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

ARTICLE *in* ORGANOMETALLICS · JANUARY 2009

3 AUTHORS, INCLUDING:

Jeroen Volbeda
Institute for heat and fuel technology
7 PUBLICATIONS   52 CITATIONS

SEE PROFILE

Auke Meetsma
University of Groningen
527 PUBLICATIONS   15,381 CITATIONS

SEE PROFILE

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

Jeroen Volbeda, Auke Meetsma, and Marco W. Bouwkamp*

Molecular Inorganic Chemistry Department, Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Received July 17, 2008

Reaction of diimine ligands $(Ph_2CN)_2C_nH_{2n}$ ($n = 2$, **a**; $n = 3$, **b**) with $FeCl_2$ or $FeBr_2$ results in formation of the corresponding high-spin ferrous complexes $\{(Ph_2CN)_2C_2H_4\}FeX_2$ (**1a**, X = Cl; **2a**, X = Br) and $\{(Ph_2CN)_2C_3H_6\}FeCl_2$ (**1b**). Dialkyl $\{(Ph_2CN)_2C_2H_4\}Fe(CH_2SiMe_3)_2$ (**3a**) was prepared by treatment of $(py)_2Fe(CH_2SiMe_3)_2$ with diimine ligand **a**. Addition of $B(C_6F_5)_3$ to **3a** at −30 °C resulted in Me_3SiCH_2 abstraction, affording $[\{(Ph_2CN)_2C_2H_4\}Fe(CH_2SiMe_3)][Me_3SiCH_2B(C_6F_5)_3]$ (**5a**). ^{19}F NMR spectroscopy revealed that this compound exists as a contact ion-pair in toluene solution. Compound **5a** decomposes at room temperature in bromobenzene-d_5 or toluene-d_8, affording dication $[\{(Ph_2CN)_2C_2H_4\}_2Fe]^{2+}$ (**6a**); at elevated temperatures in toluene-d_8 the formation of $[\{(Ph_2CN)_2C_2H_4\}Fe(CH_2SiMe_3)C_6F_5]$ (**7a**) was observed as well. Neither ferrous chloride $\{(Ph_2CN)_2C_2H_4\}FeCl_2$ 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 Brookhart[1] 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 zerovalent[5] and trivalent[6] iron species have been proposed as well. It has been shown that the pyridine-diimine iron dialkyl complex $(PDI)Fe(CH_2SiMe_3)_2$ $(PDI = 2,6-\{2,6-i-Pr_2C_6H_3NC(Me)\}_2C_5H_3N)$[7] can be converted into a monoalkyl cation by treatment with tris(pentafluorophenyl)borane and that the resulting well-defined iron alkyl cation

Scheme 1
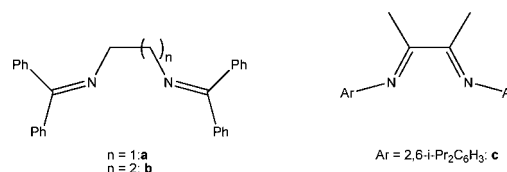
$[(PDI)Fe(CH_2SiMe_2CH_2SiMe_3)][MeB(C_6F_5)_3]$ is indeed active in the polymerization of ethylene.[8] On the other hand, it is known that treatment of PDI iron complexes with alkyl aluminum species can result in ligand redistribution reactions;[9] thus the exact nature of the active species in the MAO-activated system remains under debate.

We are thus interested in the reactivity of cationic iron alkyl complexes supported by neutral imine derived ligands. Our initial focus has been on the synthesis and reactivity of iron complexes with nonconjugated diimine ligands $(Ph_2CN)_2C_nH_{2n}$ ($n = 2$, **a**; $n = 3$, **b**; Scheme 1),[10] and the results have been compared to those previously obtained with the well-known α-diimine ligand $(2,6-i-Pr_2C_6H_3N)_2(C_2Me_2)$ (**c**, Scheme 1).[11] Included is the synthesis of neutral and cationic iron alkyl complexes with the C_2-bridged diimine ligand **a**. The alkyl cation $[\{(Ph_2CN)_2C_2H_4\}Fe(CH_2SiMe_3)]^+$ is inactive in the polymerization of olefins, but was found to reversibly bind ethylene.

* Corresponding author. E-mail: M.W.Bouwkamp@rug.nl.

(1) Small, B. L.; Brookhart, M.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049.

(2) Britovsek, G. J. P.; Gibson, V. C.; Kimberely, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 849.

(3) For recent reviews on iron-catalyzed olefin polymerization catalysis, see: Bianchini, C.; Giambastiania, G.; Guerrero Rios, I.; Mantovani, G.; Meli, A.; Segarra, A. M. *Coord. Chem. Rev.* **2006**, *250*, 1391. Gibson, V. C.; Redshaw, C.; Solan, G. A. *Chem. Rev.* **2007**, *107*, 1745.

(4) (a) Deng, L.; Margl, P.; Ziegler, T. *J. Am. Chem. Soc.* **1999**, *121*, 6479. (b) Babik, S. T.; Fink, G. *J. Mol. Catal. A* **2002**, *188*, 245. (c) Britovsek, G. J. P.; Gibson, V. C.; Spitzmesser, S. K.; Tellman, K. P.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **2002**, 1159. (d) Bryliakov, K. P.; Semikolenova, N. V.; Zudin, V. N.; Zakharov, V. A.; Talsi, E. P. *Catal. Commun.* **2004**, *5*, 45. (e) Castro, P. M.; Lahtinen, P.; Axenov, K.; Viidanoja, J.; Kotiaho, T.; Leskelä, M.; Repo, T. *Organometallics* **2005**, *24*, 3664.

(5) Scott, J.; Gambarotta, S.; Korobkov, I.; Budzelaar, P. H. M. *Organometallics* **2005**, *24*, 6298.

(6) (a) Britovsek, G. J. P.; Clentsmith, G. K. B.; Gibson, V. C.; Goodgame, D. M. L.; McTavish, S. J.; Pankhurst, Q. A. *Catal. Commun.* **2002**, *3*, 207. (b) Raucoules, R.; De Bruin, T.; Raybaud, P.; Adamo, C. *Organometallics* **2008**, *27*, 3368−3377.

