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Reactions of Five-Membered Zirconacyclocumulenes with Diisobutylaluminum Hydride

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Different products of the reaction of the five-membered zirconacyclocumulenes (zirconacyclopenta-2,3,4-trienes) Cp*$_2$Zr(η^4-1,2,3,4-RC$_4$R) (Cp* = η^5-pentamethylcyclopentadienyl, R = Me (**1a**), Me$_3$Si (**1b**), Ph (**1c**)) with *i*-Bu$_2$AlH are described which can serve as models for the elementary reaction steps of the zirconocene-catalyzed hydroalumination of disubstituted buta-1,3-diynes RC≡CC≡CR and also for the activation of zirconocene complexes in the catalytic polymerization of ethylene. In all investigated cases of reactions of complexes **1** with *i*-Bu$_2$AlH via a *cis*-hydroalumination of the central double bond, the formation of zirconacyclopentadienes with *i*-Bu$_2$Al substituents in the 3-position as intermediates must be assumed. These complexes were not isolated but subsequently stabilized in a different manner, depending on the substituents R used. For R = Me, the intermediate reacts with a second molecule of *i*-Bu$_2$AlH to give the complex of the substituted zirconacyclopentadiene with *i*-Bu$_2$AlH (**2**). This complex reacts with CO$_2$ to produce the dinuclear complex **3**, whose structure was confirmed by X-ray analysis. For R = Me$_3$Si, the C−C bond in the intermediate is cleaved ("hydroaluminolysis") with formation of the alkyne *i*-Bu$_2$AlC≡CSiMe$_3$ (detected by NMR) and the alkyne complex [Cp*$_2$Zr(η^2-Me$_3$SiCCH)]. The latter is stabilized by reaction with *i*-Bu$_2$AlH to give [Cp*$_2$Zr][(μ-η^1:η^2-Me$_3$SiCCH)(μ-H)(*i*-Bu$_2$Al)] (**4**), which was characterized by X-ray crystallography. For R = Ph, two complexes were isolated after a stepwise reaction of the unisolated hydroalumination product. The heterobimetallic complex [Cp*$_2$Zr][(μ-η^1:η^2-PhCC−CHCPh)(μ-H)(*i*-BuAl)] (**5**) was formed by interaction with *i*-Bu$_2$AlH with elimination of *i*-Bu$_3$Al. This complex can add a further 1 equiv of *i*-Bu$_2$AlH to form the trinuclear bimetallic complex [Cp*$_2$Zr][(μ-η^1:η^2-PhCC−CH=C(*i*-Bu$_2$Al)(Ph)](μ-H)(*i*-BuAlH)] (**6**). The structures of complexes **5** and **6** were determined by X-ray diffraction analysis.

Introduction

Conjugated as well as nonconjugated diynes have been reported to react with titanocene or zirconocene.[1] We investigated such reactions with 1,3-butadiynes using the complexes Cp$_2$M(L)(η^2-Me$_3$SiC$_2$SiMe$_3$) (M = Ti, L = −; M = Zr, L = THF, pyridine) as metallocene sources.[2] Some unexpected results were obtained in these studies: different modes of complexation, C−C single bond cleavage, and coupling reactions. The resulting products strongly depend on the diyne substituents R, the metal, and the stoichiometry employed. The most interesting products of these reactions were the stable five-membered metallacyclocumulenes Cp$_2$M(η^4-1,2,3,4-RC$_4$R) (R = *t*-Bu, M = Zr,[3] Ti[4]), whose structures were established by X-ray diffraction studies, which showed a planar ring system with three C=C double bonds, the central bond of which is internally coordinated to the metal center. We reported the different interactions of permethylzirconocene complexes with 1,3-butadiynes RC≡CC≡CR, in which the five-membered zirconacyclocumulenes (η^4 complexes, zirconacyclopenta-2,3,4-trienes) Cp*$_2$Zr(η^4-1,2,3,4-RC$_4$R) (R = Me, SiMe$_3$, Ph) also were the major products.[5,6]

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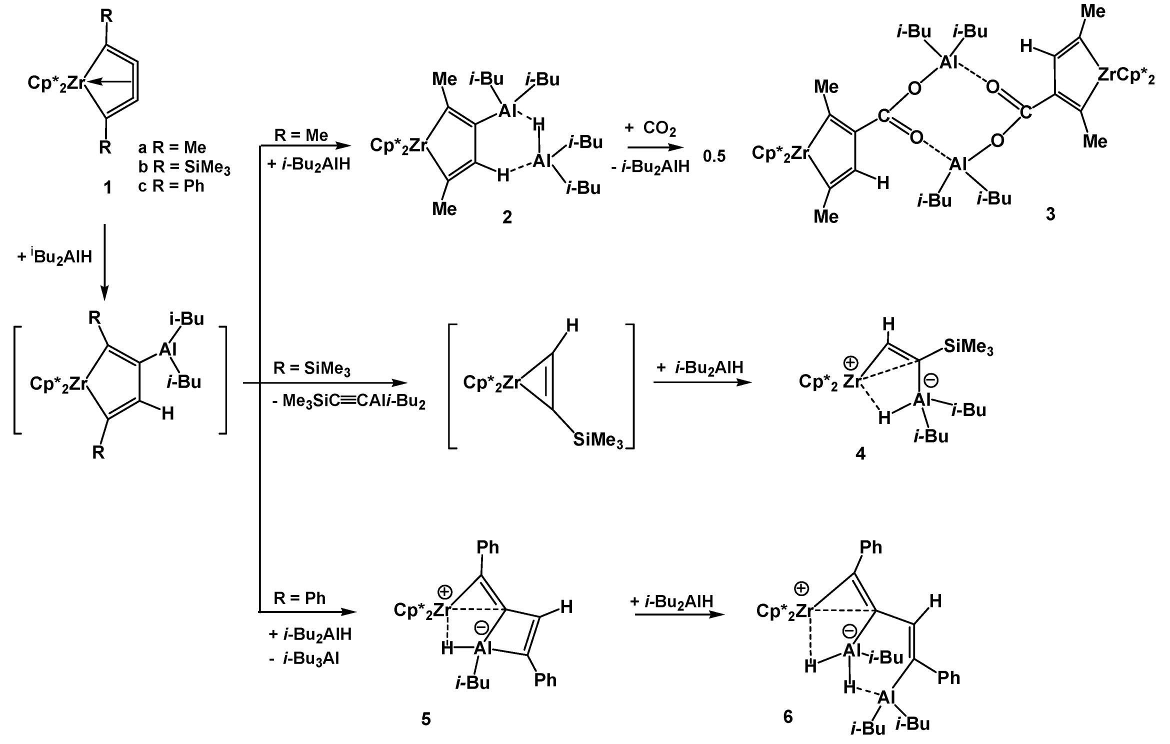
Scheme 1



