Bimetallic Titanocene or Zirconocene/Aluminium Complexes as Active Catalysts in Lactone Polymerization Reactions

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The metallocene alkyne complexes [$Cp_2M(L)(\eta^2$-$Me_3SiC_2R)$] react with diisobutylaluminium hydride at room temp. by addition of $HAl(iBu)_2$ to yield the heterobimetallic complexes [{Cp_2M}(μ-η^1:η^2-$RCCSiMe_3$)(μ-H){$Al(iBu)_2$}] [{Cp_2M}: (η^5-$C_5H_5)_2Ti$, R = Ph **1**, R = $SiMe_3$ **2**; {Cp_2M}: (η^5-$C_5H_5)_2Zr$, R = $SiMe_3$ **3**; {Cp_2M}: (ebthi)Zr, R = $SiMe_3$ **4**] {ebthi: *rac*-[1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)]}. Complexes **1**–**4** were characterized by NMR spectroscopy and **1**, **2** and **4** investigated by X-ray crystal structure analysis. Compounds **1**–**4** were tested as initiators in the ring-opening polymerization of lactones. The results are discussed in comparison to the corresponding monometallic titanocene and zirconocene alkyne complexes.

Introduction

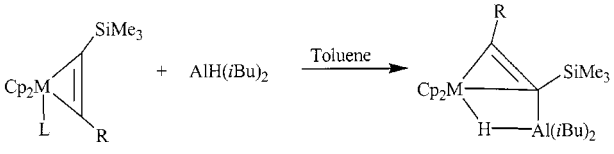
Group 4 metallocene complexes react with organoaluminium compounds to give highly active Ziegler-type catalyst systems.[1] Nevertheless, these catalysts present some disadvantages, such as the necessity of very large amounts of MAO. An approach to overcome this problem resides in the development of new activation methods to extend these active systems to other catalytic reactions. The generation of single-component catalysts, or their direct precursors, is therefore of great current interest.[2]

The reaction of metallocene-alkyne and -alkene complexes with aluminium or boron organic compounds has been intensively investigated by Erker and Binger[3] and leads to bimetallic systems of the type [{Cp_2M^1}(μ-η^1:η^2-RCCR)(μ-X){$M^2R_2^2$}] (M^1 = Zr, Hf, X = Cl, H, M^2 = Al, Ga; M^1 = Ti, X = H, M^2 = B) containing a planar tetracoordinate carbon atom bridging between a group 4 transition metal and a main group element; [$Cp_2M(PMe_3)$(alkyne)] complexes give [{Cp_2M}(μ-η^1:η^2-RCCR)(μ-H){$Al(iBu)_2$}] with diisobutylaluminium hydride.[3f] These compounds are of current interest and have been studied extensively, although compounds with a desired activation for catalytic processes were not obtained.[4]

We report here the easy synthesis of bimetallic titanium or zirconium/aluminium compounds, starting from (η^2-alkyne) metallocene complexes (alkyne = Me_3SiC_2R, R = Ph, $SiMe_3$) and their polymerization capability in the ring-opening polymerization (ROP) of lactones in comparison to the corresponding monometallic (η^2-alkyne)compounds.[11,12]

Results and Discussion

In the reaction of [$Cp_2M(L)(\eta^2$-$RC_2SiMe_3)$] {[Cp_2M]: (η^5-$C_5H_5)_2Ti$, R = Ph, $SiMe_3$, without L; [Cp_2M]: (η^5-$C_5H_5)_2Zr$, R = $SiMe_3$, L = Py; [Cp_2M]: *rac*-(ebthi)Zr, R = $SiMe_3$, without L} with diisobutylaluminium hydride in toluene (2 h) at ambient temperature, corresponding to the investigations by Erker,[3f] the bimetallic complexes [{Cp_2M}(μ-η^1:η^2-$RCCSiMe_3$)(μ-H){$Al(iBu)_2$}] **1**–**4** are formed [Equation (1)].



