Controlled Alkene and Alkyne Insertion Reactivity of a Cationic Zirconium Complex Stabilized by an Open Diamide Ligand

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The chemistry of electrophilic zirconium complexes stabilized by a sterically open diamide ligand has been studied. Treatment of $Me_2Si(NLiCMe_3)_2$ with $ZrCl_4(THF)_2$ afforded $\{Me_2Si(NCMe_3)_2\}ZrCl_2(THF)_2$ (**1**), which, in solution, was in equilibrium with a dimeric zirconium dichloride species $[\{Me_2Si(NCMe_3)_2\}ZrCl_2]_2(THF)$. Complex **1** was converted to dialkyl complexes $\{Me_2Si(NCMe_3)_2\}ZrR_2$ (R = CH_2Ph, **4**; CH_2CMe_3, **5**) using $MgBz_2(dioxane)_{0.5}$ and $LiCH_2CMe_3$, respectively, but dimethylation was unsuccessful. Alkyl abstraction from **4** using $B(C_6F_5)_3$ cleanly afforded $\{Me_2Si(NCMe_3)_2\}Zr(CH_2Ph)\{\eta^6\text{-}PhCH_2B(C_6F_5)_3\}$ (**6**), in which the anion strongly coordinates to the benzylzirconium cation via the aromatic ring. Protonolysis of **4** using $[PhMe_2NH][B(C_6F_5)_4]$ afforded the Lewis-base adduct $[\{Me_2Si(NCMe_3)_2\}Zr\{CH_2Ph)(NMe_2Ph)]^+$ (**7**), whereas $[Ph_3C][B(C_6F_5)_4]$ gave 1 equiv of Ph_3CCH_2Ph and a mixture of two cationic species, **9a**/**b**, proposed to be monomeric and dimeric benzylzirconium cations. Reaction of **4** with 0.5 equiv of the trityl reagent afforded the dizirconium complex $[\{Me_2Si(NCMe_3)_2\}_2Zr_2(CH_2Ph)_3]^+$. Cations **6**, **7**, and **9a**/**b** cleanly and rapidly reacted with 2-butyne to afford the single insertion product, $[\{Me_2Si(NCMe_3)_2\}Zr\{\eta^1,\eta^6\text{-}C(Me){=}C(Me)CH_2Ph]^+$, stabilized by a chelating π-coordination of the benzene ring of the hydrocarbyl ligand. Structurally similar insertion products were obtained from the reaction of **9a** with a range of alkenes, $[\{Me_2Si(NCMe_3)_2\}Zr\{\eta^1,\eta^6\text{-}CH_2CH(R)CH_2Ph]^+$ (R = H, Me, *n*-Bu, CH_2Ph). Benzylborate adduct **6** also underwent single alkene insertion giving $\{Me_2Si(NCMe_3)_2\}Zr\{\eta^1\text{-}CH_2CH(R)CH_2Ph\}\{\eta^6\text{-}PhCH_2B(C_6F_5)_3\}$ (R = H, Me), stabilized by anion coordination to zirconium. The dramatic effects of anion, Lewis base, solvent, and substrate variation on the rate of insertion have been rationalized in terms of the facility of anion or base dissociation from the benzylzirconium cation.

Introduction

The utility of "uniform site" metallocene-based alkene polymerization catalysts[1] has spawned an intensive academic and industrial effort to develop related catalysts in which the cyclopentadienyl groups are replaced by other ligands. Much attention has focused on nitrogen-containing ligands, such as porphyrins,[2] tetraazaannulenes,[3] tetradentate Schiff-base ligands,[4] (hydroxyphenyl)oxazolines,[5] benzamidinates,[6] pyrollyls,[7] and amido- and alkoxy-pyridines.[8,9] In contrast to the industrial application of cyclopentadienyl−amide catalysts in ethene (co)polymerization,[10] diamide catalysts have, until very recently,[11,12] been studied little, despite the straightforward synthesis of group 4 diamide com-

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plexes[13] and the wide potential for ligand variation. By simple extrapolation from cyclopentadienyl–amide catalysis[10] and due to their extreme metal electrophilicity,[14] diamide complexes might be expected to act as novel polymerization catalysts. We have recently reported that cationic zirconium complexes stabilized by amide ligands exhibit ethene and, in some cases, propene polymerization activity.[15] In order to explore the limits of steric unsaturation in diamide catalysis, we choose to synthesize cationic complexes based on the "open" diamide ligand $[Me_2Si(NCMe_3)_2]^{2-}$.[16–19]

Ligand chelation rather than bridging diamide coordination, as well as ligand robustness, were expected to be favored by the presence of *tert*-butyl substituents on nitrogen.[16,17] In comparison to the well-studied cyclopentadienyl–amide complexes, such as $[\{Me_2Si(NCMe_3)(C_5Me_5)\}MR]^+$ (M = Ti, Zr), putative diamide analogues, $[\{Me_2Si(NCMe_3)_2\}MR]^+$, should be both electronically more unsaturated (maximum of a 10- compared to 12-electron metal) and sterically more open.[19] These differences were expected to result in an extremely high sensitivity of the reactivity of such diamide-stabilized cations to donor molecule coordination. This has indeed turned out to be the case, as the new cationic complexes reported here, although generally inactive in alkene polymerization, undergo controlled single insertion reactivity with rates depending on the anion, Lewis base, and solvent, as well as the substrate.

Controlled alkyne insertion into the Zr–methyl bond of $[Cp'_2ZrMe]^+$ has previously been examined as a model[20,21] for alkene insertion: insertion of a second alkyne molecule is generally slower than the first insertion, allowing successive insertion products to be isolated in some cases.[20] Controlled insertion of alkenes into a group 4 metallocene–hydrocarbyl bond has been observed when the insertion product is particularly stabilized, for example by a chelating Lewis-base coordination.[21] During the course of our studies, the single insertion of alkenes into the Zr–benzyl bond of $Zr(CH_2Ph)_3\{PhCH_2B(C_6F_5)_3\}$ and $(C_5Me_5)Zr(CH_2Ph)_2\{PhCH_2B(C_6F_5)_3\}$ was described by Pellecchia:[22] spectroscopic and NMR evidence for stabilization of the single insertion product by chelating coordination of the 3-phenylpropyl ligand via the benzene ring was provided. Unfortunately, the NMR studies were complicated both by the rapid exchange of the different zirconium benzyl groups and by aromatic ring current effects, and no attempt was made to study the effect of anion or solvent variation on insertion. We now report the preparation of diamide-stabilized cationic benzyl complexes and the study of their single insertion reactivity with 2-butyne and alkenes.

Results

Synthesis of Dichlorozirconium Complexes. The known diamine ligand[16,17] $Me_2Si(NHCMe_3)_2$ was readily prepared by reaction of Me_2SiCl_2 with a 4-fold excess of Me_3CNH_2.[23] Deprotonation with a 2-fold excess of *n*-BuLi in hexane solution under reflux, followed by cooling to −40 °C, afforded large colorless crystals of the dilithium salt in 92% yield. Reaction of the dilithium salt with an equimolar amount of $ZrCl_4$ in toluene gave a 1:1 mixture of the known bis(ligand) complex $\{Me_2SiN(CMe_3)\}_2Zr$[17] and $ZrCl_4$. In contrast, reaction with $ZrCl_4(THF)_2$ in toluene (Scheme 1), followed by extraction of the crude residue with a THF/

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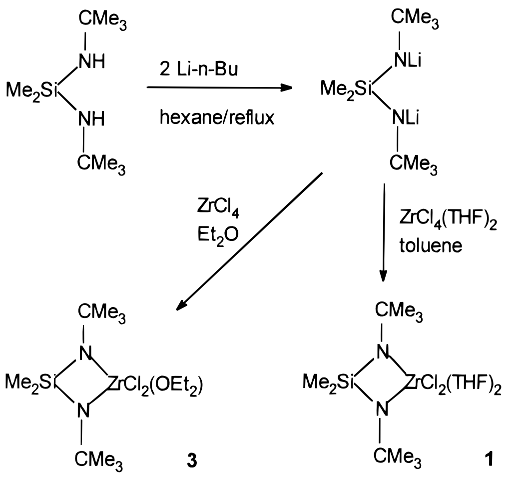
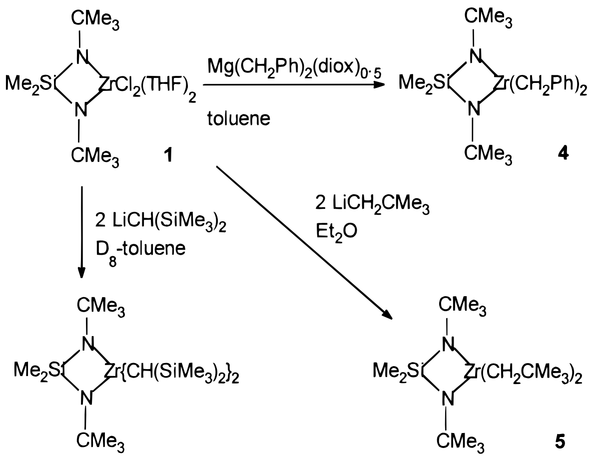
Scheme 1



Scheme 2

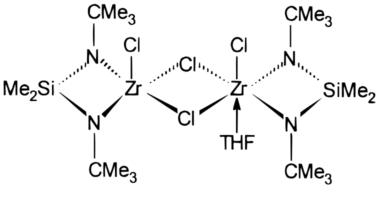


hexane mixture, afforded, in 48% yield, a colorless microcrystalline complex containing 2 equiv of THF per diamide ligand and formulated as $\{Me_2SiN(CMe_3)_2\}ZrCl_2(THF)_2$ (**1**). Pure crystalline **1** was obtained by cooling a THF solution to −40 °C.

Dissolution of complex **1** in aromatic solvents or CD_2Cl_2 resulted in partial loss of THF and the observation of resonances for approximately equal amounts (on the basis of Zr atoms) of complex **1** and a second species **2** containing 0.5 equiv of THF per zirconium (eq 1).

$$\underset{\mathbf{1}}{2\ \{Me_2Si(NCMe_3)_2\}ZrCl_2(THF)_2} \xrightleftharpoons{CD_2Cl_2} \underset{\mathbf{2}}{[\{Me_2Si(NCMe_3)_2\}ZrCl_2]_2(THF)} + 3\ THF \qquad (1)$$

Although attempts to remove the THF *in vacuo* from the crude product mixture at elevated temperatures led to decomposition, complex **2** could be obtained as a spectroscopically pure solid by cooling a dichloromethane/hexane solution of **1** to −40 °C.



Possible structure of **2**

New complexes **1** and **2** have been characterized by ^1H and ^{13}C NMR spectroscopy and, in the case of **1**, by elemental analysis. The observation of single resonances for the Si*Me*$_2$ and the C*Me*$_3$ groups in **1** is consistent with a pseudo-octahedral structure or, perhaps, a lower symmetry species undergoing rapid THF exchange. The latter is supported by the observation of a more complex pattern of resonances on cooling a toluene solution of **1** to −75 °C.

Complex **2** appears to be a dizirconium species. One possible structure with bridging chloride ligands,[18] which is consistent with the observation at 25 °C of resonances for two inequivalent C*Me*$_3$ groups and four Si*Me* groups (or, in some cases, three in a 1:1:2 ratio), is shown above. More rapid THF exchange at higher tempeartures may be responsible for the observation of a single resonance for each of the C*Me*$_3$ and Si*Me*$_2$ groups in C_7D_8 at 75 °C.

Preliminary studies using diethyl ether instead of toluene as the solvent in the reaction of $Me_2Si(NLiCMe_3)_2$ with $ZrCl_4$ have indicated that the mono-ether adduct, **3**, is cleanly formed (Scheme 1). Complex **3** was obtained in spectroscopically pure crystalline form by cooling an ether/hexane solution of the crude product. The greater steric bulk of Et_2O than THF appears to favor a five-coordinate monomeric structure for **3**. Interestingly, the base-free titanium analogue of complexes **1**−**3**, $\{Me_2Si(NCMe_3)_2\}TiCl_2$, has been shown by X-ray structural analysis to exhibit a monomeric structure with a pseudotetrahedral titanium.[17] For comparison, the complexes $\{Me_2Si(NSiMe_3)_2\}MCl_2$ (M = Zr, Hf) are believed to be polymeric in structure with bridging chloride ligands (IR evidence); formation of a soluble 1:1 adduct with diethyl ether (similar to **3**) has been reported.[18]

Dialkylzirconium Complexes. The dibenzyl complex **4** and the dineopentyl complex **5** were obtained from **1** using standard alkylation methodology, as shown in Scheme 2. Crystallization of **4** from hexane at −40 °C afforded pure yellow crystalline product in 60% yield. Cooling a pentane solution of **5** afforded colorless crystals of the dineopentyl complex, which melted on warming to 25 °C. The crystals contained 0.5 equiv of (noncoordinated) THF as a solvent of crystallization, removable *in vacuo*. The dialkyl complexes have been characterized by ^1H and ^{13}C NMR spectroscopy and, in the case of **4**, by elemental analysis. A symmetrical pseudotetrahedral geometry for the complexes is evidenced by the observation of single resonances for the Si*Me*$_2$, C*Me*$_3$, and alkyl fragments. Despite the rather high $^1J_{CH}$ coupling constant of 129 Hz for the Zr−benzyl methylene in **4**, normal η^1-benzyl coordination is suggested by the characteristic downfield location of the *ipso*-carbon resonance at δ 145.5 ppm.[24,25]

The sterically undemanding nature of this diamide ligand is reflected both in the facile formation, under NMR conditions, of a dialkyl derivative with the bulky $CH(SiMe_3)_2$ ligand (for comparison, in metallocene chemistry, only the monoalkyl derivative $(C_5H_5)_2Zr\{CH(SiMe_3)_2\}Cl$ may be obtained)[26] and the synthetic inac-

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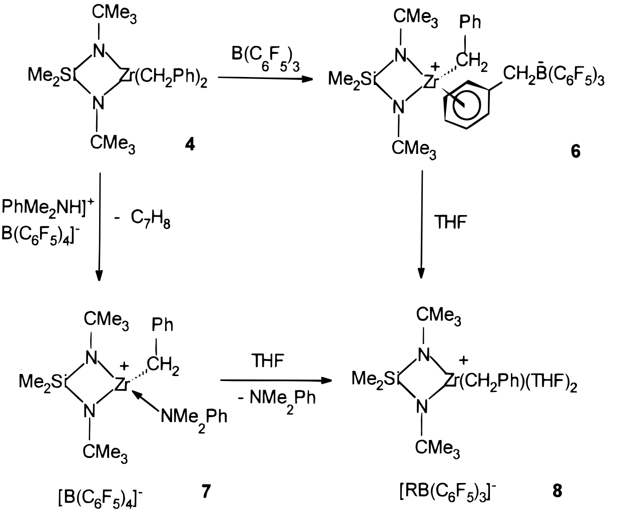
cessibility of the dimethyl complex. Reaction of dichloride **1** with a 2-fold excess of LiMe in diethyl ether afforded a poorly characterized mixture of complexes exhibiting broad methyl resonances in the region δ 1.0–0.2 ppm and containing coordinated THF. It is possible that additional LiMe or LiCl coordinates to the putative sterically open dimethylzirconium species.[27]

Preparation of Cationic Benzylzirconium Complexes. Alkyl abstraction[28–31] from dialkyl complexes using Lewis acidic reagents or protonolysis were investigated as potential routes to diamide-based cationic alkylzirconium complexes. Given the sterically open nature of the silicon-bridged diamide ligand, it was expected that the cations would exhibit distinct structural and reactive chemistry compared to the analogous metallocene cations.

