Reaction of the Lewis Acids $B(C_6F_5)_3$ and $(AlMe_2Cl)_2$ with Azazirconacycles

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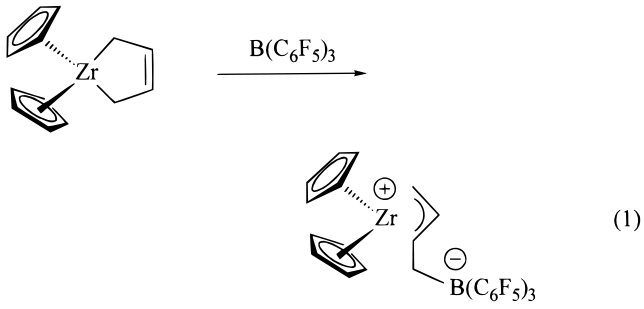
$B(C_6F_5)_3$ opens the ring of the *N*-^{t}Bu azazirconacyclobutane **2** by abstracting the carbon from the zirconium; the resulting amido cation **3** reacts slowly with ethylene to form a chelating γ-iminoalkyl zirconocene cation, **4**. Similarly, $B(C_6F_5)_3$ removes carbon from the Zr of the *N*-Ph azazirconacyclopentane **5a** and the *N*-$SiMe_3$ azazirconacyclopentane **5b**, forming amido cations that are stabilized in the solid state by coordination of phenyl substituents on N (**6**, from **5a**) or C (**8**, from **5b**); **8** slowly loses hydrogen, forming an azaallyl cation **9**. In contrast $AlMe_2Cl$ coordinates the N of the zirconaaziridines **10**, resulting in an sp^2 N coordinated to Zr through a p orbital. The structures of **4**, **6**, **8**, and **11a** have been established by X-ray crystallography.

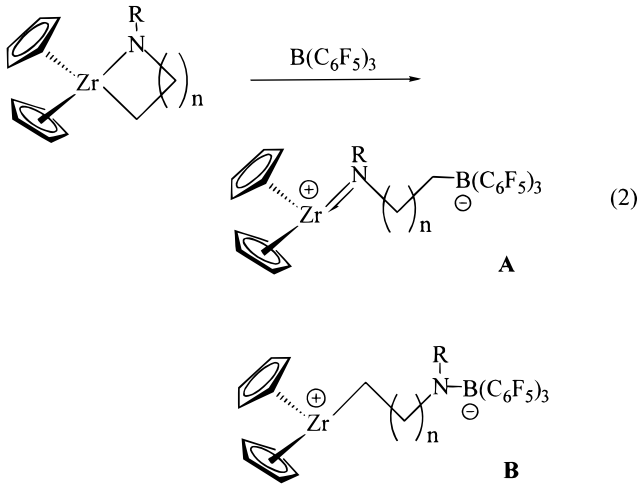
Introduction

The ability of $B(C_6F_5)_3$[1] to abstract an alkyl group from metallocene dialkyls is well-known from numerous studies relating to Ziegler/Natta polymerization of olefins.[2−4] For example, the abstraction of a methylene group from a zirconacyclopentene, illustrated in eq 1, leads to an active olefin polymerization catalyst with the counteranion tethered to the end of the growing chain.[5,6]



(1)

Because of our interest in zirconaaziridines,[7] we decided to investigate the reaction of $B(C_6F_5)_3$ and $(Me_2AlCl)_2$ with these and other azazirconacycles. As the methyl and amide ligands in $Cp_2Zr(Me)(NR_2)$ are abstracted competitively by $B(C_6F_5)_3$,[8] we expected that $B(C_6F_5)_3$ would abstract from the zirconium in eq 2 either the carbon ligand (giving **A**) or the nitrogen ligand (giving the potential zwitterionic catalyst **B**). We have found that $B(C_6F_5)_3$ treatment of several azazirconacycles removes the carbon ligand exclusively, while $AlMe_2Cl$ coordinates to the nitrogen of zirconaaziridines.



(2)

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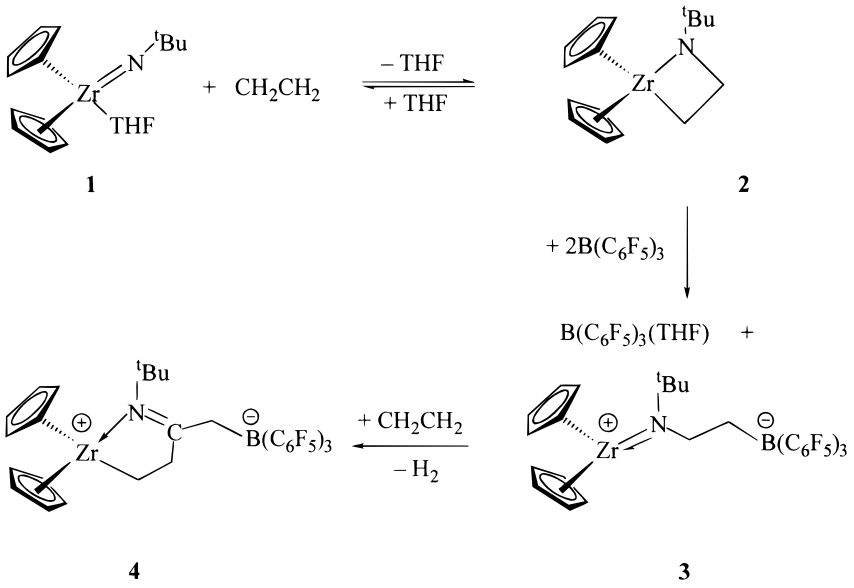
Scheme 1



Results

Reaction of the Azazirconacyclobutane 2 with $B(C_6F_5)_3$. The azazirconacyclobutane **2** is available from the reversible reaction of ethylene with the terminal imido complex **1**.[9] The addition of 2 equiv of $B(C_6F_5)_3$ to an ethylene-saturated solution of **1** in C_6D_6 results in an immediate color change from light yellow to purple; the $B(C_6F_5)_3$ adduct **3** is formed, along with $B(C_6F_5)_3$(THF) (Scheme 1).

We have not been able to isolate **3**, but the room-temperature NMR data in C_6D_6 are consistent with the structure drawn in Scheme 1. (We found no solvent suitable for low-temperature spectra in which **3** was soluble and stable.) The ^{13}C NMR resonance of the CH_2 group attached to $B(C_6F_5)_3$ is not observed in a standard spectrum because of residual coupling to the boron (an effect noticed in similar $B(C_6F_5)_3$ complexes[5a]) but can be found at δ 7.9 in the HMQC spectrum of **3**. There is no evidence for a Zr−F interaction (the ^{19}F spectrum of **3** shows only one set of *o*, *m*, and *p* resonances, respectively, for the $B(C_6F_5)_3$ moiety). There is no evidence of an agostic interaction between the Zr and a methylene C−H bond (such interactions can result in an upfield shift of the methylene ^1H NMR resonances[6a]).