(7) (a) Bouwkamp, M. W.; Bart, S. C.; Hawrelak, E. J.; Trovitch, R. J.; Lobkovsky, E.; Chirik, P. J. *Chem. Commun.* **2005**, 3406. (b) Scott, J.; Gambarotta, S.; Korobkov, I.; Budzelaar, P. H. M. *J. Am. Chem. Soc.* **2005**, *127*, 13019. (c) Cámpora, J.; Naz, A. M.; Palma, P.; Álvarez, E.; Reyes, M. L. *Organometallics* **2005**, *24*, 4878.

(8) Bouwkamp, M. W.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2005**, *127*, 9660.

(9) Scott, J.; Gambarotta, S.; Korobkov, I.; Knijnenburg, Q.; De Bruin, B.; Budzelaar, P. H. M. *J. Am. Chem. Soc.* **2005**, *127*, 17204.

(10) (a) Tripathi, S. C.; Srivastava, S. C.; Shrimal, A. K.; Singh, O. P. *Inorg. Chim. Acta* **1985**, *98*, 19. (b) Paz-Sandoval, M. A.; Domínguez-Durán, M. E.; Pazos-Mayen, C.; Ariza-Castolo, A.; Rosales-Hoz, M. J.; Contretas, R. *J. Organomet. Chem.* **1995**, *492*, 1. (c) Petrovski, Z.; Pillinger, M.; Valente, A. A.; Gonçalves, I. S.; Hazell, A.; Romão, C. C. *J. Mol. Catal. A: Chem.* **2005**, *227*, 67. (d) Kia, R.; Mirkhani, V.; Kalman, A.; Deak, A. *Polyhedron* **2007**, *26*, 1711.

(11) Bart, S. C.; Hawrelak, E. J.; Schmisseur, A. K.; Lobkovsky, E.; Chirik, P. J. *Organometallics* **2004**, *23*, 237.

Scheme 2
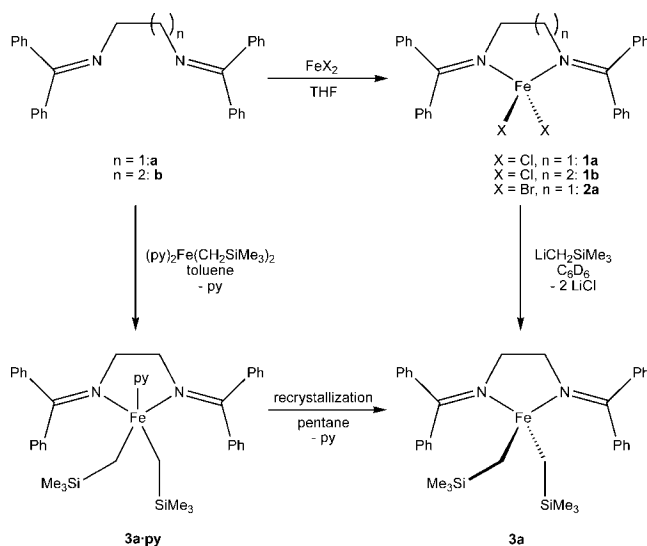
Results and Discussion

Synthesis of Iron Halide Complexes. Ferrous dichlorides {$(Ph_2CN)_2C_2H_4$}FeCl$_2$ (**1a**) and {$(Ph_2CN)_2C_3H_6$}FeCl$_2$ (**1b**) and dibromide {$(Ph_2CN)_2C_2H_4$}FeBr$_2$ (**2a**) were prepared by stirring THF suspensions of anhydrous FeCl$_2$ or FeBr$_2$ 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,b** 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-diimine complexes of this type.[11] Both compounds **1a** and **2a**[12] 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 $P2_1/c$ 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 N(11)−Fe(1)−N(12) angles of 81.88(9)° and 81.7(3)° and X−Fe(1)−X angles of 126.09(3)° and 121.39(7)°, respectively. Both compounds show a strong puckering in the Fe(1)−N(11)−C(114)−C(115)−N(12) ring, with one of the two carbon atoms of the C$_2$-spacer deviating from the ligand plane. As a result, one of the imine moieties is pushed out of the Fe(1)−N(11)−N(12) plane (Figure 1). The (C$_{ipso}$)$_2$CNCH$_2$ moieties are virtually planar, resulting in two sets of distinct phenyl groups: one that is directed toward the metal center and one that is pointing away. The metrical parameters of **1a** are similar to the corresponding ferrous chloride with an α-diimine ligand, {$(2,6-i-Pr_2C_6H_3N)_2$-(C_2Me_2)}FeCl$_2$ (**1c**),[13] with slightly larger Fe−N and Fe−Cl bond distances for the first (average Fe−N: 2.130(4) Å for **1a** and 2.1016(14) for **1c**; average Fe−Cl: 2.2588(13) Å for **1a** and 2.2222(10) for **1c**) and a larger bite angle (81.88(9)° for **1a** and 76.50(5)° for **1c**).

As expected for high-spin ($S = 2$) iron complexes, the ^{1}H NMR spectra of the ferrous complexes prepared in this study reveal paramagnetically shifted resonances. Whereas most of these are found relatively close to the resonances observed for the free diimines, two resonances integrating to 4 protons each show 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 ^{1}H NMR spectrum.

Synthesis of Neutral Iron Alkyl Complexes. Treatment of **1a** or **2a** with 2 equiv of LiCH$_2$SiMe$_3$ in benzene-d_6 solution resulted in a color change from yellow to brownish-red. ^{1}H NMR spectroscopy of the reaction mixture revealed the number of signals expected for a C_{2v} symmetric dialkyl complex {$(Ph_2CN)_2$-C_2H_4}Fe(CH$_2$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 center[7a,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)$_2$Fe(CH$_2$SiMe$_3$)$_2$[7c] 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 {$(Ph_2CN)_2C_2H_4$}-Fe(CH$_2$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 {$(Ph_2CN)_2C_2H_4$}Fe(CH$_2$SiMe$_3$)$_2$ (**3a**). The geometry of **3a** (see Figure 1 for an ORTEP representation of **3a** and Table 1 for pertinent bond distances and angles) is very similar to that of complexes **1a** and **2a**, with slightly longer Fe−N bond distances. The Fe−N and Fe−C bond distances in **3a** are slightly elongated compared with those found in {$(2,6-i-Pr_2C_6H_3N)_2(C_2Me_2)$}Fe(CH$_2$SiMe$_3$)$_2$ (**3c**).[11] As expected, iron dialkyl **3a** has a high-spin ground state (μ_{eff} = 4.9 μ_B).