Addition of cold toluene to a mixture of dibenzyl complex **4** and $B(C_6F_5)_3$ at −30 °C resulted in a virtually instantaneous intense orange color, indicating rapid alkyl abstraction.[28,29] The product exhibited high solubility in toluene and was more conveniently isolated as an orange precipitate in virtually quantitative yield on mixing hexane solutions of the reactants. Large crystals of **6** were obtained from a dichloromethane/hexane solution at −40 °C. Unfortunately, attempts to characterize **6** by X-ray structural analysis were frustrated by loss of the solvent of crystallization. The complex has been characterized by ^1H, ^{11}B, ^{13}C, and ^{19}F NMR spectroscopy as a cationic benzylzirconium species coordinated by the $[PhCH_2B(C_6F_5)_3]^-$ anion (Scheme 3).[32–34]

Scheme 3



Strong nonfluxional anion coordination in complex **6** resulted in the observation of ^1H and ^{13}C NMR resonances of inequivalent Si*Me* groups in all solvents studied at 25 °C and up to 75 °C in C_7D_8 solution (^1H NMR). 2-D NMR COSY studies in C_7D_8 solution indicated that anion coordination results in an upfield shift of the *o*- and *p*-hydrogens of the B−benzyl (overlapping resonance at δ 6.1 ppm; free anion, δ 7.24 and 6.89 ppm, respectively), while the *m*-hydrogen resonance is slightly downfield-shifted (δ 7.14 ppm; free anion, δ 7.04 ppm).[32–34] The Zr−benzyl group exhibited aromatic resonances at δ 6.69, 6.85, and 7.08 ppm (*o*-, *p*-, and *m*-hydrogens, respectively).[24,25] Caution should be exercised in drawing conclusions on the exact coordination mode of the anion and Zr−benzyl group, based on the benzyl ^1H NMR resonances, because of possible ring current effects.[22] Interestingly, the aromatic ^1H NMR resonances are highly sensitive to the solvent: in C_6D_5-Br and in CD_2Cl_2 solutions, no far-downfield B−benzyl resonances were observed.

Anion coordination to zirconium via a π-benzene interaction was clearly indicated by the characteristic downfield location of the B−benzyl *ipso*-carbon resonance at δ 160.4 ppm in **6**, compared to δ 148.5 for the free anion ($C_2D_2Cl_4$).[32] The similar shift of the *ipso*-carbon in C_6D_6 solution (δ 160.1 ppm) suggests that the solvent-dependence of the ^1H NMR resonances may reflect only very subtle structural differences. The downfield location of the Zr−benzyl *ipso*-carbon (δ 147.6) and the “normal” $^1J_{CH}$ coupling constant (123 Hz) for the methylene group at δ 52.4 ppm are consistent with η^1-benzyl coordination to zirconium.[24,25] In this context, the somewhat downfield location of the Zr−benzyl *o*-H in **6** (C_7D_8, δ 6.69 ppm) may reflect the ring current effect of the B−benzyl.

We have previously shown that unlike ^{11}B spectroscopy, which is relatively insensitive to anion coordination, ^{19}F NMR spectroscopy is a very useful probe of the coordination of alkylborate anions, $[RB(C_6F_5)_3]^-$, to cationic complexes, insensitive to solvent or ring-current effects.[15] A difference in the chemical shifts of the *meta*- and *para*-fluorine resonances [$\Delta\delta(m,p\text{-F})$] greater than

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[25] For examples of benzyl coordination in cationic complexes, see the following: (a) Pellecchia, C.; Immirzi, A.; Pappalardo, D.; Peluso, A. *Organometallics* **1994**, *13*, 3773. (b) Bochmann, M.; Lancaster, S. J. *Organometallics* **1993**, *12*, 633. (c) Bochmann, M.; Lancaster, S. J. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 807. (d) Crowther, D. J.; Borkowsky, S. L.; Swenson, D.; Meyer, T. Y.; Jordan, R. F. *Organometallics* **1993**, *12*, 2897. (e) Borkowsky, S. L.; Baenziger, N. C.; Jordan, R. F. *Organometallics* **1993**, *12*, 486. (f) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111. (g) Bhandari, G.; Kim, Y.; McFarland, J. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1995**, *14*, 738. (h) Amor, J. I.; Cuenca, T.; Galakhov, M.; Royo, P. *J. Organomet. Chem.* **1995**, *497*, 127.

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[27] LiMe coordination to lanthanide metals is well-precedented, see: Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *34*, 283.

[28] (a) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1966**, *5*, 218. (b) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245.

[29] (a) Chen, Y.-X.; Stern, C. L.; Yang, X.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 12451. (b) Deck, P. A.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 6128. (c) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015. (d) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623. (e) Siedle, A. R.; Newmark, R. A. *J. Organomet. Chem.* **1995**, *497*, 119. (f) Bochmann, M.; Lancaster, S. J.; Hursthouse, M. B.; Malik, K. M. A. *Organometallics* **1993**, *12*, 2235.

[30] (a) Ewen, J. A.; Elder, M. J. (Fina) Eur. Pat. Appl. 426 637, 1991. (b) Chien, J. C. W.; Tsai, W.-M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570.

[31] Turner, H. W.; Hlatky, G. G. (Exxon) Eur. Pat. Appl. 277 004, 1988.

[32] For examples of the coordination of $[PhCH_2B(C_6F_5)_3]^-$ to a cationic d^0 metal center, see the following: (a) Pellecchia, C.; Grassi, A.; Immirzi, A. *J. Am. Chem. Soc.* **1993**, *115*, 1160. (b) Pellecchia, C.; Immirzi, A.; Grassi, A.; Zambelli, A. *Organometallics* **1993**, *12*, 4473. (c) Pellecchia, C.; Grassi, A.; Zambelli, A. *J. Mol. Catal.* **1993**, *82*, 57.

[33] For examples of the coordination of $[B(C_6H_5)_4]^-$ to a cationic d^0 metal center, see the following: (a) Horton, A. D.; Frijns, J. H. G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1152. (b) Bochmann, M.; Jaggar, A. J.; Nicholls, J. C. *Angew. Chem., Int. Ed. Engl.* **1990**, 29, 780. (c) Bochmann, M.; Karger, G.; Jaggar, A. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1038. (d) Schaverien, C. J. *Organometallics* **1992**, *11*, 3476.

[34] For examples of the coordination of a benzene ring to a cationic group 4 metal center, see the following: (a) Lancaster, S. J.; Robinson, O. B.; Bochmann, M.; Coles, S. J.; Hursthouse, M. B. *Organometallics* **1995**, *14*, 2456. (b) Gillis, D. J.; Tudoret, M.-J.; Baird, M. C. *J. Am. Chem. Soc.* **1993**, *115*, 2543. (c) Pellecchia, C.; Grassi, A.; Immirzi, A. *J. Am. Chem. Soc.* **1993**, *115*, 1160.

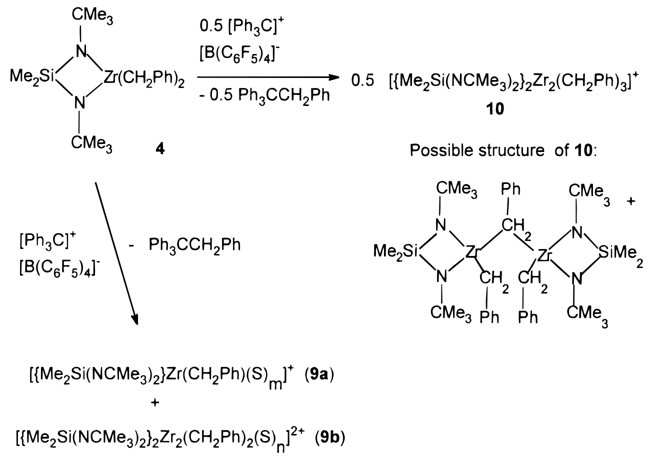
3.5 ppm is associated with coordination, whereas a value less than 3.0 ppm indicates noncoordination. In the case of **6**, anion coordination is associated with a significant downfield shift of the *m*- and *p*-fluorine resonances relative to those of the free anion, with a $\Delta\delta(m,p\text{-F})$ value of 4.1 ppm; the *ortho*-fluorine resonance is much less strongly shifted on coordination.

The high solubility of **6** in toluene or benzene solution (0.3 M) is also consistent with benzylborate anion coordination to the metal, rather than a solvent-separated ionic structure or facile anion dissociation. Strong anion coordination in **6** may also explain the high stability in chlorinated solvents: dichloromethane solutions at 25 °C decomposed slowly over several hours, whereas solutions in 1,1,2,2-tetrachloroethane were stable over several days. Solutions of **6** in bromobenzene or toluene at 25 °C remained unchanged over prolonged periods, but decomposition was accelerated in C_7D_8 at 75 °C: clean conversion over 2 h to two organometallic products and a mixture of boranes, $B(Bz)_n(C_6F_5)_{3-n}$ ($n = 1-3$) was observed by ^1H NMR spectroscopy. The zirconium products have been tentatively identified as $\{Me_2Si(NCMe_3)_2\}Zr(CH_2Ph)(C_6F_5)$ and $\{Me_2Si(NCMe_3)_2\}Zr(C_6F_5)_2$, resulting from pentafluorphenyl−benzyl exchange between zirconium and boron. There are a number of literature examples of pentafluorphenyl transfer from $[RB(C_6F_5)_3]^-$ (R = alkyl) to cationic metallocene or benzamidinate cations,[6e,29c] whereas phenyl transfer from $[B(C_6F_5)_4]^-$ and related fluorinated-tetraphenylborate anions is less common.[35]

Protonolysis of dibenzyl **4** was found to be a clean route to a cationic complex. Addition of C_6D_5Br or $C_2D_2Cl_4$ at −30 °C to a mixture of **4** and $[PhMe_2NH][B(C_6F_5)_4]$[31] at −30 °C resulted in the almost instantaneous formation of an orange complex characterized by ^1H and ^{19}F NMR spectroscopy as the benzyl cation, **7**, stabilized by coordination of the NMe_2Ph coproduct of protonolysis (Scheme 3). Although solutions of complex **7** were found to be stable over 1 h at 25 °C, no attempt was made to isolate the complex, as such efforts normally lead to poorly defined oils with less than 1 equiv of Lewis base per metal.

Coordination of NMe_2Ph is reflected in the observation of ^1H NMR resonances for inequivalent Si*Me* groups above and below the SiN_2Zr plane ($C_2D_2Cl_4$, −25 °C) and resonances (identified by 2-D COSY) for the *meta*- and *para*-phenyl hydrogens (δ 7.55 and 7.11 ppm, respectively) downfield from the trace of free aniline being present (δ 7.25 and 7.00 ppm, respectively); the shift of the *ortho*-hydrogen is identical to that of the free base. The presence of resonances for a small amount of free aniline in **7** is consistent with aniline exchange being slow on the NMR time scale. The NMe_2Ph-Zr interaction might involve either nitrogen atom or π-benzene ring coordination, but it is not possible to distinguish these alternative modes due to the the possible ring-current effect of the benzyl ligand.[4,20c,36] As expected, no evidence was found for coordination of the $[B(C_6F_5)_4]^-$ counteranion: ^{19}F NMR resonances were unperturbed from the free anion values.

Scheme 4



Both the benzylborate anion in **6** and the *N*,*N*-dimethylaniline in **7** were cleanly displaced by THF (Scheme 3). The bis(THF) adduct **8** was conveniently isolated as a colorless solid by protonolysis of **4** in THF solution, followed by precipitation and washing with hexane. Solutions of **8** exhibited ^1H and ^{13}C NMR resonances for a single highly symmetric species. However, rapid THF exchange in solution is indicated by the observation of dramatic changes in the cation ^1H NMR shifts and of averaged THF resonances on addition of excess THF.

