Reactions of ε-Caprolactone with (Alkyne)zirconocene Complexes: Investigation of Elemental Steps in Catalytic Ring-Opening Polymerization of Lactones[☆]

Dominique Thomas, Perdita Arndt*, Normen Peulecke, Anke Spannenberg, Rhett Kempe, and Uwe Rosenthal

Abteilung "Komplexkatalyse", Institut für Organische Katalyseforschung an der Universität Rostock e.V.,
Buchbinderstraße 5–6, D-18055 Rostock, Germany

The reactions of $Cp_2Zr(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (L = THF, pyridine) with ε-caprolactone, cyclohexanone and cycloheptanone result in an insertion of the carbonyl group into the zirconacyclopropene ring system of the alkyne complexes to yield the five-membered metallacyclic spiro-zirconadihydrofurane complexes **1**, **3**, **4**. The product with ε-caprolactone is not stable at room temperature and was identified only by NMR spectra and chemical reactions.

Starting from $rac\text{-}(\text{ebthi})Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ with ε-caprolactone and ethylene carbonate under analogous conditions more stable complexes (**2**, **5**) were obtained. Complexes **2** and **3** were characterized by X-ray crystal-structure analysis. Complexes **1** and **2** react with further ε-caprolactone in a catalytic ring-opening polymerization. The polymerization reactions were monitored by NMR spectroscopy.

Introduction

Group-4 transition-metal and lanthanide complexes containing one or two cyclopentadienyl ligands (metallocenes) have emerged as a new class of initiators of the polymerization of various polar monomers including methacrylate, epoxides, lactones.[1] The polymerization of lactones is known to give polyesters, which are becoming an increasingly important class of versatile biodegradable and biocompatible polymeric materials.[2] Since ε-caprolactone is rapidly polymerized by many metal complexes, little information is available on the details of the first steps in metal-mediated polymerization process. For example, only *mer*-$YCl_3(\varepsilon\text{-caprolactone})_3$,[2b] in which the caprolactone is coordinated by a carbonyl oxygen atom, has been characterized by an X-ray structure analysis. Recently, we described how (alkyne)zirconocene and -titanocene complexes are capable of polymerizing ε-caprolactone with living characteristics and high yield.[3a] Lactams react with (alkyne)titanocene or -zirconocene complexes to yield different complexes, depending on the nature of the metal and the ring size. These complexes have been discussed as elemental steps in the ring-opening polymerization.[3b]

Here we report on reactions of (alkyne)zirconocene complexes with cyclic carbonyl compounds such as ε-caprolactone, giving cyclic acetals, postulated as intermediates in the well-established ring-opening polymerization reaction.

The reactions of (alkyne)zirconocene and olefin complexes with carbonyl compounds have been well investigated.[4] For the complexes $Cp_2Zr(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (L = THF,[6] pyridine[7]) the reaction with acetone, formaldehyde or benzaldehyde[5] leads to insertion products of the carbonyl unit into the zirconacyclopropene ring of the alkyne complex giving zirconadihydrofuranes $[Cp_2Zr\{-C(SiMe_3)=C(SiMe_3)-CRR'-O-\}]$, which, in the case of the aldehydes, were additionally stabilized by

formation of a coordination dimer. Benzophenone reacted by apparent displacement of the alkyne by the ketone to give the complex $Cp_2Zr(THF)(\eta^2\text{-}O=CPh_2)$.

Results and Discussion

ε-Caprolactone (CL) reacts with $Cp_2Zr(L)(\eta^2\text{-}Me_3SiC_2\text{-}SiMe_3)$ (L = THF, pyridine) and forms, comparable to the reaction with acetone,[5a] in a single step, the five-membered metallacyclic spiroacetal **1** (Eq. 1).

L = py, THF   **1**   (1)
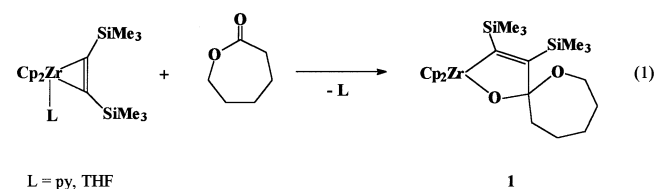
Complex **1** is an orange solid, which is not stable at room temperature and decomposes in toluene to poly-ε-caprolactone (PCL) and a mixture of as yet unidentified zirconocene complexes.

The reaction of *rac*-(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$) with ε-caprolactone yields the analogous *ansa*-metallocene compounds **2a** and **2b** (Eq. 2).
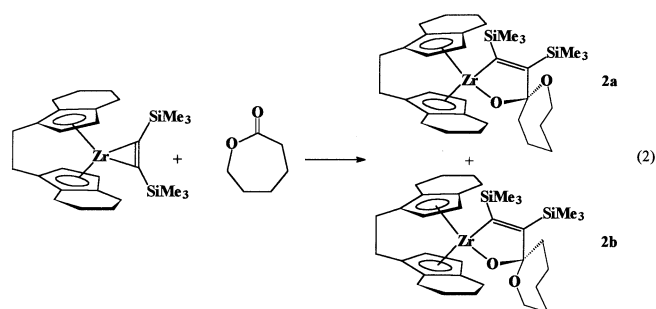
Complex **2a** crystallizes as orange yellow prisms, which, in contrast to complex **1**, are stable at room temperature under argon. It was therefore possible to obtain crystals for an X-ray structure analysis. The enhanced stability of complex **2** when compared to **1** seems to be a consequence of the steric shielding of the ebthi ligand system that has been found in other reactions, e.g., with substituted olefins[8] and with ethylene carbonate (see below). In solution complex **2** has C_1 symmetry, and both diastereomers (**2a**, **2b**) could be observed by NMR investigations. The ratio of the diastereomers formed is strongly influenced by temperature: for the product of this reaction, conducted at $-10\,°C$, we observed by NMR investigations at room temperature the stereoselective formation of the major complex **2a** (ratio **2a/2b** = 6:1), while running the same reaction at room temperature the ratio of the diastereomers formed was 1:1.