At room temperature solutions of **3** containing excess ethylene slowly form (Scheme 1) **4**, which has been isolated as a yellow crystalline solid. When examined by X-ray crystallography, crystals of **4** grown from toluene/hexanes contained a molecule of toluene and a molecule of hexane in each unit cell; both solvent molecules were disordered. (Complex **4** can be obtained solvent free by recrystallization from CH_2Cl_2/hexanes.) The molecular structure of **4** in these solvent-containing crystals is shown in Figure 1. The ^1H NMR and HMQC spectra of solutions of **4** imply that its solid-state structure is retained in solution. Again, the ^{13}C NMR resonance of the CH_2 group attached to $B(C_6F_5)_3$ is not observed in a standard spectrum but is readily apparent in the HMQC spectrum (δ 36.5).

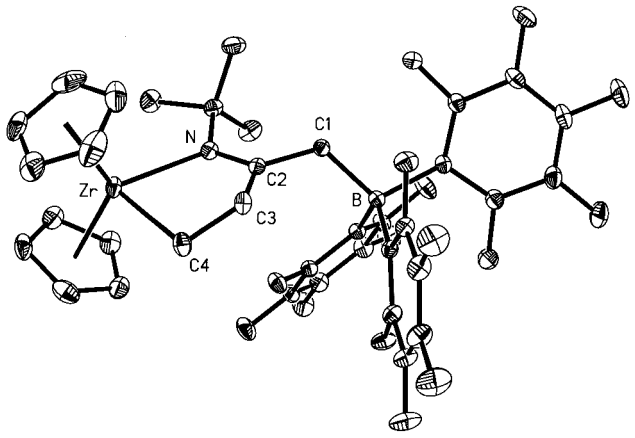


Figure 1. Molecular structure of **4**. Selected bond lengths (Å) and angles (deg): Zr−N 2.3313(17), Zr−C4 2.262(2), N−C2 1.308(2), C2−C3 1.509(3), C3−C4 1.529(3), C2−C1 1.489(3), C1−B 1.685(3), Zr−N−C2 115.35(13), Zr−C4−C3 105.53(14), N−C2−C1 127.62(18), N−C2−C3 115.94(17), C2−C1−B 121.87(15), C2−C3−C4 115.33(16), N−Zr−C4 76.19(7), C1−C2−C3 116.03(16).

Complex **4** is formally the result of the addition of two ethylenes to **1**, along with the loss of two hydrogens. ^1H NMR shows that the conversion of **3** to **4** occurs in high yield, but the solution thickens and small amounts of polyethylene precipitate. However, at room temperature ethylene-saturated solutions of **4** in C_6D_6 or CD_2Cl_2 do not yield polyethylene, so its formation during the conversion of **3** to **4** is due to a small amount of highly active impurity or decomposition product. Addition of diphenylacetylene to a freshly prepared solution of **3** almost completely suppressed polyethylene formation, presumably by trapping the active polymerization catalyst, without affecting the formation of **4**.

Reaction of the Azazirconacyclopentanes 5 ($Cp_2Zr(NRCHPhCH_2CH_2)$, R = Ph, 5a; R = $SiMe_3$, 5b) with $B(C_6F_5)_3$. Addition of 1 equiv of $B(C_6F_5)_3$ to an orange solution of the azazirconacyclopentane **5a** in benzene results (eq 3) in the formation of **6**, which precipitates as brown crystals of **6**·1.5(C_6H_6) after the addition of hexanes. Pure **6**, without molecules of solvation, can be obtained by synthesis in or recrystal-

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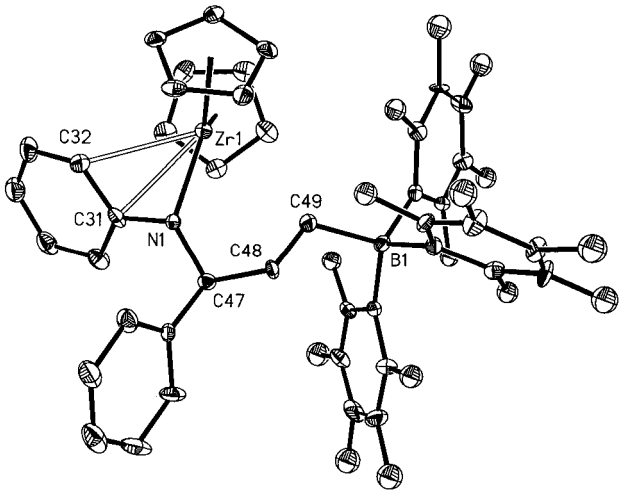
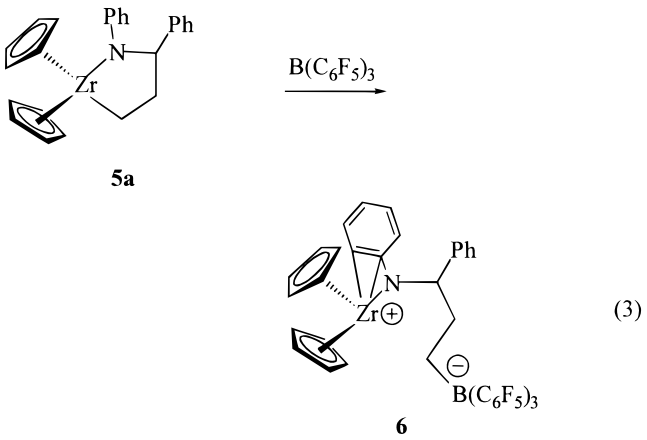


Figure 2. Molecular structure of **6**. Selected bond lengths (Å) and angles (deg): Zr1−N1 2.112(5), Zr1−C31 2.638(7), Zr1−C32 2.711(8), Zr1−C49 3.002(7), N−C31 1.384(8), N1−C47 1.466(8), C49−B1 1.668(11), Zr1−N1−C31 95.7(4), Zr1−N1−C47.

lization from toluene/hexanes. Crystals of both **6** and **6**·1.5(C_6H_6) did not give X-ray diffraction data of high quality; solution of the best data set gave the connectivity displayed in Figure 2 and drawn in eq 3, with one *N*-phenyl double bond weakly coordinated to the Zr (the Zr1−C31 bond length is 2.638(7) Å and the Zr1−C32 bond length is 2.711(8) Å).