Abstraction of a hydrocarbyl group using the trityl reagent, $[Ph_3C][B(C_6F_5)_4]$,[30] has been widely utilized in metallocene chemistry for the formation of highly electrophilic Lewis-base-free cations. Reaction with dibenzyl **6** cleanly afforded 1 equiv of Ph_3CCH_2Ph, but the organometallic product mixture was rather complex. In C_6D_5Br solution, an insoluble orange product mixture was obtained. The same mixture of two complexes (**9a** and **9b**) was conveniently formed in CD_2Cl_2 solution, in which it is soluble and relatively stable (in the absence of excess trityl reagent). The noninterconverting complexes, obtained in a 3:1 ratio (based on Zr atoms), reacted with THF to give known bis(THF) complex **8** and another THF adduct, again in a 3:1 ratio. This and the fact that the relative amount of **9a** formed in the reaction increases on decreasing the reaction concentration has led us to propose that complex **9a** is a monomeric cationic and **9b** a dimeric dicationic species (Scheme 4).

Each complex exhibits a 2:2:1 pattern of downfield resonances (δ 8.0−7.4 ppm) for the benzyl group and single $ZrCH_2$, CMe_3, and $SiMe_2$ resonances. Extensive speculation on the structures of **9a** and **9b** is unwarranted in the absence of ^{13}C NMR data (due to the low solubility) or X-ray structural data. However, the downfield location of the ring resonances of "monomeric" **9a** suggest that the presumed η^n-benzyl coordination likely involves a very significant interaction with the aromatic ring.[37] The equivalent benzyl ligands in **9b** might, perhaps, bridge the two zirconium atoms via a σ-interaction with one metal ($ZrCH_2$) and a π-interaction of the ring with the other.[37] These unusual bonding modes would be expected to be favored by the sterically open environment at zirconium.

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[35] Jia, L.; Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 842.

[36] For examples of the cooordination of NMe_2Ph to a cationic group 4 metal, see refs 4 and 19c and the following: Grossman, R. B.; Doyle, R. A.; Buchwald, S. L. *Organometallics* **1991**, *10*, 1501.

[37] A structurally characterized case of η^7-benzyl coordination to zirconium has recently been reported, see: Pellecchia, C.; Immirzi, A.; Pappalardo, D.; Peluso, A. *Organometallics* **1994**, *13*, 3773.

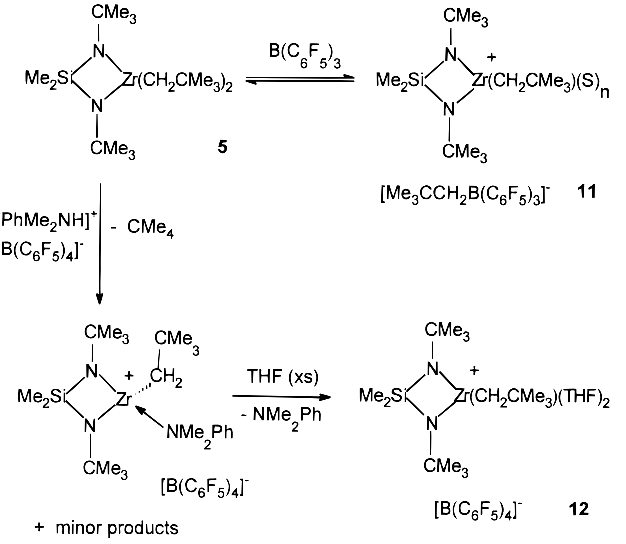
The reaction of dibenzyl **4** with 0.5 equiv of the trityl reagent at −30 °C in dichloromethane gave 0.5 equiv of Ph_3CCH_2Ph and an interesting dizirconium complex, **10**, containing three benzyl groups (Scheme 4). Attempts to obtain crystalline material were unsuccessful, and the complex was isolated as an orange solid by hexane addition to the reaction mixture. The dizirconium complex gave, with excess THF, a 1:1 mixture of recovered **4** and bis(THF) cation **8**. Complex **10** was also formed on reaction of **4** with <1 equiv of the borane or *N*,*N*-dimethylanilinium reagent, but in this case, an equilibrium mixture of **4**, the dimer, and the monometallic benzyl cations, **6** or **7**, respectively, was observed.

Resonances for two kinds of benzyl ligands in **10** in a 2:1 ratio have been identified by ^1H NMR (2-D COSY) and ^{13}C NMR spectroscopy. The rather large $^1J_{CH}$ values associated with the $ZrCH_2$ groups of 130.5 Hz (δ 53.8 ppm, 2C) and 132.5 Hz (δ 53.3 ppm, 1C) might be consistent with η^n-benzyl coordination. However, the downfield location of the *ipso*-carbon resonances at δ 144.4 (2C) and 162.2 ppm (1C) appear more in line with η^1-benzyl coordination. The observation of resonances for equivalent CMe_3 groups and two kinds of $SiMe$ groups in a 1:1 ratio is consistent with a symmetrical structure in which one benzyl group symmetrically bridges the zirconium atoms, which are also coordinated by terminal benzyl and diamide ligands.[38] Related methyl-bridged dimetallic complexes of the form $[(L_2MMe)_2(\mu\text{-}Me)]^+$ are known in metallocene and diamide chemistry.[15a,29a,39]

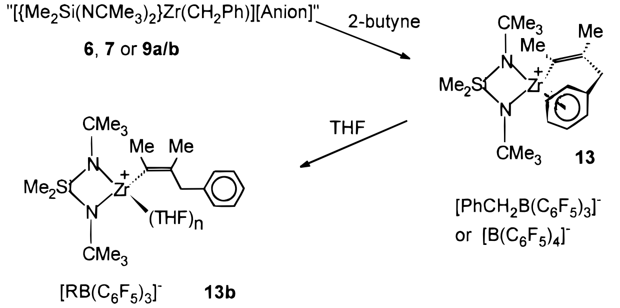
Partly driven by the mechanistic interest in the β-methyl elimination reaction, preliminary studies were also made of neopentyl group abstraction from dineopentyl complex **5**. The reaction of **5** with $B(C_6F_5)_3$ is slow at 25 °C, requiring the use of a 3-fold excess of borane and long reaction times. Under these conditions (2 h, C_6D_5Br), a pale yellow complex tentatively identified as neopentyl cation **11** was formed, contaminated by a small amount of **5**. The $[Me_3CCH_2B(C_6F_5)_3]^-$ anion exhibited resonances at δ 2.09 (BCH_2) and 0.97 ppm (CMe_3), which did not change on addition of THF. The cationic neopentyl species exhibited two CMe_3 resonances (18H, 9H) and one $SiMe_2$ resonance (6H), as expected. It is likely that the ionic complex is stabilized by weak solvent coordination. No evidence for the formation of 2-methyl-1-propene by β-methyl elimination was obtained.

Reaction of **5** with $[PhMe_2NH][B(C_6F_5)_4]$ in C_6D_5Br solution afforded one major organometallic species, as well as 1 equiv of CMe_4 (Scheme 5). The major product is tentatively proposed to be a neopentyl cation, on the basis of the observation of resonances for CMe_3 (2:1 ratio), $SiMe_2$ (1:1 ratio), and $ZrCH_2$ (δ 0.37 ppm) groups and coordinated NMe_2Ph. The *ortho*- and *para*-phenyl hydrogens (δ 6.41, 6.52 ppm, respectively) of the coordinated Lewis base are shifted upfield from the free molecule, the *meta*-hydrogen downfield (δ 7.18 ppm). Two minor species were obtained, one of which is probably the methyl cation obtained by elimination of 2-methyl-1-propene (0.1 equiv), while the identity of the other species is uncertain. Protonolysis of **5** in THF solution using $[PhMe_2NH][B(C_6H_5)_4]$, followed by product precipitation and washing with hexane, afforded bis(THF) adduct **12** as a colorless solid, characterized by ^1H and ^{13}C NMR spectroscopy (Scheme 5). Partial THF dissociation occurs on dissolution of neopentyl cation **12** in C_6D_5Br. In addition to the concentration-dependent ^1H NMR resonances of **12**, additional minor resonances were observed, which disappear with excess THF, and are tentatively ascribed to a monoTHF adduct.

Scheme 5



Scheme 6



Controlled Insertion of Unsaturated Substrates. Study of the reaction of electrophilic early transition metal (ETM) complexes with unsaturated molecules can give important information on such fundamental steps in catalysis as insertion, chain transfer, and decomposition. Understanding the effect of ligand and anion variation on these steps should assist in the development of superior catalysts. As already discussed, controlled insertion of alkenes and alkynes in metal–hydocarbyl bonds has previously been examined as a model for alkene insertion during polymerization.[20,21] We have now observed controlled alkyne and alkene insertion in diamide-stabilized complexes.

Reaction of a small excess of 2-butyne with benzylzirconium cations **6**, **7**, or **9a**/**b** afforded the cationic complex **13**, stabilized by the chelating coordination of the phenyl ring of the hydrocarbyl ligand to zirconium (Scheme 6). Assuming η^6 ring coordination, the zirconium center in the single insertion product may adopt

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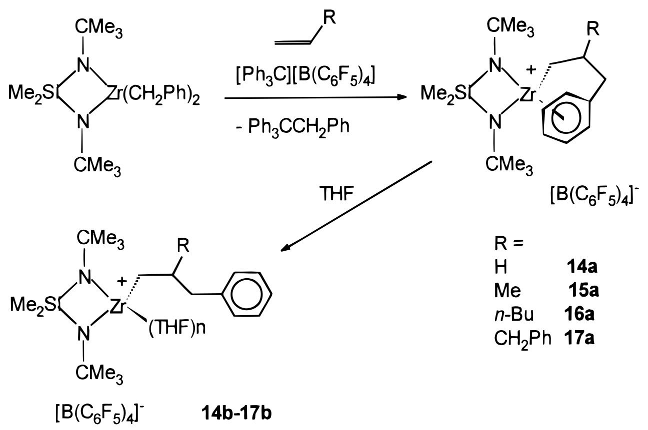
[38] For examples of different bridging benzyl coordination modes, see the following: Bhandari, G.; Rheingold, A. L.; Theopold, K. H. *Chem. Eur. J.* **1995**, *1*, 199.

[39] Bochmann, M.; Lancaster, S. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1634.

[40] (a) Horton, A. D.; Orpen, A. G. *Organometallics* **1996**, *15*, 2675. (b) Guo, Z.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1994**, *13*, 1424. (c) Hajela, S.; Bercaw, J. E. *Organometallics* **1994**, *13*, 1147. (d) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471.

Scheme 7



a formal 16-electron configuration. The reaction with **9a**/**b** in dichloromethane was almost instantaneous at 25 °C, as shown by the rapid change in the solution color from orange to yellow. The reaction of **6** with 2-butyne (3-fold excess) in C_6D_5Br solution was slightly slower (complete in 5 min) and in toluene much slower (75% in 20 min). This difference presumably reflects stronger anion coordination to zirconium (less facile dissociation) in the less polar solvent. Complex **13**, with $[BzB(C_6F_5)_3]^-$ as a noncoordinating anion, was obtained in analytically pure yellow microcrystalline form on cooling a dichloromethane/hexane solution to −40 °C.

Complex **13** has been further characterized by ^1H, ^{11}B, ^{13}C, and ^{19}F NMR spectroscopy and by the clean formation of $PhCH_2CMe{=}CHMe$ on hydrolysis. The cation exhibits resonances for inequivalent Si*Me* groups, equivalent C*Me*3 groups, and the $ZrC(Me){=}C(Me)CH_2Ph$ fragment. The far-downfield location of the phenyl group resonances at δ 8.16 (*o*-H), 8.12 (*m*-H), and 7.88 ppm (*p*-H) in the ^1H NMR spectrum (CD_2Cl_2) and the observation of free anion resonances (in particular, for $[BzB(C_6F_5)_3]^-$) are consistent with coordination of the phenyl ring of the hydrocarbyl ligand to zirconium.[32-34] The coordinated ring resonates at δ 156.8 (*ipso*-C), 136.4 (*o*/*m*-C), 130.4 (*o*/*m*-C), and 127.0 ppm (*p*-C) in the ^{13}C NMR spectrum. Addition of excess THF results in dissociation of the phenyl ring giving adduct **13b** (Scheme 6), exhibiting “normal” phenyl ^1H NMR resonances at δ 7.24 (*m*,*p*-H) and 7.13 ppm (*o*-H).

Single Insertion of Alkenes. A remarkable aspect of the fomation of **13** is that both the “monomeric” and “dimeric” isomers **9a** and **9b**, respectively, reacted to give **13**. Alkenes also gave single-insertion products, but in this case only **9a** was reactive; **9b** remained as a minor contaminant in the product. A range of alkenes afforded cationic single insertion products **14a**−**17a**, stabilized by a chelating coordination of a benzene ring (Scheme 7). In CD_2Cl_2 solution, the reaction was complete within 2−20 min at 25 °C (depending on the alkene). The products of the insertion of 1-hexene (**16a**) and allylbenzene (**17a**) were isolated as yellow solids, free of **9b**, by cation formation in the presence of excess alkene, followed by hexane addition. Repeated attempts to obtain ethene insertion product **14a** in solid form led only to unidentified decomposition products. As the complexes could not be obtained in analytically pure form, they were characterized by ^1H and (for **16a**) ^{13}C NMR spectroscopy, by the formation of the THF adducts **14b**−**17b**, and by the NMR identification of $PhCH_2CH(R)CH_3$ formed on hydrolysis.

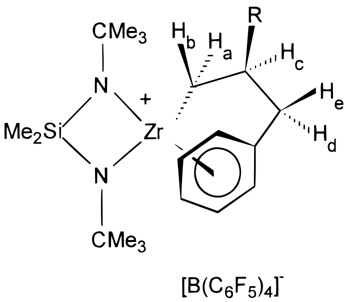


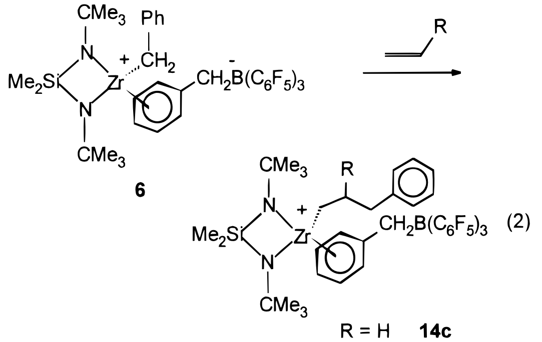
Figure 1. Hydrogen atom labeling in complexes **15a**−**17a**.

