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Zirconium(IV) Complexes Having a Rigid 1,8-Naphthalene Diamide versus a Flexible 1,3-Propylene Diamide for Olefin Polymerization

Choong Hoon Lee, Young-Hye La, and Joon Won Park*

Department of Chemistry, Center for Biofunctional Molecules, Pohang University of Science and Technology, San 31 Hyoja-dong, Pohang, 790-784, Korea

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Structure and chemical properties of zirconium(IV) complexes containing a rigid naphthalene diamide ligand ($[1,8\text{-}C_{10}H_6(NSiMe_3)_2]^{2-}$) or flexible propylene diamide ligands ($[1,3\text{-}C_3H_6(NR)_2]^{2-}$, R = $SiMe_3$, Si(*i*-Pr)$_3$) are described. The reaction of $1,8\text{-}C_{10}H_6(NHSiMe_3)_2$ with $Zr(NMe_2)_4$ in refluxing toluene yields $[1,8\text{-}C_{10}H_6(NSiMe_3)_2]Zr(NMe_2)_2$ (**1**), and the product **1** is converted to $[1,8\text{-}C_{10}H_6(NSiMe_3)_2]ZrCl_2$ (**2**) in a moderate isolation yield by the treatment with excess $ClSiMe_3$. X-ray crystallographic analysis establishes that **2** forms a dimer associated through two chloride bridges in the solid state and has a highly puckered six-membered ring with a small N−Zr−N bite angle (91.05°). The reaction of $1,3\text{-}C_3H_6(NHR)_2$ (R = $SiMe_3$, Si(*i*-Pr)$_3$) with $Zr(NMe_2)_4$ also affords $[1,3\text{-}C_3H_6(NR)_2]Zr(NMe_2)_2$. Treatment of the amide complex with excess $ClSiMe_3$ results in $[1,3\text{-}C_3H_6(NR)_2]ZrCl_2$ (**4**, R = $SiMe_3$; **5**, R = Si(*i*-Pr)$_3$) in a facile manner. The crystal structure of **5** shows that the molecule is monomeric, featuring a mirror plane that passes the zirconium atom and two chloride atoms, and the chelate and the metal form a boatlike six-membered ring with a large N−Zr−N angle (104.31°). While these zirconium(IV) diamide complexes (**2**, **4**, and **5**) exhibit moderate ethylene polymerization activity (10−90 kg of PE/($mol_{cat}\cdot atm\cdot h$)) in the presence of methylalumoxane, the diamide dimethyl compound $[1,3\text{-}C_3C_6(NSi(i\text{-}Pr)_3)_2]ZrMe_2$ (**6**) shows a high activity (300 kg of PE/($mol_{cat}\cdot atm\cdot h$)) for the ethylene polymerization when it is activated with $Ph_3CB(C_6F_5)_4$.

Introduction

A group 4 metal complex bearing bi-[1,2] or tridentate[3] diamide ligands has attracted investigators' attention as a potential alternative to the classical homogeneous Ziegler−Natta polymerization catalysts[4] that are mostly based on bis- or monocyclopentadienyl ligands. Because the diamide ligand system generates a unique metallic center in terms of the geometry and the electronic property, their group 4 metal complexes are being explored.[1,2] Recently, we reported titanium(IV) and zirconium(IV) complexes containing rigid diamide ligands derived from *N*,*N*′-disilylated 1,8-diaminonaphthalene.[5] When the lithiated diamide was applied to zirconium tetrachloride, a bis(diamide) zirconium(IV) complex, $[1,8\text{-}C_{10}H_6(NSiMe_3)_2]_2Zr$, and a mono(diamide) zirconium(IV) dichloride, $[1,8\text{-}C_{10}H_6(NSi(i\text{-}Pr)_3)_2]ZrCl_2$, were obtained. The latter complex showed meager activity for ethylene polymerization.

In this paper, we describe an amine elimination reaction leading to the less bulky mono(diamide) complex $[1,8\text{-}C_{10}H_6(NSiMe_3)_2]ZrCl_2$ and the structure as well as the polymerization activity. Also, we have prepared zirconium(IV) complexes bearing a *flexible* propylene diamide ligand ($[RN(CH_2)_3NR]^{2-}$; R = $SiMe_3$, Si(*i*-Pr)$_3$)

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(6) We carried out the NMR tube reaction of $1,8\text{-}C_{10}H_6(NHSiMe_3)_2$ and $Zr(NMe_2)_4$ in benzene-d_6 at room temperature. ^1H NMR data for the resulting complex, $[1,8\text{-}C_{10}H_6(NSiMe_3)_2]Zr(NMe_2)_2(HNMe_2)$ (**1′**): δ 7.33 (d, 2H), 7.26 (t, 2H), 6.88 (d, 2H), 2.54 (s, 12H, N*Me*$_2$), 1.84 (d, 6H, HN*Me*$_2$), 0.90 (br s, 1H, *H*NMe$_2$), 0.34 (s, 18H).

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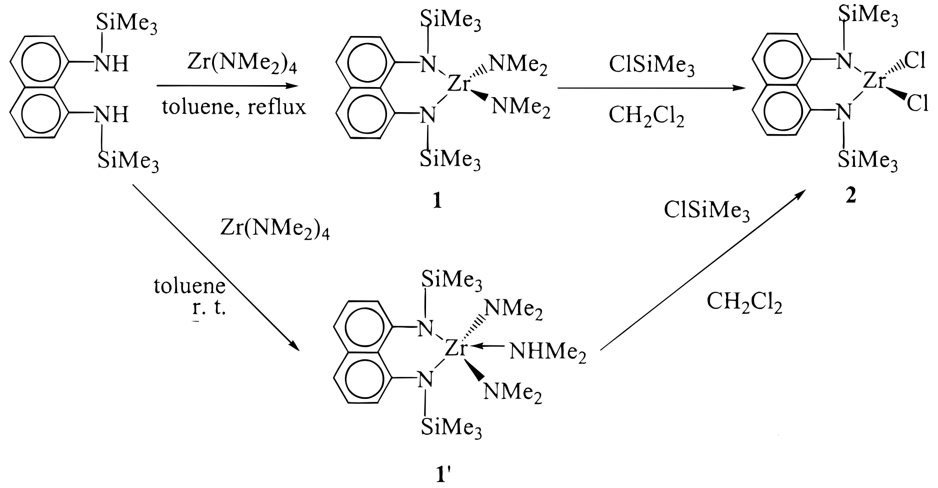
Scheme 1



to elucidate the influence of the linkage on the structure and the polymerization activity.

