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# Ferrocene-Based Olefin Polymerization Catalysts: Activation, Structure, and Intermediates

Alexandr Shafir and John Arnold*

*Department of Chemistry, University of California, Berkeley, and the Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720-1460*

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This paper describes abstraction of a benzyl group from the Zr dibenzyl complex 1,1′-Fc(NSiMe$_3$)$_2$]ZrBn$_2$ (**1**) using B(C$_6$F$_5$)$_3$ and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (**TB**). In both cases, clean formation of the corresponding cationic monobenzyl species LZrBn$^+$ (L = 1,1′-Fc(NSiMe$_3$)$_2$$^{2-}$) was observed by NMR spectroscopy. In the case of [LZrBn][BnB(C$_6$F$_5$)$_3$] (**2**), an X-ray crystal structure determination confirmed an $\eta^6$ coordination of the borate benzyl group to the cationic Zr center. Reaction of this complex with 1 equiv of C$_2$H$_2$ or RCCR (R = Me, Ph) proceeded with rapid single insertion of the olefin or acetylene into the Zr−carbon $\sigma$-bond. With ethylene or 2-butyne further insertions occur more slowly and longer chains were obtained upon addition of more monomer. Activation of **1** with **TB** leads to an active ethylene polymerization catalyst, producing 102 g of PE mmol$^{-1}$ atm$^{-1}$ h$^{-1}$. Compound **2** reacted with CH$_2$Cl$_2$ to form the dimeric [LZrCl$_2$]$_2$, which was characterized crystallographically.

## Introduction

Ferrocene derivatives have long served as scaffolds for a variety of ligands used in catalytic transformations.[1] The success of these systems is attributed mainly to the steric bulk of a ferrocene group and the fairly constrained directionality of the chelate vectors imposed by the relative rigidity of the metallocene. Additionally, many ferrocene-based ligands feature a combination of planar and central chirality, rendering them useful in asymmetric catalysis.

The bulk and the rigidity of the ferrocene group made it an attractive candidate for the design of new types of olefin polymerization catalysts. We chose diaminoferrocene as a ligand precursor on the basis of the fact that various diamide ligands are well-known to support Ti- and Zr-based olefin polymerization systems. While some of the earlier examples of group 4 diamide systems are based on nonbridged diamide ligands,[2] more recently the research in this area has been focused on more restricted linked diamide complexes. Several diamines have served as the basis for these complexes, including propylenediamine,[3,4] phenylenediamine,[5,6] biphenylenediamine,[7] and naphthalenediamine.[8,9] Perhaps the most striking example was discovered by the McConville group, who reported that a propylenediamine-based Ti dimethyl complex actively polymerized 1-hexene and, when activated with B(C$_6$F$_5$)$_3$, did so in a "living" manner.[3,4] Closely related systems incorporating additional donor atoms have also been investigated.[10] The Schrock group has developed a range of such tridentate diamido/donor ligands for group IV catalyzed 1-hexene polymerization.[11−14]

Our group recently reported the synthesis of a series of Ti and Zr complexes based on the silylated[15] and arylated[16] diaminoferrocenes (C$_5$H$_4$NHR)$_2$Fe; closely related ferrocenediamide complexes have also been prepared by other groups.[17,18] In these compounds the N-donor atoms are attached directly to the ferrocene backbone. Several features of this arrangement are notable. As is often the case with ferrocene-based ligands, diamidoferrocene provides for a fairly rigid and highly directing scaffold. Despite the low rotation barrier around the Cp(centroid)−Fe axis, all of our structurally characterized group 4 complexes featured a fully eclipsed syn-periplanar ferrocene group and an open N−M−N angle (>130°). In addition, the electron-rich ferrocene group may stabilize an extremely electron-poor Ti or Zr center. Indeed, an X-ray crystal structure

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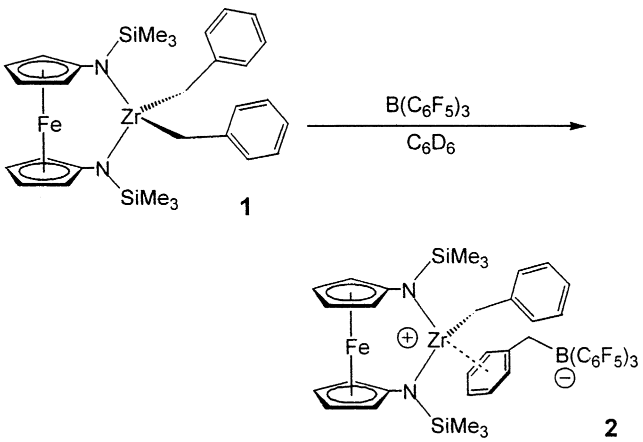
**Scheme 1**



of $[Fc(NSiMe_3)_2TiCl]_2^{2+}$ revealed a highly unusual geometry with a very short Fe−Ti distance.[19] The nature of this interaction is currently being investigated.

Preliminary study of the catalytic activity of $LTiMe_2$ (L = 1,1′-$Fc(NSiMe_3)_2$) indicated that stable cationic species could be obtained through the abstraction of a methide group with strong Lewis acids and that these cations were active catalysts for oligomerization of 1-hexene.[19] In this paper we extend this study to $LZrBn_2$ (**1**) and report the synthesis of stable cationic species of the type $[LZrBn^+][A^-]$ ($A^- = PhCH_2B(C_6F_5)^-$, $B(C_6F_5)_4^-$). Solid- and solution-state structures of these species are reported. Additionally, reactivity of these species toward unsaturated substrates is reported, including polymerization of ethylene.

## Results and Discussion

**Generation of $[LZrBn]^+$ and Its Reactivity with Ethylene and Acetylenes.** Reaction of $LZrBn_2$ (**1**; L = 1,1′-$Fc(NSiMe_3)_2^{2-}$) with $B(C_6F_5)_3$ in toluene or benzene produced the cationic $[LZrBn][BnB(C_6F_5)_3]$ (**2**) (Scheme 1). With toluene as a solvent, the product precipitated after 24 h as a red crystalline solid incorporating 1 equiv of toluene. Upon isolation, the material is only sparingly soluble in benzene and toluene; therefore, **2** was generated in situ for reactivity studies (see below).

Crystals of **2** suitable for X-ray diffraction were grown from a $C_6D_6$ solution. In the solid state, the compound exists as a close-contact ion pair with the benzylborate $[BnB(C_6F_5)_3]^-$ anion bound to zirconium in an $\eta^6$ fashion (Figure 1). The distorted-tetrahedral environment of zirconium is comprised of two nitrogen donors of the diamide ligand, a phenyl centroid, and the methylene carbon atom of the remaining $\sigma$-bound benzyl group. Alternatively, the structure may be viewed as being six-coordinate, with the phenyl ring occupying three (*fac*) coordination sites. The interatomic distance of 3.20 Å between Zr and Fe precludes any significant metal−metal interaction. In addition, the rather wide Zr−C11−C12 angle of 105.7° argues against an $\eta^2$-bound benzyl ligand. The ferrocene group is in a fully eclipsed (synperiplanar) 1,1′-conformation, but the two mean Cp planes are at a 10.85° angle to each other. The Zr atom is found 0.28 Å out of the Fe1−N1−N2 plane, and the Zr−Ph(centroid) distance is 2.34 Å.