All of the insertion products exhibited phenyl resonances in the region δ 8.1−7.8 ppm in CD_2Cl_2 solution, characteristic of a chelating ring coordination, as shown in Scheme 7,[32-34] similar to complex **13**. More upfield ring resonances were observed in C_6D_5Br solution (δ 7.52−7.38 ppm). Ring coordination was also reflected in the observation of a downfield resonance for the *ipso*-carbon at δ 159.0 ppm in **16a**, which shifted to δ 143.0 ppm in THF adduct **16b**. The α-, β-, and γ-hydrogens of the Zr−trimethylene fragment in **14a** resonated at δ 1.08, 2.62, and 3.11 ppm, respectively.[21] Such downfield resonances were found to be highly characteristic of chelating coordination and shifted upfield to δ 0.44, 2.06, and 2.44 ppm, respectively, in THF adduct **14b**.

Of course, the ^1H NMR spectra of the substituted complexes were more complicated than that of **14a**, with resonances for five inequivalent hydrogens in the three-carbon linking group. For **16a** and **17a**, 2-D COSY NMR analysis was used to assign the resonances. In the 1-hexene insertion product **16a** (Figure 1), resonances for two diasterotopic methylene groups were observed at δ 1.88/0.03 ppm (H_a, H_b, respectively, $^2J_{HH}$ = 13.5 Hz, $ZrCH_2$) and δ 3.42/2.55 ppm (H_e, H_d, respectively, $^2J_{HH}$ = 11.8 Hz, CH_2Ph), together with the −C*H*(*n*-Bu)− resonance at δ 2.41 ppm. The observation of a significant long-range coupling between H_a and H_d ($^4J_{HH}$ = 1.7 Hz), also found by Pellecchia in closely related adducts,[22] is consistent with a sterorigid W-conformation of the four bonds joining the two hydrogens.

Complex **17a** was synthesized in order to examine whether exchange of the coordinated and free benzene rings occurred. Apart from some slight broadening of the hydrocarbyl ligand resonances at 50 °C, there was no evidence for ring exchange and the inequivalency of the methyl groups on silicon was maintained. It is clear that the benzene ring coordinates strongly to the zirconium center in **14a**−**17a**, presumably affording (with amide−Zr π-bonding) a 16-electron metal center.

Complex **6** also cleanly inserted one molecule of ethene or propene into the Zr−benzyl bond, but replacement of the $[B(C_6F_5)_4]^-$ by the $[BzB(C_6F_5)_3]^-$ anion resulted both in a dramatic deceleration of the reaction and in a remarkably different product structure (eq 2). Ethene insertion in **6** was 60% complete in 60 min (4.5 mL of ethene added to 0.03 mmol of **6** in 0.7 mL CD_2Cl_2 at 25 °C), compared to 100% complete in 5 min at 25 °C for **9a**. As with 2-butyne insertion, the nature of the solvent also plays an important role, the reaction rate decreases as the solvent polarity decreases (bromobenzene-*d*5, $t_{1/2}$ of 76 min; toluene, 20% reaction in



6

R = H **14c**
R = Me **15c**

20 h). Propene insertion in **6** was even slower, with a $t_{1/2}$ of 280 min in C_6D_5Br solution.

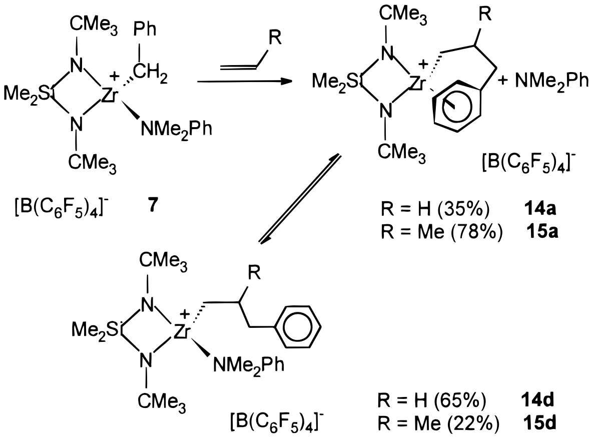
In complexes **14c** and **15c**, strong anion coordination to zirconium resulted in noncoordination of the benzene ring of the 3-phenylpropyl ligand. For **14c** (CD_2Cl_2), this was reflected in the upfield location of the phenyl resonances at δ 7.6−7.1 ppm, compared to δ 8.0 ppm in **14a**, and of the α-, β-, and γ-hydrogen resonances of the trimethylene group at δ 0.60, 1.88, and 2.45 ppm, respectively, compared to δ 1.08, 2.62, and 3.11 ppm in **14a**. Coordination of the $[BzB(C_6F_5)_3]^-$ anion was very clearly reflected in the large value of $\Delta\delta(m,p\text{-F})$ of 4.0 ppm in the ^{19}F NMR spectrum.

To complete the study of the alkene reactivity of the sterically open benzyl cations, NMe_2Ph adduct **7** was examined in C_6D_5Br solution. Single ethene insertion was complete within 11 min, whereas propene insertion required 25 min. As shown in Scheme 8, a mixture of the already discussed chelate product **14a**/**15a** and a nonchelated species with coordinated NMe_2Ph (**14d**, **15d**) was obtained. As expected, substitution of the trimethylene group favored ligand chelation, with **15a** as the major species present (78%) in the propene reaction, whereas with ethene, **14a** was the minor component (35%). The mixtures of **14a**/**14d** and **15a**/**15d** were cleanly converted to THF adducts **14b** and **15b**, respectively, with an excess of the Lewis base.

Far-upfield resonances of the *ortho*- and *para*-hydrogens of the coordinated NMe_2*Ph* ligand in **14d** were observed at δ 6.47 and 6.34 ppm, respectively, indicating strong Lewis-base coordination, perhaps even involving Ph−N rather than N−Zr coordination. The hydrocarbyl ligand in **14d** afforded a similar resonance pattern to the related adducts containing coordinated THF or $[BzB(C_6F_5)_3]^-$. For example, the α-, β-, and γ-hydrogen resonances for the trimethylene group in **14d** were located at δ 0.2 (obscured), 1.86, and 2.44 ppm, respectively.

Ethene Polymerization Reactivity? We have shown that cationic benzylzirconium complexes undergo clean single insertion reactions with alkenes and 2-butyne, the rate of insertion increasing in the series 1-alkenes < ethene < 2-butyne. The insertion rate was higher for the more poorly coordinating anion $[B(C_6F_5)_4]^-$ and in more polar solvents. Remarkably, the alkene reaction does not proceed beyond the single insertion product, with no polymerization under NMR conditions. (In some cases, a trace of polyethylene (PE) was formed almost instantaneously, but the polymer yield did not increase during the reaction and probably arose from catalysis by a trace impurity). Only for the 2-butyne reaction was there evidence for further reaction, uncharacterized product mixtures being obtained with excess alkyne over long periods. The low reactivity and lack of catalysis are presumably the result of strong coordination of the chelating hydrocarbyl ligand, the anion $[BzB(C_6F_5)_3]^-$, *N*,*N*-dimethylaniline, or solvent to the sterically open zirconium cation. The neopentyl cations appear more reactive toward ethene: cation **11** and the related *N*,*N*-dimethylaniline adduct rapidly polymerized excess ethene (minutes) under NMR conditions.

Scheme 8



7

R = H (35%) **14a**
R = Me (78%) **15a**

R = H (65%) **14d**
R = Me (22%) **15d**

The ethene polymerization activity of the electrophilic complexes was also briefly examined under high-pressure conditions. Benzyl complex **6** afforded only traces of polyethene in toluene or dichloromethane solvent (25 °C, 20 bar). The product of the reaction of dibenzyl complex **4** with the trityl reagent exhibited an activity of 330 g/g of Zr•h when tested under more forcing conditions in dichloromethane solvent (0.69 g of PE from 0.04 mmol of catalyst, 50 °C, 20 bar, 30 min).

Neopentyl cation **7** was also found to be inactive in toluene solvent, but the related cation obtained by protonolysis exhibited a (low) activity of 130 g/g of Zr•h in bromobenzene (0.37 g of PE from 0.03 mmol of catalyst, 25 °C, 20 bar, 40 min).

For comparison, dichloride complex **1**, in combination with MAO in toluene at 25 °C, showed an activity for PE of 700 g/g of Zr•h (0.70 g of PE from 0.01 mmol of catalyst, 2.0 mmol of MAO, 20 bar, 30 min). Increasing the temperature did not result in a significantly increased activity with MAO as the cocatalyst: at 44 °C, a PE activity of 370 g/g of Zr•h was observed (0.37 g of PE from 0.01 mmol of catalyst, 5.0 mmol of MAO, 3.2 bar, 120 min), whereas at 60 °C, only traces of PE were obtained. Complex **1** with MAO afforded no polypropene under similar conditions. Given the low alkene polymerization activities, no attempt was made to systematically investigate the effect of the process conditions on catalysis or to further characterize the polymers formed.

Discussion

Application of the methodology developed in metallocene chemistry has allowed a range of cationic diamide complexes of zirconium to be synthesized by alkyl abstraction. Recurring features of this chemistry are the strong anion or Lewis base coordination to the diamide cations and, in the absence of such donors, the apparent formation of oligomeric cations. These features may be traced to the high steric and electronic unsaturation of the fragment $[\{Me_2Si(NCMe_3)_2\}ZrR]^{2+}$. The maximum formal 10-electron count (including π-donation from nitrogen) for $[N_2MR]^+$ compares to 14 for metallocene analogues and 12 for cyclopentadienyl–amide cations. A benzyl ligand may, of course, provide more than two electrons,[24,25,37] but this is apparently not enough to prevent the formation of dimeric complex **10**. Whereas cationic metallocenes $[Cp'_2MR]^+$ exhibit a restricted wedgelike opening, the ligand bulk in the diamides lies close to the N–M–N plane, leaving room for two extra ligands of moderate bulk to coordinate to $[N_2MR]^+$. Thus, for example, whereas cationic alkylmetallocenes coordinate one molecule of THF,[41] diamide analogues $[N_2MR]^+$ form bis(THF) adducts. Analogous bis(alkene) adducts[1a,42] $[N_2MR(alkene)_2]^+$ might be implicated in the propagation and chain-transfer steps of polymerization by diamide catalysts.

The high degree of unsaturation at zirconium also appears to play a role in the observation of the controlled insertion of unsaturated molecules.[22] Stabilization of the single insertion products is not, as had been initially thought, *in all cases* due to blocking π-coordination of the benzene ring of the 3-phenylpropyl group to the zirconium. Such stabilization is found in the 2-butyne insertion products (both anions), as well as in alkene insertion products **14a**–**17a** with the poorly coordinating anion $[B(C_6F_5)_4]^-$. However, when the anion is $[BzB(C_6F_5)_3]^-$, the single alkene insertion product coordinates the anion strongly, resulting in a pendant ligand benzene ring. It may be postulated that stronger anion coordination to the cationic 3-phenylpropyl complex than to the cationic benzyl precursor underlies the inertness of **14c** and **15c** toward further ethene or propene insertion.

NMR study of anion and ligand effects on alkene reactivity has led to the conclusion that the relative rates of insertion are largely determined by the ease of displacement from the cation of the counteranion or Lewis base, which appears to follows the order $[B(C_6F_5)_4]^- > NMe_2Ph > [PhCH_2B(C_6F_5)_3]^-$ and, for different solvents, dichloromethane > bromobenzene > toluene. The low polymerization activity of the dichlorozirconium complex with MAO may be due to strong coordination of the anion (derived from MAO by halide abstraction) or solvent to the putative alkylzirconium cation. Vulnerability to blocking anion[43] or toluene coordination[11] might explain the generally low alkene polymerization activity of electrophilic group 4 catalysts based on sterically open and/or poorly electron-donating ligands.[44] The high activity of metallocenes and related species such as boratabenzene[45] complexes may derive from the preference of such sterically crowded complexes for coordination of alkene rather than a bulky anion or solvent/base. Higher polymerization activities in diamide-based systems[11] may require the use of ligands with bulky (but metalation-resistant) substituents on nitrogen.

Experimental Section

General Procedures. All experiments were performed under nitrogen in a Braun MB 200-G drybox or under argon using standard Schlenk techniques. Solvents were dried by refluxing over and distilling from standard reagents. Deuterated solvents and liquid alkenes were dried over 4 Å molecular sieves. $B(C_6F_5)_3$,[28] $[PhMe_2NH][B(C_6F_5)_4]$,[31] $[Ph_3CMe][B(C_6F_5)_4]$,[30] and LiNp[46] were synthesized following literature procedures. $Mg(CH_2Ph)_2(dioxane)_{0.5}$ was prepared from the reaction of $(PhCH_2)MgCl$ with dioxane. All other reagents were purchased from commercial suppliers and used without further purification.

^1H NMR spectra were recorded on a Varian XL-200 (200.0 MHz) or a Varian VXR-300 (300.0 MHz) instrument, ^{13}C NMR spectra were recorded on a Varian VXR-300 instrument (75.43 MHz), ^{11}B NMR (96.24 MHz) spectra were recorded on a Varian VXR-300 instrument, and ^{19}F NMR (188.16 or 282.24 MHz) spectra were recorded on either instrument. NMR data are listed in parts per million downfield from TMS for proton and carbon measurements and are referenced relative to an aqueous solution of $NaBF_4$ (δ −40 ppm) for boron measurements and $CF_3C_6H_5$ in C_6D_6 (δ −64 ppm) for fluorine. Elemental analyses were performed by Analytische Laboratorien, Engelskirchen, Germany.