Treatment of **1b** with LiCH$_2$SiMe$_3$ in benzene-d_6 in an NMR tube resulted in a reddish-brown, intractable mixture of products. Furthermore, dissolving (py)$_2$Fe(CH$_2$SiMe$_3$)$_2$ and the C$_3$-bridged diimine ligand (**b**) in benzene-d_6 did not result in formation of the corresponding dialkyl complex. Instead, a mixture of the starting materials was observed by ^{1}H NMR spectroscopy, even after shaking the NMR tube for 3 days at room temperature.

Synthesis of Cationic Iron Alkyl Complexes. THF-solvated cation [{$(Ph_2CN)_2C_2H_4$}Fe(CH$_2$SiMe$_3$)(THF)][BPh$_4$] (**4a′**) was prepared in reasonable yield (53%) by reaction of a 1:1 mixture of dialkyl **3a** and Brønsted acid [PhNMe$_2$H][BPh$_4$] 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-d_5. These crystals were used for a single-crystal X-ray analysis.

(13) Kervern, G.; Pintacuda, G.; Zhang, Y.; Oldfield, E.; Roukoss, C.; Kuntz, E.; Herdtweck, E.; Basset, J. M.; Cadars, S.; Lesage, A.; Copéret, C.; Emsley, L. *J. Am. Chem. Soc.* **2006**, *128*, 13545.

(14) (a) Scott, J.; Gambarotta, S.; Korobkov, I.; Budzelaar, P. H. M. *Organometallics* **2005**, *24*, 6298. (b) Fernández, I.; Trovitch, R. J.; Lobkovsky, E.; Chirik, P. J. *Organometallics* **2008**, *27*, 109.
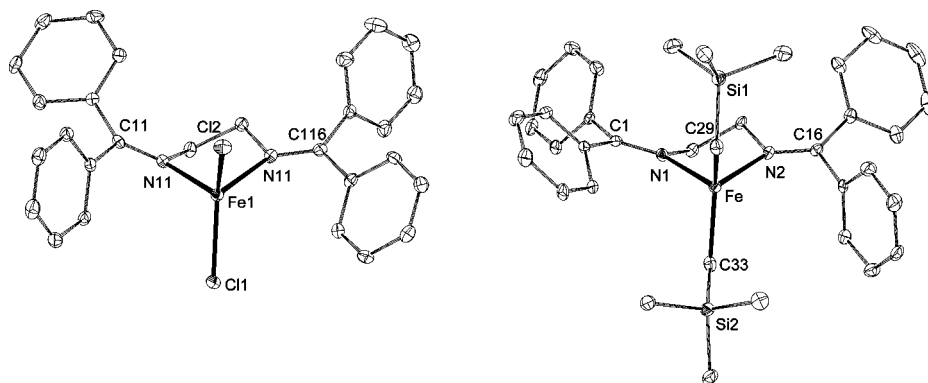
Figure 1. ORTEP representations at the 30% probability level of **1a** and **3a**. Hydrogen atoms are omitted for clarity.

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

	1a	2a	3a	4a′	6a	7a
Fe(1)−N(11)[a]	2.149(3)	2,114(8)	2.214(3)	2.120(3)	2.123(6)	2.186(5)
Fe(1)−N(12)[b]	2.112(2)	2.129(8)	2.176(3)	2.154(3)	2.095(6)	2.149(5)
Fe(1)−X[c]	2.2431(9)	2.443(2)	2.078(4)	2.055(2)	2.073(6)	2.132(7)
Fe(1)−Y[d]	2.2744(9)	2.374(2)	2.098(4)	2.024(4)	2.085(6)	2.077(6)
C(11)−N(11)[a,e]	1.296(3)	1.308(13)	1.287(5)	1.301(5)	1.306(9)	1.293(7)
C(116)−N(12)[b,f]	1.291(4)	1.295(12)	1.285(5)	1.292(5)	1.300(9)	1.292(7)
C(135)−N(13)					1.301(11)	
C(150)−N(14)					1.304(11)	
N(11)−Fe(1)−N(12)[a,b]	81.88(9)	81.7(3)	80.09(11)	81.52(11)	84.5(2)	80.34(17)
X−Fe(1)−Y[c,d]	126.09(3)	121.39(7)	131.66(16)	137.06(12)	83.5(2)	124.1(2)

[a] Fe and N(1) for **3a** and **7a**. [b] Fe and N(2) for **3a** and **7a**. [c] X = Cl11 (**1a**); Br11 (**2a**); C(29) (**3a**); O(11) (**4a′**); N(13) (**6a**); C(29) (**7a**). [d] Y = Cl12 (**1a**); Br12 (**2a**); C(29) (**3a**); C(129) (**4a′**); N(14) (**6a**); C(35) (**7a**). [e] C(1) for **3a** and **7a**; C(17) for **6a**. [f] C(16) for **3a** and **7a**; C(122) for **6a**.

contracted 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-d_8 solution of $B(C_6F_5)_3$ to a cooled solution of **3a** in toluene-d_8. This resulted in a color change from purple to yellow. After replacing the solvent with THF-d_8 a species was observed with a similar ^{1}H NMR spectrum to that of **4a′**, suggesting the initial formation of ion-pair $[\{(Ph_2CN)_2C_2H_4\}Fe(CH_2SiMe_3)][Me_3SiCH_2B(C_6F_5)_3]$ (**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 $[Me_3SiCH_2B(C_6F_5)_3]$, 599.1) in the negative-ion spectrum. Hence, similar to the α-diimine case, the coordination sphere of the iron center in **3a** is sufficiently open to allow abstraction of a Me_3SiCH_2 group,[11] and there is no indication for Me_3SiCH_2-methyl group abstraction.[8] It should be noted that, in the case of the α-diimine complex, the iron alkyl cation $[\{(2,6\text{-}i\text{-}Pr_2C_6H_3N)_2(C_2Me_2)\}Fe(CH_2Si\text{-}Me_3)]^+$ could not be observed. Instead, $\{(2,6\text{-}i\text{-}Pr_2C_6H_3N)_2$-

Figure 2. ^{1}H NMR spectrum of **1a**. The numbers represent the relative integrations; * marks the CDCl$_3$ solvent peak.