Results and Discussion

Preparation of the Zirconium(IV) Complexes Containing a Mono(naphthalenediamide) Ligand. We prepared the mono(diamide) zirconium(IV) complex through an amine elimination (Scheme 1). The reaction of 1,8-$C_{10}H_6(NHSiMe_3)_2$ with $Zr(NMe_2)_4$ in refluxing toluene afforded the monochelated amide complex [1,8-$C_{10}H_6(NSiMe_3)_2$]$Zr(NMe_2)_2$ (**1**) in a high conversion, but the isolation yield was low due to its high solubility in hydrocarbon solvents as well as polar ones. The addition of excess chlorotrimethylsilane into the bright yellow solution of **1** in CH_2Cl_2 resulted in an immediate color change to yellow-orange, indicating the conversion to [1,8-$C_{10}H_6(NSiMe_3)_2$]$ZrCl_2$ (**2**). In contrast, the amine elimination at room temperature gave the pentacoordinated amide complex (**1′**) as viscous brown oil. The ^1H NMR spectrum of **1′** shows dimethylamine (HN*Me*$_2$; δ 1.84) coordinating to the zirconium center.[6] The pentacoordinated complex is also transformed into **2** by the treatment of chlorotrimethylsilane, but the conversion is not as clean as the above case. The complication must be invoked by the side reactions between the coordinated amine and $SiMe_3Cl$.

Characterization of [1,8-$C_{10}H_6(NSiMe_3)_2$]Zr-(NMe_2)$_2$ (1) and [1,8-$C_{10}H_6(NSiMe_3)_2$]$ZrCl_2$ (2). The room-temperature ^1H NMR spectrum for the amide complex **1** displays broad resonances for all protons. When **1** is heated to 50 °C, the broad signals sharpen to give a spectrum consistent with a C_{2v}-symmetric molecule. Unlike complex **1**, the dichloride complex **2** displays sharp resonances for the naphthalene and methyl protons at room temperature. The symmetric splitting pattern of the aromatic ring for **2** reflects the chemical equivalency of both sides of the ring.

The molecular structure of **2** is shown in Figure 1, and selected bond lengths and angles are summarized in Table 1. The zirconium dichloride **2** exists as a dimer connected through two chloride bridges in the solid state, and two molecular units are related by a crystallographic inversion center. Bond distances from the zirconium atom to the nonequivalent bridging chloride centers (2.5884(10), 2.6310(9) Å) are elongated from the Zr−Cl$_{terminal}$ distance (2.4159(10) Å). The geometry of the zirconium atom can be described as a distorted square pyramid with the N(2) atom and the remaining atoms (N(1), Cl(1), Cl(2), Cl(2A)) occupying axial and basal (about 0.09 Å deviation from planarity) positions, respectively. The dihedral angle between the planes containing Si(1), N(1), Zr atoms and Zr, N(2), Si(2) atoms is about 62.5°, which reflects the Si(2) group being away from the naphthalene plane. This large twisting between two planes is a consequence of the steric crowding between *N*-trimethylsilyl substituents and the rigid naphthalene framework, which makes the chelate

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for [1,8-$C_{10}H_6(NSiMe_3)_2$]$ZrCl_2$ Dimer (2)[a]

Zr−N(1)	2.033(3)	Zr−N(2)	1.976(3)
Zr−Cl(1)	2.4159(10)	Zr−Cl(2)	2.5884(10)
Zr−Cl(2A)	2.6310(9)	Zr−Si(1)	3.1204(11)
Si(1)−N(1)	1.764(3)	Si(2)−N(2)	1.791(3)
N(1)−C(2)	1.415(4)	N(2)−C(10)	1.445(4)
N(1)−Zr−N(2)	91.05(11)	N(2)−Zr−Cl(1)	104.95(9)
N(1)−Zr−Cl(1)	104.70(9)	N(2)−Zr−Cl(2)	96.52(9)
N(1)−Zr−Cl(2)	82.92(8)	Cl(1)−Zr−Cl(2)	155.47(4)
N(2)−Zr−Cl(2A)	106.21(8)	N(1)−Zr−Cl(2A)	157.22(8)
Cl(1)−Zr−Cl(2A)	85.76(4)	Cl(2)−Zr−Cl(2A)	75.65(3)
Zr−Cl(2)−Zr(A)	104.35(3)	Cl(1)−Zr−Si(1)	94.56(4)
Zr−N(1)−C(2)	124.1(2)	Zr−N(1)−Si(1)	110.32(14)

[a] Symmetry transformations used to generate equivalent atoms: (A) $-x + 2$, $-y + 2$, $-z$.

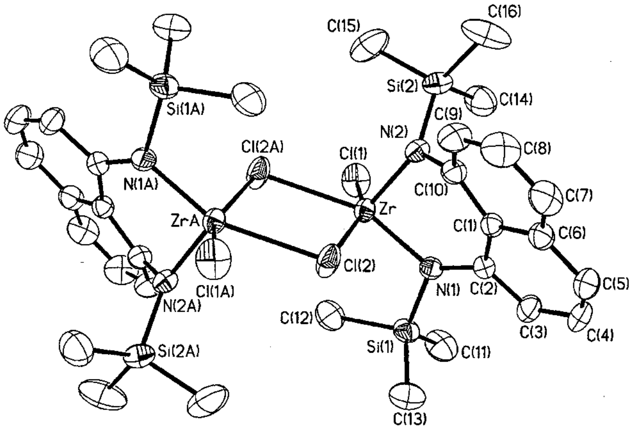
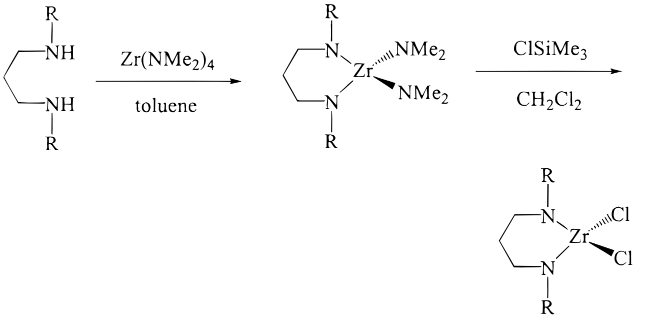


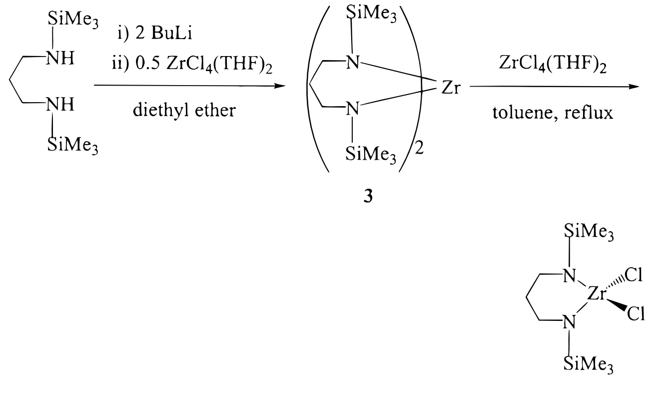
Figure 1. ORTEP diagram of [1,8-$C_{10}H_6(NSiMe_3)_2$]$ZrCl_2$ dimer (**2**).

