Reactions of Lactams with Titanocene- and Zirconocene-Alkyne Complexes as Elemental Steps in Catalytic Anionic Ring-Opening Polymerization of Lactams

Perdita Arndt*, Claudia Lefeber, Rhett Kempe, Annegret Tillack, and Uwe Rosenthal

Max-Planck-Gesellschaft, Arbeitsgruppe „Komplexkatalyse" an der Universität Rostock, Buchbinderstraße 5–6, D-18055 Rostock, Germany

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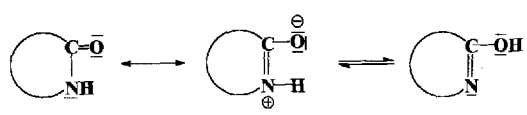
Depending on the nature of the metal and the ring size, lactams react with titanocene and zircocene complexes of bis(trimethylsilyl)acetylene $Cp_2Ti(Me_3SiC_2SiMe_3)$ and $Cp_2Zr(L)(Me_3SiC_2SiMe_3)$ (L = Py, THF) to yield different products. In the reaction of $Cp_2Zr(Py)(Me_3SiC_2SiMe_3)$ with *N*-methyl-ε-caprolactam a simple ligand exchange reaction occurs and the complex $Cp_2Zr(Me_3SiC_2SiMe_3)[O=C-N(Me)-(CH_2)_5]$ **(1)** was isolated. With β-propiolactam the alkenyl-amido complex $Cp_2Zr[-C(SiMe_3)=C(H)(SiMe_3)][-N-CO-CH_2-CH_2]$ **(2)** was obtained, which indicates that an agostic metal-hydrogen interaction has taken place. The reaction of $Cp_2Ti(Me_3SiC_2SiMe_3)$ with ε-caprolactam gives after elimination of the alkyne and molecular hydrogen the first early transition metal complex with a deprotonated coordinated ε-caprolactam in a η^2-amidate bonding fashion $Cp_2Ti-O=C=N-(CH_2)_5$ **(3)**. The obtained complexes were characterized by NMR spectra **(1, 2)** and crystal structure analysis **(1–3)** and discussed as elemental steps in anionic ring-opening polymerization of lactams catalyzed by metallocene-alkyne complexes.

Recently, we described the reactions of the titanocene- and zirconocene-alkyne complexes $Cp_2Ti(Me_3SiC_2SiMe_3)$[1] and $Cp_2Zr(L)(Me_3SiC_2SiMe_3)$ (L = THF[2], Py[3]), which can formally generate under mild conditions the unstable metallocenes, with C=N bonds in ketimines and aldimines, undergoing either hydrogen migration or C–C coupling, depending on the substituents and metals used[4].

We also reported on novel ring-opening and ring-enlargement reactions of heterocyclic C=N systems, e.g. benzoxazoles, thiazoles, and benzisoxazole, which yield zircona-heterocyclic systems[5] upon treatment with $Cp_2Zr(L)(Me_3SiC_2SiMe_3)$.

Lactams represent another type of C=N systems[6a] due to the tautomerization between lactam (keto amine) and lactim (hydroxy imine) (Scheme 1). The lactim form is much more favored in the case of cyclic than with noncyclic amides of carboxylic acids, but this equilibrium depends strongly on the ring size[6b].

Scheme 1



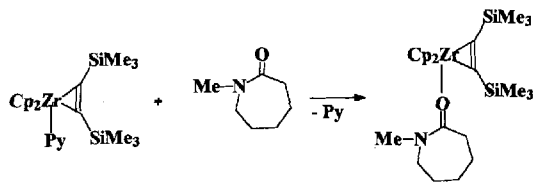
The analogous catalytic ring-opening polymerization of ε-caprolactone by mono(cyclopentadienyl)titanium complexes of the type $CpTiCl_2(OR)$[7] or cationic zirconocene complexes like $[Cp_2ZrMe]^+[B(C_6F_5)_4]^-$[8] are well-known but less is known about the structure of metallocene intermediates in these reactions.