In a similar reaction a cycloreversion of the metallacycle formed was found by heating the coupling product of the nonsymmetrically substituted alkyne tBuC≡CSiMe₃ with acetone. The kinetically preferred zirconacycle with an SiMe₃ group in the β position rearranges at higher temperature to the thermodynamically more stable α-SiMe₃ product.[5b]

Heating of pure complex **2a**, up to $50\,°C$, gave no inversion of the configuration at the acetal C and thus no complex **2b**, rather only decomposition products. It seems reasonable to assume that the ebthi ligand, in comparison to the sterically less demanding Cp ligand, prevents the cycloreversion by allowing less space for the ring-opening process. It therefore seems that there is no equilibrium between the two diastereomers and that the kinetically favoured product should be **2a**. The ratio of the formed diastereomers cannot be explained by the steric restriction coming from the ebthi ligand. The formation of **2a** as the major isomer indicates that there is no steric repulsion between the ebthi ligand and the seven-membered ring in the β position of the metallacycle due to the similarity of **2a** and **2b**. Investigations concerning coupling reactions with substituted olefins show the same stereochemical behaviour.[8]

Additionally, for comparison, other cyclic carbonyl compounds with a different number of oxygen atoms in the ring, such as ketones (no O atoms) and ethylene carbonate (two O atoms) were also investigated.

The reaction of Cp₂Zr(L)(η²-Me₃SiC₂SiMe₃) (L = THF, pyridine) with cyclohexanone yields, by an insertion of the carbonyl compound into a Zr−C bond, the metallacyclic complex **3** (Eq. 3).
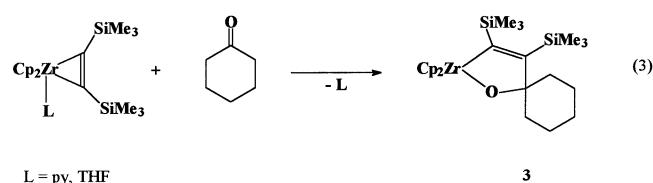
In the reaction with cycloheptanone the analogous complex **4** was obtained. Both complexes are orange solids (**3**: m.p. $136\,°C$; **4**: $138\,°C$), which were characterized using NMR spectra (**3**, **4**) and X-ray crystal-structure analysis (**3**).

In addition, the reaction of rac-(ebthi)Zr(η²-Me₃SiC₂SiMe₃) with ethylene carbonate results in an insertion of the carbonyl compound into a Zr−C bond of the zirconacyclopropene to yield the five-membered metallacyclic complex **5** (Eq. 4). Complex **5** is a yellow crystalline substance (m.p. $120\,°C$).

(4)

5
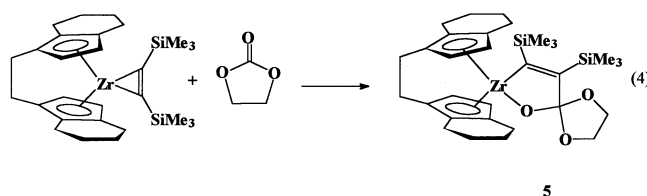
From reactions of Cp₂Zr(L)(η²-Me₃SiC₂SiMe₃) (L = THF, pyridine) with ethylene carbonate no defined product could be isolated. The ¹H-NMR spectra showed within a mixture of products the formation of a small amount of a metallacyclic complex analogous to **5** and free ethylene carbonate; no polymeric product was obtained.

Spectroscopic Characteristics

The NMR spectra of complexes **1−5** are very similar to those reported earlier for such metallacycles, obtained from reactions of (alkyne)zirconocene complexes with acyclic carbonyl compounds such as aldehydes, ketones and esters.[5] Table 1 lists the relevant NMR data in comparison to the acetone metallacycle [Cp₂Zr{−C(SiMe₃)=C(SiMe₃)−CMe₂−O−}] (**6**).

Table 1. Selected NMR data of zirconacyclic complexes **1**, **2a**, **3**, **4** and **6**

	1	**2a**	**3**	**4**	**6**[5a]
¹H NMR					
Cp	6.07		6.32	6.11	6.12
	6.16				
SiMe₃	0.19	0.35	0.13	0.20	0.19
	0.47	0.51	0.20	0.35	0.29
¹³C NMR					
$C_α, C_β$ (alkyne)	214.7	219.6	215.3	211.6	211.7
	190.0	187.4	192.8	195.3	193.5
C(CO)	106.8	105.5	93.0	95.2	89.0

These data allow a clear distinction between the C_1- (**1**, **2**) and the C_s-symmetric (**3**, **4**, **6**) complexes to be made. While the coupling of Cp₂Zr(L)(η²-Me₃SiC₂SiMe₃) with the prochiral carbonyl compound ε-caprolactone leads to a C_1-symmetric complex with two signals for the inequivalent Cp ligands (**1**: 2 s, each 5 H, δ = 6.07 and 6.16), the reaction product formed by the coupling with symmetrically substi-


(3)

L = py, THF   **3**

tuted carbonyl compounds is C_s-symmetric and exhibits one signal for the two Cp rings (**3**, **4**, **6**, cf. Table 1).

