Organometallics **2006,** *25,* 519−522

Simple Alumination Reactions of Pentamethylcyclopentadienyl Ligands in the Decamethylzirconocene−Bis(trimethylsilyl)acetylene Complex $Cp^*_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$

Vladimir V. Burlakov,[§] Perdita Arndt, Wolfgang Baumann, Anke Spannenberg, and Uwe Rosenthal*

Leibniz-Institut für Organische Katalyse an der Universität Rostock e. V.,
Albert-Einstein-Strasse 29a, D-18059 Rostock, Germany

Received September 23, 2005

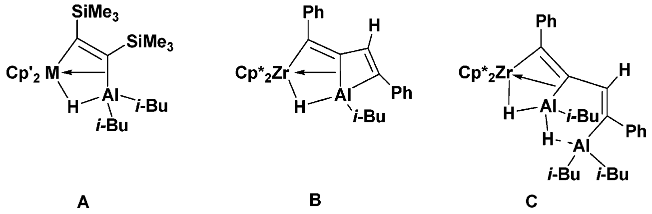
In the reaction of the decamethylzirconocene−bis(trimethylsilyl)acetylene complex $Cp^*_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**1**) with $i\text{-}Bu_2AlH$, CH bond activation, an electrophilic substitution, and alumination of the pentamethylcyclopentadienyl ligand resulted in formation of the $\eta^5\text{-}C_5Me_4CH_2{-}Al(i\text{-}Bu)_2H$ ligand. The final product contains an alkenyl complex that shows an agostic C−H···Zr interaction, $Cp^*Zr[{-}C(SiMe_3){=}CH(SiMe_3)](\mu\text{-}H)[\eta^5\text{-}C_5Me_4CH_2{-}Al(i\text{-}Bu)_2]$ (**2**). Heating complex **2** gives the heterobimetallic complex $Cp^*Zr[{-}C(SiMe_3){=}C(SiMe_3)Al(i\text{-}Bu)(\mu\text{-}H)(CH_2{-}\eta^5\text{-}C_5Me_4)]$ (**3**), which is formed by an intramolecular reaction, analogous to intermolecular reactions of titanocene- and zirconocene-alkyne complexes with $i\text{-}Bu_2AlH$, which yield the well-known heterobimetallic complexes with tetracoordinated planar carbon atoms. Both complexes were characterized by NMR spectroscopy and X-ray crystal structure analysis. Complex **2** catalyzes the ethene polymerization and the ring-opening polymerization of ε-caprolactone.

Introduction

The ability of the Lewis acids to abstract alkyl groups from metallocene alkyl compounds Cp'_2MR_2 and to form coordinatively unsaturated alkyl metal cationic complexes $[Cp'_2MR]^+$ (Cp' = substituted η^5-cyclopentadienyl) is well-documented from numerous investigations relating to Ziegler/Natta catalysts for olefin polymerization.[1] Mostly metallocenes of type Cp'_2MR_2 were investigated. These were formed by alkylation of metallocene dihalides by organoaluminum compounds, which were used as activators.[2] Recently we investigated reactions of $i\text{-}Bu_2AlH$ with different metallacycles such as metallacyclo*propene*, $Cp'_2M(\eta^2\text{-}RC_2R)$,[3] and the unusual five-memberd metalla*cyclocumulenes*, $Cp^*_2M(\eta^4\text{-}RC_4R)$,[4] all of which have two metal−carbon σ-bonds.

In detail we reported that titana- and zirconacyclopropenes of type $Cp'_2M(\eta^2\text{-}Me_3SiC_2SiMe_3)$, with M = Ti and Zr and $Cp'_2 = Cp_2$ (bis-η^5-cyclopentadienyl) and ebthi (1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl), readily react with $i\text{-}Bu_3Al$ to give isobutene and the heterobimetallic complexes **A** (Scheme 1, drawings as by Erker[5j]).[3a] A better route to these complexes is the direct reaction of the alkyne complexes with $i\text{-}Bu_2AlH$. Similar reactions of metallocene alkyne complexes with organoaluminum compounds were investigated earlier by Erker and Binger.[5] Novel bimetallic systems of the type $[Cp_2M^1](\mu\text{-}\eta^1{:}\eta^2\text{-}RCCR)(\mu\text{-}X)[M^2R^2_2]$ (M^1 = Zr, Hf, X = Cl, H, M^2 = Al; M^1 = Ti, X = H) with planar tetracoordinate carbon atoms bridging the group 4 transition metal and the aluminum were obtained.