Also the transition-metal-catalyzed ring-opening polymerization of lactams is not well investigated in this respect. In this paper we report on novel complexes of titanocene and zirconocene with lactams which can act as intermediates in their polymerization reaction.

Results and Discussion

N-Methyl-ε-caprolactam

The reaction of the complex $Cp_2Zr(Py)(Me_3SiC_2SiMe_3)$ with *N*-methyl-ε-caprolactam in ether at −10 °C yields by a ligand substitution compound **1**.



1

1 is an orange crystalline substance [m.p. 116 °C (dec.)]. The IR spectrum exhibits a ν(C=O) vibration at 1617 cm^{-1} for an "end-on" coordinated carbonyl group (Table 1). The obtained ^1H- and ^{13}C-NMR data of complex **1** are similar to those of the starting complex $Cp_2Zr(Py)(Me_3SiC_2SiMe_3)$[4]. The structure of complex **1** was confirmed by an X-ray analysis.

It shows the coordination of the *N*-methyl-ε-caprolactam by the carbonyl group and gives no evidence for an additional interaction of the N atom (Figure 1). A similar interaction is well-known, e.g. in mono-[9a] and dinuclear

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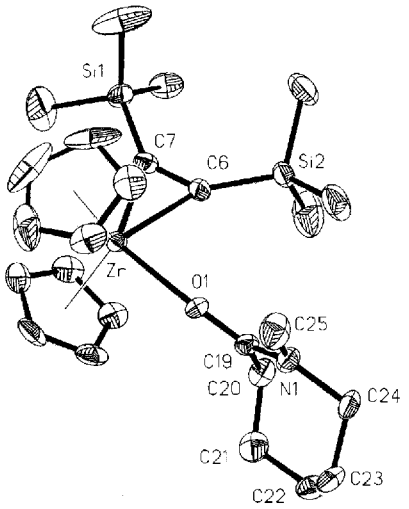
Figure 1. Molecular structure of complex **1**, shown by an ORTEP plot; the thermal ellipsoids correspond to 40% probability[a]



[a] Selected bond lengths [Å] and angles [°]: Zr–O(1) 2.290(3), O(1)–C(19) 1.249(5), Zr–C(7) 2.215(4), Zr–C(6) 2.259(4), C(7)–C(6) 1.326(6), C(7)–Si(1) 1.848(4), C(6)–Si(2) 1.834(5); Zr–C(7)–C(6) 74.6(3), C(7)–Zr–C(6) 34.46(15), Zr–C(6)–C(7) 71.0(3), C(6)–Zr–O(1) 84.61(14), C(6)–C(7)–Si(1) 139.2(4), C(7)–C(6)–Si(2) 136.5(3), Si(1)–C(7)–Zr 145.8(3), Zr–O(1)–C(19) 151.7(3).

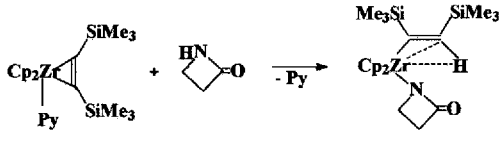
Table 1. Infrared spectral data (cm^{-1}) of **1**, **2**, **3** and **4**

Complex	ν (C=O)free	ν (C=O)coord.	ν(C_2)
1	1644	1617	1573(C≡C)
2	1718	1672	1568(C=C(H))
3	1658	1580	-
4	1658	1592	-

copper(II) complexes[9b] of ε-caprolactam. In the reactions of the complexes $Cp_2Zr(THF)(Me_3SiC_2SiMe_3)$ or $Cp_2Ti(Me_3SiC_2SiMe_3)$ with *N*-methyl-ε-caprolactam in THF under comparable conditions no defined products could be isolated.