Preparation of Neutral Precursors. $Me_2Si(NHCMe_3)_2$. Reaction of Me_2SiCl_2 (47.6 g, 370 mmol) with *t*-$BuNH_2$ (113.3 g, 1550 mmol) in hexane (700 mL) at room temperature, followed by brief reflux (10 min), filtration, solvent removal, and fractional vacuum distillation, afforded $Me_2Si(NHCMe_3)_2$ in 98% purity. ^1H NMR (C_6D_6, 25 °C): δ 1.18 (s, 18H, C*Me*$_3$), 0.51 (br, 2H, NH), 0.17 (s, 6H, Si*Me*$_2$).

$Me_2Si(NLiCMe_3)_2$. To a stirred solution of $(Me_2SiNHCMe_3)_2$ (14.7 g, 72 mmol) in hexane (200 mL) was added dropwise 93.4 mL of a 1.6 M *n*-BuLi solution in hexane (149 mmol). The mixture was then refluxed for 20 min, the solvent removed *in vacuo*, and a solution of the crude product in hexane cooled to −40 °C to give 14.3 g (3 crops, 92% yield) of colorless crystalline $Me_2Si(NLiCMe_3)_2$. ^1H NMR (C_6D_6, 25 °C): δ 1.23 (s, 18H, C*Me*$_3$), 0.41 (s, 6H, Si*Me*$_2$). ^{13}C NMR (C_6D_6, 25 °C): δ 51.6 (2C, N*C*Me$_3$), 36.8 (6C, NC*Me*$_3$), 11.3 (2C, Si*Me*$_2$).

$\{Me_2Si(NCMe_3)_2\}ZrCl_2(THF)_n$ (1, 2). Toluene (150 mL) at −78 °C was added to a mixture of $Me_2Si(NLiCMe_3)_2$ (4.01 g, 18.7 mmol) and $ZrCl_4(THF)_2$ (7.04 g, 18.7 mmol) at −78 °C, and the mixture was allowed to warm to 25 °C and stirred for 90 min. The solvent was removed *in vacuo*, and the residue was extracted with a mixture of THF and hexane. The extract was reduced to dryness and then once again extracted with a THF/hexane mixture. Colorless microcrystalline **1** (3 crops, 4.5 g, 48% yield), containing about two THF molecules per zirconium (^1H NMR), was obtained on cooling the solution to −40 °C. Solutions of the product exhibited resonances for approximately equal amounts (on the basis of Zr atoms) of two species, $\{Me_2Si(NCMe_3)_2\}ZrCl_2(THF)_2$ (**1**) and $[\{Me_2Si(NCMe_3)_2\}ZrCl_2]_2(THF)$ (**2**); the latter complex is formed on THF dissociation. Analytically pure **1** was obtained as white crystals on cooling a THF solution to −40 °C. Spectroscopically pure **2** was obtained by cooling a dichloromethane/hexane solution to −40 °C.

Complex **1**. ^1H NMR (C_7D_8, −75 °C): δ 3.96, 3.58 (m, 4H, THF), 1.60, 1.56 (s, 9H, C*Me*$_3$), 1.06 (m, 8H, THF), 0.82, 0.50 (s, 3H, Si*Me*$_2$); resonances for a minor unidentified species were

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(41) For examples of monoTHF adducts of cationic alkylmetallocenes, see ref 20c and the following: (a) Guo, Z.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1994**, *13*, 1424. (b) Borkowsky, S. L.; Jordan, R. F.; Hinch, G. D. *Organometallics* **1991**, *10*, 1268. (c) Jordan, R. F.; LaPointe, R. E.; Bradley, P. K.; Baenziger, N. *Organometallics* **1989**, *8*, 2892. (d) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111.

(42) Ystenes, M. *J. Catal.* **1991**, *129*, 383.

(43) For very recent reports of the effect of anion variation on metallocene catalysis, see refs 29a and 35 and the following: Chen, Y. X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1997**, *119*, 2582.

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(45) (a) Bazan, G. C.; Rodriguez, G.; Ashe, A. J., III; Al-Ahmad, S.; Müller, C. *J. Am. Chem. Soc.* **1996**, *118*, 2291. (b) Krishnamurti, R.; Nagy, S.; Etherton, B. P. (Occidental) World Pat. Appl. 96/23004, 1996.

(46) Schrock, R. R.; Fellman, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359.

also observed. ^{1}H NMR (C_7D_8, −25 °C): δ 3.67 (m, 8H, THF), 1.53 (br, 18H, CMe_3), 1.39 (m, 8H, THF), 0.74, 0.52 (s, 3H, SiMe_2); resonances for a minor unidentified species were also observed. ^{1}H NMR (C_7D_8, 25 °C): δ 3.68 (m, 8H, THF), 1.61 (s, 18H, CMe_3), 1.39 (m, 8H, THF), 0.62 (s, 6H, SiMe_2). ^{1}H NMR (CD_2Cl_2, 25 °C): δ 3.72 (m, 8H, THF), 1.84 (m, 8H, THF), 1.39 (obscured, CMe_3), 0.53 (obscured, SiMe_2). ^{13}C NMR (THF-d_8, 25 °C): δ 58.2 (2C, N$C\mathrm{Me}_3$), 34.5 (6C, NCMe_3), 6.8 (2C, SiMe_2). ^{13}C NMR (CD_2Cl_2, 25 °C): δ 68.9 (4C, THF), 58.7 (2C, N$C\mathrm{Me}_3$), 34.7 (6C, NCMe_3), 25.9 (4C, THF), 6.1 (2C, SiMe_2). Anal. Calcd for $C_{18}H_{40}Cl_2N_2O_2Si_2Zr$: C, 42.66; H, 7.96; Cl, 13.99; N, 5.53; Si, 5.54. Found: C, 42.45; H, 7.80; Cl, 14.20; N, 5.49; Si, 5.36.

Complex **2**. ^{1}H NMR (C_7D_8, −25 °C): δ 3.93 (m, 4H, THF), 1.66, 1.38 (s, 18H, CMe_3), 1.04 (m, 4H, THF), 0.69, 0.65, 0.52, 0.32 (s, 3H, SiMe_2). ^{1}H NMR (C_7D_8, 25 °C): δ 4.03 (m, 4H, THF), 1.63, 1.40 (br, 18H, CMe_3), 1.21 (m, 4H, THF), 0.66 (s, 6H, SiMe_2), 0.53, 0.39 (s, 3H, SiMe_2). ^{1}H NMR (C_7D_8, 75 °C): δ 4.02 (m, 4H, THF), 1.60 (s, 36H, CMe_3), 1.46 (m, 4H, THF), 0.56 (s, 12H, SiMe_2). ^{1}H NMR (CD_2Cl_2, 25 °C): δ 4.44 (m, 4, THF), 2.09 (m, 4H, THF), 1.39 (s, 36H, CMe_3), 0.61, 0.58 (s, 3H, SiMe_2), 0.53 (s, 6H SiMe_2).^{13}C NMR (CD_2Cl_2, 25 °C): δ 77.8 (2C, THF), 60.0, 59.7 (2C, N$C\mathrm{Me}_3$), 34.7, 34.6 (6C, NCMe_3), 26.0 (2C, THF), 6.5, 5.9 (2C, SiMe_2).

$\{Me_2Si(NCMe_3)_2\}ZrCl_2(OEt_2)$ (3). Diethyl ether (60 mL, −78 °C) was added to a mixture of $Me_2Si(NLiCMe_3)_2$ (1.80 g, 8.4 mmol) and $ZrCl_4$ (1.96 g, 8.4 mmol) at −78 °C, and the mixture was allowed to warm to room temperature over 2 h and stirred for 1 h. The solvent was removed *in vacuo*, and the residue was extracted with toluene. The extract was reduced to dryness and then washed with hexane to remove soluble $\{Me_2Si(NCMe_3)_2\}_2Zr$. The residue was then extacted with ether (7 mL), to which hexane (2 mL) was added. Cooling to −40 °C afforded microcrystalline **3** (3 crops, 1.60 g, 44% yield). ^{1}H NMR (C_6D_6, 25 °C): δ 3.27 (q, 4H, OEt_2), 1.54 (s, 18H, CMe_3), 1.07 (t, 6H, OEt_2), 0.57 (s, 6H, SiMe_2).

$\{Me_2Si(NCMe_3)_2\}ZrBz_2$ (4). Toluene (40 mL) at −30 °C was added to a Schlenk tube at −40 °C containing a mixture of **1** (0.83 g, 1.7 mmol) and $Mg(Bz)_2(dioxane)_{0.5}$ (0.50 g, 1.7 mmol). The mixture was allowed to warm to room temperature and then stirred for 30 min. A hexane/ether mixture (30 mL, 2:1) was added, and the reaction mixture was then filtered. The solvent was removed *in vacuo*, the residue extracted with hexane, and the extract reduced to dryness. Redissolution of the residue in minimum hexane and cooling to −40 °C afforded 0.47 g (2 crops; 60% yield) of analytically pure yellow crystalline product. ^{1}H NMR (C_6D_6, 25 °C): δ 7.09 (t, 4H, *m*-Bz), 6.86 (t, 2H, *p*-Bz), 6.72 (d, 4H, *o*-Bz), 1.83 (s, 4H, Zr$\mathrm{C}H_2$), 1.09 (s, 18H, CMe_3), 0.40 (s, 6H, SiMe_2). ^{13}C NMR (C_2D_2 Cl_4, 25 °C): δ −145.5 (2C, *ipso*-Bz), 131.0 (4C, Bz), 128.8 (4C, Bz), 121.6 (2C, Bz), 58.6 (2C, $C\mathrm{Me}_3$), 53.2 (t, $^1J_{CH}$ = 129.2 Hz, 2C, Zr$C\mathrm{H}_2$), 34.7 (6C, CMe_3), 6.1 (2C, SiMe_2). Anal. Calcd for $C_{24}H_{38}N_2SiZr$: C, 60.83; H, 8.08; N, 5.91; Si, 5.93. Found: C, 60.55; H, 7.91; N, 5.70; Si, 5.81.

$\{Me_2Si(NCMe_3)_2\}Zr(CH_2CMe_3)_2$ (5). Treatment of **1** with a 2-fold excess of $LiCH_2CMe_3$ in Et_2O (−40 °C to 25 °C), followed by hexane extraction, and crystallization from hexane at −40 °C afforded $\{Me_2Si(NCMe_3)_2\}ZrNp_2(THF)_{0.5}$ as colorless crystals which melt at room temperature. The THF-free complex **5** was obtained as a white solid by placing the above product under high vacuum (30 min, 25 °C). ^{1}H NMR (C_6D_6, 25 °C): δ 1.38, 1.20 (s, 18H, CMe_3), 0.91 (s, 4H, Zr$\mathrm{C}H_2$), 0.42 (s, 6H, SiMe_2). ^{13}C NMR ($C_2D_2Cl_4$, −20 °C): δ 80.0 (t, $^1J_{CH}$ = 104 Hz, 2C, Zr$C\mathrm{H}_2$), 57.9 (2C, N$C\mathrm{Me}_3$), 35.8, 35.3 (6C, CMe_3), 34.9 (2C, $\mathrm{ZrCH_2C}Me_3$), 31.8 (2C, $\mathrm{ZrCH_2}C\mathrm{Me}_3$), 6.6 (2C, Si$Me_2$).

$\{Me_2Si(NCMe_3)_2\}Zr\{CH(SiMe_3)_2\}_2$. The complex was prepared *in situ* in an NMR tube by reaction of **1** with a 2-fold excess of $LiCH(SiMe_2)_2$ in C_7D_8. ^{1}H NMR (C_7D_8, 25 °C): δ 1.43 (s, 18H, CMe_3), 0.50 (s, 6H, SiMe_2), 0.38, 0.34 (s, 18H, SiMe_2), −0.13 (s, 2H, Zr$\mathrm{C}H$).

Preparation of Cationic Complexes. $\{Me_2Si(NCMe_3)_2\}ZrBz\{BzB(C_6F_5)_3\}$ (6). A solution of 35 mg (0.074 mmol) of **4** in hexane (2 mL) was added dropwise to a solution of 38 mg (0.074 mmol) of $B(C_6F_5)_3$ in hexane (2 mL), resulting in the immediate precipitation of an orange solid. The mixture was stirrred for 5 min, and the solid was collected by decantation of the solvent, washing (twice) with hexane and drying *in vacuo*. A 68 mg (93% yield) amount of spectroscopically pure material was obtained. The complex was also conveniently obtained by carrying out the reaction in toluene, removal of the *solvent in vacuo*, and washing the residue (3 times) with hexane. Cooling a dichloromethane/hexane solution to −40 °C afforded large red crystals of complex **6**. ^{1}H NMR (C_6D_5Br, 25 °C): δ 7.3−6.7 (m, 10H, Bz), 3.36 (br, 2H, BCH_2), 1.95 (s, 2H, Zr$\mathrm{C}H_2$), 1.02 (s, 18H, CMe_3), 0.32, 0.22 (s, 3H, SiMe_2). ^{1}H NMR (C_7D_8, −25 °C): δ 7.14 (t, 2H, *m*-BzB), 7.08 (d, 2H, *m*-BzZr), 6.85 (t, 1H, *p*-BzZr), 6.69 (d, 2H, *o*-BzZr), 6.1 (m, 3H, *o*-BzB and *p*-BzB), 3.44 (br, 2H, BCH_2), 1.77 (s, 2H, Zr$\mathrm{C}H_2$), 0.88 (s, 18H, CMe_3), 0.26, 0.03 (s, 3H, SiMe_2); resonances assigned using a 2-D COSY experiment. ^{1}H NMR (CD_2Cl_2, 25 °C): δ 7.53 (m, 3H, Bz), 7.37 (d, 2H, *o*-Bz), 7.14 (t, 2H, *m*-Bz), 6.87 (m, 3H, Bz), 3.23 (br, 2H, BCH_2), 2.13 (s, 2H, Zr$\mathrm{C}H_2$), 1.27 (s, 18H, CMe_3), 0.54, 0.45 (s, 3H, SiMe_2). ^{13}C NMR ($C_2D_2Cl_4$, 25 °C): δ 160.4 (1C, *ipso*-BzB), 148.2 (d, 6C, C_6F_5), 147.6 (1C, *ipso*-BzZr), 138.6 (d, 3C, C_6F_5), 136.9 (d, 6C, C_6F_5), 131.2 (2C, Bz), 131.1 (1C, *p*-BzZr), 129.3 (2C, Bz), 126.4 (2C, Bz), 122.5 (1C, *p*-BzB), 61.4 (2C, $C\mathrm{Me}_3$), 52.4 (t, $^1J_{CH}$ = 122.5 Hz, 1C, Zr$C\mathrm{H}_2$), 35.1 (6C, CMe_3), 5.8, 5.4 (1C, SiMe_2); resonances for *ipso*-C_6F_5 and B$C\mathrm{H}_2$ were not observed. ^{13}C NMR (C_6D_6, 25 °C): δ 160.1 (1C, *ipso*-BzB), 148.6 (d, 6C, C_6F_5), 147.6 (1C, *ipso*-BzZr), 138.9 (d, 3C, C_6F_5), 137.4 (d, 6C, C_6F_5), 130.8 (4C, Bz), 129.0 (1C?, Bz), 126.6 (2C, Bz), 124.2 (br q, 1C, *ipso*-C_6F_5), 122.4 (1C, *p*-BzB), 60.9 (2C, $C\mathrm{Me}_3$), 52.5 (t, $^1J_{CH}$ = 122.5 Hz, 1C, Zr$C\mathrm{H}_2$), 36.2 (br q, 1C, B$C\mathrm{H}_2$), 34.6 (6C, CMe_3), 5.2, 4.7 (1C, SiMe_2); one benzyl resonances was obscured. ^{11}B NMR (C_6D_6, 25 °C): δ −12.2 ($\Delta\nu_{1/2}$ = 32.7 Hz). ^{19}F NMR (C_6D_6, 25 °C): δ −132.48 (d), −162.30 (t), −166.44 (m).