Scheme 1



More recently we investigated reactions of five-membered zirconacyclocumulenes (zirconacyclopenta-2,3,4-trienes), $Cp^*_2Zr(\eta^4\text{-}1,2,3,4\text{-}RC_4R)$, $Cp^* = \eta^5$-pentamethylcyclopentadienyl, R = Me, Me_3Si, and Ph, with $i\text{-}Bu_2AlH$. A *cis*-hydroalumination of the central double bond gave zirconacylopentadienes with

---

* Corresponding author. E-mail: uwe.rosenthal@ifok-rostock.de.

[§] On leave from the A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov St. 28, 117813, Moscow, Russia.

(1) (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. *Angew. Chem.* **1995**, *107*, 1255; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143, and references therein. (b) Janiak, C. In *Metallocenes*; Togni, A., Halterman, R. L., Eds.; Wiley-VCH: New York, 1998; Vol. 2, p 547.

(2) Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391.

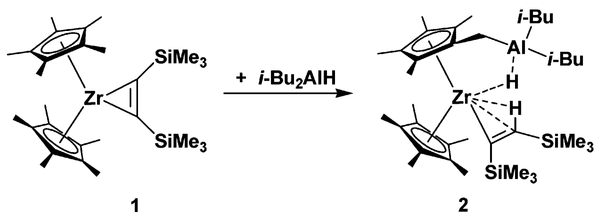
(3) (a) Arndt, P.; Spannenberg, A.; Baumann, W.; Becke, S.; Rosenthal, U. *Eur. J. Inorg. Chem.* **2001**, 2885. (b) Thomas, D.; Arndt, P.; Peulecke, N.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *Eur. J. Inorg. Chem.* **1998**, 1351. (c) Arndt, P.; Thomas, D.; Rosenthal, U. *Tetrahedron Lett.* **1997**, *38*, 5467.

(4) (a) Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *Organometallics* **2004**, *23*, 4160. (b) Rosenthal, U.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A. *Organometallics* **2005**, *24*, 456. (c) Rosenthal, U.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Shur, V. B. *Eur. J. Inorg. Chem.* **2004**, 4729. (d) Hiller, J.; Thewalt, U.; Polasek, M.; Petrusova, L.; Varga, V.; Sedmera, P.; Mach, K. *Organometallics* **1996**, *15*, 3752.

(5) (a) Erker, G. *Comments Inorg. Chem.* **1992**, *13*, 111. (b) Erker, G.; Noe, R.; Wingbergmühle, D. *Chem. Ber.* **1994**, *127*, 805. (c) Erker, G.; Albrecht, M.; Krüger, K. *Synlett* **1993**, 441. (d) Erker, G.; Albrecht, M. *Organometallics* **1992**, *11*, 3517. (e) Erker, G.; Albrecht, M.; Werner, S.; Nolte, M.; Krüger, C. *Chem. Ber.* **1992**, *125*, 1953. (f) Binger, P.; Sandmeyer, F.; Krüger, K.; Erker, G. *Tetrahedron* **1995**, *51*, 4277. (g) Binger, P.; Sandmeyer, F.; Krüger, C. *Organometallics* **1995**, *14*, 2969. (h) Erker, G.; Hoffmann, U.; Zwettler, R.; Krüger, K. *J. Organomet. Chem.* **1989**, *367*, C15−C17. (i) Röttger, D.; Erker, G. *Angew. Chem.* **1997**, *109*, 840; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 812. (j) Erker, G.; Venne-Dunker, S.; Kehr, G.; Kleigrewe, N.; Fröhlich, R.; Mück-Lichtenfeld, C.; Grimme, S. *Organometallics* **2004**, *23*, 4391.