β-Propiolactam

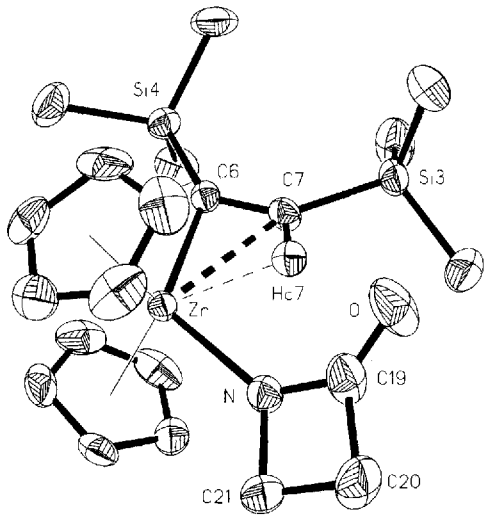
The reaction of $Cp_2Zr(Py)(Me_3SiC_2SiMe_3)$ with β-propiolactam under analogous conditions afforded complex **2**.



2

Complex **2** crystallizes as colorless prisms [m.p. 119 °C (dec.)]. In the reaction pathway the hydrogen atom is shifted from the N atom of the lactam to the alkyne unit and a zirconocene alkenyl-amido complex is formed. The $Zr-C^{\alpha}=C^{\beta}-H$ unit shows a ^{1}H-NMR signal at rather low field (δ 8.04). The ^{13}C-NMR signal of C^{α} appears at 227.0, whereas the C^{β} signal is located upfield in the normal olefinic absorption range (δ = 106.3). These spectroscopic features[10,11] of **2** together with the very low $^1J(C^{\beta}$-H) coupling constant (101 Hz) are a strong indication of the presence of an agostic metal H interaction. The alkenyl complex was characterized by an X-ray crystal structure analysis (Figure 2).

Figure 2. Molecular structure of complex **2**, shown by an ORTEP plot; the thermal ellipsoids correspond to 30% probability[a]



[a] Selected bond lengths [Å] and angles [°]: Zr–C(6) 2.242(3), Zr–C(7) 2.543(3), C(6)–C(7) 1.330(4), C(6)–Si(4) 1.852(4), C(7)–Si(3) 1.878(3), C(7)–Hc(7) 0.95(3), Zr–N 2.238(3); C(6)–Zr–C(7) 31.47(10), Si(4)–C(6)–C(7) 132.1(3), Si(3)–C(7)–C(6) 138.7(3), C(6)–Zr–N 120.26(10), Si(4)–C(6)–Zr 141.0(2).

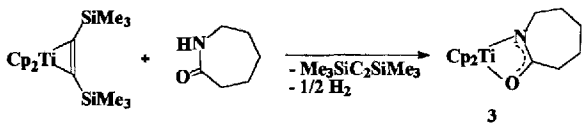
The molecular structure exhibits a coordination of the N atom of the β-propiolactam with the zirconocene moiety, which is typical of the amido bond in similar complexes[12]. The most interesting feature of the structure is the agostic interaction of the former lactam hydrogen atom. The special bonding situation is similar as found previously in complex $[Cp(\mu\text{-}\eta^1\text{:}\eta^5\text{-}C_5H_4)Zr-C^{\alpha}(SiMe_3)=C^{\beta}H(SiMe_3)]_2$[11] **A** with the same structural element [Zr–C^{α}, **2**: 2.242(3), **A**: 2.244(3); Zr–C^{β} **2**: 2.543(3), **A**: 2.566(3); C^{β}–H, **2**: 0.95(3), **A**: 1.10(3) Å; Zr–C^{α}–C^{β}, **2**: 86.9(2), **A**: 88.2(2)°].

In the reactions of $Cp_2Zr(THF)(Me_3SiC_2SiMe_3)$ or **2** in toluene with an excess of β-propiolactam a slow polymerization was observed. In the case of $Cp_2Ti(Me_3SiC_2SiMe_3)$ under the same conditions the color of the solution turned from yellow to blue and molecular hydrogen was evolved before the polymerization of the lactam occured. In comparison to the zirconocene complex the titanocene is more active in this polymerization. The IR spectra of the products exhibit broad absorption bands in the region of ν(C=O)-amides.