Scheme 2



4: R = SiMe$_3$
5: R = Si(*i*-Pr)$_3$

Scheme 3

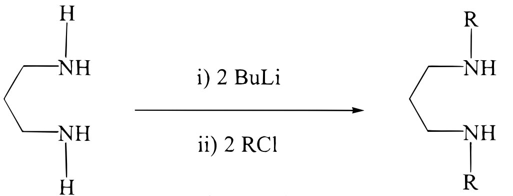


3

4

ring highly puckered. The structural feature of **2** is quite similar to that of the *N*,*N*′-bis(triisopropylsilyl)-substituted zirconium(IV) analogue [1,8-$C_{10}H_6$(NSi(*i*-Pr)$_3$)$_2$]-$ZrCl_2$ (**2′**) reported previously.[5] The Zr···Zr separation is 4.121(2) Å, which is shorter than the value observed for **2′** (4.261(2) Å), presumably reflecting the less sterically demanding trimethylsilyl substituent on the diamide ligand. The N(1)−Zr−N(2) chelate angle (91.05(11)°) is somewhat smaller than that of **2′** (94.17(13)°). Meanwhile, Zr−N (2.033(3), 1.976(3) Å) and Zr−Cl (2.4159(10), 2.5884(10) Å) bond lengths are comparable to those found in other related zirconium diamide complexes. The sum of the angles about each nitrogen (N(1) = 356.4°, N(2) = 358.6°) indicates that both nitrogen centers are sp^2-hybridized, and it can be assumed that each nitrogen atom donates four π-electrons to the electrophilic zirconium center.

Preparation of the Zirconium(IV) Complexes Containing Propylenediamide Ligands. The reaction of 1,3-diaminopropane with chlorotrimethylsilane and chlorotriisopropylsilane gives *N*,*N*′-disilylated products, which are isolated as colorless viscous oil in moderate yields (55−65%) by vacuum distillation (eq 1).



(R = SiMe$_3$, Si(*i*-Pr)$_3$) (1)

Zirconium(IV) dichloride complexes having an *N*,*N*′-disilylated 1,3-propylenediamide ligand can be obtained by the same method as used for **2**. The amine elimination between 1,3-C_3H_6(NHR)$_2$ (R = SiMe$_3$, Si(*i*-Pr)$_3$) and Zr(NMe$_2$)$_4$ in refluxing toluene affords the monochelated amide complex [1,3-C_3H_6(NR)$_2$]Zr(NMe$_2$)$_2$ as a viscous brown oil (R = SiMe$_3$) or yellow solid (R = Si(*i*-Pr)$_3$). The complex is easily converted to dichloride derivative **4** by treatment with excess chlorotrimethylsilane (Scheme 2).

Alternatively, complex **4** can be prepared from salt elimination and subsequent disproportionation (Scheme 3). When 1,3-C_3H_6(NHSiMe$_3$)$_2$ is lithiated with 2 equiv of *n*-BuLi, and the resulting solution is allowed to react with 0.5 equiv of ZrCl$_4$(THF)$_2$, a bischelated zirconium(IV) complex [1,3-C_3H_6(NSiMe$_3$)$_2$]$_2$Zr is isolated as a white crystalline solid analogous to the rigid (diamide) zirconium complex [1,8-$C_{10}H_6$(NSiMe$_3$)$_2$]$_2$Zr. The reaction of [1,3-C_3H_6(NSiMe$_3$)$_2$]$_2$Zr with 1.0 equiv of ZrCl$_4$(THF)$_2$ in toluene leads to the redistribution of the diamide ligands between the zirconium centers and the subsequent formation of **4**.

Characterization of [1,3-C_3H_6(NSiMe$_3$)$_2$]ZrCl$_2$ (4) and [1,3-C_3H_6(NSi(*i*-Pr)$_3$)$_2$]ZrCl$_2$ (5). These compounds have been characterized by NMR spectroscopy and elemental analysis. The ^{1}H and ^{13}C NMR spectra at room temperature reveal that these complexes exhibit C_{2v} symmetry in solution. Also, sharp resonances for the methyl and isopropyl protons in **4** and **5**, respectively, indicate that the rotation of the alkyl groups around the silicon−nitrogen bond is fast.

The solid-state structure of **5** was determined by X-ray crystallography. The molecular structure of **5** is shown in Figure 2, and selected bond lengths and angles are summarized in Table 2. Unlike zirconium(IV) dichlorides (**2**, **2′**) containing the rigid naphthalenediamide ligands, **5** exists as a mononuclear species with a mirror plane passing through Zr, Cl(1), Cl(2), and C(1) atoms and therefore maintains C_s symmetry in the solid state. A six-membered chelate ring is so twisted that Zr and C(1) atoms are out of a plane passing N, C(2), C(2′), and N′ atoms, resulting in a boatlike conformation. It seems that the twist relieves the steric crowding between the chlorides and the triisopropylsilyl substituents. The geometry around the zirconium atom is best described

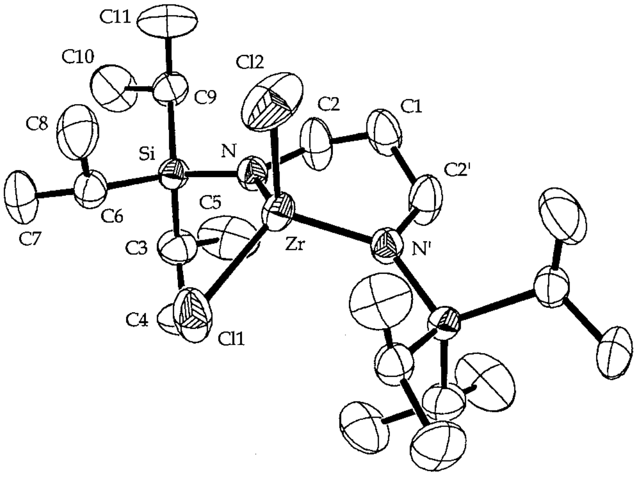


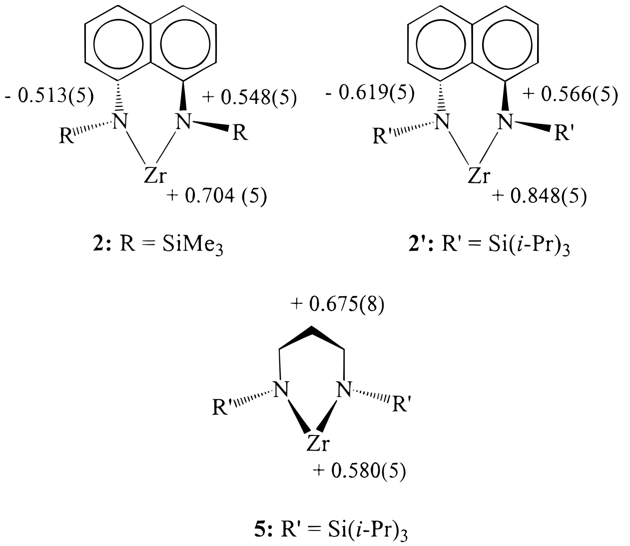
Figure 2. ORTEP diagram of [1,3-C_3H_6(NSi(*i*-Pr)$_3$)$_2$]ZrCl$_2$ (**5**).

