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# Activation of Enamido Zirconium Complexes for Ethylene Polymerization: Electrophilic Addition versus Electrophilic Abstraction Reaction

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Deprotonation of the  $\alpha$ -dimine compound {2,6-(CHMe<sub>2</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>}N=C(CH<sub>3</sub>)C(CH<sub>3</sub>)=N{2,6- $(CHMe_2)_2$ -C<sub>6</sub>H<sub>3</sub> with excess KH in THF gives dipotassium N, N-(1,2-dimethylene-1,2ethanediyl)bis(2,6-diisopropylanilide) (1) in 75% yield. Reaction of 1 with bis(2-picolyl)zirconium dichloride generated in situ by the reaction of ZrCl<sub>4</sub> and 2 equiv of (2picolyl)potassium affords [N,N-(1,2-dimethylene-1,2-ethanediyl)bis(2,6-diisopropylanilido)- $\kappa^2 N, N$ ]bis(2-picolyl)zirconium(IV) (2) in 35% yield. Similar reaction of 1 with LMCl<sub>3</sub> (L = Cp, Cp\*; M = Zr, Hf) gives the desired complexes {2,6-(CHMe<sub>2</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>}NC=(CH<sub>2</sub>)C=(CH<sub>2</sub>)N- $\{2, 6-(CHMe_2)_2-C_6H_3\}MLCl (L = Cp^*, M = Zr, 4; L = Cp^*, M = Hf, 5; L = Cp, M = Zr, 6)$  in 79%, 94% and 54% yields, respectively. Reaction of the chloride complexes with MeMgBr  $(CHMe_2)_2 - C_6H_3$  MLMe (L = Cp\*, M = Zr, 7; L = Cp\*, M = Hf, 8; L = Cp, M = Zr, 9) in 63%, 69% and 90% yields, respectively. The solid-state structure of 7 was determined. When 2, 7, or **9** is treated with 1 equiv of  $B(C_6F_5)_3$ , one observes formation of the picolyl- or methylabstracted ion-paired complex in NMR spectra. When  $Al(C_6F_5)_3$  is added to 2, 8, or 9, the aluminum atom is coordinated by the methylene functionality of the enamide ligand to form zwitterionic complexes. The solid structure of a zwitterionic complex generated by the addition of  $Al(C_3F_5)_3$  to 8 was determined and confirms the molecular connectivity. The zwitterionic complexes are active to ethylene polymerization, while the ion-paired complexes are sluggish. Complexes 2 and 6 are highly active to the ethylene polymerization when they are activated with MAO.

### Introduction

Homogeneous transition-metal complexes for olefin polymerization are ongoing topics of research in both academic and industrial fields.<sup>1,2</sup> Polyolefins made from ethylene and/or  $\alpha$ -olefins including propylene are environmentally benign and are expected to substitute plastics derived from monomers, which are produced with higher resource usage and are less ecologically benign.<sup>3</sup> The metal complexes are traditionally activated by electrophilic abstraction reaction by Lewis acids (eq 1).<sup>4</sup> The activated complex is an ion-paired complex

$$L_{n}MR_{2} \xrightarrow{A} \begin{bmatrix} u_{n}^{\oplus}MR \end{bmatrix} \begin{bmatrix} e^{\bigoplus} \\ R-A \end{bmatrix} (1)$$

$$L_{n}MR \xrightarrow{A} L_{n}M^{\oplus} - -R-A \qquad (2)$$

$$X \xrightarrow{Y-Ni-R} A \xrightarrow{A} C^{\oplus} - C^{$$

consisting of a transition-metal cation and a bulky noncoordinating anion, and the catalyst activity, lifetime, chain-transfer characteristics, and stereoregulation are strongly dependent on the nature of the ion pairs.<sup>5</sup> The preactivated complex requires two alkyls or halides. One of them is abstracted by the Lewis acid, and the monomer inserts into the remaining metal–

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alkyl bond. Recently, some different activation reactions have been reported. Chen et al. have reported that group 4 complexes bearing only one alkyl or halide can serve as efficient catalysts for olefin polymerization.<sup>6</sup> They proposed a bimetallic mechanism resembling that originally proposed by Natta and Mazzanti (eq 2). Bazan et al. and we have shown that nickel complexes containing carboxylato,7 carboxamidato,8 or enamido ligands9 can be activated by electrophilic addition reactions of Lewis acids. In those cases, the Lewis acid is added to the functional group to afford zwitterionic active complexes (eq 3).<sup>10</sup> Herein, we disclose that the novel activation reaction can be expanded to group 4 transition-metal complexes.

### **Results and Discussion**

Synthesis and Characterization. The dianionic bis(enamido) ligand, dipotassium N, N'-(1, 2-dimethylene-1,2-ethanediyl)bis(2,6-diisopropylanilide) (1) for group 4 metal complexes, which can serve as preactivated complexes for the novel activation reaction, is synthesized by the deprotonation of the  $\alpha$ -diimine compound  $\{2,6-(CHMe_2)_2-C_6H_3\}N=C(CH_3)C(CH_3)=N\{2,6-(CHMe_2)_2-C_6H_3\}N=C(CH_3)C(CH_3)=N\{2,6-(CHMe_2)_2-C_6H_3\}N=C(CH_3)C(CH_3)=N\{2,6-(CHMe_2)_2-C_6H_3\}N=C(CH_3)C(CH_3)=N\{2,6-(CHMe_2)_2-C_6H_3\}N=C(CH_3)C(CH_3)=N\{2,6-(CHMe_2)_2-C_6H_3\}N=C(CH_3)C(CH_3)=N\{2,6-(CHMe_2)_2-C_6H_3\}N=C(CH_3)C(CH_3)C(CH_3)=N\{2,6-(CHMe_2)_2-C_6H_3\}N=C(CH_3)C(CH_3)C(CH_3)=N\{2,6-(CHMe_2)_2-C_6H_3\}N=C(CH_3)C(CH_3)C(CH_3)=N\{2,6-(CHMe_2)_2-C_6H_3\}N=C(CH_3)C(CH_3)C(CH_3)=N\{2,6-(CHMe_2)_2-C_6H_3\}N=C(CH_3)C(CH_3$  $C_6H_3$  with excess KH in 75% yield (eq 4). The  $\alpha$ -diimine



compound serves well as a ligand for the late-transitionmetal catalyst.<sup>11</sup> Metalations of the ligand by reaction with ZrCl<sub>4</sub>(THF)<sub>2</sub>, TiCl<sub>4</sub>(THF)<sub>2</sub>, or HfCl<sub>4</sub>(THF)<sub>2</sub> were not successful. Fairly successful syntheses of bis(amido) complexes of group 4 have been reported.<sup>12</sup> We attributed the synthetic failure to the incompatibility of the electron-deficient metal center and the electron-rich methylene carbons on the enamido ligand. Instead of the zirconium dichloride complex, we tried to synthesize

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a bis(2-picolyl)zirconium complex (eq 5), in which ni-



trogen atoms on the picolyl ligands are expected to coordinate to the zirconium atom to block the interaction with the electron-rich methylene carbons. 2-Picolyllithium-2-picoline is obtained when 2.5 equiv of 2-picoline is reacted with n-BuLi in cold ether (86%). Addition of **1** to the bis(2-picolyl)zirconium dichloride, which is generated in situ in THF by the reaction of 2.0 equiv of 2-picolyllithium with ZrCl<sub>4</sub>(THF)<sub>2</sub>, affords successfully the desired complex [N, N-(1, 2-dimethylene-1,2-ethanediyl)bis(2,6-diisopropylanilido)- $\kappa^2 N$ ,N]bis(2picolyl)zirconium(IV) (2). The <sup>1</sup>H NMR spectrum of the crude product shows that the reaction is fairly clean but some side product signals (ca., 15%) are observed. Isolation of the product by discarding the side product was not successful. The analytically pure complex can be obtained in 35% yield when 2-picolylpotassium is used instead of 2-picolyllithium.