ε-Caprolactam

$Cp_2Ti(Me_3SiC_2SiMe_3)$ reacts in THF with ε-caprolactam with elimination of bis(trimethylsilyl)acetylene (detected by gaschromatography) and molecular hydrogen to furnish the Ti^{III} complex **3**.

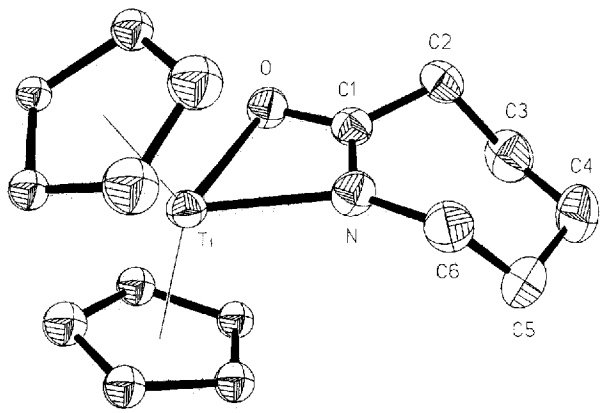
Complex **3** crystallizes as deep blue prisms [m.p. 116–119 °C (dec.)]. In the IR spectrum of **3** no bands for the $SiMe_3$ or NH groups are observed; a band at 1580 cm^{-1} is assigned to the metal-coordinated carbonyl group which



3

is shifted 78 cm^{-1} to lower wavenumber compared to that of the free ε-caprolactam (Table 1). The paramagnetic compound **3** gives no NMR data. An X-ray diffraction study was performed due to the paramagnetic nature of **3**. Crystals of complex **3** suitable for X-ray analysis were obtained by crystallization from *n*-hexane.

Figure 3. Molecular structure of complex **3**, shown by an ORTEP plot; the thermal ellipsoids correspond to 30% probability[a]



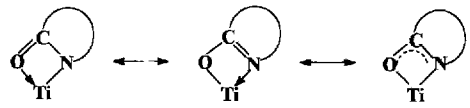
[a] Selected bond lengths (Å) and angles (°): Ti–N 2.145(5), Ti–O 2.157(4), C(6)–N 1.427(6), N–C(1) 1.308(8), C(1)–O 1.280(8), C(6)–N 1.427(6), C(1)–C(2) 1.501(8); N–Ti–O 61.3(2), Ti–O–C(1) 91.5(4), O–C(1)–N 115.9(6), C(1)–N–Ti 91.2(4), O–C(1)–C(2) 120.2(6).

The molecular structure of complex **3** (Figure 3) confirms a bent titanocene unit and a deprotonated ε-caprolactam which is coordinated in a η^2-amidate fashion[13a], giving a four-membered ring. The Ti–N [2.145(5) Å] and Ti–O [2.157(4) Å] bond lengths are nearly identical and do not show as large differences between the values as found for other η^2-amidate complexes[13]. They are shorter compared to those in the complexes **1** and **2** (Table 2). The C(1)–O distance of complex **3** is longer than that in the uncomplexed carbonyl groups of the complexes **1** and **2**, but significantly shorter than the value determined for $C(sp^2)$–O single bonds (1.35 Å). The C(1)–N distance of complex **3** is shorter than that found in the complexes **1** and **2** but significantly longer than the value observed for $C(sp^2)=N(sp^2)$ double bonds (1.26 Å). These structural data suggest the following resonance forms with some electronic delocalization in the O–C–N ligand (Scheme 2).