1 - 4

Cp_2M	R	L
(η5-$C_5H_5)_2Ti$	Ph	-
(η5-$C_5H_5)_2Ti$	$SiMe_3$	-
(η5-$C_5H_5)_2Zr$	$SiMe_3$	Py
rac-(ebthi)Zr	$SiMe_3$	-

Cp_2M	R	
(η5-$C_5H_5)_2Ti$	Ph	**1**
(η5-$C_5H_5)_2Ti$	$SiMe_3$	**2**
(η5-$C_5H_5)_2Zr$	$SiMe_3$	**3**
rac-(ebthi)Zr	$SiMe_3$	**4**

rac-(ebthi) = *rac*-[1,2-Ethylene-1,1'-bis(η5-tetrahydroindenyl)]

(1)

Complex **1** crystallizes from *n*-hexane as yellow prisms (m.p. 150–152 °C) and is stable in solution for some days even at higher temperatures. The corresponding bis(trimethylsilyl)-substituted compound **2** (brown-yellow crystals, m.p. 136 °C dec.) is less stable, it regenerates the starting

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compound [$Cp_2Ti(\eta^2$-$Me_3SiC_2SiMe_3)$] in solution at higher temperatures (80 °C, 5 h). The stable analogous zirconocene complexes **3** (light yellow needles, m.p. 142 °C) and **4** (deep yellow prism, m.p. 157−158 °C) are obtained in a similar reaction. All the above complexes were characterized by NMR spectroscopy and **1**, **2** and **4** by X-ray crystal structure analysis.

Spectroscopic Data

The most characteristic proton NMR spectroscopic feature of the compounds **1**−**4** is the high-field resonances of the bridging hydrido ligands (Table 1). The resonance signals are located in the range expected for a hydrogen atom bridging the aluminium and the transition metal center[7] [broad singlets at: δ = −3.79 (**1**), δ = −4.87 (**2**), δ = −2.46 (**3**), δ = −1.27 (**4**)].

Table 1. Selected NMR spectroscopic data of complexes **1**−**4**

	1	**2**	**3**	**4**
^{1}H NMR (δ [ppm])				
Cp	5.15	5.10	5.35	
H	−3.79	−4.87	−2.46	−1.27
^{13}C NMR (δ [ppm])				
C_α, C_β (alkyne)	230.1	234.3	240.4	243.4
	105.0	123.7	138.5	149.5

The methylene groups at aluminium give broad signals in the ^{13}C NMR spectrum which become sharper upon cooling the sample, especially for complex **2**. Besides that, no changes in the NMR spectra were observed. The ^{13}C resonances of the planar-tetracoordinated carbon atom are in the expected olefinic range [δ = 105.0 (**1**), δ = 123.7(**2**), δ = 138.5 (**3**), δ = 149.5 (**4**)]. The methylene group at the aluminium is found in the ^{13}C NMR spectrum as a broad signal at room temp.

These data of complexes **1**−**4** are in good agreement with the zirconocene/aluminium complexes [{Cp_2Zr}(μ-η^1:η^2-RCCR)(μ-H){Al(*i*Bu)$_2$}] from Erker,[3a−3f,4] and the titanocene complexes [{Cp_2Ti}(μ-η^1:η^2-$RCCSiMe_3$)(μ-H)-{Al(*i*Bu)$_2$}] described by Binger[4] and show the same structural features.

X-ray Crystal Structure Analysis of Bimetallic Ti or Zr and Aluminium Compounds

It turned out that an unambiguous characterization of the compounds **1**, **2** and **4** cannot be revealed by NMR spectroscopy as the structural element of the square-planar carbon coordination geometry does not cause any remarkable features in the NMR spectra. Compounds **1**, **2** and **4** were therefore crystallized from *n*-hexane solution by cooling to −30 °C.