Recently we reported that the titana- and zirconacyclopropenes (η^2-alkyne complexes) Cp′$_2$M(η^2-Me$_3$SiC$_2$SiMe$_3$) with M = Ti, Zr and Cp′$_2$ = Cp$_2$ (bis(η^5-cyclopentadienyl)), ebthi (1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)) readily react with *i*-Bu$_3$Al with formation of isobutene and the heterobimetallic complexes [Cp′$_2$M]-[(μ-η^1:η^2-Me$_3$SiCCSiMe$_3$)(μ-H)(*i*-Bu$_2$Al)].[7a] A better route to these complexes is the direct reaction of the alkyne complexes with *i*-Bu$_2$AlH. Such reactions can serve as a model for the titanocene- and zirconocene-catalyzed hydroalumination of alkynes, an important route to organoaluminum compounds.[8]

Because such data for the titanium- and zirconium-catalyzed hydroalumination of 1,3-butadiynes are limited,[9] after having studied the reactions of titanocene and zirconocene complexes of *alkynes* with *i*-Bu$_2$AlH we continued with similar studies with *1,3-diynes*. We report here the reactions of five-membered zirconacyclocumulenes (η^4-diyne complexes, zirconacyclopenta-2,3,4-trienes) with *i*-Bu$_2$AlH.

Results and Discussion

Complex Syntheses. The first reaction of the five-membered zirconacyclocumulene Cp*$_2$Zr(η^4-1,2,3,4-MeC$_4$-Me) (**1a**) with *i*-Bu$_2$AlH is probably *cis*-hydroalumination of the central double bond. The initial product could not be isolated, because it rapidly added a second molecule of *i*-Bu$_2$AlH to give the complex **2** (Scheme 1).

Support for the structure of complex **2** was provided by NMR measurements and its reaction with carbon dioxide. Carbon dioxide inserted into the Al−C bond of **2**, and the dinuclear complex **3** was formed after formal elimination of *i*-Bu$_2$AlH (Scheme 1). The dimeric structure of **3** was confirmed by X-ray diffraction (Figure 1).

The complex Cp*$_2$Zr(η^4-1,2,3,4-Me$_3$SiC$_4$SiMe$_3$) (**1b**) reacted with *i*-Bu$_2$AlH like **1a** in the first step, in a cis-hydroalumination of the central double bond. Subsequent C−C bond cleavage ("hydroaluminolysis") to the alkyne *i*-Bu$_2$AlC≡CSiMe$_3$ (detected by NMR) and the alkyne complex [Cp*$_2$Zr(η^2-Me$_3$SiCCH)] is the probable second step. The latter complex of a terminal alkyne reacted with a second equivalent of *i*-Bu$_2$AlH, to give the complex [Cp*$_2$Zr][(μ-η^1:η^2-Me$_3$SiCCH)(μ-H)(*i*-Bu$_2$Al)] (**4**) as the final product. The structure of **4** was confirmed by X-ray analysis. This complex is very similar to the products of the Cp′$_2$M(η^2-Me$_3$SiC$_2$SiMe$_3$) reaction with *i*-Bu$_3$Al or *i*-Bu$_2$AlH[7] mentioned above, but a terminal alkyne complex is involved.

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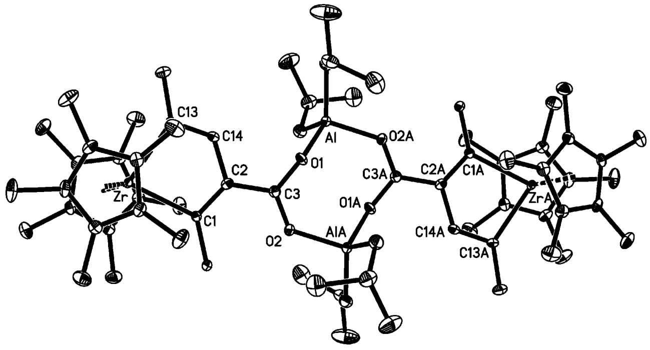

Figure 1. Crystal structure of complex **3**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Bond distances (Å): Zr−C1 = 2.271(4), Zr−C13 = 2.240(4), C1−C2 = 1.357(5), C2−C14 = 1.486(6), C13−C14 = 1.339(6), Al−O1 = 1.801(3), Al−O2 = 1.840(3).