Table 2. Selected bond lengths [Å]

	1	2	3
M-O	2.290(3)	-	2.157(4)
M-N	-	2.238(3)	2.145(5)
C-O	1.249(2)	1.215(5)	1.280(8)
N-C	1.343(6)	1.345(5)	1.308(8)

Scheme 2



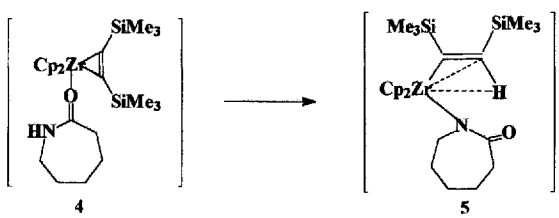
The N, C(1), O, C(6), and C(2) atoms are coplanar within experimental error, and the Zr atom is out of this plane by 0.025(9) Å. The N atom is slightly planar deviating by 0.029(6) Å from the plane through Ti, C(1), C(6).

The results described here present to our knowledge the first example of a deprotonated ε-caprolactam complex of transition metals in which the lactam is coordinated in a bidentate fashion. Isostructural, noncyclic (open) η^2-amidate zirconocene[13b] and titanocene[13c] complexes were obtained by insertion of aryl isocyanates into metal–carbon bonds and are considered as intermediates in living organotitanium(IV)-catalyzed polymerization of isocyanates[14]. Also the oxidative addition of cyclic imides such as succinimide or phthalimide involving N–H bond cleavage to give hydrido-imido complexes was described[15].

The reaction of $Cp_2Zr(Py)(Me_3SiC_2SiMe_3)$ with ε-caprolactam at −10 °C in ether yields a mixture of two complexes **4** and **5** in a ratio of 2:1, from which colorless crystals of **4** could be isolated in 51% yield. In the IR spectrum of **4** an absorption at 1592 cm^{-1} is detected for the "end-on" coordinated carbonyl group.

The ^{1}H-NMR spectrum of the main product **4** exhibits besides signals of the Cp, $SiMe_3$ and methylene groups in the typical region also at δ = 7.36 the signal of the NH unit of the caprolactam and suggests the coordination of one caprolactam and one alkyne unit with the zirconocene moiety. The data of complex **4** are in agreement with an analogous coordination of *N*-methyl-ε-caprolactam as found in complex **1**. Unfortunately, crystals which are suitable for an X-ray crystal structure analysis were not obtained.

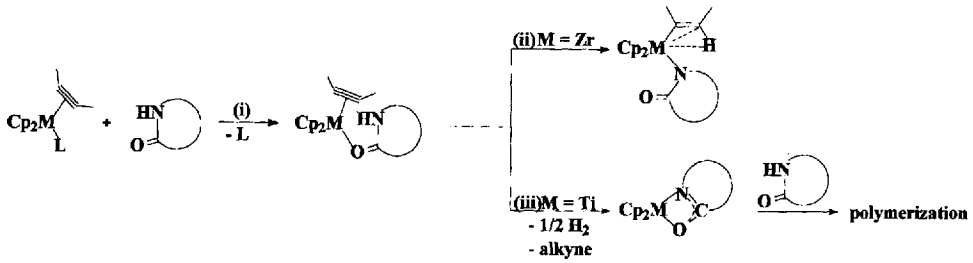
The NMR spectra of the second obtained complex **5** [^{1}H: δ = 8.00 ($Zr-C^{\alpha}=C^{\beta}-H$); ^{13}C: δ = 148.3 ($C^{\beta}$), δ = 236.1 ($C^{\alpha}$)] give some evidence for an agostic structure which was also found in the case of compound **2**. NMR measurement show, that complex **4** is slowly converted into a mixture of complexes containing also compound **5**, but no pure samples could be isolated.



4 5

In the reactions of $Cp_2Zr(THF)(Me_3SiC_2SiMe_3)$ with an excess of ε-caprolactam only a mixture of different products was obtained. The reaction of $Cp_2Ti(Me_3SiC_2SiMe_3)$ with an excess of ε-caprolactam in refluxing THF or toluene gave only complex **3** and unreacted lactam. No catalytic reactions were observed.

Scheme 3



Conclusion

The isolation of complexes **1**, **2**, and **3** gave evidence for some possible elementary steps of the reaction pathway in the catalytic anionic ring-opening polymerization of lactams with metallocene alkyne complexes (Scheme 3).