The X-ray crystal structures of the titanium complexes exhibit planar, bicyclic five-membered ring systems consisting of the metal atom, the hydridic hydrogen H, Al, C_β and C_α (Figure 1−3 and Table 2). The most remarkable structural element is the coordination geometry of the carbon atom C_β, which is bonded to C_α, M, Al and the Si atom of the $SiMe_3$ group, with all four bonds lying in one plane (mean deviation from the best plane through Ti, Al, Si, C_α **1**: 0.057 Å, **2**: 0 Å). The zirconium complex **4** shows a similar bicyclic ring system as the titanium complexes but in this case the planarity is distorted because of the steric hindrance of the ebthi ligand. The values found for the M−C_β bond lengths are in the expected range for such structural features.[3−5]

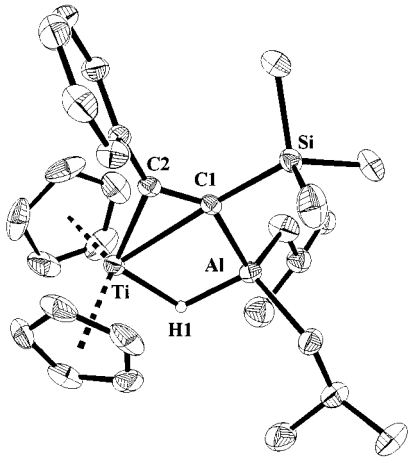


Figure 1. Molecular structure of complex **1** as an ORTEP plot at the 30% probability level; selected bond lengths (Å) and bond angles (deg):[14] Ti−Al 2.788(1), Ti−H1 1.857, Al−H1 1.628, Ti−C1 2.379(3), Ti−C2 2.111(3), C1−C2 1.315(5), Al−C1 2.098(4); Ti−H1−Al 106.1, Al−C1−Ti 76.74(11), H1−Al−C1 96.0, Ti−C1−Si 172.7(2), C1−C2−Ti 84.6(2)

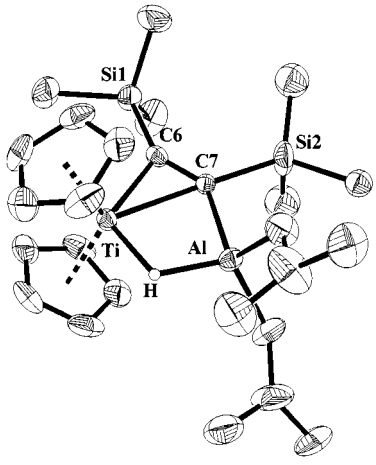


Figure 2. Molecular structure of complex **2** as an ORTEP plot at the 30% probability level; selected bond lengths (Å) and bond angles (deg):[14] Ti−Al 2.762, Ti−H 1.765, Al−H 1.624, Ti−C7 2.341(7), Ti−C6 2.127(7) C7−C6 1.311(9), Al−C7 2.145(7); Ti−H−Al 109.1, Al−C7−Ti 75.9(2), H−Al−C7 92.4, Ti−C7−Si2 177.9(4), C7−C6−Ti 82.1(5)

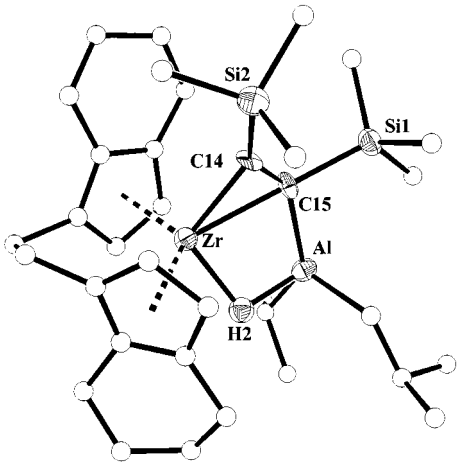
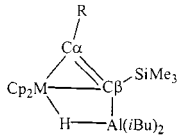