Thermal Decomposition of Complex 6. The decomposition of a 0.032 M solution of **6** in C_7D_8 in an NMR probe at 70 °C was monitored by ^{1}H NMR spectroscopy. After 2 h, a stable product distribution was observed, consisting of a 1:1 mixture of two organometallic complexes, as well as the three boranes, $BBz_n(C_6F_5)_{3-n}$ (n = 1−3). $Me_2Si(NCMe_3)_2\}ZrBz(C_6F_5)$ (50%): ^{1}H NMR (C_7D_8, 75 °C) δ 7.42 (d, 2H, *o*-Bz), 2.58 (s, 2H, Zr$\mathrm{C}H_2$), 1.27 (s, 18H, CMe_3), 0.44, 0.22 (s, 3H, SiMe_2); other resonances obscured. $\{Me_2Si(NCMe_3)_2\}Zr(C_6F_5)_2$ (50%): ^{1}H NMR (C_7D_8, 75 °C) δ 1.01 (s, 18H, CMe_3), 0.48 (s, 6H, SiMe_2). B$\mathrm{C}H_2$ resonances were observed at δ 3.41 (br, $B(Bz)(C_6F_5)_2$), 2.92 (s, $B(Bz)_2(C_6F_5)$), and 2.58 (s, $B(Bz)_3$).

$[\{Me_2Si(NCMe_3)_2\}Zr(Bz)(NMe_2Ph)][B(C_6F_5)_4]$ (7). $C_2D_2Cl_4$ or C_6D_5Br (0.7 mL) at −30 °C was added to a mixture of **4** (9.0 mg, 0.019 mmol) and $[PhMe_2NH][B(C_6F_5)_4]$ (15.2 mg, 0.019 mmol) in a reaction bottle at −40 °C. An orange solution was obtained almost instantaneously. After the mixture was warmed to 25 °C, the solution was used for NMR studies. ^{1}H NMR (C_6D_5Br, 25 °C): δ 7.2−7.0 (m, *m*-Ph), 6.88 (t, 1H, *p*-Ph), 6.70 (d, 2H, *o*-Ph), 6.67 (t, 1H, *p*-Ph), 6.34 (d, 2H, *o*-Ph), 2.54 (s, 6H, NMe_2), 1.99 (s, 2H, Zr$\mathrm{C}H_2$), 0.96 (s, 18H, CMe_3), 0.21 (s, 6H, SiMe_2). ^{1}H NMR ($C_2D_2Cl_4$, −25 °C): δ 7.55 (m, *m*-PhN), 7.22 (obscured, *m*-Bz), 7.11 (t, 1H, *p*-PhN), 6.98 (t, 1H, *p*-Bz), 6.82 (d, 2H, *o*-Bz), 6.74 (d, 2H, *o*-PhN), 3.08 (s, 6H, NMe_2), 2.11 (s, 2H, Zr$\mathrm{C}H_2$), 1.14 (s, 18H, CMe_3), 0.39, 0.27 (s, 3H, SiMe_2). The resonances were assigned using a 2-D COSY NMR experiment. ^{11}B NMR (C_6D_6, 25 °C): δ −15.8. ^{19}F NMR ($C_2D_2Cl_4$, 25 °C): δ −134.31 (d), −163.19 (t), −167.15 (m).

$[\{Me_2Si(NCMe_3)_2\}Zr(Bz)(THF)_2][B(C_6F_5)_4]$ (8). THF at 0 °C was added to a mixture of $\{Me_2Si(NCMe_3)_2\}ZrBz_2$ (30 mg, 0.062 mmol) and $[PhMe_2NH][B(C_6F_5)_4]$ (51 mg, 0.62 mmol) in a reaction bottle. Hexane was added to the resulting pale yellow solution to give a colorless oil. The oil was washed with hexane and dried *in vacuo* to give a colorless solid, shown by ^{1}H NMR spectroscopy to be a bis(THF) adduct. ^{1}H NMR (CD_2Cl_2, 25 °C): δ 7.28 (t, 2H, *m*-Bz), 7.00 (t, 1H, *p*-Bz), 6.92 (m, 2H, *o*-Bz), 4.03 (br, 8H, THF), 2.29 (br, 2H, Zr$\mathrm{C}H_2$), 2.07 (br, 8H, THF), 1.27 (s, 18H, C*Me*$_3$), 0.54 (s, 6H, Si*Me*$_2$). Addition of a large excess of THF afforded the following spectrum: δ 7.09 (t, 2H, *m*-Bz), 6.91 (d, 2H, *o*-Bz) 6.79 (t, 1H, *p*-Bz), 2.13 (s, 2H, ZrC*H*$_2$), 1.31 (s, 18H, C*Me*$_3$), 0.50 (br, 6H, Si*Me*$_2$).

Addition of an excess of THF to a solution of **6** gave an analogous THF adduct. ^{1}H NMR (C_7D_8, 25 °C): δ 7.2−6.8 (m, 10H, Bz), 3.34 (br, 2H, BC*H*$_2$), 1.89 (s, 2H, ZrC*H*$_2$), 1.03 (s, 18H, C*Me*$_3$), 0.28 (s, 6H, Si*Me*$_2$). ^{1}H NMR (C_6D_5Br, 25 °C): δ 7.2−6.8 (m, 10H, Bz), 3.27 (br, 2H, BC*H*$_2$), 1.93 (s, 2H, ZrC*H*$_2$), 1.07 (s, 18H, C*Me*$_3$), 0.33 (s, 6H, Si*Me*$_2$). ^{13}C NMR ($C_2D_2Cl_4$, −20 °C): δ 148.5 (1C, *ipso*-BzB), 148.1 (d, 6C, C_6F_5), 146.8 (1C, *ipso*-BzZr), 137.5 (d, 3C, *p*-C_6F_5), 136.4 (d, 6C, C_6F_5), 130.0 (2C, BzZr), 128.8 (2C, BzB), 127.2 (2C, BzB), 126.1 (2C, BzZr), 122.9 (2C, *p*-BzB), 74.2 (obscured, THF), 60.3 (2C, *C*Me$_3$), 54.7 (t, $^1J_{CH}$ = 117 Hz, 1C, Zr*C*H$_2$), 34.6 (6C, C*Me*$_3$), 32 (vbr, B*C*H$_2$), 25.7 (4C, THF), 6.3, 5.7 (1C, Si*Me*$_2$); resonances for *ipso*-C_6F_5 were not observed; at 25 °C, the Zr*C*H$_2$ resonance is very broad. ^{19}F NMR (C_6D_5Br, 25 °C): δ −131.89 (d), −164.93 (t), −167.89 (m).

Reaction of 4 with Trityl Reagent. CH_2Cl_2 (0.7 mL) at −40 °C was added to a mixture of **4** (2.2 mg, 4.6 μmol) and $[Ph_3C][B(C_6F_5)_4]$ (4.2 mg, 4.6 μmol) in a reaction bottle at 25 °C. ^{1}H NMR spectroscopy revealed complexes **9a** and **9b** to be present in a 73:27 ratio. At lower concentrations, the proportion of **9b** decreased. $[\{Me_2Si(NCMe_3)_2\}ZrBz][B(C_6F_5)_4]$ (**9a**): ^{1}H NMR (CD_2Cl_2, 25 °C) δ 7.97 (t, 2H, *m*-Bz), 7.61 (d, 2H, *o*-Bz), 7.44 (t, 1H, *p*-Bz), 2.53 (s, 2H, ZrC*H*$_2$), 1.39 (s, 18H, C*Me*$_3$), 0.75, 0.66 (s, 3H, Si*Me*$_2$). $[\{Me_2Si(NCMe_3)_2\}_2Zr_2Bz_2]$-$[B(C_6F_5)_4]_2$ (**9b**): ^{1}H NMR (CD_2Cl_2, 25 °C) δ 7.99 (t, 2H, *p*-Bz), 7.52 (t, 4H, *m*-Bz), 7.43 (d, 4H, *o*-Bz), 2.19 (s, 4H, ZrC*H*$_2$), 1.17 (s, 36H, C*Me*$_3$), 0.63, 0.00 (s, 6H, Si*Me*$_2$).

Addition of excess THF gave a mixture of complex **8** and another species proposed to be $[\{Me_2Si(NCMe_3)_2\}_2Zr_2(Bz)_2$-$(THF)_n][B(C_6F_5)_4]_2$. ^{1}H NMR ($CD_2Cl_2$, 25 °C): δ 1.38 (s, 36H, C*Me*$_3$), 0.63, 0.08 (s, 6H, Si*Me*$_2$); other resonances were obscured.

$[\{Me_2Si(NCMe_3)_2\}_2Zr_2Bz_3][B(C_6F_5)_4]$ (10). CH_2Cl_2 (3.0 mL) at −40 °C was added to a mixture of **4** (0.100 g, 0.21 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (97 mg, 0.11 mmol) in a reaction bottle at −40 °C. After the mixture was warmed to 25 °C and hexane was added (4 mL), an orange oil was obtained, which was washed with hexane (twice). The oil solidified on drying *in vacuo*. NMR spectroscopy showed the solid to be primarily the title complex; attempts to obtain an analytically pure sample by crystallization were unsuccessful. Addition of an excess of THF afforded a 1:1 mixture **4** and **8**. ^{1}H NMR (CD_2Cl_2, −25 °C): δ 7.39 (t, 2H, *m*-Bz), 7.26 (t, 4H, *m*-Bz), 7.10 (t, 1H, *p*-Bz), 6.99 (d, 2H, *o*-Bz), 6.95 (t, 2H, *p*-Bz), 6.68 (d, 4H, *o*-Bz), 2.27 (s, 4H, ZrC*H*$_2$), 1.13 (s, 36H, C*Me*$_3$), 1.03 (s, 2H, ZrC*H*$_2$), 0.39, 0.31 (s, 6H, Si*Me*$_2$); the resonances were assigned using a 2-D COSY experiment. ^{13}C NMR ($C_2D_2Cl_4$, 25 °C): δ 162.2 (1C, *ipso*-Bz), 148.3 (d, 6C, C_6F_5), 144.4 (2C, *ipso*-Bz), 137.9 (dm, 3C, *p*-C_6F_5), 136.5 (dm, 6C, C_6F_5), 131.9 (4C, Bz), 131.7 (2C, Bz), 126.8 (4C, Bz), 124.7 (2C, Bz), 123.6 (2C, Bz), 116.5 (1C, *p*-Bz), 60.4 (4C, *C*Me$_3$), 53.8 (t, $^1J_{CH}$ = 132.5 Hz, 1C, Zr*C*H$_2$), 53.3 (t, $^1J_{CH}$ = 130.5 Hz, 2C, Zr*C*H$_2$), 34.9 (12C, C*Me*$_3$), 6.1, 5.1 (2C, Si*Me*$_2$). ^{11}B NMR (CD_2Cl_2, 25 °C): δ −15.0 ($\Delta\nu_{1/2}$ = 24 Hz). ^{19}F NMR (CD_2Cl_2, 25 °C): δ −134.69 (m), −165.00 (m), −168.85 (m).

Reaction of a ca. 2:1 molar ratio of **4** and $B(C_6F_5)_3$ in C_6D_5Br (0.014 M in Zr) gave the following mixture (%Zr): 44% **4**; 36% **6**; 20% **10**. Reaction of a ca. 2:1 molar ratio of **4** and $[PhMe_2NH][B(C_6F_5)_4$ in C_6D_5Br (0.014 M in Zr) afforded the following mixture (%Zr): 3% **4**; 14% **7**; 83% **10**.