The first step is the coordination of the carbonyl group (i) as shown in complex **1**. The reaction ends up at this stage if *N*-alkyl-substituted lactams are used. This is in agreement with the fact that *N*-alkyl substituted 5- and 6-membered ring-lactams are not anionically polymerized. In the case of unsubstituted lactams the hydrogen shift from the lactam (ii) is supported for zirconocene by the agostic interaction as shown in compound **2**. In the case of titanocene after elimination of the alkyne and hydrogen the deprotonated lactam (lactamate) is complexed by the metallocene (iii) giving complex **3**. In the generally accepted mechanism of the anionic ring-opening polymerization of lactams this complex should be able to insert further lactam. The different reaction pathways for titanocene- and zirconocene-alkyne complexes with lactams is in agreement with recently obtained results in other reactions (Ti: elimination of the alkyne, Zr: ring-opening of the zirconacyclopropene)[16]. This is best explained by the large size of zirconium and seems to be the reason for the lower activity of the zirconocene complexes in the polymerization of β-propiolactam.

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Experimental

All operations were carried out under argon with 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. – Mass spectra: AMD 402. – NMR spectra: Bruker ARX 400. Chemical shifts referenced to signals of the used solvents: [D$_8$]THF (β-CH$_2$: δ_H = 1.73, δ_C = 25.2) or C$_6$D$_6$ (δ_H = 7.16, δ_C = 128.0). The spectra were assigned with the help of DEPT experiments. – IR: Nicolet Magna 550 (Nujol mulls using KBr plates). – Melting points: Sealed capillaries, Büchi 535 apparatus. – Elemental analyses: Leco CHNS-932 elemental analyzer. – X-ray diffraction data: CAD4 MACH3 (compound **3**) and STOE-IPDS (compounds **1** and **2**) diffractometer using graphite-monochromated Mo-K_α radiation. The crystals were sealed inside capillaries. Absorption correction was carried out by Ψ scan. The structure was solved by direct methods (SHELXS-86[17]) and refined by full-matrix least-squares techniques against F^2 (SHELXL-93[18]). XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations[19].

Preparation of Cp$_2$Zr(Me$_3$SiC$_2$SiMe$_3$)[O=C–N(Me)–(CH$_2$)$_5$] (**1**): 0.175 ml (1.36 mmol) of *N*-methyl-ε-caprolactam was added to a solution of 638 mg (1.36 mmol) of Cp$_2$Zr(Py)(Me$_3$SiC$_2$SiMe$_3$) in 10 ml of ether at −10°C. After stirring at −10°C for 30 min and subsequent stirring of the red solution at room temp. for 2 h, the solvent was removed in vacuo. The resulting red oil was dissolved in 10 ml of *n*-hexane at 40°C. Orange prisms crystallized at −15°C overnight. Yield of **1** 409 mg, 58%, m.p. 116°C (dec.). – ^{1}H NMR (C$_6$D$_6$, 300 K): δ = 0.39 [s, 18H, Si(CH$_3$)$_3$]; 0.91, 1.10, 1.20, 2.25, 2.46 (5 m, 5 × 2H, CH$_2$); 2.51 (s, 3H, Me); 5.72 (s, 10H, Cp). – ^{13}C NMR (C$_6$D$_6$, 300 K): δ = 2.2 (SiMe$_3$); 22.8, 27.2, 29.5, 35.2 and 51.7 (CH$_2$); 36.1 (Me); 106.7 (Cp). – ^{13}C NMR (C$_7$D$_8$, 230 K): δ = 2.0 and 2.2 (SiMe$_3$); 22.2, 26.7, 29.3, 34.3 and 50.7 (CH$_2$); 35.7 (Me); 106.5 (Cp); 182.1 (C=O); 197.5 and 224.5 (*C*SiMe$_3$). – C$_{25}$H$_{41}$NOSi$_2$Zr (519.0): calcd. C 58.86, H 7.96, N 2.70; found C 58.56, H 6.69, N 2.70. – MS (FAB), *m/z*: 391 [M$^+$ – *N*-methyl-ε-caprolactam], 127 [*N*-methyl-ε-caprolactam]$^+$.