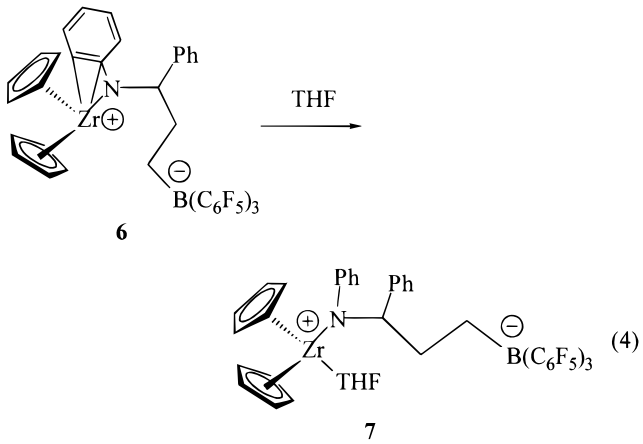


(3)

This interaction persists in solution. One aromatic ring of **6** shows five inequivalent ^{1}H and five inequivalent ^{13}C resonances at low temperature (223 K) in CD_2Cl_2. Solution coordination of the carbons pictured in eq 3 is implied by the upfield NMR shift of one ortho proton (δ 6.41 at 223 K) and its associated carbon (δ 83.9) (the ipso carbon has not been located); the other ortho proton and its carbon appear in normal locations (δ 6.82 and 119.0, respectively). As the sample is warmed to room temperature, the two pairs of ortho and meta proton resonances coalesce, presumably as a result of the dissociation of the coordinated carbons. In C_6D_6 the averaged ^{1}H signal (δ 5.87) observed for both ortho protons at room temperature is shifted even further upfield.

Such upfield shifts can be attributed to the interaction of an aryl group with a zirconium center.[10] A temperature-dependent high-field shift (δ −0.94 at 298 K, δ −2.12 at 223 K; CD_2Cl_2) of one of the methylene protons of the $CH_2B(C_6F_5)_3$ group suggests an agostic interaction with the zirconium that increases as the temperature is lowered;[6c] however, the ^{13}C NMR of the methylene carbon resonance in **6** (δ 20.3) remains about the same in the THF adduct **7** (δ 19.5) (see below). (Erker has reported a case in which displacement of an agostic $CH_2B(C_6F_5)_3$ by THF from a zirconocene cation resulted in a downfield shift of ca. 25 ppm.[5c])

Addition of ethylene (2−3 atm) to toluene solutions of **6** (25−70 °C) results (after a short induction period) in low yields of polyethylene; again, a decomposition product is probably responsible. Addition of THF to crystalline **6** or slurries of **6** in toluene causes a rapid color change from brown to yellow and the formation of **7** (eq 4), with coordination of the THF replacing coordination of the two aromatic carbons in **6**. Complex **7** is completely insoluble in aromatic solvents and CD_2Cl_2 but dissolves readily in THF. Its ^{1}H NMR shows two phenyl resonances slightly upfield from the others; however, COSY, HMQC, and HMBC experiments suggest that they belong *not* to the ortho *N*-Ph protons but to the meta *N*-Ph protons (δ 6.31, m) and ortho *C*-Ph protons (δ 6.45, d). Furthermore, no ^{13}C NMR resonances, including those of the carbons to which these protons are attached (δ 129.4 and 130.0, respectively, at 294 K), are shifted upfield; all remain unchanged even at low temperature (203 K). It is clear that neither aromatic ring in **7** is coordinated.



(4)

Addition of 1 equiv of $B(C_6F_5)_3$ to a yellow solution of **5b** in aromatic solvents immediately changes its color to purple (eq 5). From toluene a purple oil precipitates that eventually crystallizes as $Cp_2Zr(N(SiMe_3)C(Ph)HCH_2CH_2B(C_6F_5)_3)\cdot 2C_6H_5CH_3$ (**8**·2$C_6H_5CH_3$). Crystals of **8** prepared in benzene contain no benzene molecules in the crystal. The structure of **8**·2$C_6H_5CH_3$ has been determined by X-ray crystallography (Figure 3); as just seen with **6**, two carbons of the phenyl of **8** are weakly coordinated to the Zr. In **8** the Zr−C71 bond length is

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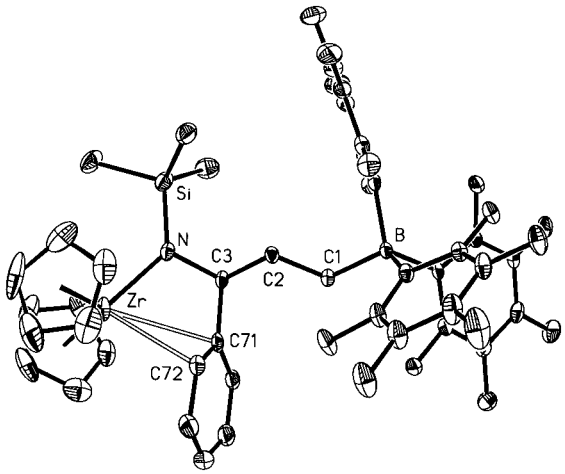
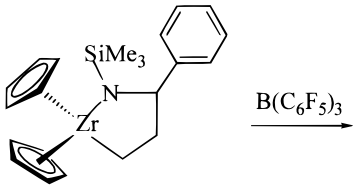
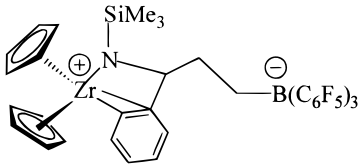


Figure 3. Molecular structure of **8**. Selected bond lengths (Å) and angles (deg): Zr−N 2.062(3), Zr−C71 2.842(4), Zr−C72 2.580(4), N−C3 1.501(4), C1−B 1.646(5), C3−C71 1.506(5), C72−C71 1.398(6), Zr−N−C3 112.2(2), N−C3−C71 110.0(3), N−C3−C2 111.5(3), C3−C71−C72 119.9(3), Zr−N−Si 130.9(2), Si−N−C3 116.0(2).

2.842(4) Å and the Zr−C72 bond length is 2.580(4) Å.