10.1021/om050821i CCC: $33.50

Scheme 2



i-Bu$_2$Al substituents in the 3-position as intermediates.[4a] These subsequently reacted further in different ways, depending on the substituents R; for example, with R = Me$_3$Si a "hydroaluminolysis" of the central double bond of the zirconacyclocumulene to *i*-Bu$_2$AlC≡CSiMe$_3$ and a bimetallic complex of type **A** was observed. With R = Ph the heterobimetallic complex **B** and the trinuclear bimetallic complex **C** were the products. All had planar tetracoordinated carbon atoms bridging between the group 4 transition metal and the aluminum atom (Scheme 1, analogous to that by Erker[5j]).[3−5] In no case was a CH bond activation observed. We report here the facile alumination of the pentamethylcyclopentadienyl ligands in the decamethylzirconocene−bis(trimethylsilyl)acetylene complex.

Results and Discussion

In the reaction of the decamethylzirconocene−bis(trimethylsilyl)acetylene complex Cp*$_2$Zr(η^2-Me$_3$SiC$_2$SiMe$_3$)[4d] with *i*-Bu$_2$AlH, with CH bond activation and alumination of the pentamethylcyclopentadienyl ligand, the alkenyl complex Cp*Zr[−C(SiMe$_3$)=CH(SiMe$_3$)](μ-H)[η^5-C$_5$Me$_4$CH$_2$−Al-*i*-Bu$_2$] (**2**) was formed (Scheme 2). This product as shown contains a C−H···Zr agostic interaction.

One can consider the Al···H···Zr hydrogen-bridged complex **2** either as a Zr(IV) alkenyl hydride, Cp*Zr(H)[−C(SiMe$_3$)=CH(SiMe$_3$)][η^5-C$_5$Me$_4$CH$_2$−Al(*i*-Bu)$_2$], or as a zwitterionic complex, Cp*Zr$^+$[−C(SiMe$_3$)=CH(SiMe$_3$)][η^5-C$_5$Me$_4$CH$_2$−Al$^-$(H)(*i*-Bu)$_2$].

Heating complex **2** gave the complex **3** together with the alkyne complex **1** in 3 to 1 ratio (Scheme 3).

Complex **3** is an analogue of the above-mentioned heterobimetallic complexes **A** (Scheme 1), which were obtained in the *inter*molecular reaction of titanocene- and zirconocene-alkyne complexes with *i*-Bu$_2$AlH. In the case of complex **3** the (*i*-Bu)Al(H)(CH$_2$−η^5-C$_5$Me$_4$) ligand has reacted *intra*molecularly with the metallacyclopropene unit, forming a compound with the typical tetracoordinated planar carbon atom.[3−5] Complex **1** was a byproduct of this reaction, but the other byproducts, hydrocarbons and organoaluminum compounds, were not identified.

Table 1. Crystallographic Data

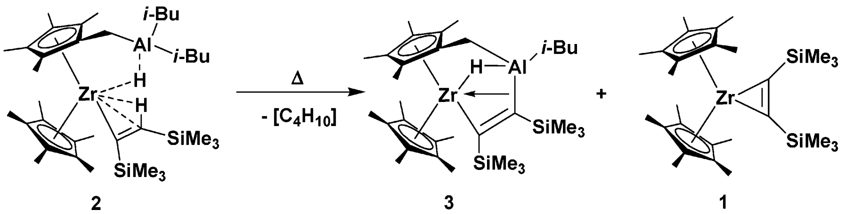
	2	3
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a [Å]	15.302(3)	10.036(2)
b [Å]	15.983(3)	11.342(2)
c [Å]	17.352(3)	16.376(3)
α [deg]		88.48(3)
β [deg]	112.55(3)	73.14(3)
γ [deg]		74.79(3)
V [Å^3]	3919.3(13)	1719.0(6)
Z	4	2
density [g·cm^{-3}]	1.143	1.190
μ(Mo Kα) [mm^{-1}]	0.385	0.433
T [K]	200	293
no. of rflns (measd)	11 437	5126
no. of rflns (indep)	6211	5126
no. of rflns (obsd)	4355	2754
no. of params	366	301
R1 (I > 2σ(I))	0.039	0.061
wR2 (all data)	0.093	0.148