$[\{Me_2Si(NCMe_3)_2\}ZrNp][NpB(C_6F_5)_3]$ (11). Reaction of **5** (THF-free) with a 3-fold excess of $B(C_6F_5)_3$ at 25 °C after 2 h afforded the title complex as the major species in solution, contaminated with a small amount of **5**. ^{1}H NMR (C_6D_5Br, 25 °C): δ 2.09 (br, 2H, BC*H*$_2$), 1.04 (s, 18H, NC*Me*$_3$), 0.97 (s, 9H, ZrCH$_2$C*Me*$_3$), 0.88 (s, 9H, ZrCH$_2$C*Me*$_3$), 0.33 (br, 6H, Si*Me*$_2$); the ZrC*H*$_2$ resonance was obscured.

$[\{Me_2Si(NCMe_3)_2\}Zr(Np)(THF)_2][B(C_6H_5)_4]$ (12). THF (1.5 mL) at −40 °C was added to a mixture of **5**·$(THF)_{0.5}$ (210 mg, 0.45 mmol) and $[PhMe_2NH][B(C_6H_5)_4]$ (203 mg, 0.46 mmol) in a reaction bottle. After the mixture was warmed to 25 °C and stirred for 30 min, hexane was added to the resulting pale yellow solution to give a colorless oil. The oil was washed with hexane and dried *in vacuo* to give a colorless solid, shown by ^{1}H NMR spectroscopy to be a bis(THF) adduct. Partial THF dissociation occurs in solution, and the exact NMR shifts are concentration-dependent. ^{1}H NMR (THF-*d*$_8$, 25 °C): δ 1.27 (s, 18H, C*Me*$_3$), 0.95 (s, 9H, C*Me*$_3$), 0.76 (s, 2H, ZrC*H*$_2$), 0.54, 0.43 (br, 3H, Si*Me*$_2$). ^{1}H NMR (C_6D_5Br, 25 °C): δ 3.36 (m, 8H, THF), 1.36 (m, 8H, THF), 1.11 (s, 18H, C*Me*$_3$), 1.04 (s, 9H, C*Me*$_3$), 0.45, 0.33 (br, 3H, Si*Me*$_2$); the ZrC*H*$_2$ resonance was obscured by resonances for a second species, believed to be a monoTHF adduct. Addition of excess THF resulted in disappearance of the “monoTHF” resonances and changes in the chemical shifts of **12**: δ 1.13 (s, 18H, C*Me*$_3$), 1.04 (s, 9H, C*Me*$_3$), 0.85 (s, 2H, ZrC*H*$_2$), 0.48, 0.32 (br, 3H, Si*Me*$_2$). ^{13}C NMR of **12** ($C_2D_2Cl_4$, 25 °C): δ 85.4 (t, $^1J_{CH}$ = 112 Hz, 1C, Zr*C*H$_2$), 71.6 (4C, THF), 59.7 (2C, N*C*Me$_3$), 36.3 (1C, ZrCH$_2$*C*Me$_3$), 35.3 (3C, CH$_2$C*Me*$_3$), 35.1 (6C, CH$_2$CMe$_3$), 25.6 (4C, THF), 7.5, 6.4 (1C, Si*Me*$_2$). Resonances for the $[BPh_4]^-$ anion are omitted.

Protonolysis of Complex 5. C_6D_5Br was added to a mixture of complex **5** (8.5 mg, 0.020 mmol) and $[PhMe_2NH]$-$[B(C_6F_5)_4]$ (15.7 mg, 0.020 mmol) at −30 °C and the reaction warmed to 25 °C. ^{1}H NMR monitoring indicated the formation of one major species, together with two minor species and a small amount of 2-methyl-1-propene (about 10% on a molar basis). Major product: ^{1}H NMR (C_6D_5Br, 25 °C) δ 7.18 (t, 2H, *m*-PhN), 6.52 (t, 1H, *p*-PhN), 6.41 (d, 2H, *o*-PhN), 2.65 (s, 6H, N*Me*$_2$Ph), 1.06 (s, 18H, C*Me*$_3$), 0.90 (s, 9H, C*Me*$_3$), 0.44 (s, 3H, Si*Me*$_2$), 0.37 (s, 2H, ZrC*H*$_2$), 0.23 (s, 3H, Si*Me*$_2$). Minor resonances: ^{1}H NMR δ 6.63, 6.32 (d, *o*-PhN), 2.57, 2.55 (s, N*Me*$_2$Ph), 1.02, 0.85 (s, C*Me*$_3$), 0.63, 0.33, 0.06 (s, Si*Me*$_2$). Addition of excess of THF afforded the cationic bis(THF) adduct **12**.

Preparation of Single Insertion Products. $[\{Me_2Si(NCMe_3)_2\}Zr\{C(Me){=}C(Me)CH_2Ph\}][Anion]$ (13) (Anion = $[B(C_6F_5)_4]^-$). A solution of 2-butyne (100 μL, 1.28 mmol) in CH_2Cl_2 (1.5 mL) at −40 °C was added to a mixture of **4** (100 mg, 0.21 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (194 mg, 0.21 mmol) in a reaction bottle at −40 °C. The solution color changed from orange to yellow on warming the stirred reaction to 25 °C. After 5 min at 25 °C, hexane (5 mL) was added, precipitating a yellow oil, which was washed twice with hexane. The oil crystallized on cooling. The resulting microcrystalline solid was spectroscopically pure. Addition of excess THF afforded **13b**.

Complex **13**. ^{1}H NMR (CD_2Cl_2, 25 °C): δ 8.16 (d, 2H, *o*-Bz), 8.12 (t, 2H, *m*-Bz), 7.88 (t, 1H, *p*-Bz), 3.84 (s, 2H, C*H*$_2$Ph), 1.89, 1.76 (s, 3H, =C*Me*), 1.27 (s, 18H, C*Me*$_3$), 0.68, 0.46 (s, 3H, Si*Me*$_2$). ^{1}H NMR ($C_2D_2Cl_4$, 25 °C): δ 8.14 (m, 2H, *o*-Ph), 8.05 (t, 2H, *m*-Ph), 7.86 (t, 1H, *p*-Ph), 3.82 (s, 2H, C*H*$_2$Ph), 1.86, 1.77 (s, 3H, =C*Me*), 1.25 (s, 18H, C*Me*$_3$), 0.67, 0.45 (s, 3H, Si*Me*$_2$). ^{1}H NMR (C_6D_5Br, 25 °C): δ 7.52−7.38 (m, 4H, Bz), 3.32 (s, 2H, C*H*$_2$Ph), 1.70, 1.53 (s, 3H, =C*Me*), 0.97 (s, 18H, C*Me*$_3$), 0.41, 0.22 (s, 3H, Si*Me*$_2$). ^{13}C NMR ($C_2D_2Cl_4$, 25 °C): δ 195.5 (1C, Zr*C*Me), 169.1 (1C, =*C*MeCH$_2$), 156.8 (1C, *ipso*-Bz), 148.2 (d, 6C, C_6F_5), 138.2 (3C, *p*-C_6F_5), 136.4 (d, 6C, C_6F_5), 136.4 (2C, Ph), 130.4 (2C, Ph), 127.0 (1C, *p*-Ph), 121.8 (m, *ipso*-C_6F_5), 60.8 (2C, *C*Me$_3$), 48.1 (1C, *C*H$_2$Ph), 35.7 (6C, C*Me*$_3$), 25.6, 22.9 (1C, =CMe), 6.7, 4.5 (2C, Si*Me*$_2$). ^{11}B NMR ($C_2D_2Cl_4$, 25 °C): δ −15.5 ($\Delta\nu_{1/2}$ = 23 Hz). ^{19}F NMR (CD_2Cl_2, 25 °C): δ −133.88 (m), −163.72 (m), −167.64 (m).

Complex **13b**. ^{1}H NMR (CD_2Cl_2, 25 °C): δ 7.24 (d, 3H, *m,p*-Bz), 7.13 (d, 2H, *o*-Bz), 3.68 (s, 2H, C*H*$_2$Ph), 1.85, 1.55 (s, 3H, =C*Me*), 1.27 (s, 18H, C*Me*$_3$), 0.52, 0.47 (s, 3H, Si*Me*$_2$). ^{13}C NMR ($C_2D_2Cl_4$, −30 °C): δ 128.8 (4C, Ph), 59.6 (2C, *C*Me$_3$), 51.8 (1C, *C*H$_2$Ph), 35.0 (6C, C*Me*$_3$), 6.4 (2C, Si*Me*$_2$); other resonances were obscured.

A spectroscopically identical cationic species, **13**, was obtained on reacting a 0.043 M solution of **7** in C_6D_5Br solution with a 3-fold excess of 2-butyne. The reaction was complete within 10 min at 25 °C; resonances for noncoordinated $PhNMe_2$ were observed (δ 6.73, 6.60, 2.66). After 1 h, 25% conversion of the product to another unidentified species was observed.

Addition of MeOH to a solution of **13** afforded MeCH═C(Me)CH_2Ph. ^1H NMR (CD_2Cl_2, 25 °C): δ 7.4−7.1 (m, 5H, Ph), 5.3 (m, 1H, ═C*H*Me), 1.60 (d, $^3J_{HH}$ = 6.6 Hz, ═CH*Me*), 1.51 (m, 3H, ═C*Me*); other resonances were obscured.

Anion = $[PhCH_2B(C_6F_5)_3]^-$. A solution of 2-butyne (20 μL, 0.26 mmol) in C_6D_5Br (1.5 mL) at −40 °C was added to a mixture of **4** (35 mg, 0.074 mmol) and $B(C_6F_5)_3$ (38 mg, 0.074 mmol) at −40 °C. The solution color changed from orange to yellow on warming to 25 °C. After 5 min at 25 °C, hexane (3 mL) was added, precipitating a yellow oil, which was washed twice with hexane. Analytically pure yellow microcrystalline product was obtained from a CH_2Cl_2/hexane solution at −40 °C. NMR monitoring of the reaction of a 0.043 M solution of **6** with a 3-fold excess of 2-butyne indicated that the reaction was much slower in toluene-d_8 (conversion 70% in 20 min, 95% in 60 min) than in C_6D_5Br (100% conversion in 5 min). Within 20 min in C_6D_5Br, further reaction afforded unidentified complexes. THF addition to **13** afforded **13b**.

Complex **13**. ^1H NMR (C_6D_5Br, 25 °C): δ 7.5−6.9 (m, Bz), 3.32 (s, 2H, BCH_2 and CH_2Ph), 1.70, 1.53 (s, 3H, ═C*Me*), 0.97 (s, 18H, C*Me*$_3$), 0.41, 0.22 (s, 3H, Si*Me*$_2$). ^{19}F NMR (C_6D_5Br, 25 °C): δ −131.79 (d), −164.74 (t), −167.62 (t). Anal. Calcd for $C_{46}H_{44}BF_{15}N_2SiZr$: C, 53.13; H, 4.26; F, 27.40; N, 2.69. Found: C, 52.86; H, 4.36; F, 27.23; N, 2.54.

Complex **13b**. ^1H NMR (C_6D_5Br, 25 °C): δ 7.3−6.8 (m, Bz), 3.58 (s, 2H, C*H*$_2$Ph), 3.28 (br, 2H, BC*H*$_2$), 1.65, 1.45 (s, 3H, ═C*Me*), 1.07 (s, 18H, C*Me*$_3$), 0.33, 0.32 (s, 3H, Si*Me*$_2$).

$[\{Me_2Si(NCMe_3)_2\}Zr\{CH_2CH_2CH_2Ph\}][B(C_6F_5)_4]$ (14a). CD_2Cl_2 (0.7 mL) was added at −30 °C to a mixture of **4** (10 mg, 0.021 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (19.4 mg, 0.021 mmol) in an NMR tube, and the reaction mixture was warmed to 5 °C. Addition of excess ethene by syringe afforded the title complex (5 min), contaminated by about 20% (Zr atoms) of **9b**. THF addition converted **14a** to complex **14b**. Repeated attempts to isolate **14a** by hexane addition to the crude product mixture in CH_2Cl_2 in a Schlenk tube led only to the isolation of a complicated mixture. In some cases, the initially deposited yellow oil suddenly turned an intense red color on removing the septum cap under an argon stream.

Complex **14a**. ^1H NMR (CD_2Cl_2, 25 °C): δ 8.03 (m, 3H, *o,m*-Ph), 7.98 (t, 1H, *p*-Ph), 3.11 (t, $^3J_{HH}$ = 6.4 Hz, 2H, C*H*$_2$Ph), 2.62 (m, 2H, CH_2C*H*$_2$Ph), 1.26 (s, 18H, C*Me*$_3$), 1.08 (m, 2H, ZrC*H*$_2$), 0.59, 0.50 (s, 3H, Si*Me*$_2$).

Complex **14b**. ^1H NMR (CD_2Cl_2, 25 °C): δ 7.25−7.05 (m, 5H, Ph), 2.44 (t, $^3J_{HH}$ = 6.5 Hz, 2H, C*H*$_2$Ph), 2.06 (m, 2H, $ZrCH_2$C*H*$_2$), 1.26 (s, 18H, C*Me*$_3$), 0.56 (s, 6H, Si*Me*$_2$), 0.44 (m, 2H, ZrC*H*$_2$).

$\{Me_2Si(NCMe_3)_2\}Zr\{CH_2CH_2CH_2Ph\}\{BzB(C_6F_5)_3\}$ (14c). Ethene (1 bar, 4.5 mL, 0.20 mmol) was added to a solution of 0.03 mmol of **6** in C_6D_5Br (0.7 mL), and the reaction was monitored by ^1H NMR spectroscopy. Clean and complete conversion to the title complex was observed within 5 h ($t_{1/2}$ = 76 min). In CD_2Cl_2, the reaction is somewhat faster (60% conversion in 60 min), and in toluene-d_8, it is noticeably slower (25% conversion in 20 h). THF addition afforded **14b**.