5b



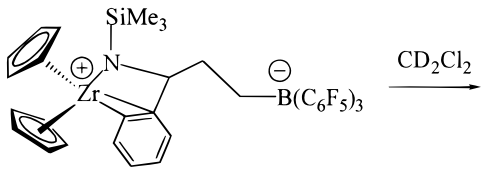
(5)

8

Purple crystalline **8** and **8**·$2C_6H_5CH_3$ dissolve in CD_2Cl_2 to form a purple solution that is unstable at room temperature (see below). As with **6**, the low-temperature (193 K) ^{1}H NMR of **8** or **8**·$2C_6H_5CH_3$ in CD_2Cl_2 shows five separate resonances for the phenyl protons, and these resonances coalesce pairwise as the temperature is raised. However, there is no upfield shift of any of the ^{1}H and ^{13}C NMR resonances of the phenyl in **8**, so there is (in contrast to the situation with **6**) no evidence that the Zr−Ph interaction persists in solution.

Cyclopentadienyl Ligand Exchange. The pairs of cyclopentadienyl ligands in **5**, **6**, **7**, and **8** are diastereotopic, and separate ^{1}H NMR resonances are expected for these ligands. The cyclopentadienyl resonances of **6** are well separated at room temperature in C_6D_6, but appear as a single extremely broad peak in CD_2Cl_2, indicating exchange; slower Cp exchange is observed for **7**. For **6** in CD_2Cl_2, from measurements between −40 and −10 °C, $\Delta H^{\ddagger} = 12.8(6)$ kcal/mol and $\Delta S^{\ddagger} = +2(3)$ eu, with an extrapolated rate constant of about $7(2) \times 10^3$ s^{-1} at 25 °C; for **7** (THF-d_8), $\Delta H^{\ddagger} = 10.6(1)$ kcal/mol and $\Delta S^{\ddagger} = -14.5(4)$ eu, with a rate constant of 66(1) s^{-1} at 25 °C.

Formation of the Azaallyl Complex 9. When purple solutions of **8** in CD_2Cl_2 remain at room temperature for several hours, a yellow product forms which appears to be the azaallyl complex **9** (eq 6).[7c,11] Although we have been unable to isolate **9**, its ^{1}H and ^{13}C NMR spectra make a convincing case for the structure drawn in eq 6. The CH_2B$(C_6F_5)_3$ protons are diastereotopic, appearing as broad humps in the ^{1}H NMR at δ 0.62 and −1.15 (raising the possibility that this methylene interacts directly with the Zr). The C2 methine resonance (δ 4.93) is downfield from that of a zirconaaziridine and near that (δ 5.02) in the allyl complex $Cp_2Zr(\eta^3$-CH_2C-(Ph)$CHCH_2B(C_6F_5)_3)$,[5a] and the carbon resonances C1, C2, and C3 (δ 154.6, 107.7, and 22.0) are remarkably similar to the corresponding ones in $Cp_2Zr(\eta^3$-CH_2C(Ph)-$CHCH_2B(C_6F_5)_3)$ (δ 147.4, 107.0, and 24.7, respectively).



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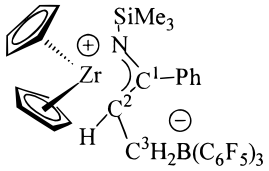
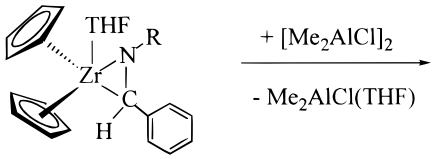


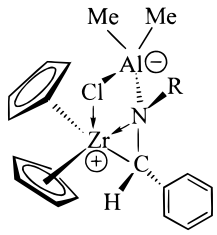
(6)

9

Reaction of Zirconaaziridines with Lewis Acids. Reaction of 2 equiv of $B(C_6F_5)_3$ with the zirconaaziridines **10** resulted in complex reaction mixtures. Addition of 1 equiv (2 equiv Al) of $(AlMe_2Cl)_2$ to hexane slurries of the zirconaziridines **10a** and **10b** results in the formation of $AlMe_2Cl$ adducts **11** and 1 equiv of $AlMe_2$-Cl(THF) (eq 7). The complexes **11** were isolated in low yield as orange-yellow crystals. The reaction of **10a** with $(AlMe_2Cl)_2$ occurs in moderate yield (^{1}H NMR), and only a small amount of **11a** has been isolated. The reaction of **10b** with $(AlMe_2Cl)_2$ is extremely clean (^{1}H NMR), but difficulties in separating **11b** from $AlMe_2Cl$(THF) have resulted in low isolated yields.



10a: R = Ph; **10b**: R = $SiMe_3$



(7)

11a: R = Ph; **11b**: R = $SiMe_3$

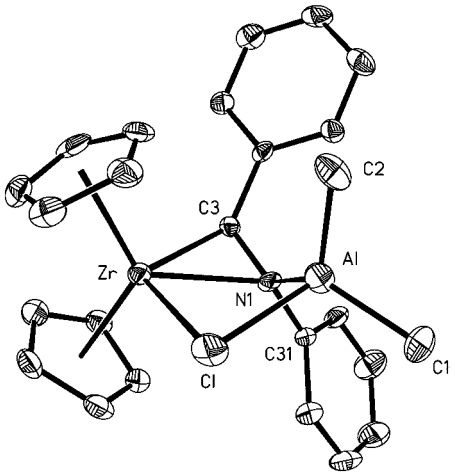
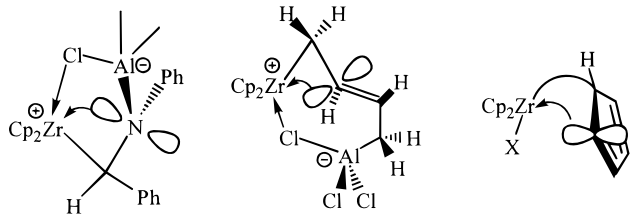


Figure 4. Molecular structure of **11a**. Selected bond lengths (Å) and angles (deg): Zr−N1 2.366(6), Zr−C3 2.297(7), Zr−Cl 2.680(3), N1−C3 1.462(9), N1−Al 1.952(7), Al−Cl 2.325(4), N1−Zr−Cl 74.3(2), Zr−N1−C3 69.2(3), Zr−Cl−Al 81.22(10), N1−C3−Zr 74.3(4).