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $[1,3\text{-}C_3H_6(NSi(i\text{-}Pr)_3)_2]ZrCl_2$ (5)[a]

Zr−N	2.0009(17)	Zr−Cl(2)	2.3943(11)
Zr−Cl(1)	2.3849(10)	Si−C(6)	1.892(2)
Si−N	1.7682(18)	Si−C(9)	1.898(2)
Si−C(3)	1.894(3)	N−C(2)	1.499(3)
N−Zr−N′	104.31(10)	N−Zr−Cl(1)	112.84(5)
N′−Zr−Cl(1)	112.84(5)	N′−Zr−Cl(2)	108.74(6)
N−Zr−Cl(2)	108.74(6)	N′−Zr−Cl(2)	108.74(6)
Cl(1)−Zr−Cl(2)	109.16(5)	N−Si−C(6)	108.09(10)
N−Si−C(3)	109.88(12)	Si−N−Zr	132.47(10)
N−C(2)−C(1)	115.1(3)	C(2)−N−Zr	112.02(15)

[a] Symmetry transformations used to generate equivalent atoms: (′) $x, -y + 3/2, z$.

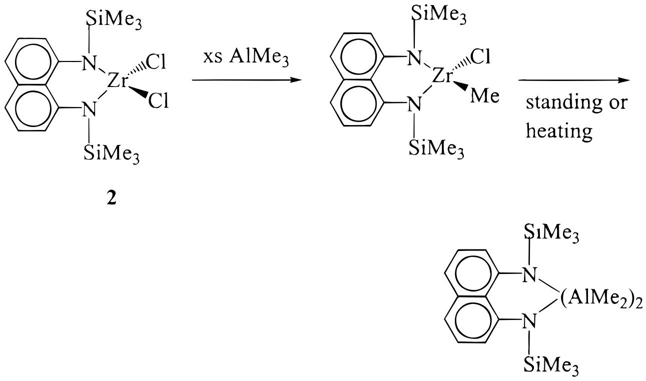
Scheme 4



2: R = $SiMe_3$ **2':** R' = $Si(i\text{-}Pr)_3$

5: R' = $Si(i\text{-}Pr)_3$

Scheme 5



as distorted tetrahedral. The N−Zr−N′ chelate angle (104.31°) is more obtuse than those of other zirconium complexes (**2**, 91.05°; **2′**, 94.17°) containing naphthalene diamide ligands, which is presumably due to the flexibility of the propylene linkage. Also, the chelate angle is wider than that (95.4°) found in a zirconium complex ($[1,3\text{-}C_3H_6(NR)_2]Zr(\eta^2\text{-}N,C{-}NC_5H_4)(CH_2CMe_2Ph)$, R = $2,6\text{-}i\text{-}Pr_2Ph$) reported by McConville and co-workers,[1c] which can be attributed to the difference of the steric bulkiness on the nitrogen atoms. The Cl(1)−Zr−Cl(2) angle (109.16°) is very close to the ideal tetrahedral value and is much larger than those found in other related zirconium amide dichlorides[1i,2e,7] as well as linked cyclopentadienylamide zirconium dichlorides.[8] The Zr−N bond distances (average 2.00 Å) are comparable to those of related zirconium diamide complexes, and each nitrogen atom is also in an sp^2-hybridized environment.

As expected, the linkage moiety of the diamide ligands has considerable influence on the structure of zirconium dichloride complexes. For easy comparison, the structural features of six-memebered chelate rings in **2**, **2′**, and **5** are schematically represented (Scheme 4).

Surprisingly, the rigid naphthalene rings themselves in **2** and **2′** are distorted from the planarity along the chelation. The induced deviation of the aromatic carbon atoms from the mean plane is as large as 0.09 Å. In particular, the chelating nitrogen atoms are forced away from the mean plane as well. Each nitrogen atom in **2** lies above and below the plane (0.548 and 0.513 Å, respectively), and the zirconium center is positioned at 0.704 Å above the plane. Consequently, the highly puckered six-membered ring is formed. Two trimethylsilyl groups are directed away from the mean naphthalene plane pointing the opposite directions to reduce steric crowding. For **2′**, the chelate ring is isostructural to that of **2**, except that the steric demand of the bulkier triisopropyl groups makes the N and Zr atoms deviate more significantly from the mean naphthalene plane. Meanwhile, the flexible propylene linkage of **5** apparently reduces the degree of distortion around the nitrogen atoms. The environment around the chelate ring in **5** is symmetric, in which Zr, C(1), and Si atoms are located 0.580, 0.675, and 0.559 Å out of the NC(2)C(2′)N′ plane. The zirconium center of **5** is less distorted than that of **2** and **2′**. Also, the silyl groups of **5** are less distorted from planarity. Therefore, the zirconium center of **5** is more protected by the diamide ligands, resulting in the monomeric form in the solid-state rather than the dimeric ones observed in **2** and **2′**. It can be concluded that the diamide ligand linked by the flexible propylene group chelates the zirconium center with a less steric stress than the rigid naphthalene cases. Combining with the higher donating ability of the aliphatic nitrogen atoms, the propylene diamide chelates seem to produce zirconium complexes of higher thermodynamic stability.

Preparation of Zirconium Alkyl Complexes. To obtain alkyl derivatives of the complexes **2**, **4**, and **5**, the reactions with excess $AlMe_3$ at room temperature were carried out and followed by ^1H NMR measurements. The reactivity for the alkylation will indicate the propensity to form the dialkylated species in the presence of methylalumoxane. The stable monomethyl product is readily and quantitatively formed for **2** (Scheme 5). Characteristic ^1H and ^{13}C NMR resonances of the Zr-Me group were observed at 0.15 and 54.1 ppm, respectively.[9] However, standing overnight at room temperature or heating the solution, the monomethyl product of **2** was transformed into a dinuclear aluminum diamide complex that was characterized before. The

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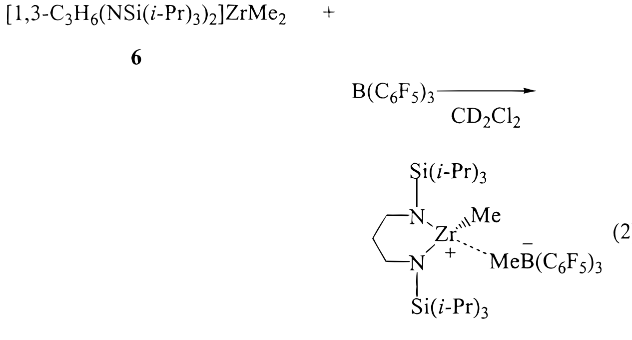
(9) NMR data for $[1,8\text{-}C_{10}H_6(NSiMe_3)_2]Zr(Me)Cl$. ^1H (C_6D_6): δ 7.35 (d, 2H), 7.29 (d, 2H), 7.09 (t, 2H), 0.57 (s, 18H), 0.15 (s, 3H, Zr-*Me*). ^{13}C (C_6D_6): δ 139.0, 135.7, 129.0, 126.7, 123.3, 54.1 (Zr-*Me*), 3.56.