Figure 3. ORTEP view of complex **4** (for clarity only atoms regarded as significant are drawn as 30% probability ellipsoids); selected bond lengths (Å) and bond angles (deg):[14] Zr−Al 2.866(4), Zr−H2 2.048, Al−H2 1.659, Zr−C15 2.384(15), Zr−C14 2.221(13), C15−C14 1.33(2), Al−C15 2.15(2); Zr−H2−Al 100.8, Al−C15−Zr 78.3(5), H2−Al−C15 96.9, Zr−C15−Si1 174.8(9), C15−C14−Zr 80.1(9)

Table 2. Selected bond lengths [Å] and angles [°][14]

	**1**	**2**	**4**
Bond lengths [Å]			
M-Al	2.788(1)	2.762	2.866(4)
M-H	1.857	1.765	2.048
Al-H	1.628	1.624	1.659
M-Cβ	2.379(3)	2.341(7)	2.384(15)
M-Cα	2.111(3)	2.127(7)	2.221(13)
Cα-Cβ	1.315(5)	1.311(9)	1.33(2)
Al-Cβ	2.098(4)	2.145(7)	2.15(2)
Bond angles [°]			
M-H-Al	106.1	109.1	100.8
Al-Cβ-M	76.74(11)	75.9(2)	78.3(5)
H-Al-Cβ	96.0	92.4	96.9
M-Cβ-Si	172.7(2)	177.9(4)	174.8(9)
Cβ-Cα-M	84.6(2)	82.1(5)	80.1(9)

Catalytic ROP of Lactones with Complexes 1−4 as Catalysts

The ROP of ε-caprolactone provides a convenient route to the synthesis of polylactones which are important for medical applications and as plastic modifiers.[6] These applications require polyesters with predictable molecular weights and low polydispersity indices, which is only possible with initiators having selectivity in terms of initiation, propagation and termination reactions.[7] For example, alkali metal alkyls or alkoxides give very fast polymerization of lactones, but inter- and intramolecular side reactions often lead to a broadening of the molecular weight distribution of the products. When aluminium alkoxides are used as initiators, the ROP has been reported to be living and generates polyesters with narrow polydispersity indices that are free of macrocycles.[8a−8c] Recently, well characterized transition metal and lanthanoid complexes containing cyclopentadienyl ligands (metallocenes) have emerged as a new class of initiators.[9] The polymerization activity (for polar monomers) was tested using mono(cyclopentadienyl)-titanium,[9] rare earth[7a] and heterobimetallic lanthanocene[7a,10a−10c] compounds. Organolanthanide complexes in general seem to be highly active and well suited as initiators for the ROP of lactones due to their Lewis acidity.[7a]

Recently, we described how (alkyne)zirconocene and titanocene complexes are capable of polymerizing ε-caprolactone with living characteristics and high yield.[11,12] (Table 3, runs 1 and 4)

The heterobimetallic complexes **1−4** are of interest in the context of the activation of catalytic systems. Polymerization reactions were carried out under the same conditions as described before;[11,12] for a high conversion it is necessary to start with a mixture of ε-caprolactone/catalyst in toluene at room temp. and add a second portion of substrate/toluene at 75 °C (Table 3, runs 2, 3 and 5). The poly-ε-caprolactone (PCL) was isolated as a colorless solid and characterized by GPC and NMR spectroscopy. The polymers formed by **1−4** are generally of high molecular weight and of moderate polydispersities ($M_w/M_n < 2.7$). The efficiency depends on the experimental conditions, with the highest value being observed for **3**.

The heterobimetallic complexes show an increase of molecular weights (runs 2 and 3, Ti) by a factor of 10 for titanium compared to their monometallic derivatives and are dependent on the metal in the metallocene unit. The lower yield of run 2 might be explained by the instability of complex **2**: as mentioned above, it forms the monometallic compound [$Cp_2Ti(\eta^2$-$Me_3SiC_2SiMe_3)$] in solution at higher temperatures (80 °C, 5 h).