Starting from the C_2-symmetric alkyne complex *rac*-(ebthi)Zr(η^2-Me$_3$SiC$_2$SiMe$_3$) we obtained as coupling products with the prochiral ε-caprolactone (see above) for which each diastereomer shows four doublets for the Cp′ protons. By coupling the C_{2v}-symmetric ethylene carbonate with *rac*-(ebthi)Zr(η^2-Me$_3$SiC$_2$SiMe$_3$) the C_1-symmetric complex **5** is formed quantitatively, as shown by NMR investigations, and the spectra exhibit four characteristic doublets in the Cp region.

Structural Investigations

Complexes **2a** and **3** were investigated by an X-ray crystal structure analysis (Figure 1 and 2).

Figure 1. Molecular structure of complex **2a**, shown by an ORTEP plot at the 30% probability level[a]
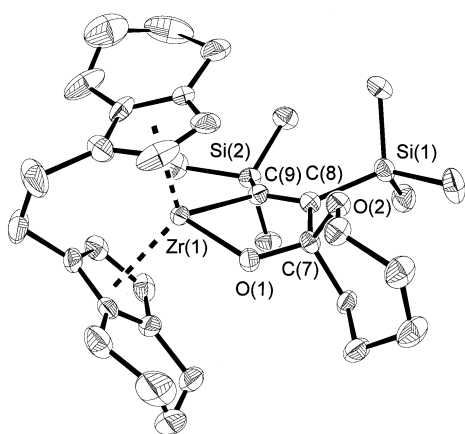
[a] Selected bond lengths [Å] and bond angles [°]: Zr1−C9 2.320(6), O1−C7 1.402(7), Zr1−O1 1.972(4), C7−C8 1.549(8), C8−C9 1.367(8), C9−Zr−O1 77.7(2), C7−O1−Zr 120.0(4), C8−C9−Zr 106.7(4).

Figure 2. Molecular structure of complex **3**, shown by an ORTEP plot at the 30% probability level[a]
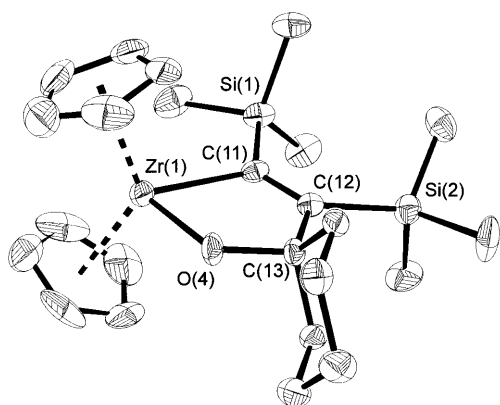
[a] Selected bond lengths [Å] and bond angles [°]: Zr1−C11 2.324(5), C11−C12 1.358(7), C12−C13 1.527(7), C13−O4 1.441(5), Zr−O4 1.922(3); C11−Zr1−O4 76.2(2), C12−C11−Zr1 110.1(4).

The obtained data for the five-membered zirconacyclic ring of complexes **2a** and **3** are listed in Table 2 and compared with those of complex **6**.

Table 2. Selected bond lengths [Å] and angles [°] for compounds **2a**, **3** and **6**

	2a	**3**	**6**[5a]
Bond lengths [Å]			
Zr−O	1.972(4)	1.922(3)	1.936(3)
Zr−C$_\alpha$	2.320(6)	2.324(5)	2.324(5)
C$_\alpha$−C$_\beta$	1.367(8)	1.358(7)	1.371(7)
C$_\beta$−CR$_2$	1.549(8)	1.527(7)	1.544(7)
O−CR$_2$	1.402(7)	1.441(5)	1.426(6)
Bond angles [°]			
O−Zr−C$_\alpha$	77.7(2)	76.2(2)	76.4(2)
Si−C$_\alpha$−Zr	125.8(2)	120.9(3)	121.6(2)
Si−C$_\alpha$−C$_\beta$	127.4(5)	129.0(4)	128.4(4)
C$_\alpha$−C$_\beta$−Si	126.6(5)	125.7(4)	125.6(4)
Si−C$_\beta$−CR$_2$	115.9(4)	115.3(4)	116.1(3)
O−CR$_2$−C$_\beta$	111.8(5)	108.2(4)	108.7(4)

Both structures correspond very well to that of the acetone product **6**[5a] and show as a result of a coupling of the alkyne with the carbonyl compound the metallacyclic ring substituted by an intact lactone or cyclohexane ring system. The C$_\alpha$−C$_\beta$ bond lengths [**2a**: 1.367(8); **3**: 1.358(7) Å] are in the expected range for C−C double bonds and the C−O distances [**2a**: 1.402(7); **3**: 1.441(5) Å] are in the C−O single-bond range. All bond lengths and angles of the five-membered zirconacycle in the three compounds compared are very similar.
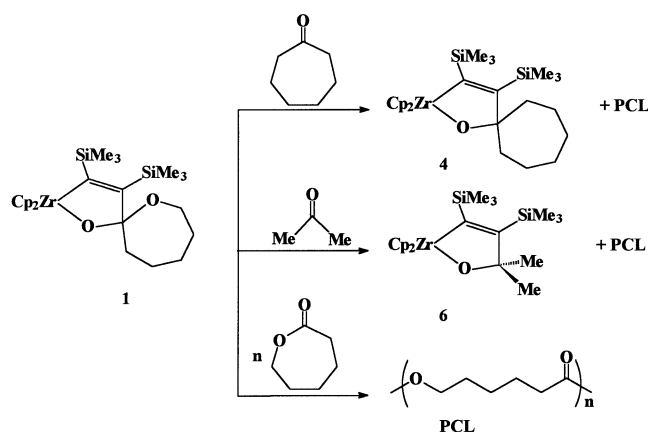
Stoichiometric Reactions