Preparation of Cp$_2$Zr[–C(SiMe$_3$)=C(H)(SiMe$_3$)][–N–CO–CH$_2$–CH$_2$] (**2**): A solution of 80 mg (1.11 mmol) of β-propiolactam in 2 ml of ether was added to a solution of 520 mg (1.11 mmol) of Cp$_2$Zr(Py)(Me$_3$SiC$_2$SiMe$_3$) in 10 ml of ether at −10°C. After stirring at −10°C for 30 min and subsequent stirring of the light green solution at room temp. for 1 h, the solvent was removed in vacuo. The residue was dissolved in a mixture of THF and *n*-hexane (2:1). Colorless prisms deposited at −15°C. Yield of **2** 412 mg, 81%, m.p. 119°C (dec.). – ^{1}H NMR (C$_6$D$_6$, 300 K): δ = 0.27 and 0.34 [2 s, 2 × 9H, Si(CH$_3$)$_3$]; 2.81 and 3.02 (2 dd, 2 × 2H, CH$_2$); 5.61 (s, 10H, Cp); 8.04 [s, ^1J(CH) = 101 Hz, 1H, CH]. – ^{13}C NMR (C$_6$D$_6$, 300 K): δ = 0.2 and 2.1 (SiMe$_3$); 39.4 and 43.7 (CH$_2$); 106.3 (CH); 108.8 (Cp); 177.4 (C=O); 227.0 (*C*SiMe$_3$). – C$_{21}$H$_{33}$NOSi$_2$Zr (461.8): calcd. C 54.49, H 7.19, N 3.03; found C 54.32, H 7.15, N 3.08. – MS (FAB), *m/z*: 461 [M$^+$].

Preparation of Cp$_2$Ti–O=C–N–(CH$_2$)$_5$ (**3**): A solution of 185 mg (1.63 mmol) of ε-caprolactam in 2 ml of THF was added to a solution of 568 mg (1.63 mmol) of Cp$_2$Ti(Me$_3$SiC$_2$SiMe$_3$) in 10 ml of THF at room temp. After stirring for 3 h the solvent was removed in vacuo from the deep blue mixture and the residue was dissolved in 10 ml of *n*-hexane. Blue prisms crystallized overnight at −40°C. Yield of **3** 402 mg, 85%, m.p. 119–120°C (dec.). – IR (nujol): 1580 ($\nu_{(C-O)}$). – C$_{16}$H$_{20}$NOTi (290): calcd. C 65.99, H 7.27, N 4.81; found C 65.47, H 7.20, N 4.90. – MS (FAB), *m/z*: 290 [M$^+$].

Preparation of Cp$_2$Zr(Me$_3$SiC$_2$SiMe$_3$)[O=C–NH–(CH$_2$)$_5$] (**4**): 133 mg (1.17 mmol) of ε-caprolactam was added to a solution of 552 mg (1.17 mmol) of Cp$_2$Zr(Py)(Me$_3$SiC$_2$SiMe$_3$) in 10 ml of ether at −10°C. After stirring at −10°C for 1 h the solvent was removed in vacuo. The residue was dissolved in 10 ml of *n*-hexane at 0°C. Colorless prisms crystallized at −40°C overnight. Yield of **4** 301 mg, 51%, m.p. 116°C (dec.). – ^{1}H NMR (C$_6$D$_6$, 300 K): δ = 0.41 and 0.46 [2 s, 2 × 9H, Si(CH$_3$)$_3$]; 1.19, 1.26, 1.34, 1.96 and 2.67 (5