$(C_2Me_2)\}Fe(CH_2SiMe_3)C_6F_5$ (**7c**) was obtained, the result of a fast C_6F_5 transfer in the initially generated ion-pair (*vide infra*).[11]

The ^{19}F NMR spectrum of **5a** in toluene-d_8 (at a concentration of 30.2 mM) revealed three resonances at δ −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 δ −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-d_8, resonances are observed at δ −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-d_8 or bromobenzene-d_5, a secondary iron species (**6a**) was observed as well. In bromobenzene-d_5 species **6a** was observed exclusively after standing for 24 h at room temperature. The compound was characterized as $[\{(Ph_2CN)_2$-$(C_2H_4)\}_2Fe][Me_3SiCH_2B(C_6F_5)_3]_2$ (**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
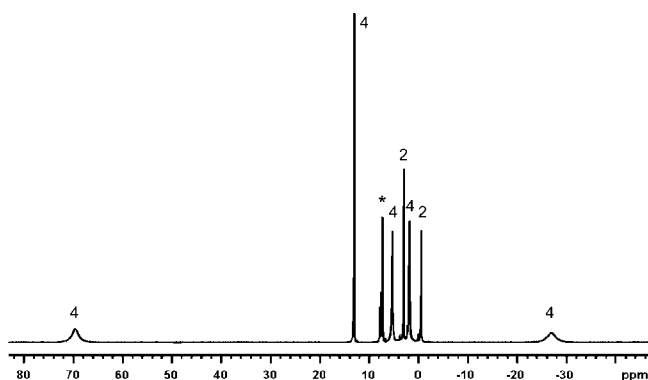
(15) (a) Sciarone, T. J. J.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Chem. Commun.* **2002**, 1580. (b) Sciarone, T. J. J.; Meetsma, A.; Hessen, B. *Inorg. Chim. Acta* **2006**, *359*, 1815. (c) Sciarone, T. J. J.; Nijhuis, C. A.; Meetsma, A.; Hessen, B. *Organometallics* **2008**, *27*, 2058.
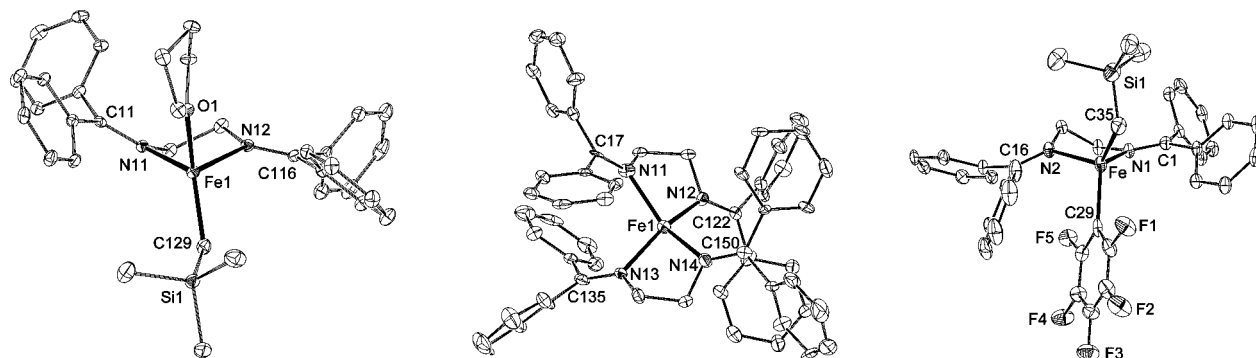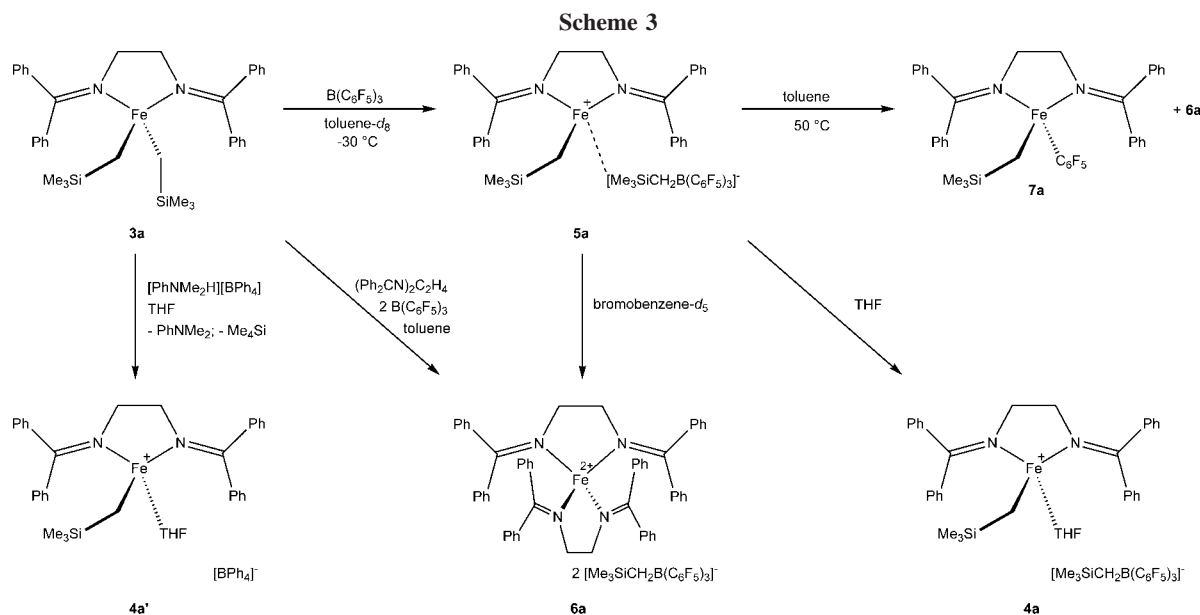
Figure 3. ORTEP representations at the 30% probability level of **4a′**, **6a**, and **7a**. Hydrogen atoms and counterions are omitted for clarity.

Scheme 3

2 equiv of $B(C_6F_5)_3$ 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 $[FeCl]_2\{\mu-(2,6-i-Pr_2C_6H_3NC\{Ph\}NC_2H_4NMe_2)\}$[15c] and in the attempted synthesis of a cationic amidinate complexes of the type $[\{PhC(N-2,6-i-Pr_2C_6H_3)_2\}Fe(CH_2SiMe_3)]^+$.[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 $(Me_3SiCH_2)_2$, suggesting concomitant formation of $[Fe(CH_2SiMe_3)_2]$.

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, $\{(Ph_2CN)_2C_2H_4\}Fe-(CH_2SiMe_3)C_6F_5$ (**7a**). Compound **7a** is highly soluble in aromatic and aliphatic solvents and could be isolated by

(16) Lee, H.; Hong, S.-D.; Park, Y.-W.; Jeong, B.-G.; Nam, D.-W.; Jung, H. Y.; Jung, M. W.; Song, K. H. *J. Organomet. Chem.* **2004**, *689*, 3402.