The reaction behaviour of [Cp$_2$Zr{−C(SiMe$_3$)=C(SiMe$_3$)−CMe$_2$−O−}] (**6**) has been well studied.[5a] In solutions containing **6** and acetone an equilibrium with an "opened form" [Cp$_2$Zr(Me$_2$CO)(η^2-Me$_3$SiC$_2$SiMe$_3$)] was proposed, the latter paving the way to numerous ligand replacements. These reactions are reversible and degenerate, and were studied by NMR methods.[5c] With another alkyne, e.g. tolan, complex **6** reacts with substitution of the silylalkyne to yield the analogous thermodynamically more stable phenyl-substituted metallacyclic complex.

In reactions of **1**, **4** and **5** with carbonyl compounds similar behaviour was expected and the stability of the complexes depending on different carbonyl compounds was investigated.

In the reaction of **1** with equimolar amounts of cycloheptanone the ε-caprolactone (CL) part of the metallacycle is substituted by cycloheptanone, and **4**, as well as poly-ε-caprolactone (PCL), are formed. It is reasonable to assume that the substitution to give **4** is slow and the free CL can react quickly with unchanged **1** to give PCL. This substitution also proceeds very well with acetone to give the corresponding metallacycle **6**.

Complex **1** alone reacts with further CL under ring-opening polymerization to PCL. **1** is thermally unstable, and decomposes at room temperature to form PCL. In contrast, the cyloheptanone complex **4** is thermodynamically so

Scheme 1

The differences in the reaction behaviour, which were observed in spite of the accordance in structural parameters of the metallacycles, can be explained on the basis of steric and/or electronic factors of the substituents of the metallacyclic ring.

NMR Investigations of the Catalytic Ring-Opening Polymerization

The (alkyne)zirconocene complexes with additional ligands $Cp_2Zr(L)(\eta^2-Me_3SiC_2SiMe_3)$ (L = THF, pyridine) and the corresponding compound without stabilizing ligands rac-(ebthi)$Zr(\eta^2-Me_3SiC_2SiMe_3)$ are active in catalytic ring-opening polymerizations of ε-caprolactone. The poly-ε-caprolactone (PCL) produced was shown to possess a very high molecular weight ($M_w = 73\,000$) and a narrow molecular weight distribution ($M_w/M_n = 1.4$) by GPC analysis.[3a] In order to learn about the polymerization mechanism, the ring-opening process was monitored directly by NMR spectroscopy (Figure 3). $Cp_2Zr(L)(\eta^2-Me_3SiC_2SiMe_3)$ (L= pyridine, THF) was treated with ε-caprolactone (1−10 equivalents) in an NMR tube. The ^{1}H- and ^{13}C-NMR spectra recorded immediately after the addition of CL showed at the initial stage the resonances arising from complex 1, which is rapidly formed and indicated by

stable that it is unreactive toward ethylene carbonate (EC) or ε-caprolactone (toluene, 75°C, 1 h). It could be handled for a short time in air. The acetone complex 6 also forms compound 4 with cycloheptanone. The comparison of stabilities and reactivities thus shows the following trend: **4 > 6 > 1**. In this series, complex 4 is the most stable and complex 1 the most reactive compound.