The complex Cp*$_2$Zr(η^4-1,2,3,4-PhC$_4$CPh) (**1c**) also reacted with 1 equiv of *i*-Bu$_2$AlH with a *cis*-hydroalumination of the central double bond, giving the unisolated zirconacyclopentadiene with *i*-Bu$_2$Al substituents in the 3-position as an intermediate. This, on reaction with a second equivalent of *i*-Bu$_2$AlH, gave with elimination of *i*-Bu$_3$Al the heterobimetallic complex [Cp*$_2$Zr][(μ-η^1:η^2-PhCC−CHCPh)(μ-H)(*i*-BuAl)] (**5**). Complex **5** reacts with a third equivalent of *i*-Bu$_2$AlH to form the trinuclear bimetallic complex [Cp*$_2$Zr][(μ-η^1:η^2-PhCCCH=C(*i*-Bu$_2$Al)(Ph)](μ-H)(*i*-BuAlH)] (**6**), which is in sum formally built up from **1c**, *i*-Bu$_2$AlH, and *i*-BuAlH$_2$ (Scheme 1). Complexes **5** and **6** were structurally characterized by X-ray diffraction analysis.

NMR Investigations. (a) ^{1}H NMR Spectroscopy. The addition of *i*-Bu$_2$AlH to the butadiyne complexes **1** occurs with formation of bridges to different bridgehead atoms. These various electron-deficient structural features can be clearly distinguished by NMR spectroscopy. In complex **2**, a CH group serving as a bridge to Al is formed. The unusual chemical shift, δ 1.20 ppm, and in particular the small coupling constant $^1J_{\mathrm{C,H}}$ (87 Hz) indicate the bonding situation ("agostic" interaction). In complexes **4**−**6**, a hydride connects aluminum with zirconium. Its proton resonance is shifted to low frequency and is found between 0 and −1.5 ppm. Interestingly, scalar couplings $J_{\mathrm{H,H}}$ over three (**4**) or four bonds (**5**) are observed, as well as a long-range CH coupling to C2 in complex **6**. A third type of bridge, connecting two Al atoms, is present in **2** and **6**. This type is characterized by δ values similar to that found for *i*-Bu$_2$AlH (3.06 ppm in C$_6$D$_6$) itself. Generally, all complexes, except **6**, appear to be C_s symmetric in solution (equivalent Cp* ligands and methyl groups in the *i*-Bu substituents), which means that the polycyclic atomic framework built up from the central metal, the butadiyne carbon atoms, and the attached Al−H group is planar (by average) and represents a symmetry plane.

(b) ^{13}C NMR spectroscopy. Due to the line broadening caused by the quadrupolar moment of the ^{27}Al nucleus (100% natural abundance), the signals of carbon atoms bonded to aluminum are easily identified. Line widths greater than 10 Hz are found for the methylene carbon atoms in the *i*-Bu substituents, whereas signal broadening for the metalated sp^2 carbons is less pronounced, although clearly noticeable (here we observed line widths up to 5 Hz). For instance, C2 in complex **2** (90.3 ppm) exhibits a 5 ppm wide resonance line; after carboxylation (complex **3**) the equivalent position (C2) gives rise to a sharp signal at 126.3 ppm. Compounds **4**−**6** are analogues to the aforementioned heterobimetallics [Cp′$_2$M][(μ-η^1:η^2-Me$_3$SiCCSiMe$_3$)(μ-H)(*i*-Bu$_2$Al)][7a] (see discussion of structure below). Therefore, similar chemical shifts for the five-membered Zr−Al ring system are observed, and a rather constant shift difference of 130 ppm is found between C$_\alpha$ and C$_\beta$. The latter, although considered formally as "planar-tetracoordinate", do not exhibit extraordinary chemical shifts but are always found in the common olefinic region. A silyl substituent leads to the expected shift toward higher frequency at the carbon in a β-position (cf. **4**, C$_\alpha$ 231.1 ppm; **5**, C$_\alpha$ 192.9 ppm). Strong shifts to high frequency occur for the Al-bound sp^2 carbons outside the zirconacycle (C3 for **5** and C4 for **6**: 178.6 and 162.0 ppm, respectively) and, as usually observed, for sp^2 carbons with σ bonds to zirconium.

Table 1. Crystallographic Data for Complexes 3−6

	3	4	5	6
cryst color, habit	yellow, prism	light yellow, prism	yellow, prism	yellow, prism
cryst syst	triclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
lattice constants				
a (Å)	9.463(2)	9.417(2)	12.539(3)	12.185(2)
b (Å)	14.051(3)	10.512(2)	22.170(4)	12.395(2)
c (Å)	14.259(3)	18.407(4)	13.364(3)	16.555(3)
α (deg)	88.73(3)	78.04(3)		74.42(3)
β (deg)	72.43(3)	88.80(3)	111.80(3)	79.57(3)
γ (deg)	70.69(3)	74.64(3)		69.31(3)
Z	1	2	4	2
cell vol, Å^3	1699.4(6)	1717.8(6)	3449.4(13)	2242.8(7)
density (g cm^{-3})	1.223	1.164	1.252	1.173
temp (K)	200(2)	293(2)	293(2)	200(2)
μ(Mo Kα) (mm^{-1})	0.377	0.399	0.370	0.314
no. of rflns				
measd	5124	5137	6964	5477
indep	5124	5137	3665	5477
obsd	3852	3208	2860	3812
no. of params	356	329	387	472
R1 ($I > 2\sigma(I)$)	0.047	0.049	0.038	0.047
wR2 (all data)	0.121	0.107	0.096	0.133

X-ray Crystal Structures. The molecular structures of complexes **3**−**6** were confirmed by X-ray crystal structure analysis. The crystallographic data are listed in Table 1.