The results of NMR studies of the ROP with titanocene initiators were disappointing. All subsequent steps of the catalytic cycles such as initiation, propagation and chain termination are very fast on the NMR time scale, and could not be detected. This is consistent with the results we obtained in the case of (alkyne)zirconocene catalysts (for propagation and termination)[12] and those obtained by other groups in monitoring lactone polymerization by NMR spectroscopy.[10b] Furthermore, no end-group signals were found.[12] This has been explained in other reports by the formation of a cyclic polymer as the termination step.[10a,10d] The corresponding heterobimetallic zirconocene(alkyne)/aluminium derivatives (**3**, **4**) (Table 3, runs 5, 7) show no significant changes in comparison to their monometallic example in the ROP. The NMR investigation of the ROP of ε-caprolactone with initiator **4** shows the formation of a five-membered metallacyclic spirozirconadihydrofuran complex, which was already described as the first step in the ROP of lactones by the monometallic

Table 3. Polymerization of ε-caprolactone (CL) in toluene at 75 °C by complexes **1**−**4** in comparison to the corresponding monometallic (η^2-alkyne) compounds (75 °C, toluene)

Run	Initiator	CL/initiator	Time [h]	Yield [%]	M_n(calcd.)	M_w(GPC)	M_n(GPC)	M_w/M_n	Efficiency[a]
1	$Cp_2Ti(Me_3SiC_2SiMe_3)$[11]	5 000	1	86	490 000	110 000	68 500	1.6	7.2
2	$Cp_2Ti(Me_3SiC_2SiMe_3)$-(μ-H)(Al*i*Bu)$_2$ (**2**)	10 000	1	67	764 000	942 900	390 000	2.4	1.9
3	$Cp_2Ti(Me_3SiC_2Ph)$-(μ-H)(Al*i*Bu)$_2$ (**1**)	50 000	1	97	5 535 000	1 072 000	410 000	2.6	13.5
4	$Cp_2Zr(Py)(Me_3SiC_2SiMe_3)$[11]	5 000	1	80	450 000	80 000	44 400	1.8	10.3
5	$Cp_2Zr(Me_3SiC_2SiMe_3)$-(μ-H)(Al*i*Bu)$_2$ (**3**)	5 000	1	82	460 000	67 570	48 170	1.4	9.7
6	(ebthi)$Zr(Me_3SiC_2SiMe_3)$[12]	5 100	1	34	190 000	−	−	−	−
7	(ebthi)$Zr(Me_3SiC_2SiMe_3)$-(μ-H)(Al*i*Bu)$_2$ (**4**)	5 000	1	10	57 000	52 760	39 680	1.3	1.4

[a] Efficiency is defined as the fraction of active initiators, calculated from the observed number of polymer chains relative to the theoretical ones, assuming that each metallocene initiates one polymer chain.

(zirconocene) alkyne complexes;[12] it is followed by a rapid polymerization. No influence of the HAl(*i*Bu)$_2$ was found. A control experiment with HAl(*i*Bu)$_2$ as catalyst gave no polymerization. This is in agreement with the fact that Al(*i*Bu)$_3$ has no catalytic activity for the ROP of ε-caprolactone.[13b]The catalytic activity of the titanocene heterobimetallic compounds can be explained by an interaction between the active species and the monomer by coordination of the exo- or endocyclic oxygen of ε-caprolactone to different metal units (Al, Ti). This could cause the increased rate of polymerization and high molecular weights of the resulting polylactones. Such an activation was demonstrated by Sheng[13a,13b] for rare-earth coordination initiators obtained in situ by adding trialkylaluminium to Ln compounds. Also, heterobimetallic lanthanide/lithium complexes have been found to be active in the polymerization of ε-caprolactone, as reported by Okuda.[10a] In this case, however, another activation mechanism involving an amide nitrogen atom was proposed.

