Reaction of diimine ligands \((\text{Ph}_2\text{CN})_2\text{C}_2\text{H}_4\) with FeCl\(_3\) or FeBr\(_3\) results in formation of the corresponding high-spin ferrous complexes \([(\text{Ph}_2\text{CN})_2\text{C}_2\text{H}_4] \text{FeCl}_3\) \((1\text{a}, \text{X} = \text{Cl}; \text{2a}, \text{X} = \text{Br})\) and \([(\text{Ph}_2\text{CN})_2\text{C}_2\text{H}_4] \text{FeBr}_3\) \((1\text{b})\). Dialkyl \([(\text{Ph}_2\text{CN})_2\text{C}_2\text{H}_4] \text{Fe}(\text{CH}_2\text{SiMe}_3)_2\) \((3\text{a})\) was prepared by treatment of \((\text{py})_2\text{Fe}(\text{CH}_2\text{SiMe}_3)_2\) with diimine ligand \(\text{a}\). Addition of \(\text{B}(\text{C}_6\text{F}_{13})_3\) to \(3\text{a}\) at \(-30^\circ\text{C}\) resulted in \(\text{Me}_6\text{SiCH}_2\) abstraction, affording \([(\text{Ph}_2\text{CN})_2\text{C}_2\text{H}_4] \text{Fe}(\text{CH}_2\text{SiMe}_3)_2][\text{Me}_6\text{SiCH}_2\text{B}(\text{C}_6\text{F}_{13})_3\] \((5\text{a})\). \(^{3}\)Fe NMR spectroscopy revealed that this compound exists as a contact ion-pair in toluene solution. Compound \(5\text{a}\) decomposes at room temperature in bromobenzene-\(d_6\) or toluene-\(d_6\), affording dication \([[(\text{Ph}_2\text{CN})_2\text{C}_2\text{H}_4] \text{Fe}]^{2+}\) \((6\text{a})\); at elevated temperatures in toluene-\(d_6\) the formation of \([(\text{Ph}_2\text{CN})_2\text{C}_2\text{H}_4] \text{Fe}(\text{CH}_2\text{SiMe}_3)_2]_2\) \((7\text{a})\) was observed as well. Neither ferrous chloride \([(\text{Ph}_2\text{CN})_2\text{C}_2\text{H}_4] \text{FeCl}_3\) activated with methylaluminoxane nor contact ion-pair \(5\text{a}\) 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 is known that treatment of \(\text{PDI}\) iron complexes with alkyl abstraction, affording \([[\text{Ph}_2\text{CN}_2\text{C}_2\text{H}_4] \text{Fe}]^{2+}\) \((6\text{a})\); at elevated temperatures in toluene-\(d_6\) the formation of \([(\text{Ph}_2\text{CN})_2\text{C}_2\text{H}_4] \text{Fe}(\text{CH}_2\text{SiMe}_3)_2]_2\) \((7\text{a})\) was observed as well. Neither ferrous chloride \([(\text{Ph}_2\text{CN})_2\text{C}_2\text{H}_4] \text{FeCl}_3\) activated with methylaluminoxane nor contact ion-pair \(5\text{a}\) 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.

\(^{9}\)M. L. Gambarotta, S.; Korobkov, I.; Budzelaar, P. H. M. \* Corresponding author. E-mail: M.W.Bouwkamp@rug.nl.


Results and Discussion

Synthesis of Iron Halide Complexes. Ferrous dichlorides ([PhCN]_2C_6H_4_2FeCl_2) (1a) and ([PhCN]_2C_6H_4FeCl_2) (1b) and dibromide ([PhCN]_2C_6H_4FeBr_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 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. Both compounds 1a and 2a 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 N(11)–Fe(1)–N(12) angles of 81.87(9)° and 81.73(9)° and X–Fe(1)–X angles of 126.09(9)° 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=CHCN)CH_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-dimine ligand, ([2,6-i-Pr_2C_6H_4N_2]_2FeCl_2) (1c), 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) Å 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 ^1H 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 ^1H NMR spectrum.

Synthesis of Neutral Iron Alkyl Complexes. Treatment of 1a or 2a with 2 equiv of LiCH_3SiMe_3 in benzene-d_8 solution resulted in a color change from yellow to brownish-red. ^1H NMR spectroscopy of the reaction mixture revealed the number of signals expected for a C_2-symmetric dialkyl complex (([PhCN]_2C_6H_4Fe(CH_3SiMe_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. Forming these reactions on a preparative scale did not allow the clean formation of dialkyl complex 3a. One explanation may be that alkylations reactions of iron halides with imine-based ligands can be susceptible to a number of side reactions, such as reduction of the iron center and alklylation of the ligand. Compound 3a, however, could be obtained in good yield (70%) by treatment of the iron-dialkyl reagent ([py]_2Fe(CH_3SiMe_3)_2) 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 ([PhCN]_2C_6H_4Fe(CH_3SiMe_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 ([PhCN]_2C_6H_4Fe(CH_3SiMe_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_4N_2]_2Fe(CH_3SiMe_3)_2) (3c). As expected, iron dialkyl 3a has a high-spin ground state (J_{tet} = 4.9 μμ).