(17) (a) Beck, S.; Lieber, S.; Schaper, F.; Geyer, A.; Brintzinger, H.-H. *J. Am. Chem. Soc.* **2001**, *123*, 1483. (b) Stahl, N. G.; Zuccaccia, C.; Jensen, T. R.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 5256. (c) Zuccaccia, C.; Stahl, N. G.; Macchioni, A.; Chen, M.-C.; Roberts, J. A.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 1448.

(18) Horton, A. D.; De With, J.; Van der Linden, A. J.; Van de Weg, H. *Organometallics* **1996**, *15*, 2672.

(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.

(20) Sciarone, T. J. J.; Nijhuis, C. A.; Meetsma, A.; Hessen, B. *Dalton Trans.* **2006**, 4896.
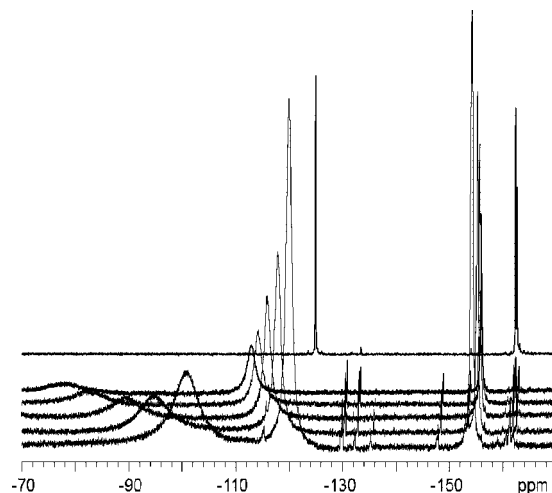
Figure 4. From bottom up: ^{19}F NMR spectra of the contact ion-pair **5a** in toluene-d_8 at 30.2, 19.4, 14.3, 11.4, and 9.19 mM, respectively, and of the THF adduct **4a** in toluene-d_8.

Scheme 4
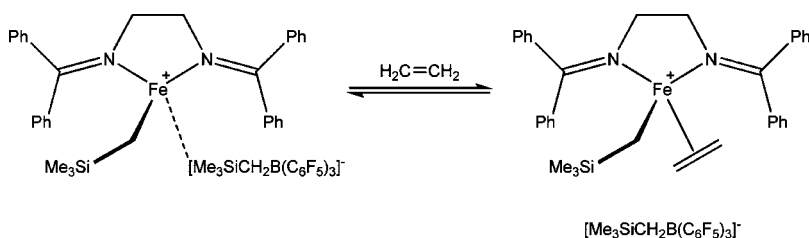
extraction with pentane. Cooling of the pentane solution to -30 °C afforded reddish-orange crystals suitable for X-ray analysis (see Figure 3 for an ORTEP representation of the molecule and Table 1 for pertinent bond distances and angles). Its structure is very similar to that of dialkyl **3a**, with shorter metal−nitrogen bond distances, a result of the increased electrophilicity of the metal center imparted by the electron-withdrawing pentafluorophenyl group. Again, a comparison of bond distances to the α-diimine analogue $\{(2,6\text{-}i\text{-}Pr_2C_6H_3N)_2(C_2Me_2)\}Fe(CH_2SiMe_3)\text{-}C_6F_5$ (**7c**) shows longer iron−nitrogen bond distances in **7a**.[11] Performing the reaction in an NMR tube shows the expected formation of $Me_3SiCH_2B(C_6F_5)_2$, which could be identified using ^{19}F NMR spectroscopy. The ^{19}F NMR spectrum of **7a** revealed two resonances at 162 and -7.3 ppm for the pentafluorophenyl group attached to the iron center. One signal, presumably the *o*-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-d_8 solution of **5a**, the ^{1}H NMR spectrum of the reaction mixture reveals a broad signal at 14.5 ppm ($\Delta\nu_{1/2} = 306$ 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 ^{19}F 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 $[\{(Ph_2CN)_2(C_2H_4)\}_2Fe][Me_3SiCH_2B(C_6F_5)_3]_2$.

Conclusions

Diimines $(Ph_2CN)_2C_nH_{2n}$ ($n = 2, 3$) are suitable ligands for the stabilization of electron-deficient iron complexes, and in case of the ligand with the C_2 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 iron alkyl complex $[\{(Ph_2CN)_2C_2H_4\}Fe(CH_2SiMe_3)][Me_3SiCH_2B(C_6F_5)_3]$ rearranges to dication $[\{(Ph_2CN)_2C_2H_4\}_2Fe]^{2+}$, the result of a ligand redistribution reaction. In toluene, at 50 °C a secondary thermolysis product was observed as well, which was identified as $\{(Ph_2CN)_2C_2H_4\}Fe(CH_2SiMe_3)C_6F_5$. 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.
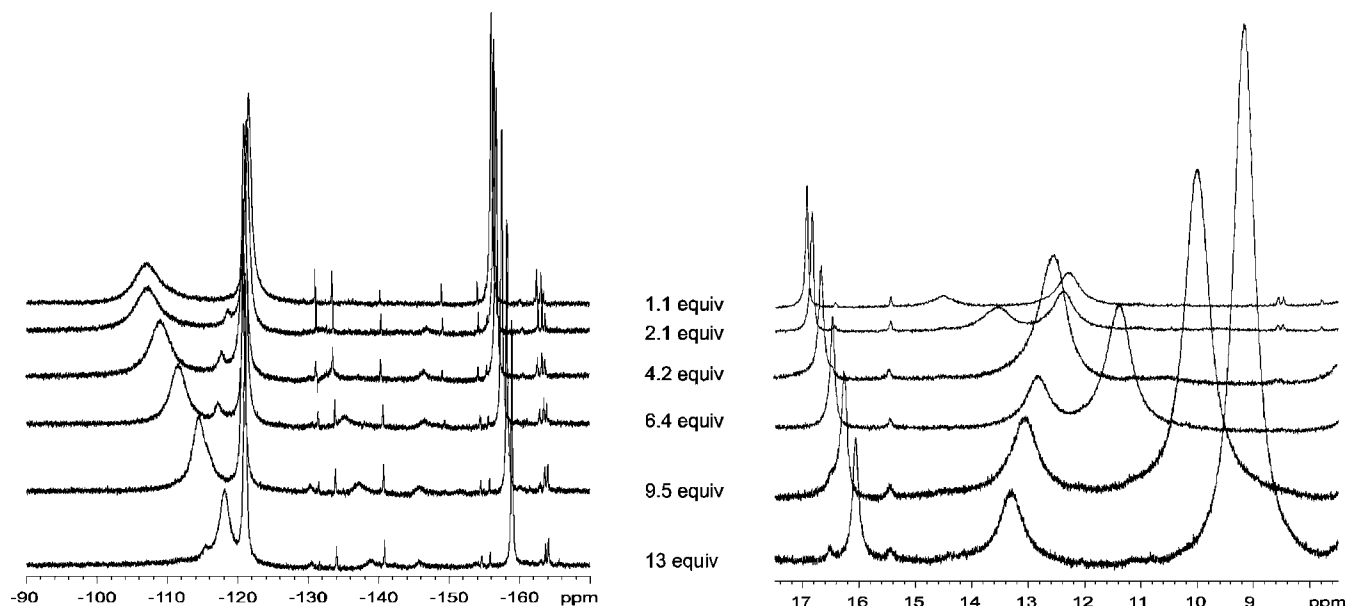