easy transmetalation reflects the instability of the zirconium complexes having the rigid linkage. When neat $AlMe_3$ was added to a white suspension of **4** in benzene, the mixture gradually turned into a dark red, clear solution. To follow the reaction, a ^1H NMR spectrum was recorded after the mixing of the reagents in C_6D_6 at room temperature. No less than six singlets were observed between 0 and 0.4 ppm, and all of those peaks must be associated with the zirconium methyl species. However, further characterization was not amenable. In the hope of increasing the selectivity, $AlMe_3$ was added to a clear solution of **4** in CD_2Cl_2 at − 50 °C, but the six signals showed up persistently. In the case of **5**, no reaction is observed even at the higher temperature. The reluctance to form the alkyl derivatives also had been found for the naphthalenediamide zirconium analogue **2′**. It seems that $AlMe_3$ is not readily accessible to the zirconium center with the bulky *N*,*N′*-bis(triisopropyl) substituents.

The reaction of **2** with 2 equiv of MeMgBr was carried out at low temperature, but only intractable product was obtained. The difficulty has been observed also for **2′**. Therefore, the ligand systems in **2** and **2′** seem not to be balanced to afford the corresponding dimethyl complexes in a facile manner. The same problem was observed for **4** when it was mixed with the Grignard reagent. Meanwhile, treating **5** with 2 equiv of MeMgBr gave the dimethyl complex $[1,3\text{-}C_3H_6(NSi(i\text{-}Pr)_3)_2]ZrMe_2$ (**6**) as a white crystalline solid in a good yield. The ^1H NMR spectrum of **6** is consistent with a species with C_{2v} symmetry. The proton and carbon NMR signals of the Zr-Me group in **6** are displayed at 0.56 and 39.5 ppm, respectively, which are very comparable to the related zirconium diamide complex $[1,3\text{-}C_3H_6(NR)_2]ZrMe_2$ (R = 2,6-*i*-Pr_2Ph; Zr−C*H*$_3$, 0.42 ppm; Zr−*C*H_3, 39.9 ppm).[1c]

Addition of $B(C_6F_5)_3$ to **6** in CD_2Cl_2 at −50 °C afforded the quantitative formation of a cationic zirconium complex $\{[1,3\text{-}C_3H_6(NSi(i\text{-}Pr)_3)_2]ZrMe\}^+\{MeB(C_6F_5)_3\}^-$ (**7**) (eq 2). The species was characterized by ^1H, ^{13}C, and ^{19}F NMR spectroscopy. The cationic complex features downfield resonances (^1H, 0.97 ppm; ^{13}C, 54.4 ppm), a characteristics of the cationic, electron-deficient Zr-Me group.[10] The downfield proton NMR resonance (1.28 ppm) and the large difference (4.3 ppm)[3h] between *p*-F and *m*-F chemical shifts of the $[MeB(C_6F_5)_3]^-$ anion suggest that there exists a *strong* interaction between the anion and the zirconium cation in dichloromethane, as observed for related cationic zirconium species.[1a,g,3f,11] It was observed that the ionic species **7** decomposed slowly to yield unidentifiable species at room temperature in several hours. The same electrophilic abstraction was tested in toluene-d_8 as well as benzene-d_6. After mixing with 1 equiv of $B(C_6F_5)_3$ at room temperature, ^1H NMR shows two new zirconium-methyl resonances with the concurrent appearance of the methyl borate resonance. The newly formed complexes were decomposed in an hour at room temperature. Therefore, nonhalogenated solvent was not able to stabilize the ionic species.

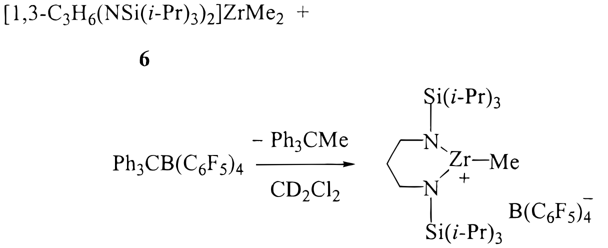


6

(2)

7

To avoid the strong interaction, a noncoordinating trityl borate, $Ph_3CB(C_6F_5)_4$, was employed. The reaction was followed with ^1H NMR spectroscopy after mixing the reagents at −50 °C. The mixing in CD_2Cl_2 gave a homogeneous orange-red solution, while the phase separation occurred in toluene-d_8. The abstracted methyl group was clearly seen at 2.13 ppm, when the spectrum was recorded at −30 °C in CD_2Cl_2. Also, it was observed that the zirconium-methyl resonance of **6** completely disappeared. Along with the resonance of the cationic Zr-Me group at 0.75 ppm, two other unidentified resonances were observed at 0.60 and 0.66 ppm. These three new methyl resonances disappeared in an hour at room temperature. The spectroscopic study elucidated that the abstraction reaction was facile even at low temperatures, but the ionic species **8** was not stable enough to survive at room temperature in dichloromethane.



6

(3)

8

Polymerization of Ethylene. Polymerization of ethylene was carried out for complexes **2**, **4**, **5**, and **6**. The results are summarized in Table 3. After activation with excess modified methylalumoxane (MMAO), the dichloride complexes **2**, **4**, and **5** show moderate activity (10−90 kg of PE/(mol$_{cat}$·atm·h)) for the ethylene polymerization. At 60 °C, the activity was slightly enhanced (entries 2, 5, and 7). However, their activities are much lower than that of Cp_2ZrCl_2 (654 kg of PE/(mol$_{cat}$·atm·h)) measured under similar conditions (entry 12). Molecular weights of the polymer samples could not be measured, because they showed low solubility even in refluxing 1,2,4-trichlorobenzene. However, melting temperatures (T_m) measured by differential scanning calorimetry (DSC) are typical of high-density polyethylene.