Figure 3. ^{13}C-NMR spectra of $Cp_2Zr(py)(\eta^2-Me_3SiC_2SiMe_3)$ with 10 equivalents of ε-caprolactone in C_6D_6; (CL = ε-caprolactone, PCL = poly-ε-caprolactone, complex 1)
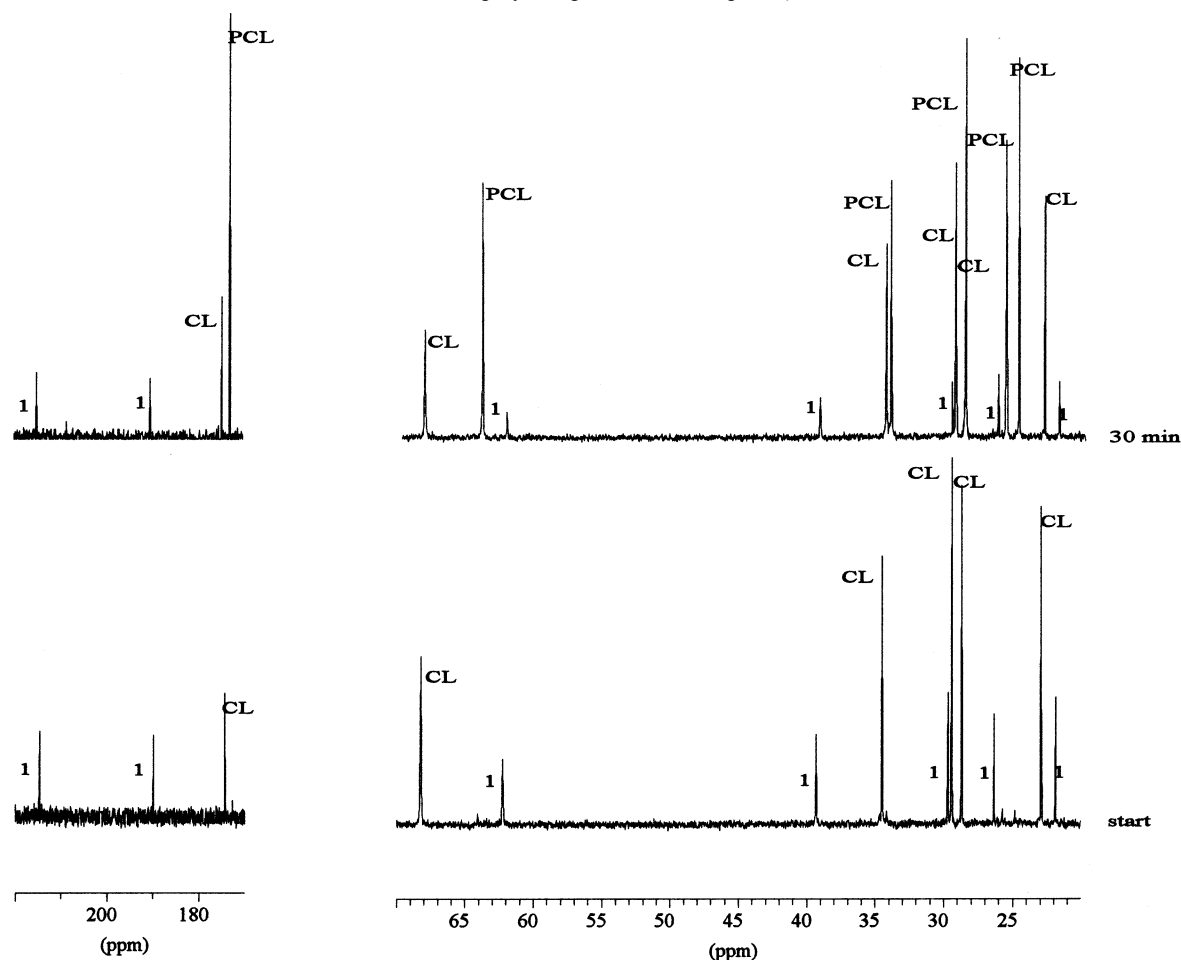
the shift of the CO signal from δ = 174.8 (free CL) to 106.8 (complex **1**). With an excess of the substrate free CL was also observed. NMR spectra taken 30 minutes after mixing showed signals arising from complex **1**, from free substrate (CL) and from poly-ε-caprolactone (PCL). The signals of monomeric ε-caprolactone (CL) disappeared within 1 h, the solution becoming highly viscous. No other species and unfortunately no end-group signals could be detected.

By combining ε-caprolactone with ethylene carbonate, polymers containing parts of PCL as well as polyethylenecarbonate (PEC) were indicated. The ^{13}C-NMR spectra of the copolymer exhibit, in addition to the carbonyl peaks of PCL (δ = 172.8), one of PEC (δ = 155.0). The amount of ethylene carbonate in the copolymer can be calculated from the ratio of the areas of these peaks and was in the range of about 8 mol-%. In contrast to this observation, ethylene carbonate is not homopolymerized in toluene or THF even at reflux (see above). Also Cp*$_2$Sm(THF)$_2$ systems, which could not polymerize ethylene carbonate, form copolymers, derived from CL and EC.[9]

Based on the results discussed for the ring-opening polymerization of ε-caprolactone by Cp*$_2$SmMe[1c] and Cp*$_2$LnOMe(THF),[1c] as well as our results mentioned above, we propose that at an early stage an exchange of the ligand L (L = THF or pyridine) takes place; ε-caprolactone approaches through the carbonyl oxygen atom. Examples of this interaction can be found in the crystallographically characterized complexes *mer*-YCl$_3$(ε-caprolactone)$_3$[2b] and Cp$_2$Zr(Me$_3$SiC$_2$SiMe$_3$)(Me-ε-caprolactam),[3b] or in the ^{1}H-NMR-spectroscopically identified initiator complex Cp*$_2$Y(OMe)(ε-caprolactone).[1c] The next step is the insertion of the carbonyl group of the lactone into the zirconacyclopropene ring system to yield the five-membered metallacyclic complex **1**. On the basis of ^{13}C-NMR studies in the initiation of the ring-opening polymerization of ε-caprolactone and δ-valerolactone by Cp*$_2$SmMe,[1c] the formation of an acetal has also been discussed.

The results of the NMR studies are disappointing. All subsequent steps of the catalytic cycles such as propagation and chain termination are very fast on the NMR time scale, and could not be detected. This is consistent with the results obtained by other groups in monitoring lactone polymerization by NMR.[1] Furthermore, no end-group signals were found. This has also been explained in some other works,[1b][1f] by the formation of a cyclic polymer as the termination step.

Conclusion

The present study demonstrated that in the reaction of the (alkyne)zirconocene complexes Cp$_2$Zr(L)(η^2-Me$_3$SiC$_2$-SiMe$_3$) (L= THF, pyridine) and *rac*-(ebthi)Zr(η^2-Me$_3$SiC$_2$-SiMe$_3$) with ε-caprolactone the five-membered spirocyclic zirconadihydrofuranes **1** and **2** are formed. Both complexes are intermediates in the catalytic ring-opening polymerization of ε-caprolactone. Complex **2** is the first well-characterized example for the formation of such an acetal, which was proposed as an elemental step of the ring-opening poly-

merization of lactones.[1] NMR studies showed that further steps of the catalytic cycle such as propagation and chain termination are very fast on the NMR time-scale and could not be detected.

The reaction of (alkyne)zirconocene complexes with other cyclic carbonyl compounds such as ketones or ethylene carbonate yields analogous metallacycles, but no polymerization was observed.