Figure 5. From top to bottom: ^{19}F NMR (left) and ^{1}H NMR (right) spectra of the reaction mixture containing compound **5a** and 1.1, 2.1, 4.2, 6.4, 9.5, and 13 equiv of ethylene in toluene-d_8, respectively.

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_8) or CaH$_2$ (chloroform-d, bromobenzene-d_5, dichloromethane). Reagents were purchased from commercial providers and used without purification unless stated otherwise. Anhydrous FeCl$_2$,[21] (Ph$_2$CN)$_2$C$_2$H$_4$,[22] (py)$_2$Fe(CH$_2$SiMe$_3$)$_2$,[7c] LiCH$_2$SiMe$_3$,[23] [PhNMe$_2$H][BPh$_4$],[24] and B(C$_6$F$_5$)$_3$[25] 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 tetramethylsilane; ^{19}F chemical shifts are reported relative to α,α,α-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 and, where possible, peak assignment. ^{1}H NMR spectra of paramagnetic complexes were recorded with a sweep width of 100 000 Hz, delay of 0 s, and acquisition time of 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 electrospray 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 closed chamber that can be evacuated, flushed, and maintained under nitrogen. Typical sample analysis: in a glovebox, the sample was taken up into a 500 mL syringe (model 1750 RNR, Hamilton) and electrosprayed via a syringe pump operating at 10 mL/min. The capillary voltage was 3.5 kV. Mass spectra were recorded from *m*/*z* 50 to 900 (example) at 10 s per scan using a step size of 0.1 Da. The sampling orifice (nozzle) was at +35 V. The skimmer was located behind the sampling. Crystals suitable for a single-crystal X-ray analysis were grown as described in the text. A crystal was mounted on a glass fiber inside a drybox and transferred under an inert atmosphere to the cold nitrogen stream of a Bruker SMART APEX CCD diffractometer. Intensity data were corrected for Lorentz and polarization effects, scale variation, decay, and absorption: a multiscan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (SADABS),[27] and reduced to F_0^2. The structures were solved by Patterson methods, and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF.[28] The positional and anisotropic displacement parameters for the non-hydrogen atoms were refined. Final refinement on F_2 was carried out by full-matrix least-squares techniques.

(21) Kovacic, P.; Brace, N. O. *Inorg. Synth.* **1960**, *6*, 172.
(22) Ariza-Castolo, A.; Paz-Sandoval, M. A.; Contreras, R. *Magn. Reson. Chem.* **1992**, *30*, 520.
(23) Lewis, H. L.; Brown, T. L. *J. Am. Chem. Soc.* **1970**, *92*, 4664.
(24) Eshuis, J. J. W.; Tan, Y. Y.; Meetsma, A.; Teuben, J. H.; Renkema, J.; Evens, G. G. *Organometallics* **1992**, *11*, 362.
(25) Pohlmann, J. L. W.; Brinckmann, F. E. Z. *Naturforsch. B* **1965**, *20*, 5.
(26) Sur, S. K. *J. Magn. Reson.* **1989**, *82*, 169.
(27) Sheldrick, G. M. *SADABS* v2, *Multi-Scan Absorption Correction Program*; University of Göttingen: Germany, 2001.
(28) Beurskens, P. T.; Beurskens, G.; De Gelder, R.; Garcı́a-Granda, S.; Gould, R. O.; Israël, R.; Smits, J. M. M. *The DIRDIF-99 Program System*; Crystallography Laboratory, University of Nijmegen: The Netherlands, 1999.

(Ph$_2$CN)$_2$C$_3$H$_6$ (b). 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 xylenes (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 (CDCl$_3$, RT): δ 7.12−7.53 (m, 20H, Ph), 3.45 (t, 4H, 6.85 Hz, CH$_2$), 2.04 (q, 2H, 6.89 Hz, CH$_2$). ^{13}C NMR (CDCl$_3$, RT): δ 140.9, 138.0 (2 × Ph C$_{ipso}$), 130.7, 129.4, 129.3, 129.2, 128.9, 128.8 (6 × Ph CH), 52.8 (CH$_2$), 33.8 (CH$_2$). Anal. Calcd for C$_{29}$H$_{26}$N$_2$: C, 86.53; H, 6.51; N, 6.96. Found: C, 86.18; H, 6.48; N, 6.95.

{(Ph$_2$CN)$_2$C$_2$H$_4$}FeCl$_2$ (1a). THF (20 mL) was added to a mixture of **a** (1.55 g; 3.99 mmol) and FeCl$_2$ (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. Layering a dichloromethane solution of the solid with pentane resulted in crystals suitable for X-ray analysis. ^{1}H NMR (CDCl$_3$, RT): δ 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 C$_{28}$H$_{24}$Cl$_2$FeN$_2$: C, 65.27; H, 4.70; N, 5.44. Found: C, 64.64; H, 4.67; N, 5.25. μ_{eff} = 5.3 μ_B.

{(Ph$_2$CN)$_2$C$_3$H$_6$}FeCl$_2$ (1b). Compound **1b** was prepared analogous to **1a**, by treating **b** (1.47 g; 3.79 mmol) with FeCl$_2$ (0.480 g; 3.78 mmol) in THF (20 mL). This afforded 1.51 g (2.85 mmol; 75%) of **1b**. ^{1}H NMR (CDCl$_3$, RT): δ 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 CH$_2$Cl$_2$/cyclohexane. Anal. Calcd for C$_{29}$H$_{26}$Cl$_2$FeN$_2$·CH$_2$Cl$_2$: C, 58.66; H, 4.60; N, 4.56. Found: C, 58.42; H, 4.59; N, 4.42.