Treatment of 1b with LiCH_3SiMe_3 in benzene-d_8 in an NMR tube resulted in a reddish-brown, intractable mixture of products. Furthermore, dissolving (py)_2Fe(CH_3SiMe_3)_2 and the C_3-bridged diimine ligand (b) in benzene-d_8 did not result in formation of the corresponding dialkyl complex. Instead, a mixture of the other iron 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_8. 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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</tr>
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 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-d₈ solution of B(C₆F₅)₃ to a cooled solution of 3a in toluene-d₈. This resulted in a color change from purple to yellow. After replacing the solvent with THF-d₈ a species was observed with a similar ¹H NMR spectrum to that of 4a', suggesting the initial formation of ion-pair [(Ph₂CN)₂C₆H₄Fe(CH₂SiMe₃)][Me₂SiCH₂B(C₆F₅)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 (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 [Me₂SiCH₂B(C₆F₅)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 Me₂SiCH₂ group,¹⁴ and there is no indication for Me₂SiCH₂-methyl group abstraction.⁵ It should be noted that, in the case of the α-diimine complex, the iron alkyl cation [(2,6-i-Pr₃C₆H₁₇)₂(C₂Me₅)Fe(CH₂SiMe₃)]⁺ could not be observed. Instead, [(2,6-i-Pr₃C₆H₁₇)₂(C₂Me₅)Fe(CH₂SiMe₃)]⁻ was obtained, the result of a fast C₂F₅ transfer in the initially generated ion-pair (vide infra).¹³

The ¹³C NMR spectrum of 5a in toluene-d₈ (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-d₈, 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-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 [(Ph₂CN)₂-(C₆H₄)₂]Fe[Me₂SiCH₂B(C₆F₅)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

Figure 2. ¹H NMR spectrum of 1a. The numbers represent the relative integrations; * marks the CDCl₃ solvent peak.

2 equiv of B(C$_6$F$_5$)$_3$ 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)$^\circ$. A similar ligand redistribution reaction was observed in the neutral ferrous amidinate complex [FeCl]$_2$\{µ-(2,6-i-Pr$_2$C$_6$H$_3$NC{Ph}NC$_2$H$_4$NMe$_2$)\}$_2$ and in the attempted synthesis of a cationic amidinate complexes of the type [(Ph$_2$CN)$_2$C$_6$H$_3$]Fe(CH$_2$SiMe$_3$)$_2$ (7a). Compound 7a is highly soluble in aromatic and aliphatic solvents and could be isolated by formation of (Me$_3$SiCH$_2$)$_2$, suggesting concomitant formation of [Fe(CH$_2$SiMe$_3$)$_2$].

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$_2$CN)$_2$C$_6$H$_3$}Fe-(CH$_2$SiMe$_3$)$_2$C$_5$F$_5$ (7a). Compound 7a is highly soluble in aromatic and aliphatic solvents and could be isolated by...

(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 cocryrstallized in the lattice. The cif file of the crystals structure determination can be found in the Supporting Information.
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 metal center imparted by the electron-withdrawing pentafluorophenyl group.

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-δ6 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-separating 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)n(C2H4)2:Fe][Me3SiCH2B(C6F5)3].

Conclusions

Diimines (Ph2CN)nC6H4 (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)nC6H4}Fe(C2H5SiMe2) rearranges to dication {(Ph2CN)nC6H4}Fe2, 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)nC6H4}Fe(C2H5SiMe2)C6F5. 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-δ6, 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$_6$, dichloromethane). Reagents were purchased from commercial providers and used without purification unless stated otherwise. Anhydrous FeCl$_3$, (Ph$_3$CN)$_2$C$_6$H$_5$ (py)$_2$Fe(2CH$_5$SiMe$_3$)$_2$, LiCH$_2$SiMe$_3$, [PhNMe$_2$H][BPh$_4$], and B(C$_6$F$_5$)$_3$ were prepared according to literature procedures. NMR spectra were recorded on Varian Inova 500, Varian Gemini VX 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; $^13$C chemical shifts are referenced relative to $^13$C methyl benzenoid ring (δ = 214 ppm), used as an external reference. For magnetically equivalent protons, the chemical shifts are followed by a ‘$^s$’ in parenthesis.