Small yellow crystals of **11a**, of poor quality, from CH_2Cl_2/hexanes solution at −20 °C, have been examined by X-ray crystallography (Figure 4). The $AlMe_2Cl$ moiety is connected by the coordination of the zirconaaziridine N to Al and by the coordination of the Cl (of the $AlMe_2$-Cl) to the Zr. The Zr−C and C−N bond lengths of the aziridine ligand are not substantially affected by Al coordination; in **10a**[7b] they are Zr−C = 2.299(5), C−N = 1.431(7) Å, and in **10b**[20] they are Zr−C = 2.26(1), C−N = 1.41(1) Å, while in **11a** they are Zr−C = 2.297(7), C−N = 1.462(9) Å. The Zr−N bond lengthens substantially upon coordination: it is 2.113(4) Å in **10a** and 2.11(1) Å in **10b**, but 2.366(6) Å in **11a**. The Zr−Cl bond in **11a** (2.680(3) Å) is significantly longer than the typical Zr−Cl distance (ca. 2.44 Å) in zirconocene alkyl chloride complexes,[12] but within the range of Zr−Cl distances observed for other chlorides bridging Al and Zr.[13]

The N of **11a** is in the plane of C3, C31, and the Al in Figure 4; the sum of the C3−N−C31, C31−N−Al, and Al−N−C3 angles is 355°. The hybridization of the N is approximately sp^2, with a filled p orbital interacting with the electrophilic Zr in a "π agostic" fashion (Figure 5).[13a] Similar interactions are known between planar carbon and zirconocene Zr in **12,**[13a] in cyclopentadienyl structures such as **13** (Figure 5),[14] and in structures with bridging methyls (which have a Zr on each side of the planar carbon).[15]



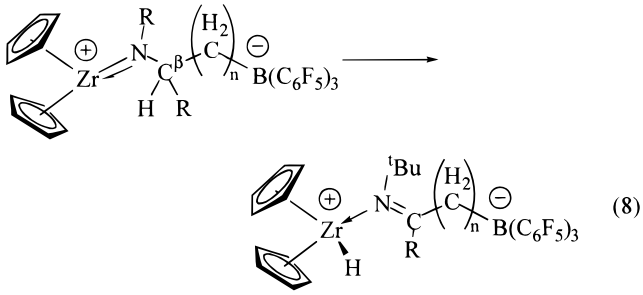
11a **12** **13**

Figure 5. Various "π agostic" interactions with zirconium: compound **11a**, this work; compound **12**, ref 13a; various compounds **13**, ref 14.

The reaction of excess $(Me_2AlCl)_2$ (C_6D_6 solution) with other azazirconacycles such as **5** in C_6D_6 resulted in immediate cleavage of the zirconacycle ligand and the formation of $Cp_2ZrMeCl$ and Cp_2ZrCl_2. These metathesis reactions probably proceed via intermediates structurally related to **11**.[15a]

Discussion

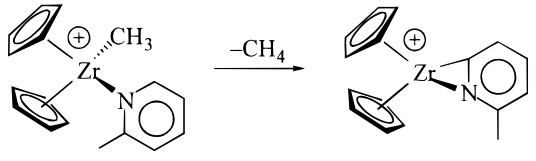
The conversions of **3** to **4** (Scheme 1) and of **8** to **9** (eq 6), and the exchange of the Cp ligands in **6**, probably all begin with a β hydrogen elimination[16] like that in eq 8.



(8)

For example, the formation of **4** from **3** can be rationalized by the route shown in Scheme 2.[17]

Such β hydride abstractions have been previously reported with the cationic zirconocene system in eq 9[18] and after $Cp_2Zr(Me)(N(CH_2)_5)$ is treated with $B(C_6F_5)_3$.[8]



(9)

After **14** is formed from **8** by β hydrogen elimination, the azaallyl **9** is plausibly formed by γ hydrogen

(11) Another zirconocene azaallyl complex has been reported: Coles, N.; Harris, M. C. J.; Whitby, R. J.; Blagg, J. *Organometallics* **1994**, *13*, 190−199.

(12) Hunter, W. E.; Hrncir, D. C.; Bynum, R. V.; Penttila, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750−755, and references therein.

(13) (a) Erker, G.; Noe, R.; Krüger, C.; Werner, S. *Organometallics* **1992**, *11*, 4174−4177. (b) Kaminsky, W.; Kopf, J.; Sinn, H.; Vollmer, H.-J *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 629−630. (c) Kopf, J.; Kaminsky, W.; Vollmer, H.-J. *Cryst. Struct. Commun.* **1980**, *9*, 197−201.

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(15) (a) Waymouth, R. W.; Potter, K. S.; Schaefer, W. P.; Grubbs, R. H. *Organometallics* **1990**, *9*, 2843−2846. (b) Waymouth, R. M.; Santarsiero, B. D.; Coots, R. J.; Bronikowski, M. J.; Grubbs, R. H. *J. Am Chem. Soc.* **1986**, *108*, 1427−1441. (c) Waymouth, R. M.; Santarsiero, B. D.; Grubbs, R. H. *J. Am Chem. Soc.* **1984**, *106*, 4050−4051.

(16) Negishi, E.; Takahashi, T. *Acc. Chem. Res.* **1994**, *27*, 124−130.

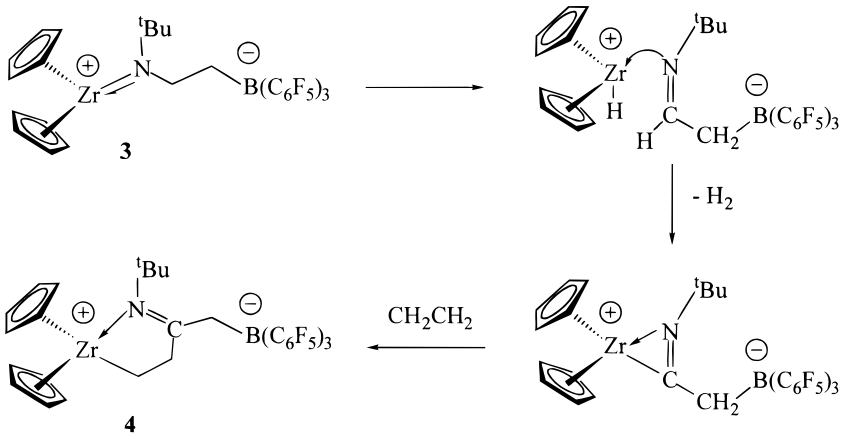
(17) A cationic iminoacyl complex like that shown in Scheme 2 has been structurally characterized: Temme, B.; Erker, G.; Fröhlich, R.; Grehl, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1480−1482.

(18) (a) Jordan. R. F.; Taylor, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 778−779. See also: (b) Nugent, W. A.; Ovenall, D. W.; Holmes, S. J. *Organometallics* **1983**, *2*, 161−162. (c) Planalp, R. P.; Andersen, R. A.; Zalkin, A. *Organometallics* **1983**, *2*, 16−20.