Structural Investigations. The most characteristic NMR spectroscopic and molecular structural feature of complex **2** is the agostic interaction of the alkenyl group Zr−Cα=CβH. ^{1}H NMR signals were observed at rather low field (6.27−8.04 ppm) and ^{13}C NMR signals due to Cα at low field (218.8−236.4 ppm), whereas the Cβ-signal is found upfield (101.1−149.1 ppm) compared to the normal olefinic range. Typical for the additional agostic interaction is the very small coupling constant ^1J(Cβ−H) (96−125 Hz). All these features, which are typical for Zr σ-alkenyl complexes with agostic Cβ-H···Zr interactions, were found earlier in complexes containing the same motif (Scheme 4).[6] The corresponding data for complex **2** are 5.03, 221.1, and 105.9 ppm with a coupling constant ^1J(Cβ−H) of 92 Hz.

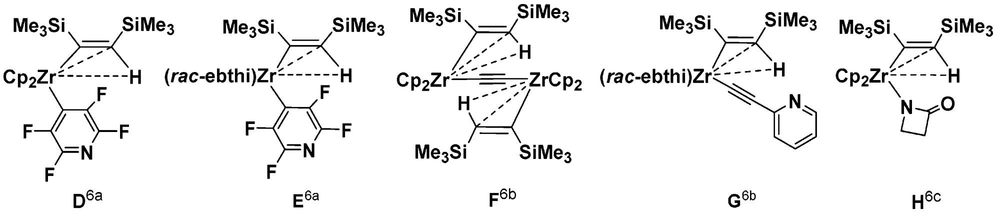
Complexes **2** and **3** were investigated by X-ray crystallography. The crystallographic data are presented in Table 1, and the molecular structures are shown in Figures 1 and 2.

The X-ray crystal structure analysis of complex **2** shows the structural element of an agostic alkenyl group Zr−Cα=CβH (Figure 1). Typical data for these complexes are acute ZrCαCβ angles (85.2−87.3°) and relatively short Zr−Cβ bond distances (2.530−2.556 Å). For complex **2** a small Zr−C1−C2 angle (85.2(2)°) and bond distances Zr−C1 (2.273(3) Å), C1−C2 (1.324(4) Å), and Zr−C2 (2.533(3) Å) were found, similar to

Scheme 3



Scheme 4



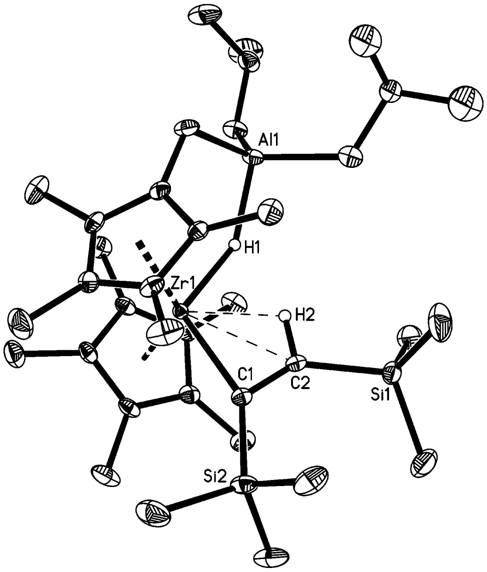


Figure 1. Crystal structure of complex **2**. Hydrogen atoms except H1 and H2 are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths [Å] and angles [deg]: C1−C2 1.324(4), C1−Si2 1.883(3), C1−Zr1 2.273(3), C2−Si1 1.887(3), C2−Zr1 2.533(3); C2−C1−Si2 125.5(3), C2−C1−Zr1 85.2(2), C1−C2−Si1 140.1(3), C1−C2−Zr1 63.4(2), Si1−C2−Zr1 156.2(2).