It is interesting to observe that the catalyst **2** bearing the trimethylsilyl groups shows much higher activity than that of the triisopropylsilyl-substituted analogue (**2′**) (entry 1 vs 3). We believe that the reduced bulkiness of the ancillary ligand in the former complex facilitates the formation of the active catalyst and/or an olefin binding to the zirconium center. Complexes **4** and **5**

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Table 3. Data for Ethylene Polymerization[a]

entry no.	catalyst	[cat] (μmol)	cocatalyst	reaction temp (°C)	time (min)	yield (g)	activity[b]	T_m[c] (°C)
1	**2**	10	MMAO	rt	30	0.41	82	131.5
2	**2**	10	MMAO	60	30	0.45	90	131.3
3	**2′**	10	MMAO	rt	30	trace[d]		131.9
4	**4**	10	MMAO	rt	30	0.05	10	129.7
5	**4**	10	MMAO	60	30	0.24	48	131.2
6	**5**	10	MMAO	rt	30	0.08	16	131.6
7	**5**	10	MMAO	60	30	0.36	72	131.0
8	**6**	10	$B(C_6F_5)_3$	0	30	0.07	14	140.2
9	**6**[e]	20	$B(C_6F_5)_3$	rt	60	0.03	1.5	136.4
10	**6**[e]	10	$Ph_3CB(C_6F_5)_4$	rt	30	1.45	290	126.8
11	**6**[e]	10	$Ph_3CB(C_6F_5)_4$	rt	60	3.17	317	128.4
12	Cp_2ZrCl_2	20	MMAO	rt	10	2.18	654	132.3

[a] MMAO (Al/M = 500) or 1.0 equiv of the borane or the borate, 50 mL toluene, 1 atm of ethylene. [b] kg PE/(mol_{cat}·atm·h). [c] Measured by differential scanning calorimetry (DSC). [d] Reference 4. [e] In the presence of triisobutylaluminum (Al/Zr = 50).

were tested to investigate the influence of the flexible linkage of the ligand on the polymerization behavior. Intriguing enough, introduction of the flexible propylene linker does not increase their activities (entries 4−7). Moreover, the dimethyl complex **6** does not show high activity when it is activated with $B(C_6F_5)_3$. Employment of triisobutylaluminum as a scavenger does not help at all. The most striking feature is the high activity of **6** (300 kg of PE/(mol_{cat}·atm·h)) when it is activated with $Ph_3CB(C_6F_5)_4$ in the presence of triisobutylaluminum. The activity is dramatically reduced in the absence of the scavenger. In contrast, the latter catalytic system is not active at all for propylene and 1-hexene.

For **2**, the relatively facile monoalkylation should be followed by the formation of a reactive cationic zirconium center in the presence of MAO. As observed in the model reaction, the desirable reaction must be in competition with a side reaction leading to the dinuclear aluminum species (Scheme 5). The latter transformation should be prominent in the presence of excess MAO. The complication may help rationalize the low observed activity in comparison with Cp_2ZrCl_2. The nonselective alkylation of **4** should be associated with the low activity of **4**. The low activity of **5** should arise from the difficulty in the alkylation. The poor polymerization activity of **6** in combination with the borane cocatalyst should originate from the strong binding of the anion to the highly electron-deficient zirconium center. High activity of **6** was realized when it was activated with a trityl borate, $Ph_3CB(C_6F_5)_4$, and when excess triisobutylaluminum was applied as a scavenger. The species **8** is not active for α-olefins such as propene and 1-hexene. The inactivity toward α-olefins must be associated with the steric hindrance of the cationic zirconium center. It is expected that propylenediamine ligands having less sterically hindered substituents such as dimethylisopropylsilyl ($SiMe_2(i\text{-}Pr)$) and methyldiisopropylsilyl ($SiMe(i\text{-}Pr)_2$) groups will generate a metallic center suitable for the polymerization of α-olefins as long as the dimethyl complex analogous to **6** can be prepared.

Summary

A rigid diamide chelate, *N*,*N*′-bis(trimethylsilyl)-1,8-diaminonaphthalene, and flexible diamide chelates, *N*,*N*′-disilylated 1,3-diaminopropane, react with $Zr(NMe_2)_4$ to yield mono(diamide) zirconium dichloride complexes. These zirconium(IV) complexes (**2**, **4**, **5**) exhibit moderate ethylene polymerization activity in the presence of MAO. The reduced bulkiness of **2** around the nitrogen atoms elevates the catalytic activity in comparison with **2′**, but the activity is significantly lower than that of Cp_2ZrCl_2. An undesirable transmetalation of **2** in the presence of excess alkyl aluminum seems to be associated with the low activity. A high activity for the polymerization was observed when the flexible diamide Zr(IV) dimethyl complex **6** was tested. When it is activated with a trityl borate, $Ph_3CB(C_6F_5)_4$, and when triisobutylaluminum is employed as a scavenger, the activity is as good as that of zirconocene dichloride. In comparison, high activity was not recorded when it was activated with $B(C_6F_5)_3$, and the low activity can be explained by the strong interaction between the anion and the zirconium center as observed in ^1H and ^{19}F NMR spectroscopy.

Experimental Sections

General Procedure. All manipulation of air- and/or moisture-sensitive compounds was carried out with use of standard Schlenk or vacuum-line techniques. Argon or nitrogen was purified by passing through columns of Ridox oxygen scavenger (R31-3, Fisher) and Linde 4-Å molecular sieves. Solids were transferred and stored in an N_2-filled Vacuum Atmospheres glovebox equipped with a HE-493 Dri-Train, a CS-40 Dri-Cold, and an oxygen analyzer (model 315, Teledyne Analytical Instruments).

Anhydrous toluene, tetrahydrofuran, and diethyl ether were purchased from Aldrich and transferred to a sodium/benzophenone ketyl mixture without prior treatment. Pentane was stirred over concentrated H_2SO_4, dried over CaH_2, and then transferred to sodium/benzophenone ketyl. Dichloromethane was dried with CaH_2. Dried deoxygenated solvents were vacuum-transferred to dry glass vessels equipped with a J-Young valve and stored under inert gas. Benzene-d_6 and toluene-d_8 were transferred from purple sodium/benzophenone ketyl. CD_2Cl_2 and $CDCl_3$ were predried under CaH_2 and vacuum-transferred. 1,8-Diaminonaphthalene, 1,3-diaminopropane, $ClSiMe_3$, $ClSi(i\text{-}Pr)_3$, *n*-BuLi (1.6 M in hexane), $ZrCl_4$, $AlMe_3$, $Al(i\text{-}Bu)_3$, and ethylene (99.5+%) were used as received from Aldrich. $ZrCl_4(THF)_2$,[12] $Zr(NMe_2)_4$,[13] and 1,8-$C_{10}H_6$-$(NHR)_2$[4] (R = $SiMe_3$) were prepared according to literature procedures. $B(C_6F_5)_3$[14] and $Ph_3CB(C_6F_5)_4$ were synthesized and recrystallized from cold pentane and dichloromethane/hexane, respectively. Methylalumoxane (Akzo, type 4) modified with

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an isobutyl group was purchased as a toluene solution, and the solid alumoxane was obtained by evaporating the solvent in a vacuum at room temperature for 24 h.

NMR spectra were recorded on Bruker DRX500 (500 MHz, ^{1}H) and DPX300 (300 MHz, ^{1}H) spectrometers. Chemical shifts are reported in δ, referenced to residual solvent signals. Elemental analyses were performed at either Galbraith Laboratories, Inc., or Pohang University of Science and Technology (Elementar Vario-EL).