The structure of **2** can be confirmed by NMR spectra and elemental analysis. An attempt to obtain single crystals suitable for X-ray crystallography was not successful. Observation of two  $=CH_2$  signals at 4.82 and 3.49 ppm as singlets ( $C_6D_6$ ) in the <sup>1</sup>H NMR spectrum (Figure 3A) suggests an enamido ligand structure as depicted in eq 5. Only one CHMe<sub>2</sub> signal, a septet (J =6.8 Hz) at 4.02 ppm, and two CH(CH<sub>3</sub>) signals, doublets at 1.45 and 1.17 ppm, are observed, due to the symmetry of the complex. A set of ring protons on the picolyl ligand are observed at 6.88 (doublet), 6.41 (triplet), 6.04 (doublet), and 5.96 ppm (triplet), and methylene protons on picolyl are observed as a singlet at 2.03 ppm. The signal observed at 82.19 ppm in the  ${}^{13}C{}^{1}H{}$  NMR spectrum is assigned unambiguously by DEPT experiments to the methylene carbon ( $CH_2=CN$ ) in the enamido ligand. Coordination of the nitrogen atom on the picolyl ligand to the zirconium cannot be confirmed by the <sup>1</sup>H or <sup>13</sup>C{<sup>1</sup>H} NMR spectra. Coordination of nitrogen to zirconium was reported in a similar complex, bis-(cyclopentadienyl)bis[(6-methyl-2-pyridinyl)methyl]zirconium(IV).13

The side product observed when 2-picolyllithium is used is very crystalline, and single crystals suitable for X-ray crystallography were obtained from a pentane

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**Figure 1.** ORTEP view of **3**, showing the atom-numbering scheme. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Zr(1)-N(1), 2.126(5); Zr(1)-N(2), 2.126(5); Zr(1)-N(5), 2.285(5); Zr(1)-C(31), 2.354(6); Zr(1)-C(32), 2.463(6); Zr(1)-C(62), 2.318-(6); N(1)-C(1), 1.407(8); N(2)-C(2), 1.425(8); C(1)-C(2), 1.485(9); C(1)-C(3), 1.332(9); C(2)-C(4), 1.351(9); C(57)-C(62), 1.444(9); N(5)-C(57), 1.352(8); C(29)-C(31), 1.446-(8); C(29)-C(30), 1.520(8); C(30)-C(32), 1.424(8); N(3)-C(29), 1.302(7); N(4)-C(30), 1.301(7); Li(1)-N(3), 1.996(13); Li(1)-N(4), 1.948(12); Li(1)-N(6), 2.087(13); N(1)-Zr(1)-N(2), 74.5(2); N(5)-Zr(1)-C(62), 59.9(2); C(31)-Zr(1)-C(32), 69.1(2); Zr(1)-C(62)-C(57), 90.6(4); N(5)-C(57)-C(62), 110.5(6); Zr(1)-N(5)-C(57), 94.4(4).

solution. The molecular structure and selected bond lengths and angles for the side product **3** are shown in



Figure 1. The complex is a distorted-octahedral ate complex bonded by a chelated picolyl ligand and two ligands derived from 1, one of which acts as a bis-(enamido) ligand while the other acts as a dialkyl ligand. A lithium ion is coordinated by the remaining nitrogens on the dialkyl ligand and by nitrogen on 2-picoline. The distances between zirconium and the two nitrogens of the enamido ligand are identical (2.126(5) Å). The bond lengths of N(1)-C(1) and N(2)-C(2) (1.407(8) and 1.425-(8) Å, respectively) are within the range of C-N singlebond lengths, and those of C(1)-C3 and C(2)-C(4)(1.332(9) and 1.351(9) Å, respectively) are within the range of C-C double-bond lengths. The two bond lengths between zirconium and carbons on the dialkyl ligand are not identical (2.354(6) and 2.463(6) Å), and both of them are longer than that of zirconium and carbon on the picolyl ligand (2.318(6) Å). When the enamido ligand acts as a dialkyl ligand with the same

composition, the C(29)-C(31) and C(30)-C(32) bond lengths change to be in the range of C-C single-bond lengths (1.446(8) and 1.424(8) Å, respectively) and those of C(29)-N(3) and C(30)-N(4) change to be in the range of C-N double-bond lengths (1.302(7) and 1.301(7) Å,respectively). The zirconium atom is placed slightly out of the N(1)-C(1)-C(2)-N(2) plane made by the enamido ligand. The dihedral angles of Zr(1)-N(1)-C(1)-C(2)and Zr(1)-N(2)-C(2)-C(1) are -14.5 and 5.1°, respectively. The zirconium is placed much more out of the C(31)-C(29)-C(30)-C(32) plane made by the dialkyl ligand and the dihedral angles of Zr(1)-C(31)-C(29)-C(30) and Zr(1)-C(32)-C(30)-C(29) are respectively -30.0 and  $42.3^{\circ}$ . In the 2-picolyl ligand, the N(5)-C(57)-C(62) angle shrinks to  $110.5(6)^{\circ}$  by the coordination of a nitrogen atom and the Zr(1)-N(5)-C(57) angle is 94.4(4)°.

In contrast to the reactions with  $ZrCl_4$  and  $HfCl_4$ , reactions of **1** with  $Cp^*ZrCl_3$ ,  $Cp^*HfCl_3$ , and  $CpZrCl_3$ give cleanly the desired bis(enamido) complexes with 79%, 94% and 54% yields, respectively (eq 6). The reaction with the corresponding titanium complex is not clean. The characteristic methylene ( $CH_2$ =) signals are observed in <sup>1</sup>H NMR spectra ( $C_6D_6$ ) as a pair of singlets at 4.7–4.8 and 3.6–3.7 ppm, conforming the ligand acts as an enamido species. The addition of MeMgBr (THF solution) in diethyl ether gives cleanly the methyl complexes **7–9** (63%, 69% and 90% yields, respectively). The methylene signals are still observed as a pair of singlets in almost the same region observed for the chloride complexes, and methyl signals are observed as a singlet at 0.6–0.7 ppm in the <sup>1</sup>H NMR spectra.



The molecular structure of **7** was confirmed by X-ray crystallography. The structure and selected bond lengths and angles are shown in Figure 2. Three independent molecules are present in a unit cell. It has a three-legged piano-stool structure. The zirconium atom is situated out of the N-C-C-N plane, and the dihedral angles Zr(1)-N(1)-C(35)-C(36) and Zr(1)-N(2)-C(36)-C(35) are 32.7 and  $-16.6^{\circ}$ , respectively. The  $CH_2=C$  bond distance (average 1.330(13) Å) and C-NAr' distance (average 1.426(8) Å) strongly support the enamido structure drawn in eq 6. The averaged Zr-N distance is 2.085(12) Å, which is shorter than that of the ate complex **3** (2.126(5) Å).

Activation Reaction. Activation studies were carried out by adding  $B(C_6F_5)_3$  or  $Al(C_6F_5)_3^{14}$  to the enamido complexes 2 and 7–9 with NMR spectroscopy. Figure 3 shows the selected region of the <sup>1</sup>H NMR spectra for 2 itself and the complexes obtained by adding  $B(C_6F_5)_3$  and  $Al(C_6F_5)_3$  to 2. The NMR spectra strongly support that the picolyl-abstracted ion-paired complex 10 is

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**Figure 2.** ORTEP view of **7**, showing the atom-numbering scheme. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Zr(1)-N(1), 2.071(5); Zr(1)-N(2), 2.077(5); Zr(1)-C(39), 2.317(6); N(1)-C(35), 1.437(7); N(2)-C(36), 1.423(8); C(35)-C(37), 1.342-(9); C(36)-C(38), 1.346(8); C(35)-C(36), 1.514(9); N(1)-C(11), 1.449(8); N(1)-Zr(1)-N(2), 85.1(2); N(1)-Zr(1)-C(39), 103.5(2); N(1)-C(35)-C(37), 121.8(7); C(37)-C(35)-C(36), 121.3(6).



**Figure 3.** <sup>1</sup>H NMR spectra ( $C_6D_6$ ) of **2** (A), **2** + B( $C_6F_5$ )<sub>3</sub> (B), and **2** + Al( $C_6F_5$ )<sub>3</sub> (C).

formed by  $B(C_6F_5)_3$  (eq 7) while the alane-added zwitterionic complex **11** is formed by  $Al(C_6F_5)_3$  (eq 8). In Figure 3B for the product of addition of  $B(C_6F_5)_3$ , one observes appearance of a broad singlet at 2.52 ppm, which is assigned to methylene protons on picolyl bonded to  $B(C_6F_5)_3$ , and the intensity of methylene protons (1.93 ppm) on the picolyl ligand bonded to zirconium is reduced by half. Two sets of picolyl ring protons are observed at 5.8-6.8 and 8.45 ppm. Signals of methylene protons on the enamido ligand are observed at 4.65 and 3.75 ppm as singlets without reduction of the intensity. A pair of rather broad septet  $CHMe_2$  signals (J = 6.8 Hz) is observed at 3.49 and 2.81 ppm due to the destroyed symmetry. However, in Figure 3C, for the product obtained by the addition of  $Al(C_6F_5)_3$ , one observes totally different patterns. In this case, the

methylene signals on the enamide shift severely to 5.33 and 3.98 ppm, with reduction of the intensity by half, and a broad singlet signal is observed at 3.21 ppm, which can be assigned to the protons on methylene bonded to Al. Only one set of picolyl ring protons is observed without reduction of intensity at 5.8-6.5 ppm, implying that both picolyl ligands are still bonded symmetrically to the zirconium. Two septet CHMe<sub>2</sub> signals are observed at 3.61 and 3.17 ppm. A strange feature of the spectrum is the observation of picolyl  $CH_2$ signals at 1.97 and 1.76 ppm. The signals are rather broad, but the splitting pattern can be analyzed as that observed for an AB spin system. The broad nature of the peaks implies that the picolyl ligand is under fluxional motion, presumably coordination-decoordination and/or change of coordination site of the nitrogens. Observation of the AB spin system signals can be interpreted by the coordination of the nitrogen atoms on the picolyl ligand. Once the nitrogen atom coordinates to the zirconium, two  $CH_2$  protons on the picolyl ligand are diastereotopic with each other, as depicted in eq 8, and each proton signal will appear separately with coupling to each other to appear as a doublet. A signal is observed severely downfield shifted at 197.41 ppm in the <sup>13</sup>C NMR spectrum, which can be assigned to the carbon on  $AlCH_2C=N$ . The shift might be attributed to the change from an enamido to an imine functionality by the coordination of alane. Both activated complexes are so stable that any decomposition is not observed in C<sub>6</sub>D<sub>6</sub> solution for several days. However, purification by recrystallization to analytically pure compounds or single crystals for X-ray crystallography failed, due to the lack of crystallinity of the complexes.