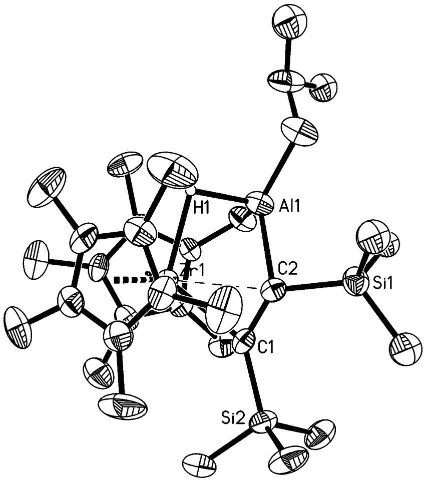


Figure 2. Crystal structure of complex **3**. Hydrogen atoms except H1 are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths [Å] and angles [deg]: C1−C2 1.348(9), C1−Si2 1.884(7), C1−Zr1 2.246(7), C2−Si1 1.901(8), C2−Al1 2.154(7), C2−Zr1 2.446(7); C2−C1−Si2 136.1(6), C2−C1−Zr1 81.7(4), C1−C2−Si1 125.7(5), C1−C2−Zr1 65.3(4), C1−C2−Al1 136.2(5), Si1−C2−Al1 96.9(3), Al1−C2−Zr1 75.4(2).

distances and angles found in the above-mentioned complexes of the same type (Scheme 4).[6]

The molecular structure of the zirconocene complex **3** shows the structural element of a bicyclic five-membered ring system consisting of Zr, hydridic hydrogen H, Al, C_β, and C_α (Figure 2). The most remarkable feature of these complexes is the coordination geometry of the carbon atom C_β, which is bonded to C_α, Zr, Al, and Si, with all four bonds lying more or less in one plane. This structural motif of planar tetracoordinated carbon atoms was often found and discussed in detail for many examples by Erker.[5] It was described as a three-center, two-electron bonding system in the σ-plane, stabilized by a perpendicular π-system. The data of complex **3** (Table 2) correspond very closely to one of these examples,[5] e.g., the complex of type **A** (Scheme 1, M = Zr, Cp'_2 = *rac*-ebthi). A comparison of selected structural data is presented in Table 2.

Table 2. Comparison of Structural Data of 3 with Complex A (Scheme 1, M = Zr, Cp'_2 = *rac*-ebthi)

	3	**A**
	Bond Distances [Å]	
Zr−C_α	2.246(7)	2.221(13)
Zr−C_β	2.446(7)	2.384(15)
C_α-C_β	1.348(9)	1.33(2)
Al−C_β	2.154(7)	2.15(2)
	Angles [deg]	
Al−C_β−Zr	75.4(2)	78.3(5)
C_β−C_α−Zr	81.7(4)	80.1(9)

For complex **3** the long Al1−C2 (2.154(7) Å) and Zr1−C2 (2.446(7) Å) bond distances support the description by a three-center Al−C−Zr bond. The C1−Si2 distance (1.884(7) Å) is compareable to that of the C2−Si1 (1.901(8) Å) bond. It was pointed out that the planarity of the five-membered ring was distorted, e.g., for complex **A** due to the steric hindrance of the ebthi ligand (mean deviation of the best plane through Zr, Al, Si, C_α, and C_β is 0.114 Å for **A**).[3a] For complex **3** the planarity is distorted, too (mean deviation of the best plane through Zr, Al, Si, C_α, and C_β is 0.177 Å for **3**; probably resulting from the special substitution of the Cp* and the resulting ring strain).