{(Ph$_2$CN)$_2$C$_2$H$_4$}FeBr$_2$ (2a). Compound **2a** was prepared analogous to **1a**, by treating FeBr$_2$ (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 (bromobenzene-d_5, RT): δ 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 C$_{28}$H$_{24}$Br$_2$FeN$_2$: C, 55.66; H, 4.00; N, 4.64. Found: C, 55.43; H, 3.96; N, 4.52.

Generation of {(Ph$_2$CN)$_2$C$_2$H$_4$}Fe(CH$_2$SiMe$_3$)$_2$ from 1a. Addition of a solution of LiCH$_2$SiMe$_3$ (9.5 mg; 0.10 mmol) in THF (0.5 mL) to **1a** (26.7 mg; 0.0518 mmol) resulted in a color change to purple. After 1 h the volatiles were pumped off. Pentane was added and removed *in vacuo* to remove residual THF. Analysis of the reaction mixture by ^{1}H NMR spectroscopy in benzene-d_6 revealed the formation of a mixture of products, one of which was identified as **3a** (see below).

Generation of {(Ph$_2$CN)$_2$C$_2$H$_4$}Fe(CH$_2$SiMe$_3$)$_2$ from 2a. LiCH$_2$SiMe$_3$ (6.6 mg; 0.070 mmol) in benzene-d_6 (0.4 mL) was added to an NMR tube with **2a** (21.4 mg; 0.0354 mmol). The resulting purple reaction mixture was analyzed by ^{1}H NMR spectroscopy and revealed the formation of **3a** (see below).

{(Ph$_2$CN)$_2$C$_2$H$_4$}Fe(CH$_2$SiMe$_3$)$_2$(py) (3a·py). In an NMR tube (py)$_2$Fe(CH$_2$SiMe$_3$)$_2$ (10.7 mg; 0.0275 mmol) and **a** (10.7 mg; 0.0275 mmol) were dissolved in benzene-d_6 (0.4 mL), resulting in a purple solution. ^{1}H NMR spectroscopy indicated the formation of **3a·py**. The volatiles were transferred to a second NMR tube charged with 4.9 mg (0.026 mmol) of ferrocene internal standard. ^{1}H NMR analysis thus revealed that during the reaction 1 equiv of free pyridine was generated. ^{1}H NMR of **3a·py** (C$_6$D$_6$, RT): δ 57.8

(4H, 13.6 Hz), 27.6 (2H, 804 Hz), 16.6 (1H, 242 Hz), 15.1 (2H, 217 Hz), 12.7 (22H, 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.

{(Ph$_2$CN)$_2$C$_2$H$_4$}Fe(CH$_2$SiMe$_3$)$_2$ (3a). Toluene (5 mL) was added to a mixture of (py)$_2$Fe(CH$_2$SiMe$_3$)$_2$ (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. ^{1}H NMR (C$_6$D$_6$, RT): δ 57.5 (4H, 601 Hz), 13 (22H, two 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$_{36}$H$_{46}$FeN$_2$Si$_2$: C, 69.88; H, 7.49; N, 4.53. Found: C, 68.35; H, 7.44; N, 4.39. μ_{eff} = 4.9 μ_B.

[{(Ph$_2$CN)$_2$C$_2$H$_4$}Fe(CH$_2$SiMe$_3$)THF][B(C$_6$H$_5$)$_4$] (4a′). THF (1 mL) was added to a mixture of **3a** (32.9 mg; 0.0532 mmol) and [PhNMe$_2$H][BPh$_4$] (23.6 mg; 0.0573 mmol). The resulting yellow-orange solution was cooled to −30 °C for 30 min and subsequently layered with pentane. After storing overnight at −30 °C orange crystals had formed. The supernatant was decanted, affording 26.1 mg (0.028 mmol; 53% yield) of orange crystals of **4a′**. ^{1}H NMR (THF-d_8; RT): δ 72.3 (4H, 833 Hz), 21.3 (9H, 170 Hz, SiMe$_3$), 13.2 (4H, 24 Hz), 10.0 (8H, 26 Hz, BPh$_4$), 8.2 (8H, 27 Hz, BPh$_4$), 7.6 (4H, 25 Hz, *p*-BPh$_4$), 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$_{36}$H$_{46}$FeN$_2$Si$_2$: C, 78.08; H, 6.88; N, 3.04. Found: C, 77.40; H, 7.08; N, 2.69. μ_{eff} = 5.2 μ_B.

Generation of [{(Ph$_2$CN)$_2$C$_2$H$_4$}Fe(CH$_2$SiMe$_3$)][Me$_3$SiCH$_2$B-(C$_6$H$_5$)$_3$] (5a). A solution of **3a** (5.9 mg; 0.0095 mmol) in toluene-d_8 and a solution of B(C$_6$F$_5$)$_3$ (4.9 mg; 0.0096 mmol) in toluene-d_8 were cooled to −30 °C. The B(C$_6$F$_5$)$_3$ solution was slowly added to the solution containing **3a**, affording an orange solution of **5a**. ^{1}H NMR (toluene-d_8, RT): δ 177.3 (4H, 857 Hz), 17.0 (4H, 56 Hz), 11.8 (9H, 228 Hz, SiMe$_3$), 4.6 (2H, 25 Hz), 2.3 (2H, 53 Hz), 1.1 (2H, 43 Hz), −1.68 (9H, 40 Hz), −26.3 (4H, 101 Hz), −45.2 (4H, 977 Hz). One signal of 2H was not observed. ^{19}F NMR (30.2 mM in toluene-d_8, RT): −99.1 (6F, 2202 Hz, *m*-F), −118.7 (6F, 969 Hz, *o*-F), −152.0 (3F, 318 Hz, *p*-F).