When an equimolar amount of  $B(C_6F_5)_3$  is added to 7 in  $C_6D_6$  solution, the <sup>1</sup>H NMR spectrum indicates that a methyl-abstracted ion-paired complex is formed (eq 9). The signal for the methyl protons is shifted from 0.63 to 1.67 ppm, and all methylene ( $CH_2$ =CN) signals (4.84 and 3.67 ppm) are still observed without reduction of intensity. The complex is so unstable in  $C_6D_6$  solution



that it decomposes at room temperature overnight to give oily precipitates. Addition of  $Al(C_6F_5)_3$  gives a more complex <sup>1</sup>H NMR spectrum, but careful inspection leads to a tentative interpretation of the formation of a mixture of a methyl-abstracted ion-paired complex and an alane-added zwitterionic complex (ratio 1/2). The ratio of the two complexes is dependent on solvent. In  $CD_2Cl_2$ , a ratio favoring the more zwitterionic complex is observed (1/6), but the ratio returns to the original value by changing the solvent to benzene. To elucidate the formation of the zwitterionic complex unambiguously, we tried to grow single crystals for X-ray crystallography, but these attempts failed.

However, addition of  $Al(C_6F_5)_3$  to the hafnium complex **8** affords a single clean complex which can be interpreted as an alane-added zwitterionic complex (eq 10). The intensity of signals of the methylene protons



on the enamido ligand is reduced by half and broad new signals appear at 3.52 and 3.24 ppm, which can be assigned as  $Al-CH_2$  signals. Two signals are observed because the two protons on a methylene carbon are diastereotopic with each other due to the chiral center on the zirconium atom. The other methylene signals shift severely from 4.92 and 3.66 ppm to 5.67 and 4.29 ppm. The complex is fairly stable. No decomposition is observed in  $C_6D_6$  solution for several days. Addition of  $B(C_6F_5)_3$  does not afford a clean complex.

Single crystals suitable for X-ray crystallography were obtained by vapor-phase addition of pentane to a toluene solution at room temperature overnight. The molecular structure with selected bond lengths and angles is shown in Figure 4. A disordered toluene molecule was found for one molecule of **14** in the crystal lattice. Measurements of bond lengths are consistent with the zwitterionic structure shown in eq 10. The AlCC–N distance (1.326(4) Å) is characteristic of a C–N double bond, while the AlC–C distance (1.466(4) Å) is indicative of a single bond. The Al–C distance (2.065(3) Å) is almost same as that observed for the nickel complex (2.053(4) Å).<sup>9</sup> The N–Hf distance on the aluminum-added side is substantially longer that that observed for the other side (2.184(3) and 2.044(3) Å, respectively).

<sup>1</sup>H NMR studies strongly support that the methylabstracted ion-paired complex **13** is formed by addition



**Figure 4.** ORTEP view of **14**, showing the atom-numbering scheme. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Hf–N(1), 2.044(3); Hf–N(2), 2.184(3); Hf–C(11), 2.205(3); N(1)–C(37), 1.432(4); N(2)–C(36), 1.326(4); C(37)–C(39), 1.326(5); C(37)–C(36), 1.486(5); C(36)–C(38), 1.466(4); C(38)–Al, 2.065(3); N(1)–Hf–N(2), 79.80(11); N(1)–C(37)–C(39), 122.6(4); C(39)–C(37)–C(36), 120.0(4); N(2)–C(36)–C(38), 123.5(4); C(37)–C(36)–C(38), 120.8(4); C(36)–C(38)–Al, 124.9(2).

of  $B(C_6F_5)_3$  to the cyclopentadienyl zirconium complex 9 while addition of  $Al(C_6F_5)_3$  affords the zwitterionic complex 15. However, both complexes decompose in  $C_6D_6$  over several hours.

Polymerization Studies. The complexes 10-15 were tested for ethylene polymerization by adding ethylene gas into an NMR cell containing a C<sub>6</sub>D<sub>6</sub> solution. In the case of the alane-added zwitterionic complex 11, rather fast ethylene consumption is observed. Added ethylene gas under atmospheric pressure disappears completely over 3 h in the <sup>1</sup>H NMR spectrum with the concomitant formation of polyethylene particles. The original <sup>1</sup>H NMR spectrum obtained before the addition of ethylene is not changed, which implies that a very small fraction of the dissolved complex acts as a catalyst. It can be postulated that it takes some time for the ethylene to coordinate and insert into the Zr-picolyl bond, because the picolyl ligand is bonded rather strongly to the zirconium by the chelation. Once it is initiated, it can act as a highly active catalyst. Similar results have been observed, with the nickel catalyst having the methallyl ligand as a leaving group.<sup>7,8</sup> In the case of the ion-paired complex **10**, very slow consumption of ethylene gas is observed. The intensity of the ethylene peak is reduced by about half overnight. The original spectrum of the complex was preserved in this case as well.

Complexes derived from the pentamethylcyclopentadienyl (Cp\*) ligand, **12** and **14**, do not show any activity, which may be attributed to the absence of any vacant site by steric congestion. The ion-paired cyclopentadienyl (Cp) complex **13** shows negligible activity as well. However, rapid ethylene consumption and formation of polyethylene precipitates are observed with the zwitterionic cyclopentadienyl complex **15**. Polymerization with carefully dried ethylene gas at room temperature

Table 1. Ethylene Polymerization Results<sup>a</sup>

entry	complex	temp (°C)	time (min)	activity (kg/(mol·h))	$M_{ m w}{}^b$	$M_{ m w}/M_{ m n}^{l}$
1	2	25	20	12 000	134 000	18 <sup>e</sup>
2	2	50	12	33 000	16 800	1.8
3	2	80	20	10 000	8000	2.1
<b>4</b> <sup>c</sup>	2	80	20	8800	7200	1.7
5	6	25	3	30 000	129 000	2.9
6	6	80	6	24 000	504 000	$11^e$
$7^d$	9	25	10	250	insoluble	
8	$Cp_2ZrCl_2$	25	4	23 000		

<sup>*a*</sup> Polymerization conditions: 30 mL of toluene, 0.5  $\mu$ mol of catalyst, Al/Zr = 5000, 60 psig of ethylene. <sup>*b*</sup> Determined by GPC in 1,2,4-trichlorobenzene at 140 °C against polystyrene standards. <sup>*c*</sup> Hexane diluent instead of toluene. <sup>*d*</sup> A 5.0  $\mu$ mol portion of the complex and Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (17.5  $\mu$ mol) were used without adding MAO under 100 psig of ethylene. <sup>*e*</sup> Bimodal distribution.

and 100 psig pressure gives 250 kg/(mol h) activity (entry 7 in Table 1).

MAO is also a Lewis acid,<sup>15</sup> and activation by either electrophilic addition or abstraction reactions are expected for 2 and the monochloride complexes 4-6. Pentamethylcyclopentadienyl (Cp\*) complexes 4 and 5 also do not show any activities in these cases, but complex 2 and the cyclopentadienyl complex 6 are highly active when they are activated with MAO. The activities are comparable with that of Cp<sub>2</sub>ZrCl<sub>2</sub> (entry 8). In the case of 2, maximum activity is observed at 50 °C. Interestingly, at low temperature (25 °C), a bimodal molecular weight distribution ( $M_w/M_n = 18$ ) is observed with rather high molecular weight ( $M_w = 134\ 000$ ), but at high temperature (50 and 80 °C) narrow molecular weight distributions are observed ( $M_w/M_n = 1.8$  and 2.1, respectively) with low molecular weight ( $M_w = 16\ 800$ and 8000, respectively). In the case of 6, the trend of molecular weight and molecular weight distribution is reversed: at low temperature (25 °C) narrow molecular weight distribution  $(M_w/M_n = 2.9)$  and low molecular weight ( $M_w = 129\ 000$ ) are observed (entry 5), while at high temperature (80 °C) broad molecular weight distributions  $(M_w/M_n = 11)$  with the appearance of a shoulder on the high molecular weight portion is observed (entry 6).