Preparation of [1,8-$C_{10}H_6(NSiMe_3)_2$]$ZrCl_2$ (2). The compound 1,8-$C_{10}H_6(NHSiMe_3)_2$ (565 mg, 1.87 mmol) in toluene (10 mL) was added to $Zr(NMe_2)_4$ (500 mg, 1.87 mmol) in toluene (15 mL) at room temperature. The reaction mixture was heated to refluxing temperature and stirred for 12 h. The volume of the solution was reduced until a yellow slurry was formed, and pentane (30 mL) was added to the solution. The resulting yellow powder (270 mg, 30.4%), [1,8-$C_{10}H_6(NSiMe_3)_2$]-$Zr(NMe_2)_2$ (**1**), was collected by the filtration, washed with cold pentane, and dried under vacuum. ^{1}H NMR (500 MHz, C_7D_8): 300 K, δ 7.10 (br s, 2H), 6.82 (br s, 2H), 6.58 (br s, 2H), 2.90, 2.73 (br s, 12H, N*Me*$_2$), 0.22 (s, 18H); 328 K, δ 7.20 (d, 2H), 7.14 (t, 2H), 6.78 (d, 2H), 2.73 (s, 12H, N*Me*$_2$), 0.20 (s, 18H). ^{13}C NMR (C_6D_6, 300 K): δ 126.3, 121.6, 119.4, 42.8, 42.4, 3.8, 1.7.

Compound **1** (300 mg, 0.625 mmol) was dissolved in CH_2Cl_2 (5 mL). Excess chlorotrimethylsilane was added to the solution at room temperature, and the reaction mixture was stirred for 30 min. All volatiles were removed under vacuum, and the resulting residue was washed with pentane three times. Drying the residue in vacuo produced yellow-orange solid **2** (120 mg, 41.3%). An analytically pure sample suitable for X-ray crystallography was obtained from the recrystallization in CH_2Cl_2 at −45 °C. ^{1}H NMR (300 MHz, C_6D_6): δ 7.27 (d, 2H), 7.11 (t, 2H), 6.71 (d, 2H), 0.39 (s, 18H). ^{13}C NMR (C_6D_6): δ 146.0, 137.4, 125.7, 124.3, 116.5, 1.2. Anal. Calcd for $C_{16}H_{24}N_2Si_2ZrCl_2$: C, 41.54; H, 5.23; N, 6.05. Found: C, 41.23; H, 5.26; N, 5.88.

Preparation of 1,3-$C_3H_6(NHSiMe_3)_2$. 1,3-Diaminopropane (3.38 mL, 40.5 mmol) in THF (150 mL) was added to a 250 mL flask equipped with a magnetic stirrer, an argon inlet, and a condenser. The solution was cooled to 0 °C, and then *n*-BuLi (55.6 mL, 89.1 mmol) in hexane was added dropwise. The reaction mixture was warmed to room temperature and stirred additionally for 5 h. The resulting solution was cooled to 0 °C again, and then $ClSiMe_3$ (11.3 mL, 89.1 mmol) was added. The mixture was heated to reflux for 2 h. After the mixture was stirred additionally for 12 h at room temperature, all volatiles were removed by drying in vacuo. The resulting residue was extracted with pentane, filtered through a Celite pad, and dried in vacuo to afford a pale yellow oil. Colorless oil (4.89 g, 55.3%) was obtained by vacuum distillation (35 °C, 30 mTorr). ^{1}H NMR (300 MHz, C_6D_6): δ 2.67 (t, 4H), 1.37 (m, 2H), 0.17 (s, NH), 0.08 (s, 18H). ^{13}C NMR (C_6D_6): δ 39.8, 39.6, 0.2. Anal. Calcd for $C_9H_{26}N_2Si_2$: C, 49.50; H, 12.00; N, 12.82. Found: C, 49.15; H, 11.81; N, 12.78.

Preparation of 1,3-C_3H_6(NHSi(*i*-Pr)$_3$)$_2$. The title compound was obtained by the same method as used for 1,3-C_3H_6-$(NHSiMe_3)_2$ except using ClSi(*i*-Pr)$_3$ as the silylating reagent. Pale yellow oil (10.1 g, 64.4%) was obtained by vacuum distillation (120 °C, 30 mTorr). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.81 (t, 4H), 1.55 (m, 2H), 1.05 (s, 6H), 1.03 (s, 36H), 0.24 (s, NH). ^{13}C NMR ($CDCl_3$): δ 40.9, 40.4, 18.6, 12.0. Anal. Calcd for $C_{21}H_{50}N_2Si_2$: C, 65.20; H, 13.03; N, 7.24. Found: C, 65.32; H, 12.96; N, 7.48.

Preparation of [1,3-$C_3H_6(NSiMe_3)_2$]$_2$Zr (3). A diethyl ether (15 mL) solution dissolving 1,3-$C_3H_6(NHSiMe_3)_2$ (1.00 g, 4.57 mmol) was cooled to 0 °C, and *n*-BuLi (6.3 mL, 10.1 mmol) was added slowly to the solution. The reaction mixture was warmed to room temperature, stirred for 1 h, and then added to $ZrCl_4(THF)_2$ (0.86 g, 2.29 mmol) dissolved in diethyl ether (15 mL) at 0 °C. The mixture was stirred additionally for 12 h at room temperature and filtered through a Celite pad. The filtrate was concentrated and stored at −45 °C overnight. Colorless crystals of **3** (0.60 g, 50%) were isolated by the filtration, washed with pentane, and dried under vacuum. ^{1}H NMR (300 MHz, C_6D_6): δ 3.33 (m, 8H), 1.89 (m, 4H), 0.24 (s, 36H). ^{13}C NMR (C_6D_6): δ 51.4, 39.7, 0.4. Anal. Calcd for $C_{18}H_{48}N_4Si_4Zr$: C, 41.24; H, 9.23; N, 10.69. Found: C, 40.77; H, 8.92; N, 10.77.

Preparation of [1,3-$C_3H_6(NSiMe_3)_2$]$ZrCl_2$ (4). Method 1. The compound 1,3-$C_3H_6(NHSiMe_3)_2$ (245 mg, 1.12 mmol) in toluene (15 mL) was added to $Zr(NMe_2)_4$ (300 mg, 1.12 mmol) in toluene (15 mL) at room temperature. The reaction mixture was refluxed for 12 h and dried in vacuo. The resulting brown oil was dissolved in CH_2Cl_2 (20 mL), and then excess $ClSiMe_3$ (0.7 mL, 5.6 mmol) was added. After the additional stirring for 30 min, all volatiles were removed under vacuum, and the resulting residue was washed with pentane three times. Drying in vacuo produced white solid **4** (200 mg, 47.1%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 3.59 (m, 4H), 2.13 (m, 2H), 0.25 (s, 18H). ^{13}C NMR (CD_2Cl_2): δ 53.4, 40.1, −0.58. Anal. Calcd for $C_9H_{24}N_2Si_2Cl_2Zr$: C, 28.55; H, 6.39; N, 7.40. Found: C, 28.32; H, 6.64; N, 7.31.