Generation of [{(Ph$_2$CN)$_2$C$_2$H$_4$}Fe(CH$_2$SiMe$_3$)(THF)][Me$_3$-SiCH$_2$B(C$_6$H$_5$)$_3$] (4a). A solution of **5a** was prepared as described above. The solvent was removed *in vacuo*, and the residue was dissolved in THF-d_8. The product was identified by ^{1}H NMR spectroscopy as the title compound. ^{1}H NMR (THF-d_8, RT): δ 72.9 (4H, 701 Hz), 21.8 (9H, 177 Hz, FeCH$_2$Si*Me*$_3$), 13.6 (4H, 46 Hz), 4.1 (2H, 90 Hz), 0.72 (2H, 16 Hz, BC*H*$_2$SiMe$_3$), −0.3 (9H, 9 Hz, BCH$_2$Si*Me*$_3$), −2.5 (2H, 54 Hz), −9.1 (4H, 76 Hz), −38.1 (4H, 593 Hz). Two signals could not be observed. ^{19}F NMR (THF-d_6, RT): δ −129.7 (d, 22 Hz, 6F, *o*-F), −164.7 (ps.t., 20 Hz, 3F, *p*-F), −166.8 (ps.t., 21 Hz, 6F, m-F). ESI-MS (35 eV, THF): neg-ion mode, *m/z* 599.1 [Me$_3$SiCH$_2$B(C$_6$F$_5$)$_3$]$^-$; pos-ion mode, *m/z* 603.3 [{(Ph$_2$CN)$_2$C$_2$H$_4$}Fe(CH$_2$SiMe$_3$)(THF)]$^+$, 531.1 [{(Ph$_2$CN)$_2$C$_2$H$_4$}-Fe(CH$_2$SiMe$_3$)]$^+$.

Decomposition of 5a in Toluene. A flask containing **3a** (0.106 g; 0.171 mmol), B(C$_6$F$_5$)$_3$ (0.087 g; 0.17 mmol), and toluene (5 mL) was stirred for 2 days at 50 °C, resulting in a brown solution and a yellow precipitate. The solution was filtered off and the solid was washed with toluene. The yellow solid was recrystallized from CH$_2$Cl$_2$/cyclohexane, affording 72.4 mg (0.0356 mmol; 21%) of yellow crystals of dication **6a**. ^{1}H NMR (CDCl$_3$; RT): δ 136.5 (4H, 587 Hz), 16.7 (4H, 20 Hz), 11.3 (4H, 60 Hz), 4.3 (2H, 20 Hz), 2.0 (2H, 19 Hz), 1.1 (2H, 25 Hz), 0.3 (9H, SiMe$_3$, 12 Hz), −1.6 (4H, 46 Hz), −31.6 (4H, 467 Hz). ^{19}F NMR (CDCl$_3$; RT): δ −128.0 (2F, 47 Hz), −163.7 (1F,

44 Hz), 165.1 (2F, 55 Hz). Anal. Calcd for C$_{106}$H$_{82}$BF$_{15}$FeN$_4$Si$_2$: C, 60.18; H, 3.91; N, 2.65. Found: C, 59.57; H, 3.70; N, 2.52. μ_{eff} = 5.8 μ_B. The brown solution that was obtained from the reaction above was combined with the portions of toluene that were used to wash compound **6a**. The solvent was removed *in vacuo*, and the resulting black oil was extracted with pentane to yield a yellow solution. Cooling to −30 °C resulted in a small amount of orange crystals of **7a**. ^{1}H NMR (C$_6$D$_6$, RT): δ 111.2 (4H, 442 Hz), 15.3 (4H, 23 Hz), 7.1 (overlapping with solvent peak, 9H, SiMe$_3$), 6.7 (4H, 56 Hz), 3.2 (2H, 23 Hz), 1.6 (2H, 26 Hz), −3.3 (4H, 43 Hz), −32.0 (4H, 372 Hz). ^{19}F NMR (C$_6$D$_6$, RT): δ 162.6 (1F, *p*-F, 144.7 Hz), −7.3 (2F, *m*-F, 59.1 Hz), one peak not found. When performing the thermolysis in toluene-d_8 and monitoring the reaction mixture by ^{19}F NMR spectroscopy, the formation of Me$_3$SiCH$_2$B(C$_6$F$_5$)$_2$ was observed.

Decomposition of 5a in Bromobenzene-d_5. 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_5 was added to the reaction mixture. Within 10 min after the addition of bromobenzene-d_5 the formation of compound **6a** was observed. The reaction was found to be complete when the reaction mixture was left overnight at room temperature.

[{(Ph$_2$CN)$_2$C$_2$H$_4$}$_2$Fe][Me$_3$SiCH$_2$B(C$_6$F$_5$)$_3$]$_2$ (6a). Toluene (20 mL) was added to a mixture of **3a** (84.3 mg; 0.136 mol), **a** (53.0 mg; 0.136 mmol), and B(C$_6$F$_5$)$_3$ (140 mg; 0.273 mmol). The color changed to orange and a precipitate formed. The solid was washed with toluene and recrystallized from CH$_2$Cl$_2$/cyclohexane, affording 103 mg (0.0497 mmol; 37%) of **6a**.

Reaction of 5a with C$_2$H$_4$. Two toluene-d_8 solutions (total amount of solvent: 0.45 g), one with B(C$_6$F$_5$)$_3$ (5.3 mg; 0.010 mmol) and the other with **3a** (6.4 mg; 0.010 mmol), were cooled to −30 °C. The borane solution was added slowly to the solution of **3a** in toluene-d_8, resulting in a color change to yellowish-orange. The solution was degassed using three freeze−pump−thaw cycles, and ethylene was added using a calibrated gas bulb (9.4 mL, 98 mmHg; 0.049 mmol). ^{1}H and ^{19}F NMR spectroscopy revealed spectra similar to that of **5a**, with the exception that a peak was observed at 12.5 ($\Delta\nu_{1/2}$ = 178 Hz) in the ^{1}H NMR spectrum for a time-average signal for bound and free ethylene and an upfield shift of the resonances in the ^{19}F NMR spectrum. In the course of the experiment a yellow precipitate starts forming, which was identified as dication **6a** by evaporating the volatiles and dissolution of the residue in THF-d_8.

Attempted Polymerization of Ethylene Using 1a/MAO. The polymerization experiment was performed in a temperature- and pressure-controlled stainless steel 1 L autoclave (Medimex). The autoclave was evacuated for 1 h at 125 °C prior to use. The reactor was cooled to 30 °C, filled with toluene (250 mL), and pressurized to 5 bar of ethylene. While stirring at 600 rpm, 1.33 mg of a 5 wt % solution of PMAO in toluene (5 mmol) and 2.6 mg (0.0050 mmol) of **1a** were injected. During the run the ethylene pressure was kept constant to within 0.2 bar of the initial pressure by replenishing flow. After 30 min reaction time the reactor was vented and the residual aluminum alkyls were destroyed by addition of 100 mL of ethanol. No substantial amount of polymer was observed.

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.