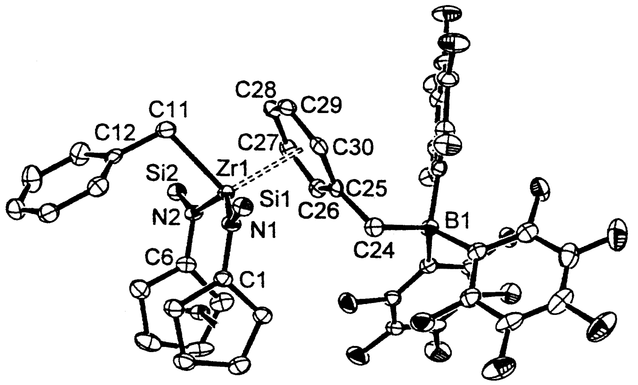


**Figure 1.** Partial ORTEP diagram of $[Fc(NSiMe_3)_2Zr(CH_2Ph)][PhCH_2B(C_6F_5)_3]$ (**2**) drawn with 50% thermal ellipsoids. For clarity, methyl groups and all hydrogen atoms are omitted. Selected bond distances (Å): Fe1−Zr1 (nonbonding) = 3.1981(7), Zr1−$Ph_{centroid}$ = 2.385(4), Zr1−N1 = 2.086(4), Zr1−N2 = 2.068(4), Zr1−C11 = 2.283(5), Zr1−C25 = 2.853(4), Zr1−C26 = 2.735(4), Zr1−C27 = 2.727(4), Zr1−C28 = 2.733(4), Zr1−C29 = 2.754(4), Zr1−C30 = 2.805(4). Selected bond angles (deg): N1−Zr1−N2 = 136.9(1), N1−Zr1−C11 = 96.0(2), N2−Zr1−C11 = 95.3(2), C11−Zr1−$Ph_{centroid}$ = 104.7(1), Zr1−C11−C12 = 105.7(3).

The coordination of a benzyl borate anion to a cationic group IV metal center in an $\eta^6$ fashion was first established by Pellecchia et al., who demonstrated this mode of binding in the solid-state structures of $[Bn_3Zr][\eta^6\text{-}PhCH_2B(C_6F_5)_3]$[20] and $[CpZrBn_2][\eta^6\text{-}PhCH_2B(C_6F_5)_3]$.[21] Following their work, several related species have been characterized in solution and in the solid state.[2,10,22−24] The Zr−Ph(centroid) distance in **2** is similar to the distances observed in related compounds, e.g. $[(Ar'O)_2ZrBn][\eta^6\text{-}BnB(C_6F_5)_3]$ (Ar′O = 2,6-disubstituted phenoxide).[22] While this mode of binding generally renders the cationic Ti or Zr species less active for olefin polymerization (as compared to their $B(C_6F_5)_4$-containing counterparts), the increased stability of these species generally facilitates the investigation of their structure and reactivity.

NMR studies of **2** in $C_6D_6$ suggest that close ion pairing is maintained in solution. The presence of the borate anion was supported by a single sharp resonance at −12.7 ppm in the $^{11}B$ NMR spectrum, a significant change from a very broad resonance at +59.2 ppm observed for the three-coordinate parent $B(C_6F_5)_3$. In the $^1H$ NMR spectrum, two new benzylic resonances at 3.05 ppm (broad) and 2.30 ppm (sharp singlet) were assigned to the boron-bound and zirconium-bound methylene groups, respectively. The ferrocene group gives rise to four resonances in the $^1H$ NMR spectrum. This is in contrast to the spectrum of $LZrBn_2$ (**1**), in which the $C_{2v}$ symmetry of the ferrocene group leads to just *two* resonances, each an AA′BB′ virtual triplet (Figure 2a).

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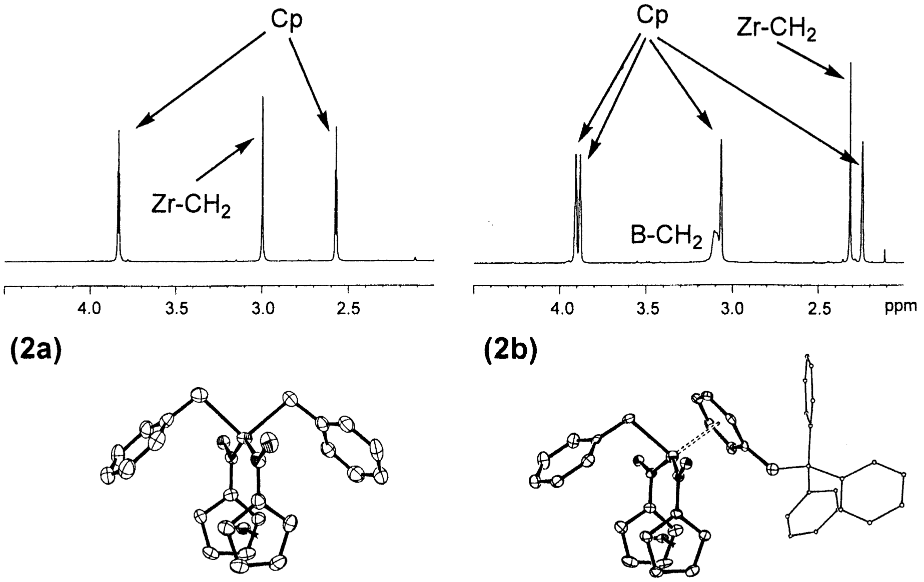
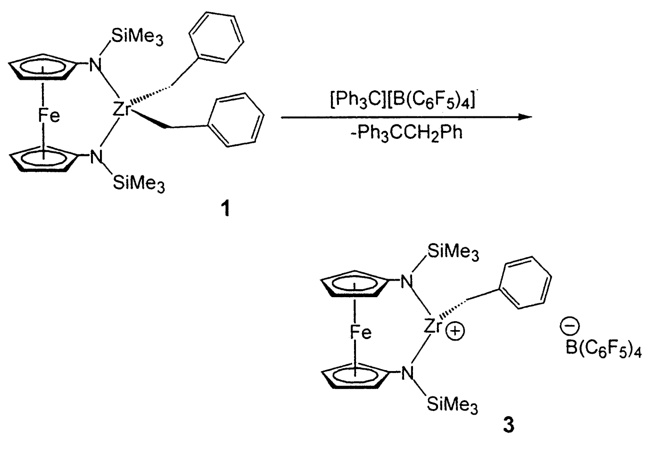


**Figure 2.** Partial $^1H$ NMR spectra of **1** (a) and **2** (b). The ORTEP diagrams below the spectra illustrate the solid-state geometry of the two molecules as determined by X-ray diffraction.

The loss of a mirror plane on going from **1** to **2** reduces the molecular symmetry to $C_s$ with the four Cp-bound hydrogens residing in distinct chemical environments (note that the two Cp rings are still related by a mirror plane) (Figure 2b). The four ferrocene resonances are comprised of a pair of six-line resonances (apparent triplets of doublets) for the 3,4-hydrogens and a pair of five-line resonances (apparent overlapping doublets of triplets) for the 2,5-hydrogens. Of note is the unusual chemical shift of one of the 2,5-ferrocene resonances at 2.23 ppm, significantly upfield from the normal chemical shift of approximately 3.5−4.5. We attribute this phenomenon in part to the ring-current effect of the zirconium-bound benzyl group, which in the solid state is bent toward one of the ortho protons of the ferrocene ring. Interestingly, this phenomenon is paralleled in the $^1H$ NMR spectrum of the parent LZrBn$_2$, where the two (equivalent) 2,5-ferrocene hydrogens appear at 2.57 ppm. The $^{13}C$ NMR spectrum of **2** is also consistent with a $C_s$-symmetric structure, showing distinct resonances for each of the five Cp carbon atoms. The Zr-bound methylene carbon appeared at 69.4 ppm; the shift for the boron-bound CH$_2$ group was inferred from a $^1H-{}^{13}C$ HMQC experiment to be at approximately 36 ppm (the resonance was not observed in the $^{13}C\{^1H\}$ spectrum due to quadrupole broadening caused by the neighboring boron nucleus).

The difference between the $^{19}F$ NMR shifts of meta and para resonances, $\Delta\delta_F(m-p)$, has been reported to be a useful tool for distinguishing between coordinated and noncoordinated $BnB(C_6F_5)_3^-$ anions.[2,10] Values >3 ppm are taken as an indication of coordination; those <3 ppm imply a free anion. For **2**, the value of $\Delta\delta_F(m-p)$ is 4.34 ppm, consistent with a coordinated $BnB(C_6F_5)_3^-$. A similar value was observed for a closely related cationic Zr system reported by Horton and de With.[24]

**Scheme 2**



Reaction of **1** with [Ph$_3$C][B(C$_6$F$_5$)$_4$] in C$_6$D$_5$Cl resulted in the clean formation of [LZrBn][B(C$_6$F$_5$)$_4$] (**3**) and 1 equiv of PhCH$_2$CPh$_3$ (Scheme 2). (We note that reactions in C$_6$D$_6$ resulted in an oily precipitate.) In contrast to the four sharp ferrocene resonances in the $^1H$ NMR spectrum of **2**, complex **3** features two broad ferrocene resonances at room temperature, suggesting a fluxional behavior in solution. The process is likely to involve the flipping of the benzyl group between two equivalent coordination sites. While in **2** the freed coordination site of the cation was occupied by a fairly tightly bound arene group of the borate anion, making the molecule static on the NMR time scale, in **3** this coordination site is most likely occupied by a weakly bound solvent molecule. The benzyl group site exchange is therefore more facile in **3** (Figure 3). Nevertheless, cooling the solution to −30 °C slows this process to a point where four ferrocene resonances are seen, consistent with a static $C_s$-symmetric conformation; at +70 °C the site exchange process is accelerated to the point where the two sides of the molecule become equivalent on the $^1H$ NMR time scale, thus imposing a time-averaged $C_{2v}$ symmetry on the cation and collapsing the ferrocene pattern to the usual pair of AA′BB′ virtual triplets.