Experimental Section

General: All operations were carried out under argon with standard Schlenk techniques. Solvents were freshly distilled prior to use from sodium tetraethylaluminate and stored under argon. Deuterated solvents were treated with sodium or sodium tetraethylaluminate, distilled and stored under argon. ε-Caprolactone (Aldrich) was dried over molecular sieves and degassed before use. − The following spectrometers were used: Mass spectra: AMD 402. − NMR spectra: Bruker ARX 400. Chemical shifts referenced to signals of the used solvents: [D_6]benzene (δ_H = 7.16, δ_C = 128.0). The spectra were assigned with the help of DEPT experiments. − Melting points: sealed capillaries, Büchi 535 apparatus. − Elemental analyses: Leco CHNS-932 elemental analyzer. − Gel permeation chromatographic (GPC) analyses of the polymers were performed using a Liquid Chromatograph 1090 HP [column: SDV 10^4 Å + 10^3 Å +100 Å (Polymer Standard Service), eluent: THF]. Molecular weights were corrected by universal calibration relative to polystyrene standards.

Preparation of 1: 1.2 mL (1.2 mmol) of a 1.0 M solution of AlH(*i*Bu)$_2$ in *n*-heptane was added to a solution of [$Cp_2Ti(\eta^2$-$PhC_2SiMe_3)$] (375 mg, 1.18 mmol) in 10 mL of toluene. The mixture was stirred for 2 h at room temp. and the color changed to brown. After evaporation of the solvents to dryness, the residue was washed twice with 2 mL of *n*-pentane and dissolved in *n*-hexane (60 °C). The solution was filtered, and after 12 h at room temp. yellow crystals formed. The crystals were washed with cold *n*-pentane and dried in vacuo to give 435 mg (75%) of **1**. M.p. 150 −152 °C. − ^{1}H NMR (C_6D_6, 297 K): δ = −3.79 (br., 1 H, μ-H), 0.11 (2 s, 9 H, $SiMe_3$), 0.47, 0.62 (m, 4 H, CH_2), 1.34, 1.36 (2 d, ^3J = 5.9/5.8 Hz, 12 H, CH_3), 2.35 (m, 2 H, CH), 5.13 (d, 2 H, Ph), 5.15 (s, 10 H, Cp), 6.83 (d, 2 H, Ph), 6.98 (t, 1 H, Ph). − ^{13}C{^{1}H} NMR (C_6D_6, 297 K): δ = 3.8 ($SiMe_3$), 26.8 (br., CH_2), 27.3 (CH), 28.8, 29.0 (CH_3), 104.9 (Cp), 123.8, 125.1, 128.0 (CH, Ph), 150.4 (*ipso-C*, Ph), 105.0(*C*-$SiMe_3$), 230.1 (*C*-Ph). − MS (70 eV): *m*/*z* (%) = 352 [$Cp_2Ti(\eta^2$-$PhC_2SiMe_3)]^+$, 178 [Cp_2Ti^+], 173 [$PhC_2SiMe_3]^+$, 141 [Al(*i*Bu)$_2]^+$. − $C_{29}H_{43}AlSiTi$ (494.61): calcd. C 70.42, H 8.76; found C 70.10, H 8.59.