Work is in progress to expand the ring-opening capability to other heterocyclic substrates and to utilize the chiral initiator for stereoselective ring openings.

Experimental Section

General: All operations were carried out under argon using standard Schlenk techniques. Prior to use, solvents were freshly distilled 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. − Mass spectra: AMD 402. − NMR spectra: Bruker ARX 400. Chemical shifts referenced to signals of the solvents used: [D$_6$]benzene (δ$_H$ = 7.16; δ$_C$ = 128.0). The spectra were assigned with the help of DEPT and COLOC experiments. − Melting points: sealed capillaries, Büchi 535 apparatus. − Elemental analyses: Leco CHNS-932 elemental analyzer.

Preparation of **1**: To a solution of 377 mg (0.80 mmol) of Cp$_2$Zr(py)(η^2-Me$_3$SiC$_2$SiMe$_3$) in 10 ml of diethyl ether was added at −10°C 92 μl (0.80 mmol) of ε-caprolactone. The mixture was stirred for 30 min at this temperature and the colour changed to orange. After concentration to dryness, *n*-hexane was added. The solution was filtered, and after 12 h at −78°C orange crystals formed. The crystals were washed with cold *n*-hexane and dried in vacuo to give 210 mg (51%) of **1**. − ^{1}H NMR (C$_6$D$_6$): δ = 0.19, 0.47 (s, 2 × 9 H, SiMe$_3$), 1.4−2.1 (m, 6 H, CH$_2$), 3.5−3.6 (m, 2 H, CH$_2$), 3.83 (m, 2 H, CH$_2$), 6.07, 6.16 (s, 2 × 5 H, Cp). − ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 4.4, 4.8 (SiMe$_3$), 21.9, 26.4, 29.7, 39.3, 62.3 (CH$_2$), 106.8 (CO), 113.1, 114.3 (Cp), 190.0 (β-*C*SiMe$_3$), 214.7(α-*C*SiMe$_3$). − MS (70 eV); *m/z* (%): 220 [Cp$_2$Zr]$^+$, 170 [Me$_3$SiC$_2$SiMe$_3$]$^+$, 114 [ε-caprolactone]$^+$. − C$_{24}$H$_{38}$O$_2$Si$_2$Zr (505.96): calcd. C 56.97, H 7.57; found C 56.83, H 7.63.

Preparation of **2a and 2b**: To a solution of 140 mg (0.266 mmol) of *rac*-(ebthi)Zr(η^2-Me$_3$SiC$_2$SiMe$_3$) in 10 ml of *n*-hexane, 28.1 μl (0.266 mmol) of ε-caprolactone was added. The colour of the reaction mixture changed from green to red-orange after a few seconds. After standing for two weeks at −78°C, red crystals separated which were suitable for X-ray structure analysis (crystals were the pure diastereomer **2a** as checked by NMR). Evaporation of the solvent at room temperature yielded 73 mg (43%) of an orange foam of **2a** and **2b**. − **2a** (major isomer): ^{1}H NMR (C$_6$D$_6$): δ = 0.35 (s, 9 H, SiMe$_3$), 0.51 (s, 9 H, SiMe$_3$), 1.4−3.2 (m, 28 H, CH$_2$), 3.57 (1 H, OCH$_2$), 3.90 (1 H, OCH$_2$), 5.12 (d, *J* = 2.8 Hz, 1 H, Cp′), 5.39 (d, *J* = 3.0 Hz, 1 H, Cp′), 6.58 (d, *J* = 3.0 Hz, 1 H, Cp′), 6.85 (d, *J* = 2.8 Hz, 1 H, Cp′). − ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 4.6, 6.2 (SiMe$_3$), 21.2, 22.6, 23.0, 23.0, 23.2, 23.3, 23.5, 24.0, 24.0, 24.6, 25.5, 28.0, 28.1, 28.9 (CH$_2$), 44.0 [CH$_2$C(O)], 60.8 (CH$_2$O), 107.7, 109.5, 110.6, 114.7, 122.1, 122.9, 129.3, 129.4 (CH) 105.5 (CO), 187.4 (β-*C*SiMe$_3$), 219.6 (α-*C*SiMe$_3$). − C$_{34}$H$_{52}$O$_2$Si$_2$Zr (640.2): calcd. C 63.79, H 8.19; found C 64.00, H 8.16. − **2b** (minor

D. Thomas, P. Arndt, N. Peulecke, A. Spannenberg, R. Kempe, U. Rosenthal

Table 3. Crystal data, data collection and structure refinement for compounds **2a** and **3**

	2a	**3**
cryst. colour	orange	yellow
cryst. system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a [Å]	9.900(2)	9.7050(12)
b [Å]	14.214(3)	18.887(3)
c [Å]	15.897(3)	13.902(2)
α [°]	99.38(2)	90
β [°]	107.07(2)	97.300(11)
γ [°]	95.01(2)	90
Z	2	4
$F(000)$ [e]	747	1032
μ [mm^{-1}]	0.348	0.547
T [K]	200(2)	293(2)
no. of rflns. (indep.)	6284	4071
no. of rflns. (obsd.)	4686	1819
no. of parameters	390	253
$R1$ [($I \geq 2\sigma(I)$)]	0.074	0.046
$wR2$ (all data)	0.226	0.095

isomer, could only be obtained in a mixture with **2a**): ^{1}H NMR (C$_6$D$_6$): δ = 0.29 (s, 9 H, SiMe$_3$), 0.34 (s, 9 H, SiMe$_3$), 5.15 (d, J = 2.7 Hz, 1 H, Cp'), 5.33 (d, J = 3.2 Hz, 1 H, Cp'), 6.35 (d, J = 3.2 Hz, 1 H, Cp'), 6.76 (d, J = 2.7 Hz, 1 H, Cp'), further signals could not be assigned. − ^{13}C\{^{1}H\} NMR (C$_6$D$_6$): δ = 5.4, 6.2 (SiMe$_3$), 39.5 [CH_2C(O)], 61.2 (CH_2O), 106.7, 108.7, 112.1, 116.5, 123.1, 123.5, 126.2, 127.3, 130.0, 130.6 (CH-ebthi), 105.0 (CO), 191.4 (β-CSiMe$_3$), 216.6 (α-CSiMe$_3$).