#### Summary

Enamido zirconium and hafnium complexes have been synthesized which have electron-rich methylene carbons in the ligand frame. Addition of  $Al(C_6F_5)_3$  to the complexes gives mainly zwitterionic complexes by electrophilic addition to the methylene carbon, while addition of  $B(C_6F_5)_3$  gives exclusively ion-paired complexes by electrophilic abstraction of the methyl or picolyl group. The ion-paired complex is sluggish for ethylene polymerization, but the zwitterionic complexes show good activity. The enamido complexes show activities comparable with that of  $Cp_2ZrCl_2$  for ethylene polymerization when they are activated with MAO.

#### **Experimental Section**

**General Remarks.** All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk techniques. Toluene, pentane, cyclohexane, THF, diethyl ether, and C<sub>6</sub>D<sub>6</sub> were distilled from benzophenone ketyl. Toluene used for the polymerization reaction was purchased from Aldrich (anhydrous grade) and purified further over Na/K alloy. Ethylene was purchased from Conley Gas (99.9%) and purified by contact with molecular sieves and copper overnight under 150 psig pressure. NMR spectra were recorded on a Varian Mercury Plus 400 or Bruker Advance DRX-500 spectrometer. <sup>19</sup>F NMR spectra were calibrated and reported downfield from external CCl<sub>3</sub>F (Bruker DRX-500) or α,α,α-trifluorotoluene (Varian Mercury 400). <sup>11</sup>B NMR spectra were calibrated and reported downfield from external BF3. OEt<sub>2</sub>. Elemental analyses were carried out on a Fisons EA1108 microanalyzer. Gel permeation chromatograms (GPC) were obtained at 140 °C in trichlorobenzene using a Waters Model 150-C+ GPC, and the data were analyzed using a polystyrene analyzing curve. Methylaluminoxane (MAO) was purchased as a solution in toluene from Akzo (7.6 wt % of Al, MMAO  ${2,6-(CHMe_2)_2-C_6H_3}N=C(CH_3)C(CH_3)=N{2,6-(CHMe_2)_2-C_6H_3}N=C(CH_3)C(CH_3)=N{2,6-(CHMe_2)_2-C_6H_3}N=C(CH_3)C(CH_3)=N{2,6-(CHMe_2)_2-C_6H_3}N=C(CH_3)C(CH_3)=N{2,6-(CHMe_2)_2-C_6H_3}N=C(CH_3)C(CH_3)=N{2,6-(CHMe_2)_2-C_6H_3}N=C(CH_3)C(CH_3)=N{2,6-(CHMe_2)_2-C_6H_3}N=C(CH_3)C(CH_3)=N{2,6-(CHMe_2)_2-C_6H_3}N=C(CH_3)C(CH_3)C(CH_3)=N{2,6-(CHMe_2)_2-C_6H_3}N=C(CH_3)C(CH_3)C(CH_3)=N{2,6-(CHMe_2)_2-C_6H_3}N=C(CH_3)C(CH_3)C(CH_3)=N{2,6-(CHMe_2)_2-C_6H_3}N=C(CH_3)C(CH_3$ type 4).  $(CHMe_2)_2$ - $C_6H_3$ }<sup>16</sup> and Al $(C_6F_5)_3$ ·(toluene)<sup>14</sup> were prepared according to the literature methods.

Dipotassium N,N-(1,2-Dimethylene-1,2-ethanediyl)**bis(2,6-diisopropylanilide)** (1).  $\{2,6-(CHMe_2)_2-C_6H_3\}N=$  $C(CH_3)C(CH_3)=N\{2,6-(CHMe_2)_2-C_6H_3\}$  (7.00 g, 17.3 mmol) and KH (3.47 g, 86.5 mmol) were stirred in THF (50 mL) under argon for 1 week at room temperature (ca, 25 °C). The evolved hydrogen gas was vented through a mercury bubbler. The excess KH was removed by filtration over Celite. The solvent was removed to leave a volume of about 10 mL. When the solution was stored in a freezer (-30 °C) overnight, a white crystalline solid was deposited. The solvent was decanted rapidly at -30 °C, and the obtained solid was dried by evacuation. The solid was triturated with pentane (50 mL) for 2 h and filtered and washed three times with pentane (20 mL). A yellow solid was obtained (6.74 g, 75%). The <sup>1</sup>H NMR spectrum indicates that a half-molecule of THF was incorporated for each dipotassium salt. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>/THF $d_8$  (10:1)):  $\delta$  7.22 (d, J = 7.6 Hz, 4 H, Ph H<sup>3</sup>), 6.95 (t, J = 7.6Hz, 2 H, Ph H<sup>4</sup>), 3.92 (septet, J = 6.7 Hz, 4 H, CHMe<sub>2</sub>), 3.09 (d, J = 3.7 Hz, 2 H, C= $\hat{C}H_2$ ), 2.49 (d, J = 3.5 Hz, 2 H, C=  $CH_2$ ), 1.48 (d, J = 6.7 Hz, 12 H,  $CH(CH_3)_2$ ), 1.31 (d, J = 6.7Hz, 12 H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>/THF-d<sub>8</sub> (10:1)):  $\delta$  170.65 (CH<sub>2</sub>CN), 156.20 (Ph C<sup>1</sup>), 142.49 (Ph C<sup>3</sup>), 122.71 (Ph C4) 118.12 (Ph C2), 67.77 (CH2=C), 27.75 (CH-(CH<sub>3</sub>)<sub>2</sub>), 25.78 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.11 (CH(CH<sub>3</sub>)<sub>2</sub>).

2-Picolyllithium-2-Picoline. n-BuLi (72.4 mmol) was added dropwise to a stirred solution of dry 2-picoline (16.85 g, 181 mmol, 2.5 equiv), purified by distillation over CaH<sub>2</sub>, in cold ether (50 mL, -20 °C). Orange crystals precipitated immediately. The mixture was stirred for 1 h. Ether was removed by evaporation. The solid was washed with pentane (50 mL) and dried under vacuum (12 g, 86%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  8.53 (dd, J = 4.2, 0.9 Hz, 1 H, picoline H<sup>3,6</sup>), 7.51 (d, J = 6.0 Hz, 1 H, picolyl H<sup>3,6</sup>), 6.78 (td J = 7.6, 1.7 Hz, 1 H), 6.60-6.41 (m, 2 H), 6.40-6.24 (m, 2 H), 5.49 (td, J =6.0, 1.1 Hz, picolyl H<sup>4,5</sup>), 3.38 (s, 2 H, picolyl CH<sub>2</sub>), 2.41 (s, 3 H, picoline CH<sub>3</sub>).  ${}^{13}C{}^{1}H$  NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  162.84 (picolyl C<sup>2</sup>), 158.91 (picoline), 149.69 (picoline), 148.34, 136.96 (picoline), 132.98, 129.26, 129.23, 129.13, 127.37, 123.70 (picoline), 121.02 (picoline), 117.47, 100.40, 57.45 (picolyl CH<sub>2</sub>), 23.78 (picoline).

**2-Picolylpotassium.** KO'Bu (7.89 g, 70.3 mmol), which had been purified by sublimation twice, was dissolved in dried 2-picoline (65 g), and *n*-BuLi (70.3 mmol) was added dropwise to the solution. An orange solid precipitated, which was filtered and washed with pentane (10 mL). The powder was dried under vacuum (7.3 g, 78%). <sup>1</sup>H NMR (400 MHz, THF-*d*<sub>8</sub>):  $\delta$  6.95 (d, J = 5.0 Hz, 1 H, H<sup>3.6</sup>), 5.97 (ddd, J = 9.0, 6.0, 2.0 Hz, 1 H, H<sup>4.5</sup>), 5.53 (d, J = 9.0 Hz, 1 H, H<sup>3.6</sup>), 4.73 (t, J = 5.0 Hz,

<sup>(15)</sup> Harlan, C. J.; Bott, S. G.; Barron, A. R. J. Am. Chem. Soc. 1995, 117, 6465.

<sup>(16)</sup> Gonioukh, A.; Popham, N. WO Patent Application 0050474 to BASF.

1 H, H<sup>4.5</sup>), 2.51 (s, 2 H, C*H*<sub>2</sub>).  ${}^{13}C{}^{1}H{}$  NMR (100 MHz, THF*d*<sub>8</sub>):  $\delta$  162.78 (C<sup>2</sup>), 149.66, 131.45, 113.86, 95.45, 58.88 (*C*H<sub>2</sub>).