The molecular structure of the zirconocene complex **3** displays a dinuclear complex with an eight-membered ring in the center, formed by dimerization of two dialkylaluminum carboxylates. Each carboxylate is the substituent in the β-position of one zirconacyclopentadiene.

The X-ray crystal structure analyses of the zirconocene complexes **4**−**6** show the same structural element: all contain in principle the more or less distorted planar, bicyclic five-membered-ring systems consisting of Zr, hydridic hydrogen H, Al, C$_\beta$, and C$_\alpha$ (Figures 2−4). As this structural key element was also found in the complexes [(η^5-C$_5$H$_5$)$_2$Ti][(μ-η^1:η^2-Me$_3$SiCCSiMe$_3$)(μ-H)(*i*-Bu$_2$Al)] (**A**)[7a] and [*rac*-(ebthi)Zr][(μ-η^1:η^2-Me$_3$SiCCSiMe$_3$)(μ-H)(*i*-Bu$_2$Al)] (**B**), [7a] a comparison is worthwhile (Table 2).

The most remarkable feature of these complexes is the coordination geometry of the carbon atom C$_\beta$, which is bonded to C$_\alpha$, M, Al, and Si or C of the attached group,

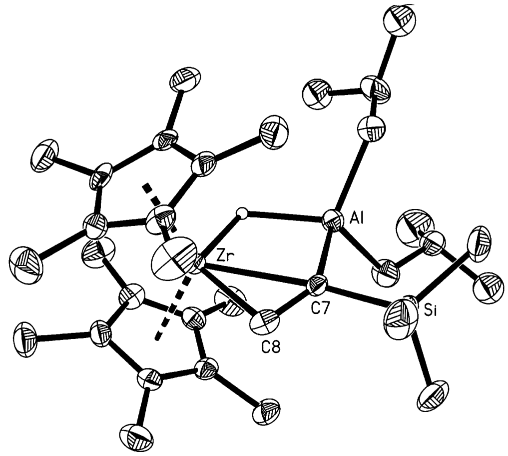

Figure 2. Crystal structure of complex **4**. Hydrogen atoms, except the bridging H atom, are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Bond distances (Å) and angles (deg): Zr−C8 = 2.132(5), Zr−C7 = 2.489(5), C7−C8 = 1.331(7), Al−C7 = 2.082(5), Zr−Al = 2.999(2); Al−C7−Zr = 81.5(2), C7−C8−Zr = 88.8(3).

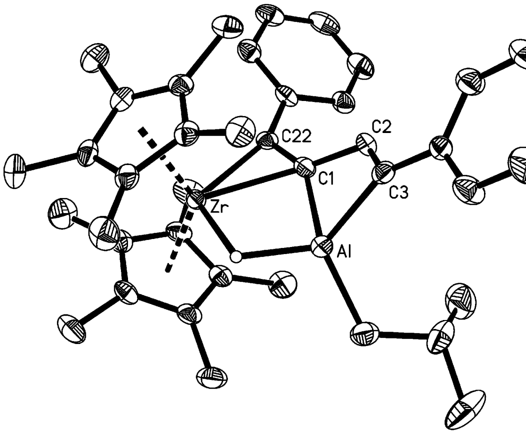

Figure 3. Crystal structure of complex **5**. Hydrogen atoms, except the bridging H atom, are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Bond distances (Å) and angles (deg): Zr−C22 = 2.237(4), Zr−C1 = 2.354(4), C1−C22 = 1.330(6), Al−C1 = 2.107(5), Al−C3 = 1.960(5), Zr−Al = 2.935(1); Al−C1−Zr = 82.1(1), C1−C22−Zr = 78.0(3).

respectively, with all four bonds lying more or less in one plane. It was pointed out that this planarity is distorted in the case of complex **B**, due to the steric hindrance of the ebthi ligand (mean deviation of the best plane through M, Al, Si, C$_\alpha$, and C$_\beta$ for **B** is 0.1142 Å, in comparison to 0.0 Å for **A**). In complex **4** the plane which is defined by Zr, Al, Si, C$_\alpha$, and C$_\beta$, is nearly planar (mean deviation 0.060 Å). As in the case of **B**, for complexes **5** and **6** the planarity is extremely distorted (mean deviation of the best plane through Zr, Al, C$_\alpha$, C$_\beta$, and C2 (**5**)/C3 (**6**): **5**, 0.223 Å; **6**, 0.116 Å). For **5** and **6** this deviation probably results from the special substitution of the group bonded to C$_\beta$ and the resulting ring strain.

The values found for the bond distances from Zr to C$_\beta$ are in the expected range for such structural features.[7d−k]

Catalytic Polymerizations of Ethylene. There is a vital interest in metallocene-catalyzed polymerization of olefins to replace expensive activators such as MAO and perfluoroaryl boron compounds by low-cost activators. Recently, we reported alkene polymerization catalyzed by zirconocene difluoride or alkyl monofluoride complexes after treatment with i-Bu$_3$Al and i-Bu$_2$AlH as cheap activators.[10] A remarkable polymerization activity was observed without any borate activation, using only i-Bu$_3$Al as cocatalyst. It was assumed that in this activation i-Bu$_3$Al alkylates the difluoride complexes in the first step with formation of the monofluoride alkyl complexes Cp′$_2$Zr(F)R or dialkyl complexes Cp′$_2$ZrR$_2$. For the zirconacyclopropene *rac*-(ebthi)Zr(η^2-Me$_3$SiC$_2$SiMe$_3$), also with two Zr−C σ bonds, after activation by i-Bu$_3$Al a very low activity was found. As mentioned above in the Introduction, zirconocene complexes such as *rac*-(ebthi)Zr(η^2-Me$_3$SiC$_2$SiMe$_3$) react very easily with i-Bu$_3$Al with formation of isobutene and i-Bu$_2$AlH, which reacts to form the heterobimetallic complex [*rac*-(ebthi)Zr][(μ-η^1:η^2-Me$_3$SiCCSiMe$_3$)(μ-H)(i-Bu$_2$Al]. [7a] This complex, however, was not active.