Preparation of **3**: An amount of 250 mg (0.54 mmol) of Cp$_2$Zr(THF)(η^2-Me$_3$SiC$_2$SiMe$_3$) was dissolved in 10 ml of THF, and cyclohexanone (56 μl, 0.54 mmol) was added to the solution. The mixture was stirred, whereupon the colour changed from orange to yellow. The solution was concentrated to dryness and the residue was dissolved in *n*-hexane. On standing at −78°C for 2 d, orange crystals deposited which were dried in vacuo to give 210 mg (79%) of **3**, m.p. 136°C. − ^{1}H NMR (C$_6$D$_6$): δ = 0.13, 0.20 (s, 2 × 9 H, SiMe$_3$), 0.90−1.0 (m, 2 H, CH$_2$), 1.30−1.41 (m, 4 H, CH$_2$), 1.61−1.70 (m, 4 H, CH$_2$), 6.32 (s, 10 H, Cp). − ^{13}C\{^{1}H\} NMR (C$_6$D$_6$): δ = 5.2, 5.4 (SiMe$_3$), 22.7, 26.1, 35.4 (CH$_2$), 93.0 (CO), 113.9 (Cp), 192.8 (β-CSiMe$_3$), 215.3 (α-CSiMe$_3$). − MS(70 eV); *m/z* (%): 220 Cp$_2$Zr$^+$, 170 [Me$_3$SiC$_2$SiMe$_3$]$^+$, 98 [cyclohexanone]$^+$. − C$_{24}$H$_{38}$OSi$_2$Zr (489.94): calcd. C 58.83, H 7.82; found C 58.53, H 8.13.

Preparation of **4**: The reaction was carried out in the same manner as described for complex **3** with an amount of 420 mg (0.89 mmol) of Cp$_2$Zr(py)(η^2-Me$_3$SiC$_2$SiMe$_3$) and cycloheptanone (104 μl, 0.89 mmol) to give 330 mg of **4** (74%), orange crystals, m.p. 138°C. − ^{1}H NMR (C$_6$D$_6$): δ = 0.20, 0.35 (s, 2 × 9 H, SiMe$_3$), 1.51 (m, 4 H, CH$_2$), 1.66 (m, 4 H, CH$_2$), 1.83 (m, 2 H, CH$_2$), 2.03 (m, 2 H, CH$_2$), 6.11 (s, 10 H, Cp). − ^{13}C\{^{1}H\} NMR (C$_6$D$_6$): δ = 5.0, 5.2 (SiMe$_3$), 22.8, 27.6, 38.4 (CH$_2$), 95.2 (CO), 113.2 (Cp), 195.3 (β-CSiMe$_3$), 211.6 (α-CSiMe$_3$). − MS(70 eV); *m/z* (%): 220 Cp$_2$Zr$^+$, 170 [Me$_3$SiC$_2$SiMe$_3$]$^+$, 112 [cycloheptanone]$^+$. − C$_{25}$H$_{39}$OSi$_2$Zr (489.94): calcd. C 59.70, H 7.82; found C 58.83, H 8.11.

Preparation of **5**: To a solution of 310 mg (0.589 mmol) of *rac*-(ebthi)Zr(η^2-Me$_3$SiC$_2$SiMe$_3$) in 3 ml of diethyl ether, 52 mg (0.589 mmol) of ethylene carbonate was added. The colour of the reaction mixture changed from green to red-orange after stirring for 5 min. Addition of 3 ml of pentane and standing for 12 h at −40°C gave 310 mg of **5** (85%), yellow crystalline solid, m.p. 120°C. − ^{1}H

NMR (C$_6$D$_6$): δ = 0.19, 0.27 (s, 2 × 9 H, SiMe$_3$), 1.1−3.4 (20 H, CH$_2$), 3.51(2 H, OCH$_2$), 3.59 (1 H, OCH$_2$), 4.91 (1 H, Cp'), 5.20 (d, 1 H, Cp'), 6.65 (d, 1 H, Cp'), 6.70 (d, 1 H, Cp'). − ^{13}C\{^{1}H\} NMR (C$_6$D$_6$): δ = 3.3 (SiMe$_3$), 5.6 (SiMe$_3$), 22.3, 22.9, 23.0, 23.1, 23.1, 23.6, 23.9, 24.6, 27.3, 27.6 (CH$_2$-ebthi), 62.3, 62.6 (CH$_2$O), 108.4, 109.4, 111.0, 118.2 (CH-ebthi) 119.0, 122.9, 123.7, 128.7, 129.5, 131.6 (C$_q$), 181.5 (β-CSiMe$_3$), 227.7 (α-CSiMe$_3$). − C$_{31}$H$_{46}$O$_3$Si$_2$Zr (614.10): calcd. C 60.63, H 7.55; found C 60.59, H 7.47.