[N,N-(1,2-Dimethylene-1,2-ethanediyl)bis(2,6-diisopropylanilido)- $\kappa^2 N, N$ ]bis(2-picolyl)zirconium(IV) (2). ZrCl<sub>4</sub>(THF)<sub>2</sub> (0.377 g, 1.00 mmol) was dissolved in cold THF  $(7.0 \text{ mL}, -20 \degree \text{C})$ , and 2-picolylpotassium (0.262 g, 2.00 mmol)was added to the solution. The mixture was stirred for 2 h at room temperature. The dipotassium salt 1 (0.480 g, 1.00 mmol) was added at room temperature to the mixture. The solution was stirred overnight. Solvent was removed under reduced pressure. The compound was extracted with cyclohexane (ca, 20 mL). The solvent was removed, and the solid was triturated with hexane (ca. 5 mL). A brownish red powder was obtained (0.344 g, 51%), which is quite pure as indicated by its <sup>1</sup>H NMR spectrum. Further purification to give an analytically pure compound was carried out by dissolving the powder in cyclohexane and hexane (60 mL, 1/1 v/v) and filtration. The solvent was removed under reduced pressure, and the powder was triturated again with hexane (0.234 g, 35%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): 7.24 (s, 6 H, Ph H<sup>3-5</sup>), 6.88 (d, J = 5.6 Hz, 2 H, picolyl H<sup>3,6</sup>), 6.41 (t, J = 7.4 Hz, 2 H, picolyl H<sup>4,5</sup>), 6.04 (d, J =7.4 Hz, 2 H, picolyl H<sup>3,6</sup>), 5.96 (t, J = 6.0 Hz, 2 H, picolyl H<sup>4,5</sup>), 4.82 (s, 2 H, enamido  $CH_2$ ), 4.02 (septet, J = 6.8 Hz, 4 H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.49 (s, 2 H, enamido CH<sub>2</sub>), 2.03 (s, 4 H, picolyl CH<sub>2</sub>), 1.45 (d, J = 6.8 Hz, 12 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.17 (d, J = 6.8Hz, 12 H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, DEPT):  $\delta$  161.35 (picolyl ipso-*C* or Ph ipso-*C*), 158.69 (picolyl ipso-*C*) or Ph ipso-C), 145.89 (CH), 145.53 (CH<sub>2</sub>=CN), 138.70 (CH), 125.61 (CH), 123.86 (CH), 123.21 (CH), 116.24 (CH), 82.19 (CH2=CN), 47.19 (picolyl CH2), 29.07 (CH(CH3)2), 27.83 (CH-(CH<sub>3</sub>)<sub>2</sub>), 24.30 (CH(CH<sub>3</sub>)<sub>2</sub>). Anal. Calcd for C<sub>40</sub>H<sub>50</sub>N<sub>4</sub>Zr: C, 70.9; H, 7.43; N, 8.26. Found: C, 71.2; H, 7.36; N, 7.93.

Ate Complex 3. The complex was isolated when synthesis of 2 was tried with 2-picolyllithium-2-picoline instead of 2-picolylpotassium. Thus, ZrCl<sub>4</sub>(THF)<sub>2</sub>, picolyllithium-2-picoline, and 1 were reacted according to the same procedure. After the solvent was removed, the residue was extracted with toluene. The toluene was removed, and the solid was triturated with hexane. Orange cubic crystals were deposited from the filtrate when it was stored at room temperature overnight. <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ ):  $\delta$  7.47 (d, J = 4.4 Hz, 1 H), 7.25–7.00 (m, 13 H), 6.84 (t, J = 7.6 Hz, 1 H), 6.83 (d, J = 4.0 Hz, 1 H), 6.53 (t, 7.6 Hz, 1 H), 6.35 (t, J = 6.4 Hz, 1 H), 6.08 (d, J = 7.6 Hz, 1 H), 6.05 (t, J = 6.4 Hz, 1 H), 4.74 (s, 2 H, C=CH<sub>2</sub>), 3.97 (septet, J = 6.8 Hz, 2 H, CHMe<sub>2</sub>), 3.77 (septet, J = 6.8 Hz, 2 H, CHMe<sub>2</sub>), 3.37 (s, 2 H, C=CH<sub>2</sub>), 3.01 (br septet, J = 6.8 Hz, 2 H, CHMe<sub>2</sub>), 2.61 (br-septet, J = 6.8 Hz, 2 H, CHMe<sub>2</sub>), 2.54 (br s, 2 H, picolyl CH<sub>2</sub>), 2.39 (s, 2 H, CH<sub>2</sub>C=N), 1.64 (s, 2 H,  $CH_2C=N$ ), 1.53 (d, J = 6.8 Hz, 6 H,  $CH(CH_3)_2$ ), 1.36 (d, J =6.8 Hz, 6 H,  $CH(CH_3)_2$ ), 1.35 (d, J = 6.8 Hz, 6 H,  $CH(CH_3)_2$ ), 0.90 (br d. 12 H. CH(CH<sub>3</sub>)<sub>2</sub>), 1.28 (br. 12 H. CH(CH<sub>3</sub>)<sub>2</sub>), 0.87 (d, J = 6.8 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  178.43, 165.89, 160.18, 158.15 (picoline), 148.96 (picoline), 148.61, 147.14, 145.72, 145.28, 144.07, 139.32, 138.72, 137.78, 137.60 (picoline), 125.95, 125.04, 124.37, 124.13, 124.11, 123.70 (picoline), 122.74, 121.28 (picoline), 117.30, 82.25 (C=*C*H<sub>2</sub>), 67.01 (br, Zr-*C*H<sub>2</sub>C=N), 44.52 (picolyl CH2), 28.84, 28.42 (br), 27.93, 27.82, 24.82, 24.68 (br), 24.45 (br), 23.86, 23.86 (br), 23.71 (br), 23.28 (br). Anal. Calcd for C<sub>68</sub>H<sub>89</sub>LiN<sub>6</sub>Zr: C, 75.0; H, 8.24; N, 7.72. Found: C, 75.3; H, 8.17; N, 7.31.

Chloro[*N*,*N*-(1,2-dimethylene-1,2-ethanediyl)bis(2,6diisopropylanilido)- $\kappa^2$  *N*,*N*](pentamethylcyclopentadienyl)zirconium(IV) (4). The dipotassium salt 1 (0.166 g, 0.345 mmol) and Cp\*ZrCl<sub>3</sub> (0.115 g, 0.345 mmol) were weighed in a vial inside a glovebox. Toluene (5 mL) was added, and the resulting solution was stirred overnight at room temperature. The solution was filtered over Celite. The solvent was removed under vacuum to give a red solid (0.180 g, 79%), which is quite pure, as shown by its <sup>1</sup>H NMR spectrum. Analytically pure compound was obtained by recrystallization in pentane solution in a freezer (-30 °C) overnight. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.3–7.1 (m, 6 H, Ph H<sup>3–5</sup>), 4.83 (s, 2 H, C=CH<sub>2</sub>), 3.72 (s, 2 H, C=CH<sub>2</sub>), 3.39 (septet, J = 6.8 Hz, 2 H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.20 (septet, J = 6.8 Hz, 2 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.66 (s, 15 H, Cp\* CH<sub>3</sub>), 1.39 (d, J = 6.8 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.34 (d, J = 6.8 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.31 (d, J = 6.8 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.31 (d, J = 6.8 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.31 (d, J = 6.8 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.31 (d, J = 6.8 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.31 (d, J = 6.8 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.32 (<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  150.58, 145.59, 144.56, 143.61, 126.36, 124.88, 124.52, 123.68, 93.75 (CH<sub>2</sub>=C), 30.44, 28.24 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.85, 26.09, 25.21, 24.06 (CH(CH<sub>3</sub>)<sub>2</sub>), 11.19 (Cp\* CH<sub>3</sub>). Anal. Calcd for C<sub>38</sub>H<sub>53</sub>ClN<sub>2</sub>Zr: C, 68.7; H, 8.04; N, 4.22. Found: C, 68.5; H, 8.15; N, 4.65.

Chloro[N,N-(1,2-dimethylene-1,2-ethanediyl)bis(2,6diisopropylanilido)- k<sup>2</sup>N,N](pentamethylcyclopentadienyl)hafnium(IV) (5). The dipotassium salt 1 (0.508 g, 0.983 mmol) and Cp\*HfCl<sub>3</sub> (0.413 g, 0.983 mmol) were weighed in a vial inside a glovebox. Cold THF (15 mL, -30 °C) was added, and the resulting solution was stirred overnight at room temperature. The solvent was removed under vacuum. Pentane (12 mL) and toluene (4 mL) were added to the residue, and the solution was filtered over Celite. The solvent was removed under vacuum to give a dark yellow solid (0.700 g, 94%), which is quite pure, as shown by its <sup>1</sup>H NMR spectrum. Analytically pure compound was obtained by recrystallization in pentane solution in a freezer (-30 °C) overnight. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.25–7.12 (m, 6 H, Ph H<sup>3-5</sup>), 4.86 (s, 2 H, C=C $H_2$ ), 3.65 (s, 2 H, C=C $H_2$ ), 3.45 (septet, J = 6.8 Hz, 2 H,  $CH(CH_3)_2$ ), 3.27 (septet, J = 6.8 Hz, 2 H,  $CH(CH_3)_2$ ), 1.69 (s, 15 H, Cp\* CH<sub>3</sub>), 1.41 (d, J = 6.8 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.34 (d, J = 6.8 Hz, 12 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.31 (d, J = 6.8 Hz, 6 H, CH- $(CH_3)_2$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  149.71, 145.56, 144.96, 144.45, 126.37, 124.89, 123.61, 123.21, 93.11 (CH<sub>2</sub>= C), 30.19, 28.14 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.88, 26.20, 25.28, 24.05 (CH-(CH<sub>3</sub>)<sub>2</sub>), 10.99 (Cp\* CH<sub>3</sub>). Anal. Calcd for C<sub>38</sub>H<sub>53</sub>ClHfN<sub>2</sub>: C, 60.7; H, 7.10; 3.73. Found: C, 60.4; H, 7.35; N, 3.98.