Complex **14c**. ^1H NMR (C_6D_5Br, 25 °C): δ 7.3−6.8 (m, Ph), 3.36 (br, 2H, BC*H*$_2$), 2.44 (t, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*$_2$Ph), 1.79 (m, 2H, $ZrCH_2$C*H*$_2$), 1.00 (s, 18H, C*Me*$_3$), 0.50 (m, 2H, ZrC*H*$_2$), 0.35, 0.32 (s, 3H, Si*Me*$_2$). ^1H NMR (CD_2Cl_2, 25 °C): δ 7.6−7.1 (m, 10H, Ph), 3.21 (m, 2H, BC*H*$_2$Ph), 2.45 (t, $^3J_{HH}$ = 6.3 Hz, 2H, CH_2C*H*$_2$Ph), 1.88 (m, 2H, $ZrCH_2$C*H*$_2$), 1.26 (s, 18H, C*Me*$_3$), 0.60 (m, 2H, ZrC*H*$_2$), 0.59, 0.50 (s, 3H, Si*Me*$_2$). ^{19}F NMR (C_6D_5Br, 25 °C): δ −132.21 (d), −161.69 (t), −165.7 (t).

Complex **14b**. ^1H NMR (C_6D_5Br, 25 °C): δ 3.25 (s, 2H, BCH_2), 2.50 (t, 2H, C*H*$_2$Ph), 2.05 (m, 2H, $ZrCH_2$C*H*$_2$), 1.12 (s, 18H, C*Me*$_3$), 0.45 (br, 6H, Si*Me*$_2$); other resonances were obscured. ^{19}F NMR (C_6D_5Br, 25 °C): δ −131.92 (d), −165.01 (t), −167.94 (t).

$[\{Me_2Si(NCMe_3)_2\}Zr\{CH_2CH_2CH_2Ph\}(NMe_2Ph)][B(C_6F_5)_4]$ (14d). Ethene (1 bar, 4.5 mL, 0.20 mmol) was added to a solution of 0.03 mmol of **7** in C_6D_5Br (0.7 mL) (in an NMR tube with a septum cap), and the reaction was monitored by ^1H NMR spectroscopy. Clean and complete conversion to a mixture of **14d** (65%) and **14a** (35%) was observed within 11 min. Addition of excess THF afforded **14b**.

Complex **14d**. ^1H NMR (C_6D_5Br, 25 °C): δ 7.3−7.0 (m, Ph), 6.47 (t, 1H, *p*-PhN), 6.34 (d, 2H, *o*-PhN), 2.51 (m, N*Me*$_2$Ph), 2.44 (t, $^3J_{HH}$ = 7.1 Hz, 2H, C*H*$_2$Ph), 1.86 (m, 2H, $ZrCH_2$C*H*$_2$), 1.00 (s, 18H, C*Me*$_3$), 0.40, 0.22 (s, 3H, Si*Me*$_2$), 0.2 (obscured, ZrC*H*$_2$).

Complex **14a**. ^1H NMR (C_6D_5Br, 25 °C): δ 0.95 (s, 18H, C*Me*$_3$), 0.69 (t, 2H, ZrC*H*$_2$?), 0.31, 0.25 (s, 3H, Si*Me*$_2$); resonances for free NMe_2Ph were also observed.

Under similar conditions in $C_2D_2Cl_4$, a 50:50 mixture of **14d** and **14a** was obtained. THF addition afforded **14b**. In CD_2Cl_2, **14d** was the major product, but significant decomposition was evident after 1 h.

Complex **14d**. ^1H NMR ($C_2D_2Cl_4$, 25 °C): δ 3.05 (m, N*Me*$_2$Ph), 2.48 (t, 2H, C*H*$_2$Ph), 1.96 (m, 2H, $ZrCH_2$C*H*$_2$), 1.23 (s, 18H, C*Me*$_3$), 0.61, 0.44 (s, 3H, Si*Me*$_2$), 0.38 (obscured, ZrC*H*$_2$); other resonances were obscured.

Complex **14a**. ^1H NMR ($C_2D_2Cl_4$, 25 °C): δ 7.98 (m, 5H, CH_2*Ph*), 2.62 (m, 2H, C*H*$_2$CH$_2$Ph), 1.23 (s, 18H, C*Me*$_3$), 1.06 (m, 2H, ZrC*H*$_2$), 0.57, 0.48 (s, 3H, Si*Me*$_2$); other resonances were obscured.

$[\{Me_2Si(NCMe_3)_2\}Zr\{CH_2CH(Me)CH_2Ph\}][B(C_6F_5)_4]$ (15a). Addition of a small excess of propene to the solution in CD_2Cl_2 obtained on reacting **4** with $[Ph_3C][B(C_6F_5)_4]$ afforded the title complex (complete in 20 min), contaminated by **9b**. ^1H NMR (CD_2Cl_2, 25 °C): δ 8.1−7.9 (m, 5H, Ph), 3.42 (m, 1H, H_d), 2.7−2.5 (m, 2H, H_c and H_e), 2.55 (t, 1H), 1.26 (s, 18H, C*Me*$_3$), 1.17 (obscured, CH*Me*), 0.60, 0.50 (s, 3H, Si*Me*$_2$), 0.22 (t, $^2J_{ab}$ = $^3J_{bc}$ = 13.1 Hz, H_b); resonance for H_a obscured.

$\{Me_2Si(NCMe_3)_2\}Zr\{CH_2CH(Me)CH_2Ph\}\{BzB(C_6F_5)_3\}$ (15c). Propene (1 bar, 4.5 mL, 0.20 mmol) was added to a solution of 0.03 mmol of **6** in C_6D_5Br (0.7 mL), and the reaction was monitored by ^1H NMR spectroscopy. Clean and complete conversion to the title complex was observed within 20 h ($t_{1/2}$ = 280 min). THF addition afforded **15b.** In CD_2Cl_2, insertion was somewhat faster (60% conversion in 60 min), and in toluene-d_8, the reaction was noticeably slower (25% conversion in 20 h).

Complex **15c**. ^1H NMR (C_6D_5Br, 25 °C): δ 7.3−6.8 (m, Ph), 3.33 (br, 2H, BC*H*$_2$), 2.44 (dd, $^2J_{HH}$ = 12.6 Hz, $^3J_{HH}$ = 6.0 Hz, 1H, CH_2Ph), 2.14 (m, 1H, CH_2Ph), 1.93 (octet, $^3J_{HH}$ = 6.7 Hz, 1H, C*H*Me), 1.04, 0.98 (s, 9H, C*Me*$_3$), 0.88 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CH*Me*), 0.48 (d, 2H, $^3J_{HH}$ = 6.1 Hz, $ZrCH_2$), 0.36, 0.29 (s, 3H, Si*Me*$_2$). ^{19}F NMR (C_6D_5Br, 25 °C): δ −131.78 (d), −161.36 (t), −165.42 (t).

Complex **15b**. ^{19}F NMR (C_6D_5Br, 25 °C): δ −131.92 (d), −165.03 (t), −167.95 (t).

$[\{Me_2Si(NCMe_3)_2\}Zr\{CH_2CH(Me)CH_2Ph\}(NMe_2Ph)][B(C_6F_5)_4]$ (15d). Propene (1 bar, 4.5 mL, 0.20 mmol) was added to a solution of 0.03 mmol of **7** in C_6D_5Br (0.7 mL), and the reaction was monitored by ^1H NMR spectroscopy. Clean and complete conversion to a 22:78 mixture of **15d** and **15a** was observed within 25 min.

Complex **15d**. ^1H NMR (C_6D_5Br, 25 °C): δ 6.47 (t, 1H, *p*-PhN), 6.34 (d, 2H, *o*-PhN), 2.5 (vbr, N*Me*$_2$Ph), 0.96 (s, C*Me*$_3$), 0.42, 0.21 (s, 3H, Si*Me*$_2$); other resonances were obscured.

Complex **15a**. ^1H NMR (C_6D_5Br, 25 °C): δ 7.5−7.0 (m, Ph), 2.88 (dd, $^2J_{de}$ = 11.6 Hz, $^3J_{cd}$ = 5.0 Hz, 1H, H_d), 0.96 (s, 18H, C*Me*$_3$), 0.69 (t, 2H, ZrC*H*$_2$), 0.32, 0.27 (s, 3H, Si*Me*$_2$), −0.12 (t, $^3J_{HH}$ = 13.1 Hz, H_a); other resonances were obscured.

$[\{Me_2Si(NCMe_3)_2\}Zr\{CH_2CH(n\text{-}Bu)CH_2Ph\}][B(C_6F_5)_4]$ (16a). A solution of 1-hexene (100 μL, 0.80 mmol) in CH_2Cl_2 (1.5 mL) at −30 °C was added to a mixture of **4** (100 mg, 0.21 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (194 mg, 0.21 mmol) at −30 °C.

The solution color changed to yellow on warming to 25 °C (2 min), after which hexane (5 mL) was added, precipitating a yellow oil. Hexane washing (twice) and drying *in vacuo* afforded a yellow solid which was spectroscopically pure. THF addition afforded **16b**.

Complex **16a**. ^{1}H NMR (CD_2Cl_2, −20 °C): δ 7.96 (m, 5H, Ph), 3.42 (ddd, $^2J_{de} = 11.8$ Hz, $^3J_{cd} = 5.5$ Hz, $^4J_{ad} = 1.7$ Hz, 1H, H_d), 2.55 (t, 1H, $^3J_{ce} = 11.8$ Hz, H_e), 2.41 (m, 1H, $^3J_{bc} = 13.5$ Hz, H_c), 1.88 (dt, $^2J_{ab} = 13.5$ Hz, 1H, H_a), 1.21 (s, 18H, CMe_3), 0.86 (obscured, 3H, CH_3), 0.57, 0.46 (s, 3H, $SiMe_2$), 0.03 (t,1H, H_b); resonances were assigned using a 2-D COSY experiment. ^{13}C NMR ($C_2D_2Cl_4$, 25 °C): δ 159.0 (1C, *ipso*-Ph), 134.7, 131.2 (2C, Ph), 125.6 (1C, *p*-Ph), 60.4 (2C, CMe_3), 55.9 (1C, CH), 55.6, 43.0, 41.7 (1C, CH_2), 35.5, 35.4, (3C, CMe_3), 29.6, 22.9 (1C, CH_2), 14.4 (1C, CH_3), 6.1, 5.6 (1C, $SiMe_2$); anion resonances omitted. ^{11}B NMR ($C_2D_2Cl_4$, 25 °C): δ −15.5 ($\Delta\nu_{1/2}$ = 23 Hz). ^{19}F NMR (CD_2Cl_2, 25 °C): δ −133.88 (m), −163.63 (m), −167.58 (m).

Complex **16b**. ^{13}C NMR (C_2D_2 Cl_4, 25 °C): δ 143.0 (1C, *ipso*-Ph), 130.0, 128.2 (2C, Ph), 125.9 (1C, *p*-Ph), 64.9 (1C, CH_2), 59.7 (2C, CMe_3), 45.5 (1C, CH_2), 44.4 (1C, CH), 38.8 (1C, CH_2), 35.0 (6C, CMe_3), 30.3, 23.6 (1C, CH_2), 14.7 (1C, CH_3), 7.0 (2C, $SiMe_2$); anion resonances omitted.

[{$Me_2Si(NCMe_3)_2$}Zr{$CH_2CH(CH_2Ph)_2$}][$B(C_6F_5)_4$] (17a). A solution of allylbenzene (100 μL, 0.75 mmol) in CH_2Cl_2 (1.5 mL) at −30 °C was added to a mixture of **4** (70 mg, 0.15 mmol) and [Ph_3C][$B(C_6F_5)_4$] (135 mg, 0.15 mmol) at −30 °C. The solution color changed to yellow on warming to 25 °C (5 min), after which hexane (5 mL) was added, precipitating a yellow oil. Hexane washing (twice) and drying *in vacuo* afforded a yellow solid. THF addition afforded **17b**.

Complex **17a**. ^{1}H NMR ($C_2D_2Cl_4$, −25 °C): δ 8.01 (t, 1H, PhZr), 7.94 (m, 1H, PhZr), 7.85 (m, 3H, PhZr), 7.30 (t, 2H, *m*-Ph), 7.21 (t, 1H, *p*-Ph), 7.12 (d, 2H, *o*-Ph), 3.24 (m, 1H, H_d), 2.62 (m, 2H, CH_2Ph), 2.52 (m, 2H, H_c and H_e), 1.78 (d, $^2J_{ab} = 13.4$ Hz, 1H, H_a), 1.16, 1.10 (s, 9H, CMe_3), 0.49, 0.42 (s, 3H, $SiMe_2$), 0.05 (t, 1H, $^2J_{bc} = 12.7$ Hz, H_b); resonances were assigned using a 2-D COSY experiment.

Complex **17b**. ^{1}H NMR (CD_2Cl_2, 25 °C): δ 2.53 (d, $^2J_{HH} = 6.4$ Hz, 4H, CH_2Ph), 2.40 (m, $ZrCH_2CH$), 1.33 (s, 18H, CMe_3), 0.68 (d, 2H, $^2J_{HH} = 6.7$ Hz, $ZrCH_2$), 0.52 (s, 6H, $SiMe_2$).

Procedure for Polymerization Testing. A 25 mL steel autoclave with a glass liner was used for screening the ethene polymerization activity. A toluene (10 mL) solution of the cationic complex (0.03 mmol) or a mixture of complex **1** (0.01 mmol), MAO (2.0 mmol; 10% solution in toluene), and toluene (10.5 mL) were loaded into the autoclave in the glovebox. The autoclave was then placed in a constant temperature bath and pressurized with ethene (20 bar). The reaction was stopped by rapidly venting the system, followed by decanting the product mixture under air. The polyethene remaining in the autoclave was washed out with toluene, and the toluene fractions were combined and added to methanol. The polyethene was removed by filtration, stirred with MeOH and then 1 N HCl solution, filtered again, washed with water followed by acetone, and then dried (vacuum, 70 °C, 3 days). The low ethene polymerization activities in the small autoclave were consistent with the results obtained in a 1 L steel autoclave under conditions of higher dilution and lower pressure (3 bar). Cationic complexes were freshly prepared and immediately introduced into the 25 mL autoclave; no alkylaluminium scavenger was utilized.

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