Preliminary Catalytic Polymerization Studies. In metallocene-catalyzed polymerization of olefins there is a vital interest in replacement of expensive activators such as MAO or perfluoroarylboron compounds by low-cost activators. For the zirconacyclopropene complex *rac*-(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$) activation by *i*-Bu_3Al resulted in only a very low activity. As mentioned above, this complex reacts very readily with *i*-Bu_3Al with formation of isobutene and *i*-Bu_2AlH, which forms the heterobimetallic complex **A** (Scheme 1, M = Zr, Cp'_2 = *rac*-ebthi).[3a] This complex, however, was not active. In the present study, in first experiments it was found that in contrast complex **2** is active in the polymerization of ethylene (1.1 bar) without the need for any additional activator (55 kg polymer/mol·h). A greater activity was found for complex **C** (Scheme 1) (100 kg polymer/mol·h).[4a] No experiments were carried out in the presence of additional aluminum reagent or activators. Further investigations are in progress.

The titana- and zirconacyclopropenes $Cp'_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ are active catalysts for the catalytic ring-opening polymerization of ϵ-caprolactone.[3b] Addition of *i*-Bu_3Al or *i*-Bu_2AlH, in which complexes of type **A** (Scheme 1, M = Ti) were formed, provides additional activation, showing an increase in the polymer molecular weight and in the activity, compared to the starting complexes.[3a] In preliminary experiments, complex **2** was tested as a catalyst in the ring-opening polymerization of ϵ-caprolactone at 60 °C. The yield of polymer was 22%, M_w = 75 000. The yields are lower and the observed molecular weight is comparable to those obtained at 75 °C with the zirconocene complexes $Cp_2Zr(Py)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (80%, M_w = 80 000) and **A** (Scheme 1, Cp′ = Cp) (82%, M_w = 67 570).[3a]

---

[6] (a) Jäger-Fiedler, U.; Arndt, P.; Baumann, W.; Spannenberg, A.; Burlakov, V. V.; Rosenthal, U. *Eur. J. Inorg. Chem.* **2005**, 2842. (b) Thomas, D.; Peulecke, N.; Burlakov, V. V.; Heller, B.; Baumann, W.; Spannenberg, A.; Kempe, R.; Rosenthal, U.; Beckhaus, R. *Z. Anorg. Allg. Chem.* **1998**, *624*, 919. (c) Arndt, P.; Lefeber, C.; Tillack, A.; Rosenthal, U. *Chem Ber.* **1996**, *129*, 1281.

Conclusion

In the reaction of Cp*$_2$Zr(η^2-Me$_3$SiC$_2$SiMe$_3$) (**1**) with *i*-Bu$_2$AlH the Cp* ligand is not inert, giving an electrophilic substitution and the formation of the η^5-C$_5$Me$_4$CH$_2$−Al(*i*-Bu)$_2$ ligand in complex **2**. In a subsequent reaction this ligand forms the η^5-C$_5$Me$_4$CH$_2$−Al(*i*-Bu)H ligand, reacting *intra*molecularly with the metallacyclopropene unit to the heterodinuclear complex **3** with tetracoordinated planar carbon atoms. The formation of **2**, described as a zwitterionic complex, Cp*Zr$^+$-[−C(SiMe$_3$)═CH(SiMe$_3$)][η^5-C$_5$Me$_4$CH$_2$−Al$^-$(H)(*i*-Bu)$_2$], is very similar to the reaction of **1** with the other Lewis acid B(C$_6$F$_5$)$_3$, in which an electrophilic substitution gives the complex Cp*Zr$^+$[−C(SiMe$_3$)═CH(SiMe$_3$)][η^5-C$_5$Me$_4$CH$_2$−B$^-$-(C$_6$F$_5$)$_3$].[7]

Experimental Section

General Procedures. All operations were carried out under argon with standard Schlenk techniques. Prior to use nonhalogenated solvents were freshly distilled from sodium tetraethylaluminate and stored under argon. Deuterated solvent (C$_6$D$_6$) was treated with sodium tetraethylaluminate, distilled, and stored under argon. The following spectrometers were used: mass spectra, AMD 402; NMR spectra, Bruker ARX 400. Chemical shifts (^{1}H, ^{13}C) are given relative to SiMe$_4$ and are referenced to signals of the used solvent (benzene-*d*$_6$, $\delta_H = 7.16$, $\delta_C = 128.0$); the spectra were assigned with the help of DEPT, NOE, and shift correlation experiments. This section gives only the key resonances; full details can be found in the Supporting Information. Melting points: sealed capillaries, Büchi 535 apparatus. Elemental analyses: Leco CHNS-932 elemental analyzer.