Chloro(cyclopentadienyl)[N,N-(1,2-dimethylene-1,2ethanediyl)bis(2,6-diisopropylanilido)-k<sup>2</sup>N,N]zirconium-(IV) (6). The dipotassium salt 1 (0.283 g, 0.588 mmol) and CpZrCl<sub>3</sub> (0.155 g. 0.588 mmol) were weighed in a vial inside a glovebox, and cold THF (7 mL, -30 °C) was added. The mixture was stirred at room temperature overnight. The resulting solution was filtered over Celite, and the solvent was removed under vacuum. The residue was dissolved in pentane, and the solution was stored overnight at -30 °C. Red microcrystalline solid was deposited (0.190 g, 54%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.3–7.6 (m, 6 H, Ph H<sup>3-5</sup>), 5.95 (s, 5 H, Cp), 4.69 (s, 2 H, C=C $H_2$ ), 3.62 (s, 2 H, C=C $H_2$ ), 3.51 (septet, J= 6.8 Hz, 2 H,  $CH(CH_3)_2$ ), 3.46 (septet, J = 6.8 Hz, 2 H,  $CH(CH_3)_2$ ), 1.38 (d, J = 6.8 Hz, 6 H,  $CH(CH_3)_2$ ), 1.29 (d, J =6.8 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.29 (d, J = 6.8 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.25 (d, J = 6.8 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ 151.89 (CH<sub>2</sub>CN), 145.57, 144.28, 142.72 (Ph C<sup>1,3,5</sup>), 126.99, 124.92, 124.16 (Ph C<sup>2,4,6</sup>), 116.28 (Cp), 92.20 (CH<sub>2</sub>= C), 28.90, 28.57 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.25, 25.94, 25.49, 24.73 (CH-(*C*H<sub>3</sub>)<sub>2</sub>). Anal. Calcd for C<sub>33</sub>H<sub>43</sub>ClN<sub>2</sub>Zr: C, 66.7; H, 7.29; N, 4.71. Found: C, 67.0; H, 7.18; N, 5.05.

Methyl[*N*,*N*-(1,2-dimethylene-1,2-ethanediyl)bis(2,6diisopropylanilido)-  $\kappa^2 N$ ,*N*](pentamethylcyclopentadienyl)zirconium(IV) (7). Compound 4 (0.150 g, 0.226 mmol) was dissolved in diethyl ether (5.0 g), and 1.0 equiv of MeMgCl in THF was added at room temperature. The color changed from red to dark yellow upon addition. After the solution was stirred at room temperature for 2 h, all volatiles were removed under vacuum. The compound was extracted with pentane (10.0 g). Red single crystals, which are suitable for X-ray crystallography and elemental analysis, were grown from the solution at -30 °C overnight. The yield was 0.091 g (63%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.3–7.1 (m, 6 H, Ph H<sup>3–5</sup>), 4.88 (s, 2 H, C=CH<sub>2</sub>), 3.70 (s, 2 H, C=CH<sub>2</sub>), 3.51 (septet, *J* = 6.8 Hz, 2 H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.03 (septet, *J* = 6.8 Hz, 2 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.60 (s, 15 H, Cp\* CH<sub>3</sub>), 1.42 (d, *J* = 6.8 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.39 (d, J = 6.8 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.28 (d, J = 6.8 Hz, 6 H, CH-(CH<sub>3</sub>)<sub>2</sub>), 1.27 (d, J = 6.8 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.63 (s, 3 H, Zr– CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  152.91, 145.72, 144.60, 144.27, 126.42, 125.27, 123.94, 122.29, 91.73 (CH<sub>2</sub>=C), 34.96 (Zr–CH<sub>3</sub>), 30.10, 28.75 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.93, 26.81, 25.57, 24.75 (CH(CH<sub>3</sub>)<sub>2</sub>), 11.25 (Cp\* CH<sub>3</sub>). Anal. Calcd for C<sub>39</sub>H<sub>56</sub>N<sub>2</sub>Zr: C, 72.7; H, 8.76; N, 4.35. Found: C, 72.9; H, 8.84; N, 4.50.

Methyl[N,N-(1,2-dimethylene-1,2-ethanediyl)bis(2,6diisopropylanilido)- k<sup>2</sup>N,N](pentamethylcyclopentadienyl)hafnium(IV) (8). Compound 5 (0.695 g, 0.924 mmol) was dissolved in diethyl ether (10.0 g), and 1.0 equiv of MeMgCl in THF was added at room temperature. The color changed from red to dark green upon addition. After the solution was stirred at room temperature for 2 days, all volatiles were removed under vacuum. The compound was extracted with pentane (30.0 g). Yellow-green crystals were obtained from the solution at -30 °C overnight. The yield was 0.468 g (69%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.3–7.1 (m, 6 H, Ph H<sup>3–5</sup>), 4.92 (s, 2 H, C=CH<sub>2</sub>), 3.66 (s, 2 H, C=CH<sub>2</sub>), 3.55 (septet, J = 6.8 Hz, 2 H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.07 (septet, J = 6.8 Hz, 2 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.62 (s, 15 H, Cp\* CH<sub>3</sub>), 1.42 (d, J = 6.8 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.41(d, J = 6.8 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.28 (d, J = 6.8 Hz, 6 H, CH- $(CH_3)_2$ , 1.27 (d, J = 6.8 Hz, 6 H,  $CH(CH_3)_2$ ), 0.53 (s, 3 H, Hf-CH<sup>3</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  151.20, 145.43, 144.50, 144.40, 126.04, 124.78, 123.43, 120.92, 91.11 (CH<sub>2</sub>=C), 39.42 (Hf-CH<sub>3</sub>), 29.44, 28.21 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.58, 26.42, 25.16, 24.22 (CH(CH<sub>3</sub>)<sub>2</sub>), 10.63 (Cp\* CH<sub>3</sub>). Anal. Calcd for C<sub>39</sub>H<sub>56</sub>HfN<sub>2</sub>: C, 64.0; H, 7.71; N, 3.83. Found: C, 63.8; H, 7.80, N; 3.95.

(Cyclopentadienyl)(Methyl)[N,N'-(1,2-dimethylene-1,2ethanediyl)bis(2,6-diisopropylanilido)-k<sup>2</sup>N,N]zirconium-(IV) (9). The complex was prepared according to the same method and conditions as for 7. A red glassy solid was obtained, which was shown to be quite pure by its NMR spectra (90%). Purification by recrystallization to give an analytically pure complex failed. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.3-7.1 (m, 6 H, Ph H<sup>3,4,5</sup>), 5.85 (s, 5 H, Cp), 4.73 (s, 2 H,  $CH_2=C$ ), 3.58 (s, 2 H,  $CH_2=C$ ), 3.58 (septet, J = 6.8 Hz, 2 H,  $CH(CH_3)_2$ ), 3.33 (septet, J = 6.8 Hz, 2 H,  $CH(CH_3)_2$ ), 1.38 (d, J = 6.8 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.34 (d, J = 6.8 Hz, 6 H, CH- $(CH_3)_2$ ), 1.35 (d, J = 6.8 Hz, 6 H,  $CH(CH_3)_2$ ), 1.19 (d, J = 6.8Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.67 (s, Zr-CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ 153.49 (CH<sub>2</sub>C-N), 145.14, 143.67, 143.21 (Ph C<sup>1,3,5</sup>), 126.56, 124.77, 123.91 (Ph C<sup>2,4,6</sup>), 114.72 (Cp), 89.64 (CH<sub>2</sub>= C), 30.54 (Zr-CH<sub>3</sub>), 28.68, 28.37 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.16, 26.04, 25.60, 24.56 (CH(CH<sub>3</sub>)<sub>2</sub>).