Exposing a solution of **2** in C$_6$D$_6$ to 1 atm of ethylene led, after 2 min, to the consumption of 1 equiv of ethylene and formation of the monoinsertion product **4** (Scheme 3). This new species is $C_s$ symmetric, as evidenced by four ferrocene resonances in the $^1H$ NMR spectrum (4.01, 3.85, 3.04, and 2.66 ppm). The singlet

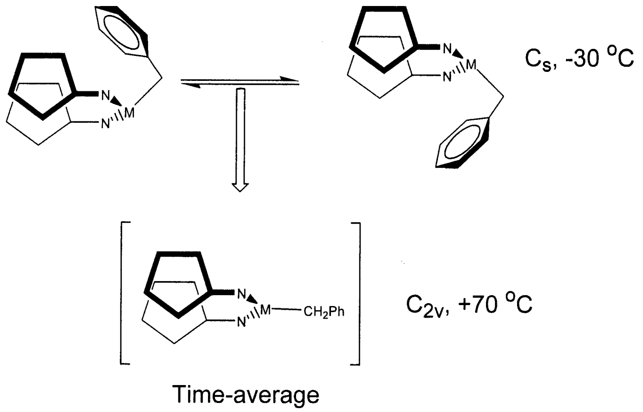
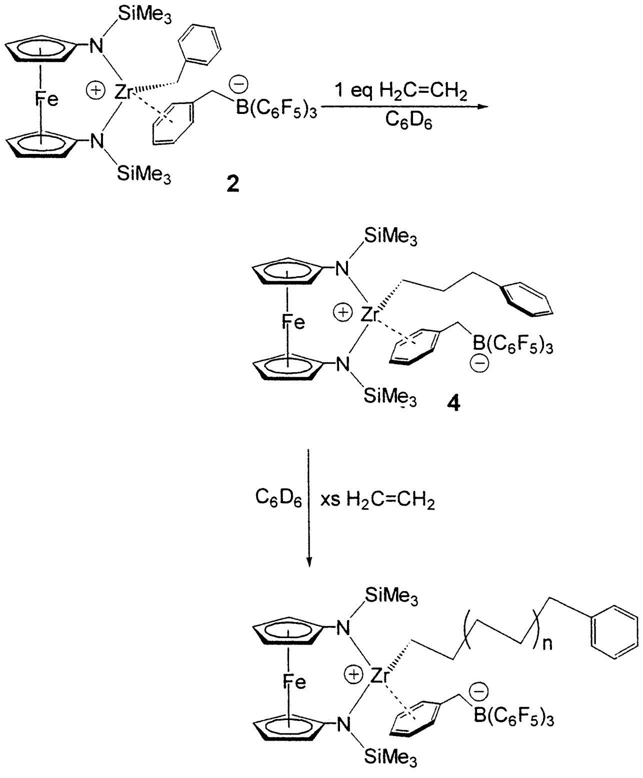


**Figure 3.** Fluxionality of the LMBn$^+$ species leading to a time-averaged $C_{2v}$-symmetric structure. The possible molecule of coordinated solvent is omitted from this illustration.

### Scheme 3



corresponding to the zirconium-bound benzyl methylene group in **2** was replaced by three methylene multiplets at 2.30, 1.00, and 0.98 ppm for the newly formed propylphenyl ligand. To confirm the stoichiometry of this reaction, the mixture was hydrolyzed with 1 M HCl and the organic products were analyzed using GC-MS. The only products observed were propylbenzene and toluene; the presence of the latter was attributed to hydrolysis of the benzylborate anion.

Even though subsequent insertions of ethylene were slower, the formation of longer chains was observed when ethylene was present in excess. With approximately 2 equiv of ethylene, di- and triinsertion products were detected by $^1$H NMR spectroscopy after 20 min. Each of the new species exhibited a set of four ferrocene resonances. The aliphatic protons of the growing polymer chain appeared as a multiplet at 0.8–1.3 ppm. The GC-MS analysis of the hydrolysis products revealed, in addition to propyl-, pentyl-, and heptylbenzene, small amounts of higher molecular weight alkylbenzenes, all conforming to the general formula $Bn(CH_2CH_2)_nH$ (Figure 4). No other types of hydrocarbons were observed by GC-MS, suggesting that the rate of $\beta$-H elimination is negligible in this system.[25]

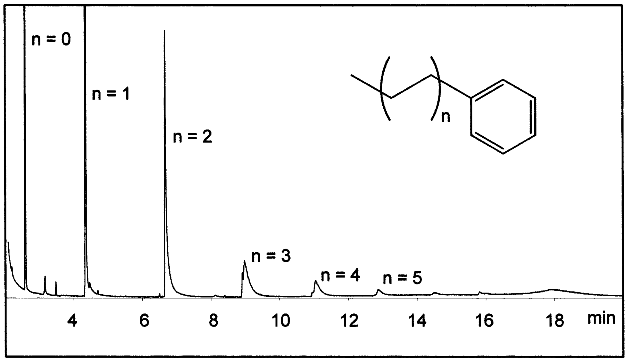
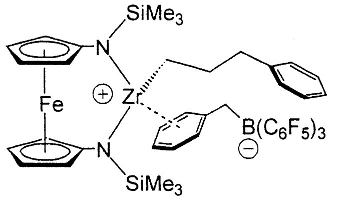
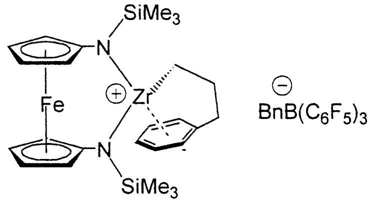


**Figure 4.** GC-MS trace of the hydrolysis products of the reaction between **2** and approximately 2 equiv of ethylene. The peaks correspond to the series $PhCH_2(CH_2CH_2)_nH$.

Two different structures can be envisioned for **4**. The benzylborate anion could bind zirconium in an $\eta^6$ fashion, leaving a dangling $\gamma$-phenylpropyl ligand (**4A**).



**4A**



**4B**

Alternatively, the increased flexibility of the three-methylene chain could allow the cation to be stabilized through an $\eta^6$ binding of the pendant $\gamma$-phenyl group to zirconium. Such binding would result in a separated ion pair (**4B**). Both types of structures are known in the literature, and the result often depends on the exact nature of the inserted molecule (e.g. ethylene vs propylene) and the counterion ($BnB(C_6F_5)_3$ vs $B(C_6F_5)_4$).[22–24,26] To probe the role of the anion, we attempted the preparation of the $B(C_6F_5)_4$-containing analogue of **4**. By using an anion incapable of binding to zirconium in an $\eta^6$ fashion, we expected to produce a type **B** structure; nonetheless, we were unable to obtain