Preparation of 2: 1.2 mL (1.2 mmol) of a 1.0 M solution of AlH(*i*Bu)$_2$ in *n*-heptane was added to a solution of [$Cp_2Ti(\eta^2$-$Me_3SiC_2SiMe_3)$] (405 mg, 1.16 mmol) in 10 mL of toluene. The mixture was stirred for 2 h at room temp. and the color changed to green-brown. After evaporation of the solvents to dryness, the oil was washed twice with 1 mL of cold *n*-pentane and dissolved in a small amount of *n*-hexane. After filtration the solvent was removed in vacuo until the first yellow-brown crystals formed. Upon cooling to −78 °C for 12 h a brown precipitate formed which was filtered off, washed with cold *n*-pentane and dried in vacuo to give 400 mg (76%) of **2**. M.p.: 136 °C (dec.). − ^{1}H NMR (C_6D_6, 297 K): δ = −4.87 (br., 1 H, μ-H), 0.29, 0.33 (2 s, 18 H, $SiMe_3$), 0.46, 0.60 (m, 4 H, CH_2), 1.30, 1.35 (2 d, ^3J = 6.5 Hz, 12 H, CH_3), 2.31 (m, 2 H, CH), 5.10 (s, 10 H, Cp). − ^{13}C{^{1}H} NMR (C_6D_6, 297 K): δ = 2.0, 3.6 ($SiMe_3$), 25.8 (br, CH_2), 25.7 (CH), 27.4, 27.5 (CH_3), 102.5 (Cp), 123.7, 234.3 (*C*-$SiMe_3$). − ^{1}H NMR ([D_8]toluene, 192 K): δ = −5.05 (br., 1 H, μ-H), 0.18, 0.18 (2 s, 18 H, $SiMe_3$), 0.43, 0.56 (br., 4 H, CH_2), 1.32, 1.40 (2 d, 12 H, CH_3), 2.30 (m, 2 H, CH), 5.10 (s, 10 H, Cp). − ^{13}C{^{1}H} NMR ([D_8]toluene, 192 K): δ = 2.0, 3.6 ($SiMe_3$), 26.5 (br., CH_2), 27.0 (CH), 28.8, 28.9 (CH_3), 103.5 (Cp), 123.7, 234.3 (*C*-$SiMe_3$). − MS (70 eV): *m*/*z* (%) =348 [$Cp_2Ti(\eta^2$-$Me_3SiC_2SiMe_3)]^+$, 178 [Cp_2Ti^+], 173 [$Me_3SiC_2SiMe_3]^+$, 141 [Al(*i*Bu)$_2]^+$. − $C_{26}H_{47}AlSi_2Ti$ (490.69): calcd. C 63.64, H 9.65; found C 63.09, H 9.23.

Preparation of 3: 1.1 mL (1.1 mmol) of a 1.0 M solution of AlH(*i*Bu)$_2$ in *n*-heptane was added to a solution of [$Cp_2Zr(Py)(\eta^2$-$Me_3SiC_2SiMe_3)$] (503 mg, 1.07 mmol) in 10 mL of toluene. The

mixture was stirred for 2 h at 40 °C and the color changed to light green. After evaporation of the solvents to dryness. the residue was solved in a small amount of *n*-hexane. Upon cooling to −78 °C for 12 h light yellow-green crystals were formed which were filtered off, washed with cold *n*-pentane and dried in vacuo to give 410 mg (71%) of **3**. M.p.: 142 °C. − ^{1}H NMR (C_6D_6, 297 K): δ = − 2.46 (br., 1 H, μ-H), 0.34, 0.35 (2 s, 18 H, $SiMe_3$), 0.39, 0.60 (m, 4 H, CH_2), 1.29, 1.34 (2 d, ^3J = 6.4 Hz, 12 H, CH_3), 2.28 (m, 2 H, CH), 5.35 (s, 10 H, Cp). − $^{13}C\{^1H\}$ NMR (C_6D_6, 297 K): δ = 3.5, 4.7 ($SiMe_3$), 26.8 (br., CH_2), 27.2 (CH), 28.6, 28.9 (CH_3), 104.6 (Cp), 138.5, 240.4 (*C*-$SiMe_3$). − MS (70 eV): *m*/*z* (%) = 534 [M^+], 220 [Cp_2Zr^+], 170 [$Me_3SiC_2SiMe_3]^+$. − $C_{26}H_{47}AlSi_2Zr$ (534.03): calcd. C 58.48, H 8.87; found C 58.23, H 8.60.