**B**(**C**<sub>6</sub>**F**<sub>5</sub>)<sub>3</sub> + 2 (10). Complex 2 (20.3 mg, 0.030 mmol) was dissolved in C<sub>6</sub>D<sub>6</sub>, and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (15.4 mg, 0.030 mmol) was added to the solution. NMR studies were carried out with the solution. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  8.46 (d, J = 5.2 Hz, 1 H), 7.30-6.90 (m, 7 H), 6.70 (t, J = 7.4 Hz, 1 H), 6.54 (t, 7.2 Hz, 1 H), 6.51 (d, J = 5.2 Hz, 1 H), 6.38 (d, J = 7.6 Hz, 1 H), 6.06 (t, J = 6.2 Hz, 1 H), 5.96 (t, J = 6.4 Hz, 1 H), 4.65 (s, 2 H, CH2=C), 3.49 (br s, 2 H, CHMe2), 3.48 (s, 2 H, CH2=C), 2.81 (br septet, J = 6.8 Hz, 2 H, CHMe<sub>2</sub>), 2.52 (br s, 2 H, BCH<sub>2</sub>), 1.93 (s, 2 H, Zr-CH<sub>2</sub>), 1.28 (br d, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.10 (br d, 12 H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.51 (br d, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>).  ${}^{13}C{}^{1}H{}$  NMR  $(100 \text{ MHz}, C_6 D_6)$ :  $\delta$  167.79, 162.48, 165.8 (br), 155.8 (br, NC= CH<sub>2</sub>), 148.6 (dm,  ${}^{1}J_{CF} = 240$  Hz), 146.29, 144.97 (br), 144.62 (br), 144.31, 141.85, 140.44, 139.0 (dm,  ${}^{1}J_{CF} = 250$  Hz), 137.1 (dm,  ${}^{1}J_{CF} = 250$  Hz), 127.56, 127.34, 125.54, 123.99, 124 (br, ipso-C in C<sub>6</sub>F<sub>5</sub>), 87.8 (br, NC= $CH_2$ ), 50.76 (Zr $CH_2$ ), 29.71, 29.54, 27.25, 25.43, 24.98, 23.6 (br, CH<sub>2</sub>B). <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>, 376 MHz):  $\delta$  -39.21 (br s), -67.34 (t,  ${}^{3}J_{FF} = 20$  Hz), -71.493 (t,  ${}^{3}J_{\text{FF}} = 20$  Hz) ppm.  ${}^{11}\text{B}{}^{1}\text{H}$  NMR (C<sub>6</sub>D<sub>6</sub>, 128 MHz):  $\delta - 14.4$ .

**Al**(**C**<sub>6</sub>**F**<sub>5</sub>)<sub>3</sub> + **2** (**11**). A C<sub>6</sub>D<sub>6</sub> solution for NMR studies was prepared according to the same procedure as for **10**. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.3–6.8 (m, 6 H), 6.45 (d, *J* = 5.2 Hz, 2 H, picolyl H<sup>3.6</sup>), 6.40 (t, *J* = 7.6 Hz, 2 H, picolyl H<sup>4.5</sup>), 5.94 (d, *J* = 8.4 Hz, 2 H, picolyl H<sup>3.6</sup>), 5.90 (t, *J* = 7.6 Hz, 2 H, picolyl H<sup>4.5</sup>), 5.33 (s, 1 H, CH<sub>2</sub>=C), 3.98 (s, 1 H, CH<sub>2</sub>=C), 3.61 (septet, *J* = 6.8 Hz, 2 H, CHMe<sub>2</sub>), 3.21 (s, 2 H, Al–CH<sub>2</sub>), 3.17 (septet, *J* = 6.8 Hz, 2 H, *CH*Me<sub>2</sub>), 1.97 (br d, *J* = 11 Hz, 2 H), 1.76 (br d, *J* = 11 Hz, 2 H), 1.18 (d, *J* = 6.8 Hz, 6 H, CH(*CH*<sub>3</sub>)<sub>2</sub>), 1.14 (d, *J* = 6.8 Hz, 6 H, CH(*CH*<sub>3</sub>)<sub>2</sub>), 0.94 (d, *J* = 6.8 Hz, 6 H, CH-(*CH*<sub>3</sub>)<sub>2</sub>), 0.77 (d, *J* = 6.8 Hz, 6 H, CH(*CH*<sub>3</sub>)<sub>2</sub>), <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ 197.41 (AlCH<sub>2</sub>*C*), 159.27, 157.12, 150.4 (dm, <sup>1</sup>*J*<sub>CF</sub> = 230 Hz), 145.79, 144.85, 142.14, 142.07, 141.36, 140.45, 140.04, 139.1 (dm, <sup>1</sup>*J*<sub>CF</sub> = 240 Hz), 137.0 (dm, <sup>1</sup>*J*<sub>CF</sub> = 240 Hz), 127.30, 125.04, 124.68, 124.56, 118.32, 100.42 (NC= *C*H<sub>2</sub>), 51.99 (Zr *C*H<sub>2</sub>), 29.73, 29.04, 27.70, 25.94, 24.35, 23.62. <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>, 376 MHz): δ -27.60 (d, <sup>3</sup>*J*<sub>FF</sub> = 19 Hz), -63.01 (t, <sup>3</sup>*J*<sub>FF</sub> = 19 Hz), -70.05 (s).

**B**(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> + 7 (12). Compound 7 (16.1 mg, 25 μmol) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (12.8 mg, 25 μmol) were dissolved in C<sub>6</sub>D<sub>6</sub> in an NMR tube at room temperature. The complex is so unstable in C<sub>6</sub>D<sub>6</sub> solution that it decomposes overnight to give oily precipitates. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.06 (m, 4 H, Ph H<sup>3.5</sup>), 6.94 (m, 2 H, Ph H<sup>4</sup>), 4.84 (s, 2 H, C=CH<sub>2</sub>), 3.67 (s, 2 H, C=CH<sub>2</sub>), 2.82 (septet, *J* = 6.8 Hz, 2 H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.40 (septet, *J* = 6.8 Hz, 2 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.67 (s, 3 H, BCH<sub>3</sub>), 1.49 (s, 15 H, Cp\* CH<sub>3</sub>), 1.23 (d, *J* = 6.8 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.22 (d, *J* = 6.8 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.06 (d, *J* = 6.8 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.65 (d, *J* = 6.8 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>19</sup>F NMR (470 MHz, C<sub>6</sub>D<sub>6</sub>): δ –133.34 (d, *J* = 21 Hz, *o*-F), -161.53 (dd, *J* = 21 Hz, *p*-F), -166.59 (dd, *J* = 21 Hz, 6, *m*-F).

**B**(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> + **9** (13). Compound **9** (17.3 mg, 30 μmol) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (15.4 mg, 30 μmol) were dissolved in C<sub>6</sub>D<sub>6</sub> in an NMR cell at room temperature. The complex decomposed in C<sub>6</sub>D<sub>6</sub> solution over several hours. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.01-(m, 4 H, Ph H<sup>3.5</sup>), 6.90 (m, 2 H, Ph H<sup>4</sup>), 5.91 (s, 5 H, Cp), 4.63 (s, 2 H, CH<sub>2</sub>=C), 3.67 (s, 2 H, CH<sub>2</sub>=C), 2.93 (septet, *J* = 6.8 Hz, 2 H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.24 (septet, *J* = 6.8 Hz, 2 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.71 (br, 3 H, BCH<sub>3</sub>), 1.19 (d, *J* = 6.8 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.04 (d, *J* = 6.8 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.03 (d, *J* = 6.8 Hz, 6 H, CH-(CH<sub>3</sub>)<sub>2</sub>), 0.80 (d, *J* = 6.8 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>).

Al( $C_6F_5$ )<sub>3</sub> + 8 (14). Compound 8 (60 mg, 82  $\mu$ mol) and Al- $(C_6F_5)_3$  (toluene) (51 mg, 82  $\mu$ mol) were dissolved in toluene (2 mL) in a vial inside a glovebox. After it was stirred for 3 min at room temperature, the solution was filtered over Celite. The filtrate was evacuated under vacuum to remove the solvent. Trituration with pentane gave a yellow powder (77 mg, 77%). Single crystals suitable for X-ray crystallography were obtained by vapor-phase addition of pentane to a toluene solution at room temperature overnight.<sup>13</sup>C{<sup>1</sup>H} NMR data could not be obtained due to the compound's low solubility in C<sub>6</sub>D<sub>6</sub> and decomposition in polar solvents such as CDCl<sub>3</sub> and CD<sub>2</sub>Cl<sub>2</sub>. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.2-6.8 (m, 6 H, Ph  $H^{3-5}$ ), 5.67 (s, 1 H, C=CH<sub>2</sub>), 4.29 (s, 1 H, C=CH<sub>2</sub>), 3.52 (d, J= 6.5 Hz, 1 H, CCH<sub>2</sub>Al), 3.24 (d, J = 6.5 Hz, 1 H, CCH<sub>2</sub>Al), 2.90 (septet, *J* = 6.8 Hz, 1 H, C*H*(CH<sub>3</sub>)<sub>2</sub>), 2.78 (septet, *J* = 6.8 Hz, 1 H,  $CH(CH_3)_2$ ), 2.38 (septet, J = 6.8 Hz, 1 H,  $CH(CH_3)_2$ ), 1.88 (septet, J = 6.8 Hz, 1 H,  $CH(CH_3)_2$ ), 1.39 (d, J = 6.8 Hz, 3 H,  $CH(CH_3)_2$ , 1.38 (s, 15 H, Cp\* CH<sub>3</sub>), 1.21 (d, J = 6.8 Hz, 3 H,  $CH(CH_3)_2$ ), 1.13 (d, J = 6.8 Hz, 3 H,  $CH(CH_3)_2$ ), 1.08 (d, J =6.8 Hz, 3 H,  $CH(CH_3)_2$ ), 1.05 (d, J = 6.8 Hz, 3 H,  $CH(CH_3)_2$ ), 0.85 (d, J = 6.8 Hz, 3 H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.84 (d, J = 6.8 Hz, 3 H,  $CH(CH_3)_2$ ), 0.61 (d, J = 6.8 Hz, 3 H,  $CH(CH_3)_2$ ), 0.58 (s, 3 H, Hf-CH<sub>3</sub>). <sup>19</sup>F NMR (470 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -123.12, -157.20, -164.22.