Preparation of Complex 2. *i*-Bu$_2$AlH (1.0 mmol, 1 mL of a 1.0 M solution in toluene) was added to a solution of complex **1**[4d] (0.461 g, 0.87 mmol) in 10−15 mL of *n*-hexane The blue-green solution was filtered and allowed to stand in an argon atmosphere at 20 °C. After 24 h the greenish solution was evaporated in a vacuum to dryness. *n*-Hexane (3 mL) was added to the oily residue, and the resulting mixture was cooled to −78 °C. After 2 days light green crystals had formed, which were separated from the mother liquor by decantation, washed with cold *n*-hexane, and dried in a vacuum to give 0.374 g (64%) of **2**, mp 153−155 °C under Ar. Anal. Calcd for C$_{36}$H$_{67}$AlSi$_2$Zr: C, 64.12; H, 10.02. Found: C, 64.30; H 9.47. ^{1}H NMR (C$_6$D$_6$, 297 K): δ −0.64 (br, 1H, μ-H); 0.38 (s, 9H, β-SiMe$_3$); 0.44 (s, 9H, α-SiMe$_3$); 1.38 (s, 3H, Cp-CH$_3$); 1.56 (s, 3H, Cp-CH$_3$); 1.60 (dd, 1H, Cp-CH$_2$); 1.70 (s, 15H, C$_5$Me$_5$); 1.76 (s, 3H, Cp-CH$_3$); 1.80 (d, 1H, Cp-CH$_2$); 2.06 (s, 3H, Cp-CH$_3$); 5.03 (d, 1H, ═CH, $^2J_{H,H} = 4.1$ Hz). ^{13}C NMR (C$_6$D$_6$, 297 K): δ 2.1 (β-SiMe$_3$); 5.8 (α-SiMe$_3$); 8.1 (br, Cp-CH$_2$); 10.6; 11.7; 11.9; 13.7 (4 Cp-CH$_3$); 12.5 (C$_5$*Me*$_5$); 105.9 (═CHSiMe$_3$ $^1J_{C,H} = 92.2$ Hz); 116.9 (*C*$_5$Me$_5$); 221.1 (═CSiMe$_3$). ^{29}Si NMR (C$_6$D$_6$, 297 K): δ −3.4 (β-Si); −9.2 (α-Si, $^3J_{Si,H} = 20.2$ Hz). MS (70 eV, *m*/*z*): 360 [Cp$_2$Zr]$^+$.