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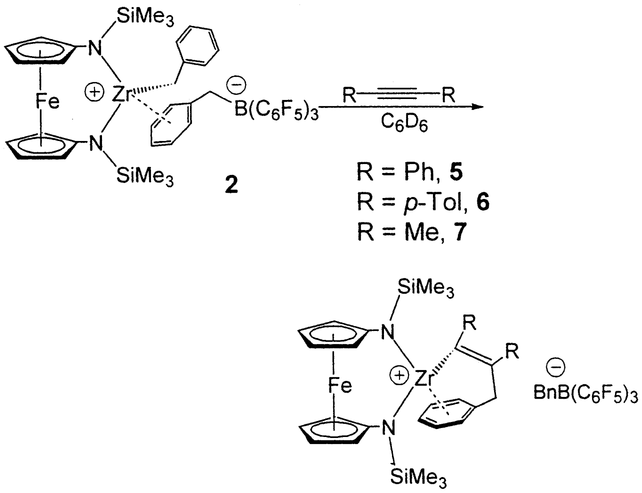
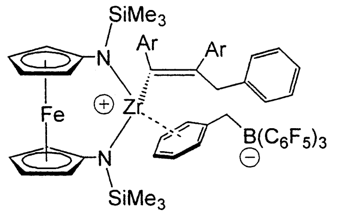
**Scheme 4**



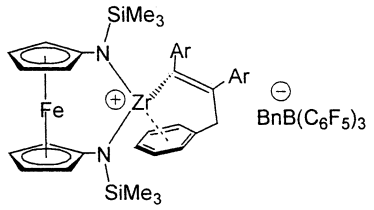
an ethylene monoinsertion product with compound **3**. Instead, introducing ethylene into an NMR tube containing a solution of **3** in $C_6D_5Cl$ resulted in the immediate formation of a polyethylene plug at the top of the solution. Indeed, compound **3** proved to be a competent ethylene polymerization catalyst, producing 102 g of PE $mmol^{-1}$ $atm^{-1}$ $h^{-1}$. Presumably, the initially formed type **B** monoinsertion product $[LZr(CH_2)_3Ph][B(C_6F_5)_4]$ (**4′**) inserted additional molecules of ethylene very rapidly. The strikingly different behavior of **4** and **4′** suggests that their structures are different, and the much-reduced reactivity of **4** argues well for the benzylborate-stabilized structure of type **4A**. Additionally for **4**, the value $\Delta\delta_F(m-p)$ was found to be 4.20 ppm, confirming coordination of the anion (see above).

Considering the slow rate of insertion of ethylene in **2**, it was not surprising to find this species to be inert toward substituted alkenes, such as 1-hexene. Nonetheless, we found **2** to be quite reactive toward disubstituted acetylenes, as shown in Scheme 4. Addition of diphenylacetylene or di-*p*-tolylacetylene to a $C_6D_5Cl$ or $C_6D_6$ solution of **2** resulted in the immediate formation of a red solution of $[LZrC(Ar){=}C(Ar)CBn][BnB(C_6F_5)_3]$ (**5**, Ar = Ph; **6**, Ar = *p*-tol). The $^1H$ NMR spectrum of **5** in $C_6D_5Cl$ featured four ferrocene ABCD multiplets (4.45, 4.16, 2.72, and 2.70 ppm), a broad $CH_2{-}B$ peak and a sharp $Ph{-}CH_2(C{=}C)$ methylene singlet. In the aromatic region one of the phenyl groups appeared downfield at 7.99 (o), 7.56 (m), and 6.85 (p) ppm, while another appeared upfield at 6.79 (m), 6.70 (p), and 6.40 ppm. In the spectrum of the *p*-tol derivative **6** the downfield resonances appear unchanged while the three aromatic upfield peaks are replaced by two doublets at 6.67 and 6.35 ppm. This allowed for the assignment of the downfield resonances to the $PhCH_2C{=}C$ phenyl group, while the upfield resonances were assigned to one of the vinylic phenyl $ArC{=}C$ groups. The signals for the second vinylic aryl group were obscured by the solvent and benzylborate aromatic resonances. Further support for the identity of **5** was obtained from a GC-MS analysis of the products of hydrolysis of the reaction mixture with 1 M HCl. The only product observed had a *m*/*z* ratio of 270 corresponding to the expected stilbene derivative $Ph(H)C{=}C(CH_2Ph)Ph$.

As was the case with the ethylene insertion product **4**, two possible structures are possible for **5** and **6**. The Zr cation can be stabilized either by an $\eta^6$ binding of the benzylborate anion (**A**) or by an $\eta^6$ binding of the allylphenyl ligand $-C{=}CCH_2Ph$ (**B**). To probe the role of the anion, a compound was synthesized in which $BnB(C_6F_5)_3^-$ was replaced with $B(C_6F_5)_5^-$ by reacting **3** with diphenylacetylene in $C_6D_5Cl$. The $^1H$ NMR spectrum of the resulting compound $[LZrC(Ph){=}C(Ph)CH_2Ph][B(C_6F_5)_4]$ (**5′**) was essentially identical with the spectrum of **5** in $C_6D_5Cl$ (but obviously lacked the benzylborate resonances). Neither **5** nor **5′** reacted with additional equivalents of PhCCPh or with ethylene. The similarities in the spectroscopic and chemical behavior of the two compounds are consistent with both belonging to the same structural type. Since complex **5′** cannot have a type **A** structure, both must be of type **B** with the pendant $C(Ph){=}C(Ph)CH_2Ph$ ligand stabilizing the cation in an $\eta^6$ fashion. The downfield shifts of the ortho and meta $-C{=}CCH_2Ph$ phenyl resonances (8.00 and 7.58 ppm) are also consistent with the spectral data for related compounds.[23,26]



**(5 or 6)A**

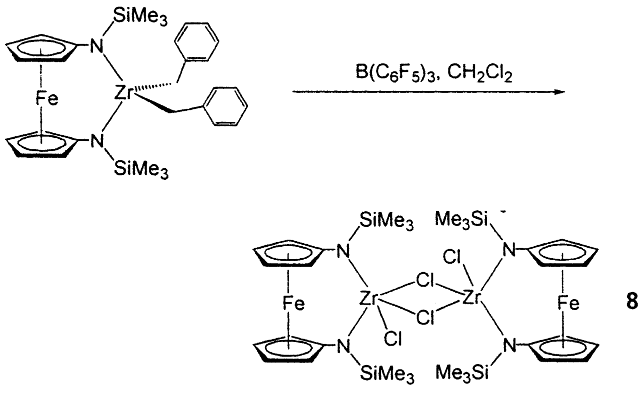


**(5 or 6)B**

Solutions of type **B** self-stabilized salts are expected to contain “free” $BnB(C_6F_5)_3^-$ anion. The $^1H$ NMR spectra of **5** and **6** in $C_6D_5Cl$ contained a $BCH_2$ methylene resonance at 3.29 ppm. Addition of approximately 0.5 equiv. of $[NEt_4][BnB(C_6F_5)_3]$ to the solutions of these salts did not change their $^1H$ NMR spectra, with the exception of the expected increase in the intensity of the $BCH_2$ peak and the appearance of $NEt_4$-related resonances. This experiment supports the formulation of **5** and **6** as separated ion pairs. Finally, the $\Delta\delta_F$(m−p) value ($^{19}F$ NMR) for **5** was found to be 2.97 ppm, consistent with a noncoordinated $BnB(C_6F_5)_3$. The value is essentially identical to that of the free $[NEt_4][BnB(C_6F_5)_3]$ (see Experimental Section).

While it is most likely that the cationic portions of **5** and **6** are stabilized through the coordination of pendant $-C{=}CCH_2Ph$ phenyl groups, the two other phenyl groups present in the $-C(Ph){=}C(Ph)CH_2Ph$ fragment could potentially serve this role. To address this problem, **2** was reacted with 2-butyne in $C_6D_6$, producing $[LZrC(Me){=}C(Me)CBn][BnB(C_6F_5)_3]$ (**7**) (Scheme 4), which separated from solution as a red oil. The cationic

**Scheme 5**



portion of **7** contains only one phenyl group as a part of the C(Me)=C(Me)CH$_2$Ph moiety.