Preparation of 4: 0.7 mL (0.7 mmol) of a 1.0 M solution of $AlH(iBu)_2$ in *n*-heptane was added to a solution of [(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$)] (378 mg, 0.72 mmol) in 10 mL of toluene were added of $AlH(iBu)_2$ as a solution in *n*-heptane (1.0 M). The light yellow solution was stirred for 2 h at room temp. After evaporation to dryness. the residue was dissolved in 5 mL of *n*-hexane. After filtration and cooling to −40 °C for 12 h crystals formed, which were filtered off and dried in vacuo to give 234 mg (48%) of **4**. M.p.: 157−158 °C. − ^{1}H NMR (C_6D_6, 297 K): δ = −1.27 (br., 1 H, μ-H), 0.48, 0.50 (2 s, 18 H, $SiMe_3$), 0.63−0.72 (m, 4 H, CH_2), 1.20, 1.29, 1.38, 1.43 (4 d, ^3J = 6.4 Hz, 12 H, CH_3), 2.23 (m, 2 H, CH), 4.38, 5.51, 5.54, 6.35 (4 d, *J* = 2.5 Hz, 4 H, CH ebthi). − $^{13}C\{^1H\}$ NMR (C_6D_6, 297 K): δ = 3.5, 4.7 ($SiMe_3$), 26.8 (br., CH_2), 27.1 (CH), 28.6, 28.9 (CH_3), 99.2, 100.46, 103.0, 104.8 (CH, ebthi), 116.7, 119.2, 122.1, 124.0, 126.4, 126.2 (q-C, ebthi) 149.5, 243.4 (*C*-$SiMe_3$). − $C_{36}H_{61}AlSi_2Zr$ (668.25): calcd. C 64.71, H 9.20; found C 63.99, H 9.02.

Polymerization of ε-Caprolactone: A stirred 5 M solution of the monomer in toluene (5 mL) was heated to 75 °C and an appropriate amount of the initiator complex dissolved in toluene was added. Ten minutes later a further amount of lactone dissolved in toluene was added. After one hour the reaction mixture was worked up by dropwise addition of a tenfold volume of methanol. The poly(ε-caprolactone)s were filtered off and dried in vacuo until the weight remained constant.

PCL: ^{1}H NMR (C_6D_6, 297 K): δ = 1.5, 1.41, 1.17 (3 m, 6 H, CH_2); 2.11, 3.98 (2 t, 4 H, CH_2).

X-ray Crystallographic Study of Complexes 1, 2 and 4: Diffraction data were collected on a STOE-IPDS diffractometer using graphite-monochromated Mo-K_α radiation. Crystal data, details of the data collections and structure refinement are compiled in Table 4. The structures were solved by direct methods (SHELXS-86: G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467) and refined by full-matrix least-squares techniques against F^2 (SHELXL-93: G. M. Sheldrick, University of Göttingen, Germany, **1993**).
Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-157428 (**1**), -157429 (**2**), -157430 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax (internat.): +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 4. Crystal data, data collection and structure refinement for compounds **1**, **2** and **4**

	1	**2**	**4**
Cryst. color	yellow	yellow	yellow
Cryst. system	orthorhombic	monoclinic	monoclinic
Space group	*Pbca*	*C*2/*m*	$P2_1$
Lattice constants			
a [Å]	9.867(2)	20.713(4)	9.448(2)
b [Å]	20.212(4)	14.630(3)	18.131(4)
c [Å]	28.261(6)	9.979(2)	11.581(2)
α [°]	90.00	90.00	90.00
β [°]	90.00	105.19(3)	108.46(3)
γ [°]	90.00	90.00	90.00
Z	8	4	2
F(000) [e]	2128	1064	716
μ [mm^{-1}]	0.392	0.416	0.401
Temp. [K]	293(2)	293(2)	293(2)
No. of rflns. (meas.)	10532	2957	5651
No. of rflns. (indep.)	2982	1562	2951
No. of rflns. (obsd.)	2290	1092	1182
No. of parameters	290	148	361
*R*1 [$I \geq 2\sigma(I)$]	0.042	0.056	0.049
w*R*2 (all data)	0.110	0.152	0.110

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[14] Values without standard deviations were determined by the program XP (Siemens Analytical X-ray Instruments, Inc.).

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