**Al**(**C**<sub>6</sub>**F**<sub>5</sub>)<sub>3</sub> + **9** (**15**). Compound **9** (17.3 mg, 30  $\mu$ mol) and Al(C<sub>6</sub>**F**<sub>5</sub>)<sub>3</sub>·(toluene) (18.6 mg, 30  $\mu$ mol) were dissolved in C<sub>6</sub>D<sub>6</sub> in a NMR tube. The complex decomposed in C<sub>6</sub>D<sub>6</sub> solution over several hours. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.2–6.6 (m, 6 H, Ph H<sup>3–5</sup>), 5.58 (s, 5 H, Cp), 5.06 (m, 2 H, CH<sub>2</sub>=C), 3.82 (m, 2 H, CH<sub>2</sub>=C), 3.25 (br, 2 H, CCH<sub>2</sub>Al), 2.98 (septet, *J* = 6.8 Hz, 1 H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.83 (septet, *J* = 6.8 Hz, 1 H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.80 (septet, *J* = 6.8 Hz, 1 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.72 (septet, *J* = 6.8 Hz, 1 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.37 (d, *J* = 6.8 Hz, 3 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.23 (d, *J* = 6.8 Hz, 3 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.06–0.84 (m, 12 H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.87 (s, 3 H, Zr–CH<sub>3</sub>), 0.58 (d, *J* = 6.8 Hz, 3 H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.48 (d, *J* = 6.8 Hz, 3 H, CH(CH<sub>3</sub>)<sub>2</sub>).

Al( $C_6F_5$ )<sub>3</sub> + 7. Compound 7 (19.3 mg, 30  $\mu$ mol) and Al- $(C_6F_5)_3$ ·(toluene) (18.6 mg, 30  $\mu$ mol) were dissolved in  $C_6D_6$  in an NMR tube at room temperature. The <sup>1</sup>H NMR spectrum can be tentatively interpreted as a mixture of a methylabstracted ion-paired complex and alane-added zwitterionic complex (ratio 1/2). Signals assigned to the zwitterionic complex are given in italics. <sup>1</sup>H NMR (500 MHz,  $C_6D_6$ ):  $\delta$ 7.13-6.77 (m, 6 H, Ph H<sup>3-5</sup>), 5.60 (s, 1 H, C=CH<sub>2</sub>), 4.84 (s, 2 H, C=CH<sub>2</sub>), 4.32 (s, 1 H, C=CH<sub>2</sub>), 3.68 (s, 2 H, C=CH<sub>2</sub>), 3.43  $(d, J = 6.9 Hz, 1 H, CCH_2AI), 3.19 (d, J = 6.9 Hz, 1 H, CCH_2AI),$ 2.90 (septet, J = 6.8 Hz, 1 H,  $CH(CH_3)_2$ ), 2.88 (septet, J = 6.8Hz, 2 H,  $CH(CH_3)_2$ ), 2.78 (septet, J = 6.8 Hz, 1 H,  $CH(CH_3)_2$ ), 2.35 (septet, J = 6.8 Hz, 1 H,  $CH(CH_3)_2$ ), 2.34 (septet, J = 6.8Hz, 2 H,  $CH(CH_3)_2$ ), 1.62 (septet, J = 6.8 Hz, 1 H,  $CH(CH_3)_2$ ), 1.48 (s, 15 H, Cp\* CH<sub>3</sub>), 1.39 (d, J = 6.8 Hz, 3 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.38 (s, 3 H,  $Zr-CH_3$ ), 1.31 (s, 15 H,  $Cp^* CH_3$ ), 1.23 (d, J =6.8 Hz, 3 H,  $CH(CH_3)_2$ , 1.21 (d, J = 6.8 Hz, 12 H,  $CH(CH_3)_2$ ), 1.10 (d, J = 6.8 Hz, 3 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.09 (d, J = 6.8 Hz, 12 H,  $CH(CH_3)_2$ ), 1.04 (d, J = 6.8 Hz, 3 H,  $CH(CH_3)_2$ ), 0.86 (d, J =6.8 Hz, 3 H,  $CH(CH_3)_2$ ), 0.79 (s, 3 H,  $Zr-CH_3$ ), 0.75 (d, J =6.8 Hz, 3 H,  $CH(CH_3)_2$ , 0.73 (d, J = 6.8 Hz, 3 H,  $CH(CH_3)_2$ ), 0.60 (d, J = 6.8 Hz, 3 H,  $CH(CH_3)_2$ ). <sup>19</sup>F NMR (470 MHz,  $C_6D_6$ ):  $\delta -123.20, -156.21, -157.32, -163.92, -164.24$ .

**Ethylene Polymerization.** In a drybox, in a dried 70 mL glass reactor was added 30 mL of toluene. Activated complex prepared by mixing a complex (0.5  $\mu$ mol) and MAO (0.89 g, Al/Zr = 5000) in the reactor. The reactor was assembled and brought out from the drybox. The reactor was immersed in an oil bath whose temperature had been set to a given value, and the mixture was stirred for 15 min. Ethylene was fed under 60 psig pressure. After the polymerization reaction was conducted for a given time, the reaction was quenched by venting ethylene gas and pouring the mixture into acetone. White precipitates were collected by filtration and dried under vacuum. Table 1 summarizes the polymerization results.

**Crystallographic Studies.** Crystals coated with grease (Apiezon N) were mounted inside a thin glass tube with epoxy glue and placed on an Enraf-Nonius CCD single-crystal X-ray diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.710$  73 Å). The structures were solved by direct methods (SHELXS-97)<sup>17</sup> and refined against all  $F^2$  data (SHELXS-97). All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were

 Table 2. Crystallographic Parameters<sup>a</sup>

	3	7	14
formula	C <sub>68</sub> H <sub>89</sub> Li-	C <sub>117</sub> H <sub>168</sub> -	C <sub>64</sub> H <sub>64</sub> Al-
	N <sub>6</sub> Zr	N <sub>6</sub> Zr <sub>3</sub>	$F_{15}HfN_2$
fw	1088.61	1932.23	1351.64
<i>a</i> , Å	12.8688(4)	19.3649(2)	17.3514(3)
<i>b</i> , Å	24.2011(7)	17.9860(3)	12.5037(2)
<i>c</i> , Å	21.0004(9)	31.4958(4)	29.1875(6)
α, deg	90	90	90
$\beta$ , deg	97.2330(10)	97.6226(9)	101.0644(6)
$\gamma$ , deg	90	90	90
V, Å <sup>3</sup>	6488.3(4)	10873.0(3)	6214.72(19)
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
$D(\text{calcd}), \text{ g cm}^{-3}$	1.114	1.180	1.445
Ζ	4	4	4
$\mu$ , mm <sup>-1</sup>	0.211	0.330	1.777
no. of data collected	17376	38409	24002
no. of unique data	9284	23350	13840
no. of variables	702	1177	763
R (%)	0.0567	0.0654	0.0366
R <sub>w</sub> (%)	0.1347	0.1566	0.0438
goodness of fit	0.961	0.918	0.698

<sup>*a*</sup> All data collected at 293(2) K with Mo Kα radiation.  $R(F) = \sum ||F_0| - |F_c|| / \sum |F_0|$  with  $F_0 > 2.0\sigma(I)$ ;  $R_w = [\sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0)^2]^2]^{1/2}$  with  $F_0 > 2.0\sigma(I)$ .

treated as idealized contributions. The crystal data and refinement results are summarized in Table 2.

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**Supporting Information Available:** Complete details for the crystallographic studies of **3**, **7** and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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<sup>(17)</sup> Sheldrick, G. M. SHELXL-97, Program for the Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997.