Table 3. Crystallographic data of **1**, **2**, and **3**

	1	2	3
formula	$C_{25}H_{41}NOSi_2Zr$	$C_{21}H_{33}NOSi_2Zr$	$C_{16}H_{20}NOTi$
mol. mass	518.99	462.88	290.23
cryst. color	orange	colourless	blue
cryst. descript	prism	prism	prism
cryst. size (mm)	0.4 × 0.3 × 0.2	0.5 × 0.5 × 0.4	0.4 × 0.3 × 0.2
cryst. system	monoclinic	triclinic	orthorombic
space group	$P2_1/n$	$P2_1/c$	$Pca2_1$
lattice constants			
a (Å)	15.389(2)	16.736(2)	10.4640(10)
b (Å)	9.843(2)	8.643(2)	16.8810(10)
c (Å)	19.642(2)	17.255(2)	8.3050(10)
α (deg)	90	90	90
β (deg)	112.24(1)	101.820(10)	90
γ (deg)	90	90	90
Z	4	4	4
temp. (K)	200(2)	293(2)	173(2)
μ (mm^{-1})	0.502	0.557	0.575
abs. cor.	no	no	Ψ scan
transm.(%)			
min./max.			93.8 / 99.9
θ range (deg)	2.12 - 24.37	2.41 - 24.33	2.41 - 23.45
largest diff. (e $Å^{-3}$)			
peak / hole	0.5 / -1.0	0.2 / -0.5	0.3 / -0.2
no. of rflns. (measd.)	7997	7083	2246
no. of rflns. (indep.)	4414	3840	1164
R (int)	0.064	0.0386	0.0349
no. of rflns. (obsd.) ($I > 2\sigma(I)$)	2675	2577	908
R1 ($I > 2\sigma(I)$)	0.094	0.068	0.041
no. of parameters	241	541	102
wR2 (all data)	0.074	0.175	0.111

m, 5 × 2H, CH_2); 5.78 (s, 10H, Cp); 7.36 (s, 1H, NH). – ^{13}C NMR (C_6D_6, 300 K): δ = 1.8 and 4.4 ($SiMe_3$); 23.4, 29.9, 31.3, 36.3 and 47.6 (CH_2); 110.5 (Cp); 182.8 (C=O); 136.1 and 227.0 ($CSiMe_3$). – $C_{23}H_{41}NOSi_2Zr$ (504.9): calcd. C 57.09, H 7.78, N 2.77; found C 57.11, H 7.75, N 2.70. – MS (FAB), *m/z*: 391 [M^+ – ε-caprolactam], 113 [ε-caprolactam].

NMR-Spectroscopic Data of $Cp_2Zr[-C(SiMe_3)=C(H)(SiMe_3)][-N-CO-(CH_2)_5]$ (**5**): Crude sample: ^1H NMR (C_6D_6, 300 K): δ = 0.32 and 0.36 [2 s, 2 × 9H, $Si(CH_3)_3$]; 1.30, 2.22 and 2.43 (5 m, 5 × 2H, CH_2); 6.01 (s, 10H, Cp); 8.00 (s, 1H, CH). – ^{13}C NMR (C_6D_6, 300 K): δ = 2.0 and 3.7 ($SiMe_3$); 23.5, 30.1, 30.6, 37.0 and 42.3 (CH_2); 111.4 (Cp); 177.0 (C=O); 148.3 (CH); 236.1 ($CSiMe_3$).

Polymerization of β-Propiolactam: A solution of 80 mg (0.23 mmol) of $Cp_2Ti(Me_3SiC_2SiMe_3)$ and 165 mg (2.31 mmol) of β-propiolactam in 10 ml of toluene was heated with stirring and at reflux for 4 h. Then the solvent was removed in vacuo and the residue was washed with water and pentane. Yield: 140 mg (85%) of a white powder.

According the same procedure described above 120 mg (0.25 mmol) of **2** and 185 mg (2.5 mmol) of β-propiolactam yielded 100 mg (56%) of a light yellow powder.

X-ray Structure Determination of Compounds **1**, **2**, *and* **3**: Crystal data are summarized in Table 3.

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[19] Further details of the structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-405473, -405472, and -405493.

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