In this work the well-defined zirconacyclopenta-2,3,4-trienes Cp*$_2$Zr(η^4-1,2,3,4-RC$_4$R) were studied as another type of zirconocene complex with two Zr−C σ bonds

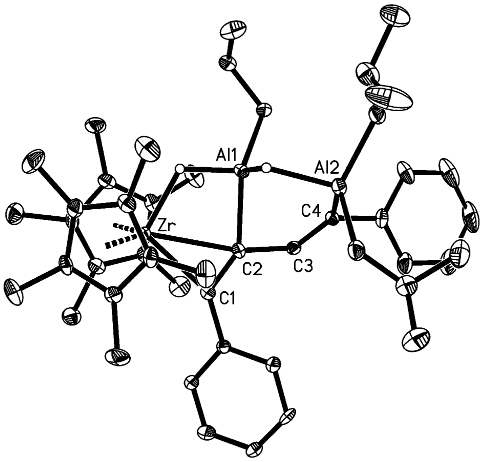

Figure 4. Crystal structure of complex **6**. Hydrogen atoms, except the bridging H atoms, are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Bond distances (Å) and angles (deg): Zr−C1 = 2.219(5), Zr−C2 = 2.448(5), C1−C2 = 1.329(7), Al1−C2 = 2.067(5), Al2−C4 = 2.037(6), Zr−Al1 = 2.929(2); Al1−C2−Zr = 80.4(2), C2−C1−Zr = 83.2(3).

Table 2. Selected Structural Data for the Complexes [*rac*-(ebthi)Zr](μ-η^1:η^2-Me$_3$SiCCSiMe$_3$)-(μ-H)[Al(i-Bu)$_2$] (B)[7a] and 4−6

	B[7a]	4	5	6
	Bond Distances (Å)			
Zr−C$_\alpha$	2.221(13)	2.132(5)	2.237(4)	2.219(5)
Zr−C$_\beta$	2.384(15)	2.489(5)	2.354(4)	2.448(5)
C$_\alpha$-C$_\beta$	1.33(2)	1.331(7)	1.330(6)	1.329(7)
Al−C$_\beta$	2.15(2)	2.082(5)	2.107(5)	2.067(5)[l]
	Bond Angles (deg)			
Al−C$_\beta$−Zr	78.3(5)	81.5(2)	82.1(1)	80.4(2)
C$_\beta$−C$_\alpha$−Zr	80.1(9)	88.8(3)	78.0(3)	83.2(3)

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[10] (a) Becke, S.; Rosenthal, U. (Bayer AG) Ger. Offen. DE 199 32 409 A1 (18.01.2001). (b) Becke, S.; Rosenthal, U. (Bayer AG) U.S. Patent 6,303,718 B1 (16.10.2001). (c) Becke, S.; Rosenthal, U.; Arndt, P.; Baumann, W.; Spannenberg, A. (Bayer AG) Ger. Offen. DE 101 10 227 A1 (05.09.2002).

Table 3. Polymerization of Ethylene with Zirconium Complexes as Catalysts

cat.	temp, °C	activity, kg of polymer/(mol h)[a]
2	40	0
2	90 → room temp[b]	220
4	40	0
4	90 → room temp[b]	105
6	40	100

[a] Conditions: 1.1 bar, 15 min; 0.04 mmol of complex in 20 mL of toluene. [b] Activation for 2 h at 90 °C under an ethylene atmosphere.

Table 4. Ring-Opening Polymerization of ϵ-Caprolactone with Zirconium Complexes as Catalysts[a]

	ϵ-cl:cat. = 5000:1		ϵ-cl:cat. = 10 000:1	
complex	yield (%)	mol mass (M_w)	yield (%)	mol mass (M_w)
$Cp_2Zr(Py)(\eta^2\text{-}Me_3SiC_2SiMe_3)$	80	80 000	n.e.	n.e.
$[Cp_2Zr](\mu\text{-}\eta^1{:}\eta^2\text{-}Me_3SiC_2SiMe_3)\text{-}(\mu\text{-}H)[Al(^iBu)_2]$	82	67 570	n.e.	n.e.
4	58.5	842 000	2	26 100
2	99.8	753 000	95.7	528 000
6	98.0	825 000	98.8	1 083 000

[a] All experiments in toluene at 75 °C (1 h) with an initial concentration of ϵ-caprolactone (ϵ-cl) of 5 mol/L.

which are activated by *i*-Bu_2AlH via different complexes. These complexes formed in reaction with *i*-Bu_2AlH (**2**, **4**, and **6**) were tested in the polymerization of ethylene without any additional activators. The obtained results are summarized in Table 3.

Only complex **6** was active without thermal activation at 90 °C, whereas the other complexes required such activation. The reason for this result is under investigation.