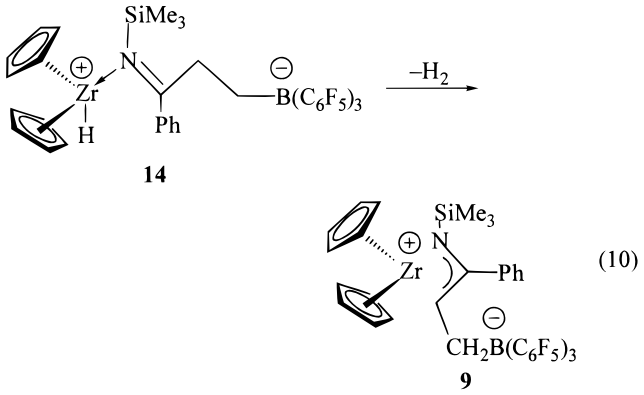
(19) Such substituents increase the rate of β hydrogen abstraction in the formation of zirconaaziridines from zirconocene alkyl amides (see ref 11).

(20) Buchwald, S. L.; Watson, B. T.; Wannamaker, M. W.; Dewan, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 4486-4494.

Scheme 2. Speculative Mechanism for Formation of 4 from 3

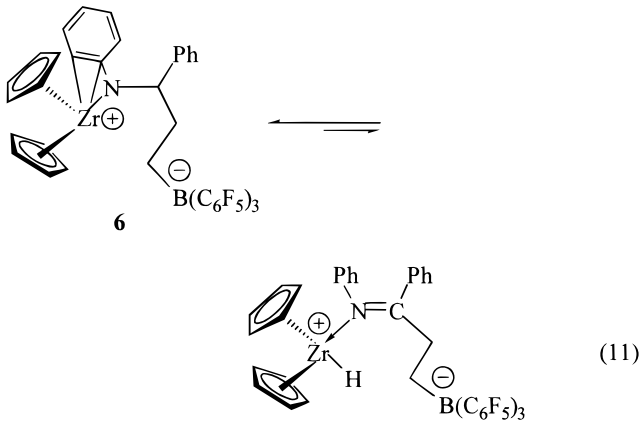


abstraction and H_2 loss (eq 10).



(10)

The exchange of the Cp ligands in **6** and **7** requires that β hydrogen elimination remove the chiral center, as shown in eq 11. The ease with which this process occurs may be due to the phenyl substituents on both nitrogen and carbon.[19]



(11)

Conclusions

While Me_2AlCl coordinates to the nitrogen of the zirconaaziridine **10**, $B(C_6F_5)_3$ exclusively abstracts the carbon (possibility **A** in eq 2 in the Introduction) rather than the nitrogen (possibility **B**) from the zirconium of the azazirconacyclobutane **2** and the azazirconacyclopentanes **5**. Carbon abstraction can be explained either by electronic stabilization of the cationic products (by π donation from the nitrogen of the amido cations **A**) or by steric constraints (bulky substituents are present on all of these nitrogens).

Experimental Section

Manipulations were conducted under N_2 or Ar using standard Schlenk techniques and Vacuum Atmospheres inert atmosphere boxes; solvents were dried and degassed. Complexes **1**,[9] **2**,[9] **5b**,[20] and **10**[7b,20] were prepared according to published procedures. Complex **5a** was prepared from **10a** in an analogous manner as for **5b** from **10b** and recrystallized from toluene/hexanes. Cp_2ZrCl_2, generously provided by Boulder Scientific, $(AlMe_2Cl)_2$ (Texas Alkyls), and polymer grade ethylene (Matheson) were used as received. $B(C_6F_5)_3$ (Boulder Scientific) was used as received or purified via recrystallization/sublimation (additional purification did not affect results). HMQC, HMBC, and COSY experiments were performed at 500 MHz; ^{19}F NMR spectra were recorded at 282 MHz; ^{13}C NMR spectra were recorded at 75 MHz; ^{1}H NMR spectra were recorded at 500 MHz unless otherwise noted. NMR spectra were taken at room temperature unless otherwise noted; HMQC results are reported as δ ^{13}C/δ ^{1}H.

$Cp_2ZrN(^tBu)CH_2CH_2B(C_6F_5)_3$ (3). $Cp_2Zr(N^tBu)(THF)$ (**1**) (0.040 g, 0.11 mmol) was dissolved in C_6D_6 (1 mL); $B(C_6F_5)_3$ (0.11 g, 0.215 mmol) was dissolved in C_6D_6 (1.5 mL). Both solutions were saturated with ethylene and combined under an ethylene atmosphere, giving a dark blue-violet color immediately. ^{1}H NMR (C_6D_6): δ 5.81 (s, 10 H), 2.14 (br, 2 H), 2.02 (br, 2 H), 0.57 (s, 9 H). ^{13}C NMR (C_6D_6): δ 115.7 (C_5H_5), 32.0/2.14 (CH_2) 59.6 ($C(CH_3)_3$), 29.4 ($C(CH_3)_3$), 7.9/2.02 (CH_2). ^{19}F NMR ($C_6D_5CD_3$): δ −132.1 (d, J_{FF} = 20 Hz) −158.2 (t, J_{FF} = 20 Hz), −163.3 (m).

Attempts to obtain low-temperature NMR spectra in toluene-d_8 resulted in separation of **3** as an oil and loss of signal. Attempts at preparing **3** in CD_2Cl_2 resulted in rapid decomposition.

Preparation of 4 from 1 via 3. $Cp_2Zr(N^tBu)(THF)$ (**1**) (0.20 g, 0.55 mmol) in toluene (18 mL) and $B(C_6F_5)_3$ (0.56 g, 1.09 mmol) in toluene (12 mL) were saturated with ethylene and combined as above; the solution was allowed to sit overnight at room temperature and turned a light yellow/green. After some toluene was removed (to a volume of ca. 8 mL), hexane (ca. 12 mL) was added and the solution cooled to −20 °C for 3 weeks; a night at room temperature gave yellow crystalline product containing toluene and hexanes. Yield: 80 mg (17%). Higher yields of analytically pure material were obtained by recrystallization of similarly prepared reaction mixtures from CH_2Cl_2/hexanes. ^{1}H NMR (CD_2Cl_2; 300 MHz): δ 6.28 (s, 10 H), 2.92 (br, 2 H), 2.76 (t, 2 H, J = 6.6 Hz.), 1.35 (t, 2 H, J = 6.6 Hz.), 0.92 (s, 9 H). ^{13}C NMR (CD_2Cl_2): δ 209.5 (C=N), 113.2 (C_5H_5), 59.7 (CCH_3), 45.2/1.35 (CH_2), 41.9/2.76 (CH_2), 36.5/2.92 ($CH_2B(C_6F_5)_3$), 27.1 (CCH_3). ^{19}F NMR (CD_2Cl_2): δ −131.0 (br),

