. Calcd for C25H36Cl2Fe2N2: C, 58.66; H, 4.60; N, 4.56. Found: C, 58.42; H, 4.49; N, 4.42. Generation of \((\text{Ph}_2\text{CN})_2\text{C}_6\text{H}_4\) \(\text{FeBr}_2\) (2a). Compound 2a was prepared analogous to 1a, by treating FeBr2 (0.179 g; 0.830 mmol) with a (0.324 g; 0.833 mmol) in THF (10 mL). This afforded 0.36 g (0.60 mmol; 72%) of 2a.1'H NMR (thromobenzene-\(d_6\), RT): \(\delta = 70.1\) (4H, 663 Hz), 14.1 (4H, 28 Hz), 5.8 (4H, 85 Hz), 2.6 (2H, 29 Hz), 1.7 (4H, 75 Hz), –2.4 (2H, 40 Hz), –36.1 (4H, 413 Hz). Anal. Calcd for C26H16Br2FeN2: C, 55.66; H, 4.00; N, 4.64. Found: C, 55.43; H, 3.96; N, 4.52.

\((\text{Ph}_2\text{CN})_2\text{C}_6\text{H}_4\) \(\text{FeCl}_2\) (3a) 

A three-necked flask equipped with a reflux condenser was charged with benzophenone (4.07 g; 22.3 mmol), diaminopropane (0.92 mL; 11 mmol), a catalytic amount of p-toluenesulfonic acid, and xylene (60 mL). The reaction mixture was warmed to reflux and stirred overnight, affording a yellow solution. Removal of the solvent by rotary evaporation afforded a yellow oil, which, upon addition of pentane and overnight cooling to –30 °C, turned solid. The pentane was decanted, and the off-white solid was dried in vacuo. Recrystallization from chloroform/pentane afforded 2.45 g (6.08 mmol; 56%) of the title compound.1'H NMR (CDCl3, RT): \(\delta = 7.12 – 7.53\) (m, 20H, Ph), 3.45 (t, 4H, 6.85 Hz, CH2), 2.04 (q, 2H, 6.89 Hz, CH2).13C NMR (CDCl3, RT): \(\delta = 140.9, 138.0\) (2 \(\times\) Ph CH3). 130.7, 129.4, 129.3, 129.2, 128.9, 128.8 (6 \(\times\) Fe CH2), 52.8 (CH2), 33.8 (CH3). Anal. Calcd for C29H24FeN2: C, 86.53; H, 6.51; N, 6.96. Found: C, 86.18; H, 6.48; N, 6.95.
(4H, 13.6 Hz), 27.6 (2H, 804 Hz), 16.6 (1H, 242 Hz), 15.1 (2H, 217 Hz), 12.7 (2H, overlapping signals), 3.7–1.3 (6H, overlapping signals), −3.2 (2H, 51 Hz), −53.3 (4H, 1403 Hz). Two signals of 4H were not observed.

\[(\text{Ph}_2\text{C}_5\text{N})_2\text{CH}_4\text{FeCH}_2\text{SiMe}_2\text{O}_2(3a)\]. Toluene (5 mL) was added to a mixture of (py)_2Fe(CH_3SiMe) (75.5 mg; 0.193 mmol) and a (64.0 mg; 0.164 mmol), resulting in a purple solution. The reaction mixture was stirred for 2 h, after which the solvent was removed in vacuo. To the resulting purple oil was added toluene (5 mL), which was pumped off to remove residual pyridine. The solid was dissolved in pentane and filtered through a pad of Celite. Concentration of the solution and cooling at −30 °C resulted in 71.5 mg (0.116 mmol, 70%) of purple crystals of the title compound. ^1H NMR (CD_6D_8, RT): δ 57.4 (6H, 101 Hz), 13 (2H, overlapping signals), 2.9 (4H, 97 Hz), 2.0 (4H, 110 Hz), 0.9 (2H, 30 Hz), −3.2 (2H, 50 Hz), −53.3 (4H, 901 Hz). One signal of 4H was not observed. Anal. Calcd for C_45H_34FeN_2Si_3: C, 78.88; H, 7.49; N, 4.53. Found: C, 78.35; H, 7.44; N, 4.39. \( \mu_{\text{eff}} = 4.9 \mu\text{B} \).

Generation of \([(\text{Ph}_2\text{CN})_2\text{C}_2\text{H}_6\text{Fe}(\text{CH}_3\text{SiMe}_3))\text{THF}\] (5a). \( \text{NMR (CD}_6\text{D}_8, \text{RT): } \delta 72.3 (4H, 833 Hz), 21.3 (9H, 170 Hz, SiMe_3), 13.2 (4H, 24 Hz), 10.0 (8H, 26 Hz, BPh), 8.2 (8H, 27 Hz, BPh), 7.6 (4H, 25 Hz, p-BPh), 3.8 (2H, 67 Hz), 1.68 (4H, overlaps with THF) −1.9 (2H, 33 Hz), −8.8 (4H, 61 Hz), −36.4 (4H, 726 Hz). One signal of 2H was not observed. Anal. Calcd for C_46H_36FeN_2Si_3: C, 78.08; H, 6.88; N, 3.04. Found: C, 77.4; H, 7.08; N, 2.69. \( \mu_{\text{eff}} = 5.2 \mu\text{B} \).

Decomposition of 5a in Bromobenzene-d_6. Compound 5a was generated in an NMR tube as described above. After checking that compound 5a had been generated cleanly, the toluene was pumped off and bromobenzene-d_6 was added to the reaction mixture. Within 10 min after the addition of bromobenzene-d_6, the formation of 6a was observed. The reaction was found to be complete when the reaction mixture was left overnight at room temperature.

Decomposition of 5a in Toluene-d_6. Compound 5a was generated in an NMR tube as described above. After checking that compound 5a had been generated cleanly, the toluene was pumped off and bromobenzene-d_6 was added to the reaction mixture. Within 10 min after the addition of bromobenzene-d_6, the formation of 6a was observed. The reaction was found to be complete when the reaction mixture was left overnight at room temperature.

**Supporting Information Available:** Crystallographic data for compounds 1a, 2a, 3a, 4a, 6a, and 7a. This material is available free of charge via the Internet at http://pubs.acs.org.