Ring-Opening Polymerization. For the catalytic ring-opening polymerization of ϵ-caprolactone we showed the titana- and zirconacyclopropenes $Cp'_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ to be active catalysts.[7b,c] Later we found an additional activation by *i*-Bu_3Al or *i*-Bu_2AlH, in which the complexes $[Cp'_2Ti][(\mu\text{-}\eta^1{:}\eta^2\text{-}Me_3SiCCSiMe_3)(\mu\text{-}H)(i\text{-}Bu_2Al)]$ [7a] were formed. These showed an increase in the polymer molecular weights and in the activity compared to the starting complexes.[7a]

Complexes **2**, **4**, and **6** were tested as catalysts in the ring-opening polymerization of ϵ-caprolactone. The results are summarized in Table 4 and compared to the results obtained with the zirconocene complexes $Cp_2Zr(Py)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ and $[Cp'_2Zr][(\mu\text{-}\eta^1{:}\eta^2\text{-}Me_3SiCCSiMe_3)(\mu\text{-}H)(i\text{-}Bu_2Al)]$.[7a] The best catalytic activity was found for complex **2** and **6**.

Conclusion

The complexes **4**−**6** as products of the reaction of the five-membered zirconacyclocumulenes (zirconacyclopenta-2,3,4-trienes) $Cp^*_2Zr(\eta^4\text{-}1,2,3,4\text{-}RC_4R)$ (R = Me_3Si (**1b**), and Ph (**1c**)) with *i*-Bu_2AlH are further examples of compounds with “planar-tetracoordinate” carbon atoms. Although initally considered “pathological”,[7] this bonding mode has meanwhile been proven to be very common, if not typical, for such heterobimetallic complexes.

Experimental Section

Preparation of Complex 2. *i*-Bu_2AlH (3.05 mL of a 1.0 M solution in *n*-heptane, 3.05 mmol) was added to a solution of **1a** (0.669 g, 1.52 mmol) in 10 mL of *n*-hexane. The resulting red-orange mixture was warmed for 3−5 min to 50 °C and filtered. Subsequent cooling to −78 °C gave after 2 days orange crystals of **2**, which were separated from the mother liquor by decantation, washed with a small amount of cold *n*-hexane, and dried under vacuum. The yield of **2** is 0.906 g (82%); mp 127−129 °C under Ar. Anal. Calcd for $C_{42}H_{74}Al_2Zr$: C, 69.65; H, 10.30. Found: C, 69.23; H 10.04. ^1H NMR (C_6D_6, 297 K): δ 0.62 (m, 8H, CH_2); 1.20 (s, 1H, $=CH$); 1.35 (d, $^3J = 6.5$ Hz, 6H, CH_3); 1.36 (d, $^3J = 6.6$ Hz, 6H, CH_3); 1.38 (d, $^3J = 6.5$ Hz, 12H, CH_3); 1.53 (s, 30H, Cp*); 2.32 (m, 2H, CH); 2.37 (m, 2H, CH); 2.44 (s, 3H, 4-CH_3); 2.72 (s, 3H, 1-CH_3); 3.77 (br., 1H, AlH). $^{13}C\{^1H\}$ NMR (C_6D_6, 297 K): 11.2 (Cp*); 22.3 (br, CH_2); 23.1 (1-CH_3); 26.0 (br, CH_2); 27.7, 27.7 (2 × CH); 28.6, 28.7, 29.0, 29.3 (4 × CH_3); 32.6 (4-CH_3); 90.3 ($C2_{Al}$) 117.5 (Cp*); 148.3 ($=CH$ [3], $^1J_{C,H} = 87$ Hz, $^3J_{CH} = 10$ Hz); 185.4 ($C4_{Zr}$), 226.2 ($C1_{Zr}$). MS (70 eV, *m*/*z*): 440 $[M - 2\text{-}i\text{-}Bu_2Al]^+$, 360 $[Cp_2Zr]^+$.

Preparation of Complex 3. Complex **2** (0.274 g, 0.38 mmol) was dissolved in 5−7 mL of *n*-hexane under Ar, and the orange solution was filtered. Argon was carefully removed in vacuo, and the flask was filled with gaseous CO_2 at room temperature. After 1 day the resulting yellow solution was cooled to −78 °C; within 2 days at this temperature yellow crystals appeared which were separated from the mother liquor by decantation, washed with a small amount of cold *n*-hexane, and dried under vacuum to give 0.080 g (34%) of **3**, mp 246−248 °C dec under Ar. Anal. Calcd for $C_{70}H_{110}Al_2Zr_2O_4$: C, 67.15; H, 8.86. Found: C, 66.83; H 8.57. ^1H NMR (C_6D_6, 297 K): δ 0.57 (d, $^3J = 7.0$ Hz, 8H, CH_2); 1.39 (d, $^3J = 6.5$ Hz, 24H, CH_3); 1.72 (s, 60H, Cp*); 1.91 (dq, $^4J = 1.6$ Hz, $^6J = 0.6$ Hz, 6H, 13-CH_3); 2.36 (q, $^6J = 0.6$ Hz, 6H, 1-CH_3); 2.38 (m, 4H, CH); 7.14 (q, $^4J = 1.6$ Hz, 2H, $=CH$ [14]); $^{13}C\{^1H\}$ NMR (C_6D_6, 297 K): 11.4 (Cp*); 22.5 (br., CH_2); 26.6 (1-CH_3); 26.8 (CH); 28.0 (13-CH_3); 28.9 (CH_3); 118.8 (Cp*); 122.7 (CH [14], $^1J_{CH} = 150$ Hz), 126.3 (C2); 169.0 (CO); 204.0 (C13), 237.6 (C1). IR (Nujol mull, cm^{-1}): 1552 ($\nu_{C=O}$).