Table 1. Summary of Crystallographic Data for Compounds 4, 6, 8, and 11a

	4	6	8	11a
empirical formula	$C_{42.50}H_{36}BF_{15}NZr$	$C_{52}H_{34}BF_{15}NZr$	$C_{54}H_{45}BF_{15}NSiZr$	$C_{25}H_{27}AlClNZr$
fw	947.75	1059.83	1123.03	495.13
temperature, K	203(2)	213(2)	203(2)	293(2)
crystal system	monoclinic	monoclinic	triclinic	orthorhombic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$Pbca$
a, Å	12.8543(6)	20.9775(14)	13.0474(6)	13.2367(11)
b, Å	21.9755(10)	21.3518(14)	13.4594(6)	15.576(2)
c, Å	15.8173(7)	20.6737(14)	16.9094(8)	23.120(2)
α, deg	90	90	87.3920(10)	90
β, deg	113.8070(10)	95.4880(10)	69.1730(10)	90
γ, deg	90	90	66.5280(10)	90
V, Å^3	4087.9(3)	9217.5(11)	2529.7(2)	4766.8(8)
Z	4	8	2	8
d_{calc}, g/cm^3	1.540	1.527	1.474	1.380
λ (Mo Kα), Å	0.71073	0.71073	0.71073	0.71073
μ, mm^{-1}	0.370	0.337	0.334	0.621
no. of data collected	28337	69017	17633	13269
no. of unique data	9064	21376	10520	5032
no. of data/restraints/params	9064/16/599	21376/0/1057	10519/0/664	5031/0/263
GOF on F^2	1.033	1.062	1.039	1.034
R1, wR2 ($I > 2\sigma(I)$)	0.0357, 0.0907	0.0958, 0.1748	0.0640, 0.1361	0.0892, 0.1471
R1, wR2(all data)	0.0455, 0.0960	0.2809, 0.2225	0.1028, 0.1556	0.2478, 0.1861

−161.3 (t, J_{FF} = 20 Hz), −165.4 (m). Anal. Calcd for $C_{36}H_{25}BF_{15}NZr$ (858.6): C, 50.36; H, 2.93; N, 1.63. Found: C, 50.52; H, 3.30; N, 1.34.

$Cp_2ZrNPhCHPhCH_2CH_2B(C_6F_5)_3$ (6). A solution of $B(C_6F_5)_3$ (1.0 g, 1.95 mmol) in toluene (15 mL) was added to a solution of **5a** (0.80 g, 1.9 mmol) in toluene (20 mL) with stirring for 20 min at room temperature; the mixture turned dark brown. About half the toluene was removed under vacuum, hexanes were added (ca. 10 mL), and the solution was allowed to stand overnight, forming reddish brown crystalline **6** that was isolated by filtration and dried under vacuum. Yield: 1.0 g (54%). Carrying out the reaction in benzene resulting in the formation of brown crystalline **6**·1.5(C_6H_6) (by X-ray diffraction), which lost benzene under vacuum (by ^{1}H NMR). ^{1}H NMR (C_6D_6; 300 MHz): δ 7.02 (m, 2 H), 6.90 (m, 3 H), 6.67 (m, 2 H), 6.21 (m, 1 H), 5.87 (br, obs, 2 H), 5.75 (s, 5 H), 4.98 (s, 5 H), 4.04 (d, 1 H), 2.00 (m, 1 H), 1.84 (m, 1 H), 1.23 (br, 1 H), −0.71 (br, 1 H). ^{1}H NMR (**6**·1.5(C_6H_6); CD_2Cl_2; 500 MHz; 223 K): δ 7.65 (br, 1 H), 7.36 (br, obs, 1 H), 7.34 (s, 1 H, residual C_6H_6), 7.20 (m, 3 H), 7.12 (m, 2 H), 7.01 (m, 2 H), 6.83 (br, 1 H), 6.63 (s, 5 H), 6.41 (br, 1 H), 5.49 (s, 5 H), 4.22 (m, 1 H), 1.60 (m, 2 H), 1.49 (m, 1 H), −2.12 (br, 1 H). HMQC (CD_2Cl_2; 223 K): δ 139.4/7.65, 139.2/7.36, 129.0/7.20, 127.7/7.12, 127.0/7.01, 126.5/7.20, 119.0/6.83, 116.5/6.63, 115.7/5.49, 83.9/6.41, 70.4/4.22, 38.5/(1.60, 1.49), 20.3/(1.60, −2.12). ^{19}F NMR: δ −130.5 (br), −159.0 (t, J_{F-F} = 20 Hz), −163.4 (br). Anal. Calcd for $C_{43}H_{25}BF_{15}NZr$ (942.68): C, 54.79; H, 2.67; N, 1.49. Found: C, 55.00; H, 2.33; N, 1.28.

$Cp_2ZrNPhCHPhCH_2CH_2B(C_6F_5)_3$(THF) (7). Addition of THF to solid **6** or slurries of **6** in toluene produced a rapid color change from brown to yellow and clean formation of **7**. Compound **7** is insoluble in aromatic solvents, and CH_2Cl_2 and was recrystallized from THF/toluene or THF/CH_2Cl_2 to yield yellow blocks. ^{1}H NMR (THF-d_8): δ 7.06 (m, 6 H), 6.68 (s, 5 H), 6.45 (d, 2 H, J_{H-H} = 7.14), 6.31 (m, 2 H), 6.13 (s, 5 H), 5.65 (m, 1 H), 1.71 (m, obs, 1 H), 1.50 (m, 1 H), 1.28 (m, 1 H), 0.29 (m, 1 H). HMQC (THF-d_8): δ 130.0/6.45, 129.4/6.45, 115.5/6.13, 115.0/6.68, 80.5/5.65, 34.8/(1.71, 1.28), 19.5/(1.50, 0.29). ^{19}F NMR (THF-d_8): δ −133.0 (d, J_{F-F} = 22.6 Hz), −167.2 (t, J_{F-F} = 19.7 Hz), −169.4 (m).