Method 2. A toluene (25 mL) solution dissolving [1,3-C_3H_6-$(NSiMe_3)_2$]$_2$Zr (200 mg, 0.38 mmol) and $ZrCl_4(THF)_2$ (140 mg, 0.37 mmol) was refluxed for 24 h. Drying the solution in vacuo produced a white solid. The ^{1}H NMR spectrum of the solid is almost the same as that obtained from method 1, but shows relatively large amount of impurities.

Preparation of [1,3-C_3H_6(NSi(*i*-Pr)$_3$)$_2$]$ZrCl_2$ (5). The compound 1,3-C_3H_6(NHSi(*i*-Pr)$_3$)$_2$ (1.45 g, 3.75 mmol) in toluene (20 mL) was added to $Zr(NMe_2)_4$ (1.00 g, 3.74 mmol) in toluene (15 mL) at room temperature. The reaction mixture was stirred and refluxed for 12 h. Drying the mixture in vacuo produced pale yellow solid [1,3-C_3H_6(NSi(*i*-Pr)$_3$)$_2$]$Zr(NMe_2)_2$. ^{1}H NMR (300 MHz, C_6D_6): δ 3.53 (m, 4H), 2.94 (s, 12H), 1.73 (m, 2H), 1.20 (s, 6H), 0.17 (s, 36H). ^{13}C NMR (C_6D_6): δ 44.5, 42.6, 34.4, 19.1, 13.0.

After the above solid was dissolved in CH_2Cl_2 (20 mL), excess chlorotrimethylsilane (1.90 mL, 12.7 mmol) was added at room temperature, and the solution was stirred for 30 min. All volatiles were removed under vacuum, and the resulting residue was washed with pentane three times. Drying in vacuo produced a pale yellow solid **5** (1.8 g, 88%). Analytically pure white microcrystals suitable for X-ray crystallography were obtained from the recrystallization in diethyl ether at −45 °C. ^{1}H NMR (300 HMz, C_6D_6): δ 3.45 (m, 4H), 2.02 (m, 2H), 1.32 (m, 6H), 1.13 (d, 36H). ^{13}C NMR (C_6D_6): δ 50.7, 36.0, 18.9, 13.0. Anal. Calcd for $C_{21}H_{48}N_2Si_2Cl_2Zr$: C, 46.12; H, 8.85; N, 5.12. Found: C, 45.71; H, 8.97; N, 5.33.

Reaction of 2, 4, and 5 with $AlMe_3$. An appropriate amount (30 μmol) of **2**, **4**, or **5** in C_6D_6 (0.6 mL) was mixed with excess $AlMe_3$ (200 μmol) at room temperature. Each sample was transferred into an NMR tube after the mixing, and its ^{1}H NMR spectrum was recorded immediately.

Preparation of [1,3-C_3H_6(NSi(*i*-Pr)$_3$)$_2$]$ZrMe_2$ (6). MeMgBr (0.70 mL, 2.1 mmol, 3 M in ether) was slowly added to the white suspension of **5** (514 mg, 0.940 mmol) in diethyl ether (30 mL) at −45 °C. The reaction mixture was gradually warmed to room temperature and stirred overnight. The resulting pale yellow solution was dried under vacuum to afford a pale yellow solid. The solid was extracted with pentane, and the filtrate was concentrated and cooled to −45 °C. White crystalline solid **6** (350 mg, 73.6%) was isolated by the filtration, washing with cold pentane, and drying in vacuo. ^{1}H NMR (300 MHz, C_6D_6): δ 3.38 (m, 4H), 1.90 (m, 2H), 1.32 (m, 6H), 1.19 (d, 36H), 0.56 (s, 6H, Zr-*Me*). ^{13}C NMR (C_6D_6): δ 50.1, 39.5 (Zr-*Me*), 37.0, 19.1, 12.9. Anal. Calcd for $C_{23}H_{54}N_2Si_2Zr$: C, 54.58; H, 10.76; N, 5.54. Found: C, 53.90; H, 10.40; N, 5.36.

Generation of the Cationic Zirconium Complex [1,3-C_3H_6(NSi(*i*-Pr)$_3$)$_2$ZrMe]$^+$[MeB(C_6F_5)$_3$]$^-$ (7). In a glovebox, an NMR tube was charged with complex **6** (25.2 mg, 50.0 μmol) and $B(C_6F_5)_3$ (25.6 mg, 50.0 μmol). CD_2Cl_2 (0.6 mL) was slowly added to the tube at −50 °C. NMR spectra were recorded at 0 °C. ^{1}H NMR (500 MHz, CD_2Cl_2, 273 K): δ 3.79 (br s, 4H), 2.32 (br s, 2H), 1.38 (sept, 6H), 1.28 (br s, 3H, B-*Me*), 1.09 (d, 36H), 0.97 (s, 3H, Zr-*Me*). ^{13}C NMR (CD_2Cl_2, 273 K): 149.4, 147.6, 140.2, 138.2, 136.4, 123.5, 54.4 (Zr-*Me*), 52.0, 37.1, 21.5 (B-*Me*), 18.8, 12.7. ^{19}F NMR (CD_2Cl_2, 273 K): −132.6 (br d, *ortho*-F), −160.4 (br s, *para*-F), −164.7 (br s, *meta*-F).

Polymerization of Ethylene. In a glovebox a 100 mL Schlenk tube was charged with the catalyst together with MAO and toluene. Typically, each solid catalyst (10 μmol) was added to a MAO (0.29 g, 5.0 mmol) solution in toluene (50 mL). The mixture was stirred at room temperature for 10 min. Ethylene gas was then allowed into the tube, and its pressure was maintained continuously at 1 atm by means of bubbling. The polymerization was quenched by stopping the ethylene supply and subsequent addition of methanolic solution of 1 M HCl. The white precipitate was filtered and washed with an aqueous solution of 1 M HCl, copious methanol, and acetone. The resulting powder was finally dried in an oven at 80 °C for 12 h.

X-ray Crystallographic Determination for 2 and 5. Crystals of **2** and **5** were obtained by recrystallization from methylene chloride and diethyl ether, respectively. Each crystal sealed in a capillary tube was mounted on a Siemens SMART diffractometer equipped with a graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation source and a CCD detector. Fifteen frames of two-dimensional diffraction image were collected and processed to deduce a cell parameter and orientation matrix. Data collection was performed at 293 K. A total of 1271 frames of two-dimensional diffraction images were collected, and each was measured for 20 s. The frame data were processed to produce conventional intensity data by the program SAINT. The intensity data were corrected for Lorentz and polarization effects. An absorption correction was also applied based on ψ scans. The structures were solved by a combination of Patterson and difference Fourier methods provided by the program package SHELXTL. All the non-hydrogen atoms were refined anisotropically.

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Supporting Information Available: Tables S1−S8 listing full experimental details for data collection and refinement, atomic coordinates, bond distances and bond angles, and anisotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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