The $^1$H NMR spectrum of **7** in CD$_2$Cl$_2$ contained four ferrocene resonances with the expected ABCD spin pattern. The two inequivalent methyl groups appeared at 1.84 and 1.37 ppm, exhibiting mutual long-range coupling with $^5J = 0.83$ Hz. The only product detected by the GC-MS analysis of the hydrolyzed reaction mixture was Me(H)C=C(CH$_2$Ph)Me, consistent with the proposed formulation of **7**. In the aromatic region the $^1$H NMR spectrum contained two sets of benzyl resonances, one assigned to the benzylborate anion and the other to the C(Me)=C(Me)CH$_2$Ph group. The latter appeared at 8.16 (o), 7.82 (m), and 7.41 (p) ppm; the downfield shift of these resonances can be associated with an $\eta^6$ mode of binding of this phenyl group to zirconium. The B$-$*CH$_2$* peak appeared at 2.88 ppm, and the addition of approximately 1 equiv of [NEt$_4$][BnB(C$_6$F$_5$)$_3$] to the sample resulted in the increase in the integration of this peak from 2H to 4H and the appearance of NEt$_4$-related resonances. As was the case with **5** and **6**, such addition of the "free" borate did not lead to any other changes in the $^1$H NMR spectrum. This suggests that in solution compound **7** is structurally similar to **5** and **6** with a type **B** self-stabilized cationic portion and that the pendant C=CCH$_2$*Ph* is indeed involved in the $\eta^6$ binding to zirconium.

Compound **7** reacted with additional equivalents of 2-butyne. Reaction of **2** with approximately 5 equiv of 2-butyne in C$_6$H$_6$ led, after 24 h, to the formation of a mixture of products. Hydrolysis of this mixture, and subsequent analysis by GC-MS, revealed the presence of the single-insertion product Me(H)C=C(Me)CH$_2$Ph as well as higher oligoacetylenes. Interestingly, while the triple- and quadruple-insertion products were found, GC-MS showed no evidence for the double-insertion product.

**Reaction of LZrBn$^+$ with CH$_2$Cl$_2$.** We have previously reported that the reaction of LTiMe$^+$ with CH$_2$Cl$_2$ produced the dimeric dication LTi($\mu$-Cl)$_2$TiL$^{2+}$.[19] The highly unusual geometry of the species prompted an attempt to generate the related hitherto unknown Zr analogue. Leaving a mixture of solutions of LZrBn$_2$ and B(C$_6$F$_5$)$_3$ in CH$_2$Cl$_2$ undisturbed for 18 h resulted in the formation of a yellow crystalline solid. X-ray diffraction analysis showed the solid to be the neutral [LZrCl$_2$]$_2$ (**8**) (Scheme 5) rather than the dicationic [LZr($\mu$-Cl)]$_2$$^{2+}$. In the solid state the compound exists as a dimer residing on a crystallographic inversion center (Figure 5). Each five-coordinate zirconium atom is bound to two bridging chlorides, one terminal chloride, and two nitrogen atoms of the Fc(NSiMe$_3$)$_2$$^{2-}$ ligand. The ferrocene group is in the fully eclipsed synclinal conformation, but the two Cp rings are at a 10.72° angle to each other, with the Cp$-$Cp wedge opening toward the zirconium atom. The compound is virtually insoluble in nonpolar solvents and CH$_2$Cl$_2$ but dissolved well in THF. The $^1$H NMR spectrum of **8** in THF-*d*$_8$ contains two virtual triplets for the ferrocene group. This pattern is indicative of a solution $C_{2v}$ symmetry, which is in contrast to the solid-state structure, where each ferrocene group possesses a local $C_s$ symmetry. This discrepancy can be explained by the coordination of THF molecules to the Zr center and the formation of monomeric LZrCl$_2$(THF)$_x$ complexes. In that case a fluxional process could render each ferrocene group $C_{2v}$ symmetric. Interestingly, the 2,5- (but *not* the 3,4-) ferrocene resonances in both $^1$H and $^{13}$C{$^1$H} NMR spectra of **8** are slightly broadened, presumably due to this fluxional process. Previous attempts to prepare this material in a more direct fashion, using salt metathesis reactions related to those that are successful in the Ti case, were in vain.[15]

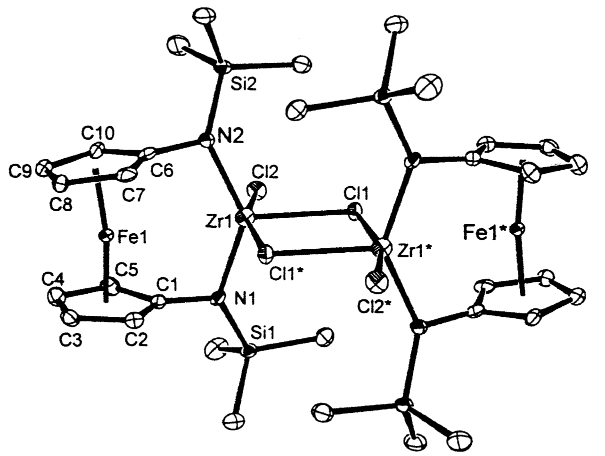


**Figure 5.** ORTEP diagram of [Fc(NSiMe$_3$)$_2$ZrCl($\mu$-Cl)]$_2$ (**8**) shown with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Zr1$-$Zr1* (nonbonding) = 4.1270(8), Zr1$-$Fe1 (nonbonding) = 3.2229(7), Zr1$-$Cl1 = 2.519(1), Zr1$-$Cl1* = 2.707(1), Zr1$-$Cl2 = 2.430(1), Zr1$-$N1 = 2.046(4), Zr1$-$N2 = 2.046(4). Selected bond angles (deg): N1$-$Zr1$-$N2 = 136.7(1), Cl1$-$Zr$-$Cl1* = 75.75(4), Cl1$-$Zr1$-$Cl2 = 88.68(4), Cl2$-$Zr$-$Cl1* = 164.15(4).

Activation of halogenated solvents by cationic Ti and Zr complexes is not unprecedented,[27,28] but the exact mechanism of this process remains unknown. Hydrolysis and subsequent GC-MS analysis of the mixture revealed the presence of 1,2-diphenylethane ("bibenzyl", *m/z* 182), possibly suggesting a SET mechanism for CH$_2$Cl$_2$ activation.

## Conclusions

We have shown that abstraction of a benzyl group from the ferrocene-containing Zr complex Fc(NSiMe$_3$)$_2$-

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$ZrBn_2$ ($LZrBn_2$, **1**) using $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$ resulted in formation of the stable cationic species [LZrBn][A] (**2**, A = $BnB(C_6F_5)_3$; **3**, A = $B(C_6F_5)_3$). Compound **2** was found to be a close-contact ion pair and in the solid state contained an $\eta^6$-coordinated benzylborate anion. The compound was found to cleanly insert ethylene and acetylene, and the rare ethylene single-insertion product **4** was observed by $^1H$ NMR. In solution, **4** appears to have an $\eta^6$-coordinated benzylborate anion; however, the related acetylene-insertion products feature noncoordinate benzylborate, as evidenced by $^1H$ and $^{19}F$ NMR spectroscopy. Finally, the “free” cationic $LZrBn^+$ proved to be an active ethylene polymerization catalyst.

## Experimental Section

**General Considerations.** Standard Schlenk-line and glovebox techniques were used unless otherwise indicated. Pentane, toluene, benzene, $Et_2O$, and $CH_2Cl_2$ were dried by passing through a column of activated alumina and degassed with argon prior to use. PhCl was stirred over $CaH_2$ and distilled. $Fc(NHSiMe_3)_2$,[15] $Zr(CH_2Ph)_4$,[29] $Ti(CH_2Ph)_4$,[30] $B(C_6F_5)_3$,[31] and $[Ph_3C][B(C_6F_5)_4]$[32] were prepared according to published procedures. $C_6D_6$ and THF-$d_8$ were vacuum-transferred from sodium/benzophenone. $C_6D_5Cl$ and $CD_2Cl_2$ were vacuum-transferred from $CaH_2$. $^1H$ NMR spectra were recorded on a Bruker AMX-300 or DRX-500 spectrometer. $^{13}C$, $^{19}F$, and $^{11}B$ NMR data were recorded on a Bruker DRX-500 spectrometer. $^1H$ NMR chemical shifts are given relative to $C_6D_5H$ (7.16 ppm), $CDHCl_2$ (5.32 ppm), and THF-$d_7$ (1.73 ppm). Due to overlap with aromatic resonances, the residual solvent protons in $C_6D_5Cl$ were difficult to observe. Therefore, all $^1H$ NMR spectra in this solvent were referenced to an external $SiMe_4$ (0.00 ppm) in $C_6D_5Cl$ standard. $^{13}C\{^1H\}$ NMR spectra are relative to $C_6D_6$ (128.3 ppm), $CD_2Cl_2$ (58.3 ppm), THF-$d_8$ (25.3 ppm), and $C_6D_5Cl$ (*C*Cl, 134.2 ppm). $^{11}B$ NMR spectra are referenced to external $BF_3{\cdot}Et_2O$ in $C_6D_6$ (0.00 ppm). $^{19}F$ NMR spectra are relative to $C_6D_5CF_3$ at −64.0 ppm in $C_6D_6$. Peak assignment was aided by 2D $^1H-^1H$ TOCSY and $^1H-^{13}C$ HMQC experiments. Elemental analyses were determined at the Microanalytical Laboratory of the College of Chemistry, University of California, Berkeley. Single-crystal X-ray structure determinations were performed at CHEXRAY, University of California, Berkeley.