Polymerization of ε-*Caprolactone in an NMR Tube:* In a 5-mm NMR tube the catalyst (20−30 mg) was dissolved in C$_6$D$_6$ (0.6 ml). ε-Caprolactone (1−10 equivalents) was placed at the upper end of the tube to prevent early mixing. The NMR tube was closed and vigorously shaken just before running the spectra.

X-ray-Crystallographic Study of Complexes **2 and 3**: 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 3. 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**). Further details of the crystal-structure investigations are available on request from the Cambridge Crystallographic Data Centre, on quoting the depository number CCDC-101309. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44(0)1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

☆ Dedicated to Dr. habil. *Erhard Kurras* on the occasion of his 70th birthday.
[1a] J. Okuda, I. L. Rushkin, *Macromolecules* **1993**, *26*, 5530−5532. − [1b] J. Okuda, K. C. Hulitzsch, *Macromol. Rapid Commun.* **1997**, *18*, 809−815. − [1c] H. Yasuda, E. Ihara, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1745−1767 and references therein. − [1d] M. Hayakawa, M. Mitani, T. Yamada, T. Mukaiyama, *Macromol. Chem. Phys.* **1997**, *198*, 1305−1317. − [1e] T. Mukaiyama, M. Hayakawa, K. Oouchi, M. Mitani, T. Yamada, *Chem. Lett.* **1995**, 737−738 and references therein. − [1f] K. C. Hultzsch, T. P. Spaniol, J. Okuda, *Organometallics* **1997**, *16*, 4845−4856.
[2a] D. Seebach, H.-M. Müller, *Angew. Chem.* **1993**, *105*, 483−509; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 457−476. − [2b] W. J. Evans, J. L. Shreeve, R. J. Doedens, *Inorg. Chem.* **1993**, *32*, 245−246.
[3a] P. Arndt, D. Thomas, U. Rosenthal, *Tetrahedron Lett.* **1997**, *38*, 5467−5468. − [3b] P. Arndt, C. Lefeber, R. Kempe, U. Rosenthal, *Chem. Ber.* **1996**, *129*, 1281−1285. −
[4a] G. Erker, F. Rosenfeldt, *J. Organomet. Chem.* **1982**, *224*, 29−42. − [4b] G. Erker, U. Dorf, P. Czisch, J. Petersen, *Organometallics* **1986**, *5*, 668−676. − [4c] S. Buchwald, R. Nielsen, *Chem. Rev.* **1988**, *88*, 1047−1058. − [4d] E. Negischi, T. Takahashi, *Synthesis* **1988**, 1−19. − [4e] H. Yasuda, T. Okamoto, K. Matsuoka, Y. Nakamura, Y. Kai, N. Kanehisa, N. Kasai, *Organometallics* **1989**, *8*, 1139−1152. − [4f] G. Erker, *Angew. Chem.* **1989**, *101*, 411−426; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 397−412. − [4g] H. Alt, C. Denner, *J. Organomet. Chem.* **1990**, *390*, 53−60. − [4h] T. Takahashi, N. Suzuki, M. Hasegawa, Y. Nitto, K. Aoyagi, M. Saburi, *Chem. Lett.* **1992**, 331−334. − [4i] S. Buchwald, R. Broene, *Science* **1993**, *261*, 1696−1701. − [4k] E. Negishi, T. Takahashi, *Acc. Chem. Res.* **1994**, *27*, 124−130. − [4l] G. Erker, L. Lopez, M. Berlekamp, D. Kowalski, *Angew. Chem.* **1994**, *106*, 1168−1170; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1114−1116. − [4m] G. Erker, M. Berlekamp, L. Lopez, M. Grehl, B. Schönecker, R. Krieg, *Synthesis* **1994**, 214−222. − [4n] E. Hey-Hawkins, *Chem. Rev.* **1994**, *94*, 1661−1717. − [4o] M. Hasegawa, Y. Nitto, M. Saburi, *J. Organomet. Chem.* **1994**, *473*, 117−128. − [4p] M. Maier, T. Oost, *J. Organomet. Chem.* **1995**, *505*, 95−107.
[5a] U. Rosenthal, A. Ohff, W. Baumann, A. Tillack, V. V. Burlakov, V. B. Shur, *J. Organomet. Chem.* **1994**, *484*, 203−207. − [5b] C.

Lefeber, A. Ohff, A. Tillack, W. Baumann, R. Kempe, V. V. Burlakov, U. Rosenthal, *J. Organomet. Chem.* **1995**, *501*, 189−194. − [5c] W. Baumann, A. Ohff, M. Ebener, *Helv. Chim. Acta* **1996**, *79*, 454−460. − [5d] N. Peulecke, A. Ohff, A. Tillack, W. Baumann, R. Kempe, V. V. Burlakov, U. Rosenthal, *Organometallics* **1996**, *15*, 1340−1343.

[6] U. Rosenthal, A. Ohff, M. Michalik, H. Görls, V. V. Burlakov, V. B. Shur, *Angew. Chem.* **1993**, *105*, 1228−1230; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1193−1195.

[7] U. Rosenthal, A. Ohff, W. Baumann, A. Tillack, H. Görls, V. V. Burlakov, V. B. Shur, *Z. Anorg. Allg. Chem.* **1995**, *621*, 77−83.

[8] S. Mansel, D. Thomas, C. Lefeber, D. Heller, R. Kempe, W. Baumann, U. Rosenthal, *Organometallics* **1997**, *16*, 2886−2890.

[9] W. J. Evans, H. Katsumata, .*Macromolecules* **1994**, *27*, 4011−4013.

[98078]