$Cp_2ZrN(SiMe_3)CHPhCH_2CH_2B(C_6F_5)_3$ (8). A solution of $B(C_6F_5)_3$ (0.18 g, 0.35 mmol) in toluene (10 mL) was added to a solution of **5b** (0.15 g, 0.35 mmol) in toluene (10 mL) with stirring at room temperature; the mixture turned purple, and after several minutes a purple oil formed. After several hours the oil crystallized into purple blocks of **8**·2($C_6H_5CH_3$) (by X-ray diffraction and ^{1}H NMR) that were isolated by filtration, washed with hexanes, and dried under vacuum. Yield: 0.3 g (83%). Carrying out the reaction in benzene proceeded similarly to give crystalline **8** (by ^{1}H NMR and elemental analysis). ^{1}H NMR (CD_2Cl_2; 500 MHz; 193 K): δ 8.10 (pt, meta, 1 H, J_{obs} = 7.55), 7.84 (d, ortho, 1 H, J_{H-H} = 7.65), 7.78 (t, para, 1 H, J_{H-H} = 7.45), 7.75 (d, ortho, 1 H, J_{H-H} = 7.95), 7.62 (pt, meta, 1H; J_{obs} = 7.00), 6.72 (s, 5 H), 5.68 (s, 5 H), 4.06 (m, 1 H), 1.26 (br, 1 H), 0.84 (br, 2 H), 0.45 (br, 1 H), −0.17 (s, 9 H). HMQC (CD_2Cl_2, 253 K): δ 117.1/(6.72, 5.69), 70.6/4.06, 39.0/(1.26, 0.84), 16.7/(0.84, 0.45), 2.5/-0.17. ^{19}F NMR (CD_2Cl_2): δ −131.9 (d, J_{FF} = 20 Hz), −163.3 (t, J_{FF} = 20 Hz), −166.3 (m). Anal. Calcd for $C_{40}H_{29}BF_{15}NSiZr$ (938.76): C, 51.18; H, 3.11; N, 1.49. Found: C, 51.35; H, 2.82; N, 1.24.

Formation of the Azaallyl 9 from 8. Purple solutions of **8** in CH_2Cl_2 at room temperature turn yellow and cleanly convert to **9** (>90%) after several hours. (At higher temperatures multiple products form.) Attempts at crystallizing **9** from CH_2Cl_2 or toluene by cooling or addition of hexanes resulted in formation of a yellow oil. ^{1}H NMR (CD_2Cl_2): δ 7.44 (m, 4 H), 7.14 (m, 1 H), 6.36 (s, 5 H), 5.86 (s, 5 H), 4.93 (m, 1 H), 0.62 (m, 1 H), 0.03 (s, 9 H), −1.14 (m, 1 H). HMQC (CD_2Cl_2): δ 112.0/6.36, 108.9/5.86, 107.7/4.93, 22.0/(0.62, −1.14), 3.7/0.03. ^{13}C NMR (CD_2Cl_2): δ 154.6 (*C*−Ph). ^{19}F NMR (CD_2Cl_2): δ −131.7 (d, J_{FF} = 20 Hz), −159.6 (t, J_{FF} = 20 Hz), −164.1 (m).

$AlMe_2Cl$ Adduct 11a. To a suspension of **10a** (0.57 g, 1.2 mmol) in hexanes (30 mL) was added a solution of $(AlMe_2Cl)_2$ (2.5 mL, 2.75 mmol, 1.1 M in hexanes). Over 30 min the **10a** dissolved and formed a yellow solution. Cooling it to −78 °C resulted in the formation of an oily yellow-orange solid, which was isolated by filtration. The solid was dissolved in CH_2Cl_2 (5 mL, pretreated with 0.1 mL of 1.1 M $[AlMe_2Cl]_2$ solution) and kept cold as hexanes (ca. 15 mL) were added. Cooling the solution to −78 °C overnight resulted in the formation of an orange oil; warming the oil and solution to −20 °C over 3−4 h gave crystalline orange **11a**, for which adequate analysis could not be obtained. Yield: 50 mg (8.4%). ^{1}H NMR (C_6D_6; 300 MHz): δ 7.29 (br, 4 H), 7.0 (m, 4 H), 6.83 (t, 2 H), 5.54 (s, 5 H), 5.42 (s, 5 H), 4.40 (s, 1 H), − 0.15 (s, 3 H), − 0.35 (s, 3 H). ^{13}C NMR (C_6D_6): δ 112.4 (C_5H_5), 110.3 (C_5H_5), 73.5 (*C*HPh), 0.2 (AlCH_3), −1.9 (AlCH_3).

$AlMe_2Cl$ Adduct 11b. To a suspension of **10b** (0.52 g, 1.1 mmol) in hexanes (40 mL) was added $(AlMe_2Cl)_2$ (2.1 mL, 2.3 mmol, 1.1 M in hexanes). Over 5 min the **10b** dissolved and formed a yellow solution. After filtering and concentrating (to ca. 15 mL) the solution was cooled to −20 °C for several hours. A yellow crystalline product formed that was separated from the supernatant liquid, dissolved in hexanes (40 mL), filtered, and cooled to −20 °C; repeating this process gave analytically pure **11b**. Yield: 80 mg (14.8%). ^{1}H NMR (C_6D_6; 300 MHz): δ 7.24 (t, 2 H), 7.08−6.85 (br, 3 H), 5.64 (s, 5 H), 5.43 (s, 5 H), 4.31 (s, 1 H), 0.36 (s, 9 H), 0.08 (s, 3 H), −0.13 (s, 3 H). ^{13}C NMR (C_6D_6): δ 112.1 (C_5H_5), 108.3 (C_5H_5), 68.2 (*C*HPh), 5.4 (SiCH_3), 2.6 (AlCH_3), 1.0 (Al-CH_3). Anal. Calcd for $C_{22}H_{31}$-

ClNSiZr (491.23): C, 53.79; H, 6.36; N, 2.85. Found: C, 53.75; H, 6.26; N, 2.73.

X-ray Structure Determinations. Crystal data collection and refinement parameters are summarized in Table 1. Data were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector. The structures were solved using direct methods and standard difference map techniques and refined by full matrix least-squares procedures using SHELXTL.[21] Hydrogen atoms on carbon were included in calculated positions.

(21) Sheldrick, G. M. *SHELXTL*, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data; University of Göttingen: Göttingen, Federal Republic of Germany, 1981.

Acknowledgment. Financial support for this work was provided by Dr. John Birmingham (Boulder Scientific Co.) and NSF Grant CHE-98-96151. The authors thank J. Tunge and G. Parkin for helpful discussions, G. Parkin for help with X-ray diffraction studies, and D. Ramage for initial studies on the interaction of **5a** with aluminum Lewis acids.

Supporting Information Available: Tables giving atomic coordinates, bond lengths and angles, anisotropic displacement parameters and hydrogen coordinates for **4**, **6**, **8**, and **11a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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