**$[NEt_4][BnB(C_6F_5)_3]$.** A solution of BnMgCl (1.6 mL, 1.1 M in $Et_2O$, 1.8 mmol) was added to a solution of $B(C_6F_5)_3$ (900 mg, 1.75 mmol) in 30 mL of THF cooled to −60 °C. The reaction mixture was warmed to ambient temperature over a period of 1 h, at which point the solvent was removed under vacuum, affording a foamy white solid. The solid was dissolved in $CH_2Cl_2$, and a solution of $NEt_4Cl$ (390 mg, 1.80 mmol) in $CH_2Cl_2$ was added. The resulting mixture was filtered, and the solvent was removed in vacuo, affording 1.06 g (83%) of the product. $^1H$ NMR ($CD_2Cl_2$): $\delta$ 6.93 (t, 2H, *m*-Ph), 6.82 (t, 1H, *p*-Ph), 6.76 (d, 2H, *o*-Ph), 3.07 (q, 8H, $J_{HH} = 7.2$ Hz, $NCH_2CH_3$), 2.80 (br s, 2H, $BCH_2$), 1.25 (tt, 12H, $J_{HH} = 7.2$ Hz, $J_{HN} = 1.8$ Hz) ppm. $^{19}F$ NMR ($C_6D_5Cl$): $\delta$ −131.49 (d, *o*-F), −164.34 (t, *p*-F), −167.37 (m, *m*-F) ppm.

**$[Fc(NSiMe_3)_2ZrBn)][BnB(C_6F_5)_3]$ (2).** A solution of $B(C_6F_5)_3$ (240 mg, 469 $\mu$mol) in 3.5 mL of toluene was added to a Schlenk flask containing a solution of $LZrBn_2$ (**1**; 280 mg, 443 $\mu$mol) in 3.5 mL of toluene. The resulting orange solution was thoroughly mixed by shaking and then was allowed to stand for 24 h. At this point the large red crystals which appeared in the flask were collected by filtration. Drying of the crystals in vacuo led to a partial loss of solvent and powdering of the crystals. The crystals were found by $^1H$ NMR to contain 1 equiv of toluene. Yield (based on the formulation **2**$\cdot PhCH_3$): 418 mg, 76%. $^1H$ NMR ($C_6D_6$): $\delta$ 7.16 (d, 2H, *o*-Ph, $ZrCH_2Ph$), 6.85 (m, 2H, *m*-Ph, $ZrCH_2Ph$), 6.78 (m, 2H, *m*-Ph, $BCH_2Ph$), 6.59 (m, 2H, two overlapping *p*-Ph), 6.49 (d, 2H, *o*-Ph, $BCH_2Ph$), 3.90 (m, 2H, Fc), 3.87 (m, 2H, Fc), 3.09 (m, 2H, Fc), 3.08 (s br, 2H, B−C$H_2$), 2.30 (s, 2H, Zr−C$H_2$), 2.24 (m, 2H, Fc), 0.08 (s, 18H, $SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ 156.4, 148.7 (br d, $J_{C-F} = 247$ Hz), 142.4, 139.0 (br d, $J_{C-F} = 249$ Hz), 137.5 (br d, $J_{C-F} = 254$ Hz), 130.6, 129.8, 129.3, 125.6, 123.3, 88.0 (*ipso*-Fc), 75.9 (Fc), 72.4 (Fc), 70.4 (Fc), 69.4 ($Zr-CH_2$), 69.3 (Fc), 36 (B−*C*$H_2$, not directly observed, value obtained from a $^1H-^{13}C$ HMQC experiment), 1.1 ($SiMe_3$) ppm. $^{11}B$ NMR ($C_6D_6$): $\delta$ −12.7 ppm. $^{19}F$ NMR ($C_6D_6$): $\delta$ −132.10 (d, *o*-F), −161.49 (t, *p*-F), −165.81 (m, *m*-F) ppm. Anal. Calcd for $C_{48}H_{40}BF_{15}FeN_2Si_2Zr{\cdot}C_7H_8$: C, 53.45; H, 3.91; N, 2.27. Found: C, 53.60; H, 4.04; N, 2.27.

**Observation of $[Fc(NSiMe_3)_2ZrBn][B(C_6F_5)_4)]$ (3).** A solution of $[Ph_3C][B(C_6F_5)]$ (42 mg, 45 $\mu$mol) in 0.8 mL of $C_6D_6$ was added to a solution of **1** (28 mg, 44 $\mu$mol) in 0.8 mL of $C_6D_6$. The resulting cloudy mixture was allowed to stand undisturbed for 10 min, resulting in the formation of a layer of a red oil. The supernatant solution was decanted, and the oil was dissolved in 0.6 mL of $C_6D_5Cl$. In addition to **3** the solution contained a small amount (approximately 5%) of $Ph_3CCH_2Ph$ ($CH_2$ at 3.83 ppm). $^1H$ NMR of **3** at +70 °C ($C_6D_5Cl$): $\delta$ 7.42 (t, 2H, *m*-Ph), 7.15 (t, 1H, *p*-Ph), 6.66 (d, 2H, *o*-Ph), 4.43 (virt t, 4H, Fc), 3.15 (virt t, 4H, Fc), 3.03 (s, 2H, Ph*C*$H_2$), −0.07 (s, 18H, $SiMe_3$) ppm. $^1H$ NMR of **3** at −30 °C ($C_6D_5Cl$): $\delta$ 7.50 (br s, 2H, *m*-Ph), 7.20 (t, 1H, *p*-Ph), 6.66 (d, 2H, *o*-Ph), 4.60 (br s, 2H, Fc), 4.21 (br s, 2H, Fc), 4.38 (br s, 2H, Fc), 3.10 (s, 2H, Ph*C*$H_2$), 3.02 (br s, 2H, Fc), 0.06 (s, 18H, $SiMe_3$) ppm.

**Observation of $[Fc(NSiMe_3)_2Zr(CH_2CH_2CH_2Ph)][BnB(C_6F_5)_3]$ (4).** To a solution of **1** (14 mg, 22 $\mu$mol) in 0.3 mL of $C_6D_6$ was added a solution of $B(C_6F_5)_3$ (12 mg, 23 $\mu$mol) in 0.3 mL of $C_6D_6$. The resulting orange solution was transferred to an NMR tube capped with a rubber septum. Through the septum ethylene (approximately 1.2 equiv) was injected using a syringe. The $^1H$ NMR spectrum was recorded after 2 min. $^1H$ NMR: $\delta$ 7.16−7.14 (m, 4H), 4.01 (m, 2H, Fc), 3.85 (m, 2H, Fc), 3.31 (br d, 2H, B-*C*$H_2$), 3.04 (m, 2H, Fc), 2.66 (m, 2H, Fc), 2.31 (m, 2H, $CH_2$), 1.00 (m, 4H, $CH_2$), −0.02 (s, 18H, $SiMe_3$) ppm. $^{19}F$ NMR ($C_6D_6$): $\delta$ −131.99 (d, *o*-F), −161.71 (t, *p*-F), −165.92 (m, *m*-F) ppm.