Preparation of Complex 4. *i*-Bu_2AlH (2.30 mL of a 1.0 M solution in *n*-heptane, 2.30 mmol) was added to a solution of **1b** (0.646 g, 1.16 mmol) in 15 mL of *n*-hexane. After 24 h the yellow solution was evaporated to 3−4 mL and filtered. When the filtrate was cooled to −78 °C for 2 days, light yellow crystals formed, which were separated from the mother liquor by decantation, washed with a small amount of cold *n*-hexane, and dried under vacuum. The yield of **4** is 0.454 g (65%), mp 133−134 °C under Ar. Anal. Calcd for $C_{33}H_{59}AlSiZr$: C, 65.83; H, 9.88. Found: C, 65.43; H 9.57. ^1H NMR (C_6D_6, 297 K): δ −0.66 (br, 1H, μ-H); 0.49 (s, 9H, $SiMe_3$); 0.56 (m, 4H, CH_2); 1.35, 1.37 (2d, $^3J = 6.4$ Hz, 6H each, 2 × CH_3); 1.71 (s, 30H, Cp*); 2.44 (m, 2H, CH); 9.95 (d, $^3J_{H,H} = 2.4$ Hz, $^3J_{H,Si} = 9.5$ Hz, 1H, $=CH$). $^{13}C\{^1H\}$ NMR (C_6D_6, 297 K): δ 4.8 ($SiMe_3$); 12.3 (Cp*); 26.3 (br, CH_2); 27.3 (CH); 28.7, 29.4 (2 × CH_3); 115.2 (Cp*); 122.2 ($=CSiMe_3$); 231.1 ($=CH$, $^1J_{C,H} = 161$ Hz, $^3J_{CH} = 3$ Hz). ^{29}Si NMR (C_6D_6, 297 K): 0.2 ($^2J_{Si,H} = 6.3$ Hz, $^3J_{Si,H} = 9.5$ Hz). MS (70 eV, *m*/*z*): 360 $[Cp_2Zr]^+$.

The mother liquor was evaporated under vacuum to dryness to give an oily mixture of **4** and *i*-$Bu_2AlC{\equiv}CSiMe_3$; the latter is presumably dimeric, as indicated by ^1H NOE NMR observations. ^1H NMR (C_6D_6, 297 K): δ 0.09 (s, 9H, $SiMe_3$); 0.55 (d, $^3J = 7$ Hz, 4H, CH_2); 1.24 (d, $^3J = 6.5$ Hz, 12H, CH_3); 2.24 (m, 2H, CH). $^{13}C\{^1H\}$ NMR (C_6D_6, 297 K): δ −1.0 ($SiMe_3$); 25.8 (br, CH_2); 26.9 (CH); 28.2 (CH_3); 148.2 ($\equiv CSi$); $\equiv CAl$ not observed. ^{29}Si NMR (C_6D_6, 297 K): δ −15.9.

Preparation of Complex 5. Complex **1c** (0.221 g, 0.39 mmol) was dissolved in 10 mL of toluene under Ar, and *i*-Bu_2AlH (0.78 mL of a 1.0 M solution in *n*-heptane, 0.78 mmol) was added. After 15 h the red-yellow solution was evaporated under vacuum. *n*-Hexane (7−8 mL) was added to the oily residue, and the resulting mixture was warmed to 60 °C for 7 h. The solution was filtered and allowed to stand under an argon atmosphere at −78 °C. After 1 day yellow crystals had formed which were separated from the mother liquor by decanting, washed with cooled *n*-hexane, and dried under vacuum to give 0.205 g of a mixture of **5** (73%) and **6** (27%). After repeated recrystallizations from *n*-hexane 0.06 g of pure **5** was isolated. Mp: 210−212 °C dec under Ar. Anal. Calcd for $C_{40}H_{51}AlZr$: C, 73.91; H, 7.91. Found: C, 73.55; H, 7.62. ^1H NMR (C_6D_6, 297 K): δ −0.90 (br, 1H, μ-H); 0.79 (d, ^3J = 7.4 Hz, 2H, CH_2); 1.22 (d, ^3J = 6.6 Hz, 6H, CH_3); 1.79 (s, 30H, Cp*); 2.30 (m, 1H, CH); 7.12 (m, 1H, *p*-3-Ph); 7.17 (m, 1H, *p*-22-Ph); 7.29 (m, 2H, *m*-3-Ph); 7.41 (m, 2H, *m*-22-Ph); 7.66 (m, 4H, *o*-Ph); 8.89 (d, ^4J = 0.9 Hz, 1H, =CH [2]). $^{13}C\{^1H\}$ NMR (C_6D_6, 297 K): δ 12.5 (Cp*); 27.2 (CH); 28.5 (CH_3); 30.2 (br, CH_2); 115.7 (Cp*); 126.2 (*p*-22-Ph); 127.2 (*p*-3-Ph); 128.1 (*o*-3-Ph); 128.5 (*m*-22-Ph); 128.8 (*m*-3-Ph); 131.0 (*o*-22-Ph); 133.3 (C1); 136.9 (=CH [2], $^1J_{CH}$ = 156 Hz); 141.4 (*i*-22-Ph); 142.0 (*i*-3-Ph); 178.6 (C3); 192.9 (C22). MS (70 eV, *m*/*z*): 648 $[M]^+$, 360 $[Cp_2Zr]^+$.