Preparation of Complex 3. Complex **2** (1.24 g, 1.84 mmol) was heated at 160 °C for 10 min. The solid melted with gas evolution. The residue was cooled to rt, and the light green tar-like material was dissolved in *n*-hexane (4−5 mL) under Ar. The green solution was filtered, concentrated to 2−3 mL, and cooled to −78 °C. After 2 days green crystals had formed, which were isolated by filtration to give 0.23 g (20%) of complex **3**, which was identified by NMR spectroscopy and X-ray analysis. Mp: 190−192 °C (dec) under Ar. Anal. Calcd for C$_{32}$H$_{57}$AlSi$_2$Zr: C, 62.38; H, 9.32. Found: C, 62.53; H, 9.06. An NMR spectroscopic investigation of the crude thermolysis product showed a 3 to 1 ratio of complexes **3** and **1**. ^{1}H NMR (C$_6$D$_6$, 297 K): δ −1.43 (br, 1H, μ-H); 0.52 (s, 9H, β-SiMe$_3$); 0.58 (s, 9H, α-SiMe$_3$); 0.94 (dd, 1H, Cp-CH$_2$); 1.29 (s, 3H, Cp-CH$_3$); 1.48 (d, 1H, Cp-CH$_2$); 1.72 (s, 15H, Cp*); 1.81 (s, 3H, C-CH$_3$); 1.85 (s, 3H; Cp-CH$_3$); 2.33 (s, 3H, Cp-CH$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 297 K): δ 6.2 (β-SiMe$_3$); 7.2 (α-SiMe$_3$); 10.3 (br, Cp-CH$_2$); 11.3; 11.8; 13.7; 14.6 (4 Cp-CH$_3$); 12.1 (C$_5$*Me*$_5$); 114.6 (*C*$_5$Me$_5$); 142.3 (Al-*C*SiMe$_3$); 246.0 (Zr-*C*SiMe$_3$). ^{29}Si NMR (C$_6$D$_6$, 297 K): δ −2.9 (β-Si); −14,9 (α-Si). MS (70 eV, *m*/*z*): 444 [M − Me$_3$SiC$_2$SiMe$_3$]$^+$, 360 [Cp$_2$Zr]$^+$, 155 [Me$_3$SiC$_2$SiMe$_3$ − Me]$^+$.

Polymerization of Ethylene. Complex **2** (0.027 g, 0.04 mmol) was dissolved in 20 mL of toluene under Ar. Argon was carefully removed in a vacuum, and the flask with solution was filled with ethylene. The solution was stirred in the closed flask for 3 h at 90 °C. Following cooling to room temperature, the polymerization started and ethylene was supplied as consumed (1.1 bar). The solution was stirred for 15 min, and then the ethylene was removed in a vacuum. The polymer was filtered, washed with toluene, and dried in vacuo. Yield of polyethylene: 0.550 g, identified by infrared spectra.

Polymerization of ϵ-Caprolactone. Complex **2** (0.027 g, 0.04 mmol) was dissolved in 10 mL of toluene under argon. A 1 mL portion of this solution (0.004 mmol) was added to a solution of ϵ-caprolactone (2.12 mL, 2.290 g, 20 mmol) in 0.88 mL of toluene. The mixture was stirred and warmed to 60 °C. After 1 h to the reaction mixture was added an excess of methanol. The poly-ϵ-caprolactone was separated and dried in vacuo until the weight remained constant. Yield: 0.506 g (22%), identified by infrared spectra in comparison to earlier obtained samples.[3]

The molecular masses of poly-ϵ-caprolactones were measured by GPC [Hewlett-Packard liquid chromatograph 1090 HP (SDV column 10^4 Å + 10^3 Å + 100 Å (Polymer Standard Service), eluent THF] and were corrected by the universal calibration relative to polystyrene standards.

X-ray Crystallographic Study of Complexes 2 and 3. Data were collected with a STOE-IPDS diffractometer using graphite-monochromated Mo Kα radiation. The structures were solved by direct methods (SHELXS-86)[8] and refined by full-matrix least-squares techniques against F^2 (SHELXL-93, SHELXL-97).[9] XP (Bruker-AXS) was used for structure representations.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft (Research Training Group 1213 and the SPP 1118, Project-Nr RO 1269/6) and the Russian Foundation for Basic Research (Project Code 05-03-32515) for support of this work. We thank our technical staff, in particular Petra Bartels and Regina Jesse, for skilled assistance.

Supporting Information Available: Tables of crystallographic data in cif format, including bond lengths and angles of compounds **2** and **3**. Detailed NMR spectroscopic data with full assignments for compounds **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050821I

---

[7] Burlakov, V. V.; Pellny, P.-M.; Arndt, P.; Baumann, W.; Spannenberg, A.; Shur, V. B.; Rosenthal, U. *Chem. Commun.* **2000**, 241.

[8] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A 46*, 467.

[9] Sheldrick, G. M. *SHELXL-93*; University of Göttingen: Göttingen, Germany, 1993. Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.