**$[Fc(NSiMe_3)_2Zr(C(Ph){=}C(Ph)CH_2Ph)][BnB(C_6F_5)_3]$ (5).** A Schlenk tube was charged with **1** (250 mg, 0.396 mmol), diphenylacetylene (72 mg, 0.40 mmol), and 8 mL of benzene. The resulting solution was added to a solution of $B(C_6F_5)_3$ (205 mg, 0.400 mmol) in 8 mL of benzene. A red mixture formed immediately, from which a dark red oil separated after 10 min. At this point the solvent was removed in vacuo and the red sticky solid was washed with two 10 mL portions of pentane. Drying the resulting sticky solid in vacuo at 50 °C for 30 min resulted in 467 mg of a yellow flaky solid of **5** (350 mmol, 90%). $^1H$ NMR ($C_6D_6$): $\delta$ 7.74 (d, 2H, 6.9 Hz), 7.34 (t, 2H, 7.6 Hz), 7.28 (d, 2H, 7.3 Hz), 7.07−7.02 (m, 6H), 6.97 (m, 1H), 6.92 (t, 1H, 7.3 Hz), 6.71 (t, 2H, 7.6 Hz), 6.63 (m, 2H), 6.38 (m, 2H), 4.24 (m, 2H, Fc), 4.08 (m, 2H, Fc), 3.95 (s, 2H, Ph−*C*$H_2$), 3.45 (br s, 2H, B−*C*$H_2$), 2.63 (m, 2H, Fc), 2.60 (m, 2H, Fc), 0.03 (s, 18H, $SiMe_3$) ppm. $^1H$ NMR ($C_6D_5Cl$): $\delta$ 7.99 (d, 2H, *o*-Ph, *Ph*$CH_2C{=}C$), 7.56 (t, 2H, *m*-Ph, *Ph*$CH_2C{=}C$), 7.2−6.9 (m, 9H), 6.88 (t, 1H, *p*-Ph, *Ph*$CH_2C{=}C$), 6.84 (t, 1H, *p*-Ph), 6.79 (t, 2H, *m*-Ph, *Ph*C=C), 6.70 (t, 1H, *p*-Ph, *Ph*C=C), 6.39 (d, 2H, *o*-Ph, *Ph*C=C), 4.45 (m, 2H, Fc), 4.16 (m, 2H, Fc), 4.11 (s, 2H, Ph*C*$H_2C{=}C$), 3.29 (s, br, 2H, B*C*$H_2$), 2.72 (m, 2H, Fc), 2.70 (m, 2H, Fc), 0.06 (s, 18H, $SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$

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204.6, 168.6, 154.6, 149.2 (br d, $J_{C-F} = 238$ Hz), 149.0, 141.8, 140.1, 138.3 (br d, $J_{C-F} = 238$ Hz), 137.3 (br d, $J_{C-F} = 238$ Hz), 132.4, 131.6, 128.6, 125.6, 123.9, 123.4, 87.9 (Fc$_{ipso}$), 77.2 (Fc), 71.2 (Fc), 70.7 (Fc), 68.4 (Fc), 47.2 (Ph$CH_2$C=C), 33 (B$CH_2$, not directly observed, value obtained from a $^1$H−$^{13}$C HMQC experiment), 0.8 ($SiMe_3$) ppm. $^{11}$B NMR ($C_6D_6$): $\delta$ −12.8 ppm. $^{19}$F NMR ($C_6D_6$): −131.53 (d, *o*-F), −164.40 (t, *p*-F), −167.33 (m, *m*-F) ppm. Anal. Calcd for $C_{67}H_{62}BF_{15}FeN_2Si_2Zr$: C, 56.32; H, 3.81; N, 2.12. Found: C, 55.89; H, 3.81; N, 2.12.

**Observation of [Fc(NSiMe$_3$)$_2$Zr(C(Ph)=C(Ph)CH$_2$Ph)][B(C$_6$F$_5$)$_4$] (5′).** A solution of $[Ph_3C][B(C_6F_5)]$ (42 mg, 45 $\mu$mol) in 0.3 mL of $C_6D_6$ was added to a vial containing **1** (28 mg, 44 $\mu$mol) and diphenylacetylene (8 mg, 45 $\mu$mol) dissolved in 0.3 mL of $C_6D_6$. A layer of red oil separated from the resulting solution after 10 min. The supernatant solution was decanted, and the oil was redissolved in $C_6D_5Cl$. According to $^1$H NMR spectroscopy the solution contained **5′** as well as residual $Ph_3CCH_2Ph$ (approximately 5%, $CH_2$ at 3.83 ppm). $^1$H NMR of **5′** ($C_6D_5Cl$): $\delta$ 8.01 (d, 2H, *o*-Ph, *Ph*CH$_2$C=C), 7.57 (t, 2H, *m*-Ph, *Ph*CH$_2$C=C), 7.2−6.9 (m, 5 *Ph*C=C protons overlapping with solvent), 6.89 (t, 1H, *p*-Ph, *Ph*CH$_2$C=C), 6.81 (t, 2H, *m*-Ph, *Ph*C=C), 6.72 (t, 1H, *p*-Ph, *Ph*C=C), 6.40 (d, 2H, *o*-Ph, *Ph*C=C), 4.43 (m, 2H, Fc), 4.11 (m, 2H, Fc), 4.10 (s, 2H, Ph$CH_2$C=C), 2.70 (m, 2H, Fc), 2.64 (m, 2H, Fc), −0.10 (s, 18H, $SiMe_3$) ppm.

**Observation of [Fc(NSiMe$_3$)$_2$Zr(C(*p*-tol)=C(*p*-tol)CH$_2$Ph)][BnB(C$_6$F$_5$)$_3$] (6).** Addition of a solution of $B(C_6F_5)_3$ (24 mg, 46 $\mu$mol) in 0.3 mL of $C_6D_5Cl$ to a vial containing **1** (28 mg, 44 $\mu$mol) and di-*p*-tolylacetylene (9.5 mg, 46 $\mu$mol) dissolved in 0.3 mL of $C_6D_5Cl$ afforded a clear red solution. $^1$H NMR ($C_6D_5Cl$): $\delta$ 7.97 (d, 2H, *o*-Ph), 7.55 (t, 2H, *m*-Ph), 6.67 (d, 2H, *m*-tol), 6.35, (d, 2H, *o*-tol), 4.45 (m, 2H, Fc), 4.16 (m, 2H, Fc), 4.14 (s, 2H, Ph$CH_2$C=C), 3.29 (s br, 2H, B$CH_2$), 2.78 (m, 2H, Fc), 2.73 (m, 2H, Fc), 2.04 (s, 3H, Me), 1.93 (s, 3H, Me), 0.07 (s, 18H, $SiMe_3$) ppm. $^{13}$C{$^1$H} NMR ($C_6D_5Cl$): $\delta$ 205.7, 168.5, 154.8, 149.0, 148.8 (br d, $J_{C-F} = 236$ Hz), 138.5, 138.1, 138.0 (br d, $J_{C-F} = 238$ Hz), 137.1, 137.0 (br d, $J_{C-F} = 236$ Hz), 135.6, 132.4, 131.7, 131.4, 128.1, 123.8, 123.2, 87.8 (*ipso*-Fc), 77.0 (Fc), 71.0 (Fc), 70.5 (Fc), 68.6 (Fc), 47.2 (Ph$CH_2$C=C), 33 (br, B−$CH_2$, not directly observed, value obtained from a $^1$H−$^{13}$C HMQC experiment), 21.04 (Me), 20.7 (Me), 0.9 ($SiMe_3$) ppm.