Magnetic susceptibility measurements were performed by a Faraday magnetometer. Mass spectra were recorded on a Fisons Instruments QMass 2010 mass spectrometer (CI, ESI) source equipped with a gas curtain, which is contained in a closed chamber that can be evacuated, flushed, and maintained under a nitrogen atmosphere over columns of alumina, using standard Schlenk and vacuum line techniques or in an MBraun glovebox. Sensitivity compounds were performed under a nitrogen atmosphere. ICP-MS and ICP-OES analysis were performed on a Perkin-Elmer Elan 6100 DSQ ICP-MS spectrometer. Mass spectra were recorded on a Finnigan MAT TSQ-7000 triple quadrupole mass spectrometer. FT-IR spectra were recorded on a Bruker FT-IR spectrometer using standard Nujol mulls. FT-NIR spectra were recorded on a Bruker Vertex 70 FT-NIR spectrometer using standard NaCl pellets. Raman spectra were recorded on a Perkin-Elmer Lambda 900 spectrometer using a Glan-Taylor polarizer.

Catalysts were synthesized and characterized as described in the Supporting Information. Details will be given in the full publication. 

(Ph$_3$CN)$_2$C$_6$H$_5$. An orange-yellow solid, 21.7 mg (0.038 mmol) was obtained. 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 extraction was filtered through a pad of Celite, affording a yellow solution. The solution was removed in vacuo and a yellow powder was obtained. The compound was extracted using dichloromethane. The extraction was filtered through a pad of Celite, affording a yellow solution. The solution was removed in vacuo and a yellow powder was obtained. The compound was extracted using dichloromethane. The extraction was filtered through a pad of Celite, affording a yellow solution.

(Ph$_3$CN)$_2$C$_6$H$_5$FeCl$_2$. Compound 1b was prepared analogous to 1a, by treating 1b (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). 

(Ph$_3$CN)$_2$C$_6$H$_5$FeBr$_2$. 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.

(Ph$_3$CN)$_2$C$_6$H$_5$Fe(C$_6$H$_5$SiMe$_3$)$_2$. A solution of a mixture of products, one of which was identified as 1a (see below).

(Ph$_3$CN)$_2$C$_6$H$_5$Fe(CH$_2$SiMe$_3$)$_2$. A mixture of products, one of which was identified as 1a (see below).
(4H, 13.6 Hz), 27.6 (2H, 804 Hz), 16.6 (1H, 242 Hz), 15.1 (2H, 217 Hz), 12.7 (2H, overlapping signals), 3.7–13.3 (6H, overlapping signals), –3.2 (2H, 51 Hz), –53.3 (4H, 1403 Hz). Two signals of 4H were not observed.

\((\text{Ph}_{3}\text{C}_2\text{N})_2\text{C}_2\text{H}_4\text{Fe}(\text{CH}_3\text{SiMe}_3)_2(3a)\). Toluene (5 mL) was added to a mixture of \((\text{py})_2\text{Fe}((\text{CH}_3\text{SiMe})_3; (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 \(-30^\circ C\) resulted in 71.5 mg (0.116 mmol, 70%) of purple crystals of the title compound. 1H NMR (CD$_2$D$_2$RT): δ 5.75 (4H, 601 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. Calc'd for C$_{36}$H$_{58}$F$_{22}$N$_2$: C, 69.08; H, 7.49; N, 4.53. Found: C, 68.35; H, 7.44; N, 4.39.

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<td>-1.9 (2H, 33 Hz), -1.88 (4H, 61 Hz, SiMe$_3$), -36.4 (4H, 726 Hz)</td>
<td>-1.9 (2H, 33 Hz), -1.88 (4H, 61 Hz, SiMe$_3$), -36.4 (4H, 726 Hz)</td>
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</tbody>
</table>

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 compound 6a was observed. The reaction was found to be complete when the reaction mixture was left overnight at room temperature.

<table>
<thead>
<tr>
<th>生成物</th>
<th>(\delta) cm$^{-1}$</th>
<th>7.6 (4H, 25 Hz, BPh$_{2}$)</th>
<th>13.2 (4H, 24 Hz), 10.0 (8H, 26 Hz, BPh$_{3}$)</th>
<th>7.6 (4H, 25 Hz, BPh$_{3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1H NMR (THF-$d_8$)</td>
<td>δ 7.23 (4H, 833 Hz), 21.3 (9H, 170 Hz, SiMe$<em>3$), 13.2 (4H, 24 Hz), 10.0 (8H, 26 Hz, BPh$</em>{3}$), 8.2 (8H, 27 Hz, BPh$<em>{3}$), 7.6 (4H, 25 Hz, BPh$</em>{3}$), 3.8 (2H, 67 Hz), 1.68 (4H, overlaps with THF)</td>
<td>-1.9 (2H, 33 Hz), -1.88 (4H, 61 Hz, SiMe$_3$), -36.4 (4H, 726 Hz)</td>
<td>-1.9 (2H, 33 Hz), -1.88 (4H, 61 Hz, SiMe$_3$), -36.4 (4H, 726 Hz)</td>
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</tr>
</tbody>
</table>

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.

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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.