Preparation of Complex 6. (a) From 1c and *i*-Bu$_2$AlH. *i*-Bu$_2$AlH (1.45 mL of a 1.0 M solution in *n*-heptane, 1.45 mmol) was added to a solution of **1c** (0.264 g, 0.47 mmol) in 5−7 mL of toluene. After 3 days the red-yellow solution was evaporated under vacuum and *n*-hexane was added to the oily residue. The resulting mixture was allowed to stand under an argon atmosphere at room temperature to give yellow crystals after 2 days, which were separated from the mother liquor by decantation, washed with cold *n*-hexane, and dried under vacuum. The yield of **6** is 0.252 g (68%). Mp: 183−185 °C dec under Ar. Anal. Calcd for $C_{46}H_{70}Al_2Zr$: C, 72.77; H, 8.91. Found: C, 72.20; H, 8.56. ^1H NMR (C_6D_6, 297 K): δ −0.35 (br, 1H, Zr−H−Al); 0.45 (dd, ^2J = 13.7 Hz, ^3J = 6.9 Hz, 1H, CH_2); 0.62 (dd, ^2J = 13.7 Hz, ^3J = 7.1 Hz, 1H, CH_2); 0.85 (m, 2H; CH_2); 0.87 (m, 1H; CH_2); 1.13 (m, 1H; CH_2); 1.14 (d, 3H; CH_3); 1.18 (d, 3H; CH_3); 1.33 (d, 3H; CH_3); 1.34 (d, 3H; CH_3); 1.38 (d, 3H; CH_3); 1.42 (d, 3H; CH_3); 1.71 (s, 15H, Cp*); 1.75 (s, 15H, Cp*); 2.18 (non, 1H, CH); 2.34 (m, 1H, CH); 2.53 (m, 1H, CH); 4.47 (br, 1H, Al−H−Al); 7.05 (m, 1H, *p*-4-Ph); 7.14 (m, 1H, *p*-1-Ph); 7.27 (m, 2H, *m*-4-Ph); 7.37 (m, 2H, *m*-1-Ph); 7.62 (m, 2H, *o*-4-Ph); 7.74 (s, 1H, =CH [3]); 7.75 (m, 2H, *o*-1-Ph). $^{13}C\{^1H\}$ NMR (C_6D_6, 297 K): δ 12.3, 12.4 (2 × Cp*); 23.0 (br), 23.3 (br), 26.1 (br, 3 × CH_2); 27.0, 27.1, 27.7 (3 × CH); 27.4, 28.3, 28.7, 28.8, 28.8, 29.2 (6 × CH_3); 116.8, 117.2 (2 × Cp*); 117.4 (C2); 125.9 (*p*-4-Ph); 127.0 (*o*-4-Ph); 127.8 (*p*-1-Ph); 128.0 (*m*-1-Ph); 128.7 (*m*-4-Ph); 132.1 (*o*-1-Ph); 139.1 (*i*-1-Ph); 142.9 (=CH [3], $^1J_{CH}$ = 154 Hz); 149.9 (*i*-4-Ph); 162.0 (C4); 209.4 (C1). MS (70 eV, *m*/*z*): 648 $[M - i\text{-}Bu_2AlH]^+$, 360 $[Cp_2Zr]^+$.

The mother liquor was evaporated under vacuum to dryness to give an oily mixture, in which Al(*i*-Bu)$_3$ predominated (NMR measurements).

(b) From 5 and *i*-Bu$_2$AlH. Complex **5** (ca. 0.05 g, 0.09 mmol) was dissolved in 1 mL of C_6D_6 under Ar, and *i*-Bu$_2$AlH (0.09 mL of a 1.0 M solution in *n*-heptane,0.09 mmol) was added. After 2 h at room temperature the red-yellow solution was evaporated under vacuum. The residue was dissolved in 0.6 mL of C_6D_6 and transferred to an NMR tube. NMR spectroscopic measurements indicated the formation of practically pure **6**.

Polymerization of Ethylene. (a) For Complexes 2 and 4. A 0.04 mmol amount of of complex **2** or **4** was dissolved in 20 mL of toluene under Ar. Argon was carefully removed under vacuum, and the flask with solution was filled with ethylene. The solution was stirred in the closed flask for 2 h at 90 °C. After the solution was cooled 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 under vacuum. The polymer was filtered, washed with toluene, and dried in vacuo.

(b) For Complex 6. A 0.032 g amount (0.04 mmol) of complex **6** was dissolved in 20 mL of toluene under Ar. Argon was carefully removed under vacuum, and the flask with solution was filled with ethylene. The solution was stirred for 15 min at 40 °C, and ethylene was supplied as consumed (1.1 bar). After 15 min the ethylene was removed. The polymer was filtered, washed with toluene, and dried in vacuo.

Polymerization of ϵ-Caprolactone. A 5 M solution of ϵ-caprolactone in toluene was added to an appropiate amount of solid catalyst. The mixture was stirred and warmed to 75 °C. After 1 h the reaction mixture was treated by addition of an excess of methanol. The poly-ϵ-caprolactone was separated and dried in vacuo until the weight remained constant.

The molecular masses of poly-ϵ-caprolactones were measured by the GPC method on a Hewlett-Packard 1090 HP liquid chromatograph (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 3−6. Data were collected with a STOE-IPDS diffractometer using graphite-monochromated Mo Kα radiation. The structures were solved by direct methods (SHELXS-86)[11] and refined by full-matrix least-squares techniques against F^2 (SHELXL-93).[12] XP (BRUKER-AXS) was used for structure representations.

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Supporting Information Available: Tables of crystallographic data in cif file format, including bond lengths and angles of compound **3** (data_ks052), **4** (data_ks277), **5** (data_897), and **6** (data_ks068). This material is available free of charge via the Internet at http://pubs.acs.org.

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