**[Fc(NSiMe$_3$)$_2$Zr(C(Me)=C(Me)CH$_2$Ph)][BnB(C$_6$F$_5$)$_3$] (7).** Addition of 2-butyne (36 $\mu$L, 460 $\mu$mol) to a solution of **1** (280 mg, 443 $\mu$mol) in 5 mL of $C_6H_6$ followed by a solution of $B(C_6F_5)_3$ (235 mg, 460 $\mu$mol) in 5 mL of $C_6H_6$ resulted after 2 min of stirring in the formation of a red cloudy solution. The mixture was allowed to settle, producing a layer of dark red oil at the bottom of the flask. The supernatant solution was decanted, and the oil was washed with two 10 mL portions of pentane. Upon drying in vacuo at 50 °C for 30 min the product was isolated as a yellow powder. Yield: 428 mg (358 $\mu$mol, 81%). $^1$H NMR ($CD_2Cl_2$): $\delta$ 8.15 (m, 2H), 7.82 (m, 2H), 7.41 (m, 1H), 6.94 (m, 2H), 6.86 (m, 1H), 6.82 (m, 2H), 4.99 (m, 2H, Fc), 4.44 (m, 2H, Fc), 3.95 (s, 2H, Ph−$CH_2$), 3.51 (m, 2H, Fc), 3.05 (m, 2H, Fc), 2.88 (br s, 2H, B−$CH_2$), 1.84 (q, 3H, $^5J = 0.8$ Hz, C=C*Me*), 1.38 (q, 3H, $^5J = 0.8$ Hz, *Me*C=C), 0.12 (s, 18H, $SiMe_3$) ppm. $^{13}$C{$^1$H} NMR ($CD_2Cl_2$): $\delta$ 206.9, 170.0, 157.4, 148.6 (br d, $J_{C-F} = 246$ Hz), 137.9 (br d, $J_{C-F} = 242$ Hz), 136.8 (br d, $J_{C-F} = 242$ Hz), 133.1, 131.8, 129.1, 127.2, 125.8, 90.0 (*ipso*-Fc), 77.4 (Fc), 71.5 (Fc), 70.5 (Fc), 69.0 (Fc), 48.7 (Ph$CH_2$C=C), 35 (B−$CH_2$, not directly observed, value obtained from a $^1$H−$^{13}$C HMQC experiment), 19.2 (C=C*Me*), 19.1 (*Me*C=C), 0.9 ($SiMe_3$) ppm. Anal. Calcd for $C_{52}H_{46}BF_{15}FeN_2Si_2Zr$: C, 52.13; H, 3.87; N, 2.34. Found: C, 52.40; H, 3.80, N, 2.28.

**Reaction of 2 with Several Equivalents of 2-Butyne.** The reaction was set up in a manner identical with the synthesis of **7**, but approximately 5 equiv of 2-butyne was used. The mixture was allowed to react for 24 h, at which point the volatile fraction was removed under reduced pressure, affording an orange powder. $^1$H NMR of the powder showed several ferrocene-containing compounds. GC-MS analysis of a hydrolyzed mixture (1 M HCl) showed peaks consistent with the single-insertion product Me(H)C=C(Me)CH$_2$Ph (*m*/*z* 146), as well as triple- and quadruple-insertion products (*m*/*z* 254 and 308, respectively).

**Table 1. Crystallographic Data for 2 and 8**

| | **2**·$C_6D_6$ | **8**·$CH_2Cl_2$ |
|---|---|---|
| mol formula | $C_{54}H_{46}N_2BF_{15}FeSi_2Zr$ | $C_{17}H_{28}N_2Si_2ZrFeCl_4$ |
| fw | 1221.99 | 605.4 |
| cryst color, habit | yellow block | yellow plate |
| cryst size (mm) | 0.28 × 0.21 × 0.18 | 0.32 × 0.24 × 0.12 |
| cryst syst | triclinic | triclinic |
| space group | $P\bar{1}$ | $P\bar{1}$ |
| $a$ (Å) | 13.1328(3) | 10.8988(3) |
| $b$ (Å) | 13.7959(3) | 10.9214(4) |
| $c$ (Å) | 16.6316(4) | 12.2609(4) |
| $\alpha$ (deg) | 80.143(1) | 112.123(1) |
| $\beta$ (deg) | 79.695(1) | 101.207(1) |
| $\gamma$ (deg) | 62.849(1) | 105.035(1) |
| $V$ (Å$^3$) | 2624.2(1) | 1234.16(7) |
| $Z$ | 2 | 2 |
| $D_c$ (g cm$^{-3}$) | 1.546 | 1.629 |
| temp (°C) | −131 | −160 |
| radiation ($\lambda$, Å) | Mo K$\alpha$ (0.710 69) | |
| $\mu$ (cm$^{-1}$) | 6.13 | 15.45 |
| $T_{min}/T_{max}$ | 0.786 | 0.720 |
| $R_{merge}$ | 0.040 | 0.057 |
| $R$, $R_w$, $R_{all}$ | 0.040, 0.050, 0.056 | 0.034, 0.042, 0.038 |
| GOF | 1.25 | 1.72 |
| largest shift/error | 0.00 | 0.00 |
| max, min peak in diff map (e Å$^{-3}$) | 0.66/−1.35 | 0.86/−0.96 |

**[Fc(NSiMe$_3$)$_2$ZrCl($\mu$-Cl)]$_2$ (8).** A solution of **1** (190 mg, 300 $\mu$mol) in 1.7 mL of $CH_2Cl_2$ was added to a solution of $B(C_6F_5)_3$ (156 mg, 305 $\mu$mol) in 1.7 mL of $CH_2Cl_2$. The resulting yellow solution was left undisturbed for 18 h, at which point yellow crystals were collected. The crystals were found to incorporate 1 equiv of $CH_2Cl_2$, but this solvent was quickly lost upon drying under vacuum. Yield: 114 mg, 74%. $^1$H NMR (THF-$d_8$): $\delta$ 4.59 (virt t, 4H, Fc), 3.27 (br, virt t, 4H, Fc), 0.21 (s, 18H, $SiMe_3$) ppm. $^{13}$C{$^1$H} NMR (THF-$d_8$): $\delta$ 87.3 (*ipso*-Fc), 72.0 (Fc), 68.4 (br, Fc), 0.5 ($SiMe_3$) ppm. Anal. Calcd for $C_{32}H_{52}N_4Cl_4Fe_2Si_4Zr_2$: C, 36.92; H, 5.03; N, 5.38. Found: C, 37.12; H, 5.23; N, 5.18.

**Procedure for Ethylene Polymerization by 3.** A Schlenk tube was charged with 46 $\mu$mol of complex **1** and 46 $\mu$mol of $[Ph_3C][B(C_6F_5)_4]$ (42 mg). In the tube was added 5 mL of $C_6H_5Cl$,and the mixture was stirred for 2 min. At this point the flask was evacuated briefly and then refilled with ethylene. The flask was warmed immediately, and a thick mixture formed. After 5.0 min the reaction mixture was quenched with acidified MeOH (30 mL). The resulting white polyethylene was isolated by filtration, washed with additional portions of MeOH, and dried for 10 h at 100 °C.

**General Procedures for X-ray Crystallography.** Pertinent details for the individual compounds can be found in Table 1. Crystals of **2** were grown from a $C_6D_6$ solution. Crystals of **8** were formed when a solution of **2** in $CH_2Cl_2$ was allowed to stand undisturbed for 24 h. A crystal of appropriate size was mounted on a glass capillary using Paratone-N hydrocarbon oil. The crystal was transferred to a Siemens SMART diffractometer/CCD area detector,[33] centered in the beam, and cooled by a nitrogen flow low-temperature apparatus that had been previously calibrated by a thermocouple placed at the same position as the crystal. Preliminary orientation matrix and cell constants were determined by collection of 60 10 s frames, followed by spot integration and

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(33) SMART: Area-Detector Software Package; Siemens Industrial Automation, Madison, WI, 1995.

least-squares refinement. An arbitrary hemisphere of data was collected, and the raw data were integrated using SAINT.[34] Cell dimensions reported in Table 1 were calculated from all reflections with $I > 10\sigma$. Data were analyzed for agreement and possible absorption using XPREP.[35] An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS.[36] The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. The structures were solved and refined with the teXsan software package.[37] All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included as fixed contributions. ORTEP diagrams were created using the ORTEP-3 software package.[38]

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**Supporting Information Available:** Text and tables giving details of the X-ray crystallographic data for **2** and **8**; data are also available as an electronic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(34) SAINT: SAX Area Detector Integration Program, V4.024; Siemens Industrial Automation, Madison, WI, 1995.

(35) XPREP: Part of SHELXTL Crystal Structure Determination Package, V5.03; Siemens Industrial Automation, Madison, WI, 1995.

(36) SADABS: Siemens Area Detector ABSorption Correction Program; Siemens Industrial Automation, Madison, WI, 1996.

(37) TeXsan: Crystal Structure Analysis Software Package; Molecular Structure Corp., The Woodlands, TX, 1992.

(38) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.