Organocalcium Compounds with Catalytic Activity for the Ring-Opening Polymerization of Lactones

Matthias Westerhausen,*[a] Stefan Schneiderbauer,[a] Alexander N. Kneifel,[a] Yvonne Söltl,[a] Peter Mayer,[a] Heinrich Nöth,[a] Zhiyuan Zhong,[b] Pieter J. Dijkstra,[b] and Jan Feijen[b]

Dedicated to the memory of Ron Snaith

Keywords: N ligands / Calcium / O ligands / Ring-opening polymerization / Tin

The equimolar reaction of calcium bis[bis(trimethylsilyl)amide] with 2,2,6,6-tetramethylheptane-3,5-dione (Htmhd) in THF yields liquid mononuclear [Ca(tmhd){N(SiMe$_3$)$_2$}(THF)$_3$] (**1**). A similar reaction in toluene with a stoichiometric ratio of 2:3 gives the dinuclear complex [{(THF)Ca}$_2$(tmhd)$_2$(μ-tmhd){μ-N(SiMe$_3$)$_2$}] (**2**). The calcium atoms of these complexes are in a distorted octahedral environment. In **2** the complex consists of two octahedra connected by a common face of one nitrogen base and two oxygen atoms; the bridging Ca–N bond lengths are extremely large. The metalation of the tetradentate Jacobsen reagent with calcium bis[bis(trimethylsilyl)amide] in 1,2-dimethoxyethane (DME) gives the corresponding calcium complex **3**, nearly quantitatively, as its DME adduct. The calcium atom is in an unusual trigonal prismatic coordination sphere. The metathesis reaction of **3** with tin(II) chloride yields the corresponding yellow tin(II) complex with the metal atom in a distorted square-pyramidal environment. Complexes **2** and **3** show catalytic reactivity in the ring-opening polymerization of cyclic esters such as lactones and lactides.
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Introduction

The expectations that organocalcium chemistry might have a wide variety of applications[1] has led to intensive research efforts on this topic. Organocalcium compounds have been investigated for use as combustion improvers and smoke inhibitors, and as an additive for diesel fuels and fuel oils.[2] Another field of interest is the MOCVD (*M*etal *O*rganic *C*hemical *V*apour *D*eposition) process to produce, for example, thin films of calcium sulfide[3] or titanate.[4] There are also investigations on these compounds as sol-gel precursors.[5] Another important application for organocalcium compounds focuses on their use as initiators for the anionic ring-opening polymerization of cyclic esters and lactones.[6] These arbitrarily chosen examples illustrate the wide spectrum of interest in these compounds. Whereas for the MOCVD processes the main requirements of these compounds are volatility and thermal stability, the demands for ring-opening polymerization concern their reactivity towards cyclic esters and their solubility in common organic solvents such as ethers and hydrocarbons.

Due to the lack of redox reactivity, which is the key step in many catalytic cycles with transition metals, the alkaline-earth metals always show the oxidation state of +2. For their use as polymerization initiators and catalysts the organocalcium complexes should therefore have vacant coordination sites, which can be filled by weakly bonding ligands, or have unusual or distorted coordination spheres at the metal center. Furthermore, we have to design organocalcium compounds in a special reactivity range to have sufficient reactivity for the ring opening of cyclic esters but to prevent side reactions with the already formed polymer or with the solvent (such as ether cleavage reactions).

Polymeric cyclic esters such as D,L-lactide or ε-caprolactone are used for tissue engineering and as materials for surgical sutures. Orthopedic applications as well as the use for controlled-release systems for pharmaceuticals are also under investigation. The demand for these materials is extremely high with respect to toxicity and immunogenic, allergic and thrombogenic reactions. Furthermore, the polymeric materials should be sterilizable and have suitable mechanical properties.[7] Polylactides are amongst the most important biodegradable polymers. Due to the fact that the anionic polymerization initiator remains in the polymeric material, organometallic compounds based on calcium are the ideal starting materials for ring-opening polymerization.

For the purpose of investigating organocalcium compounds with respect to ring-opening polymerization we have chosen heteroleptic β-diketonates of calcium with reactive bis(trimethylsilyl)amide ligands. Homoleptic calcium

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[a] Department Chemie, Ludwig-Maximilians-Universität Munich
München, Germany
[b] Department of Chemical Technology and Institute for Biomedical Technology, University of Twente,
Enschede, The Netherlands

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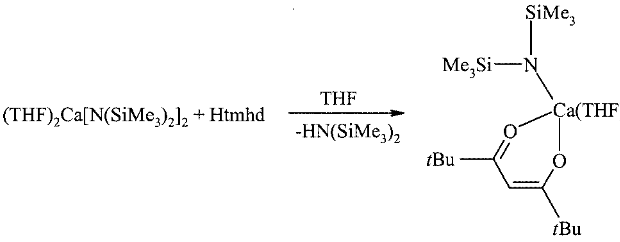
bis(tetramethylheptane-3,5-dionate) was prepared from calcium diethoxide and tetramethylheptane-3,5-dione (Htmhd) and crystallized as a dimeric bis(ethanol) complex or as a solvent-free trimer.[8] This trimer was monomerized by addition of strong mono- or bidentate N-donors.[9]

Results and Discussion

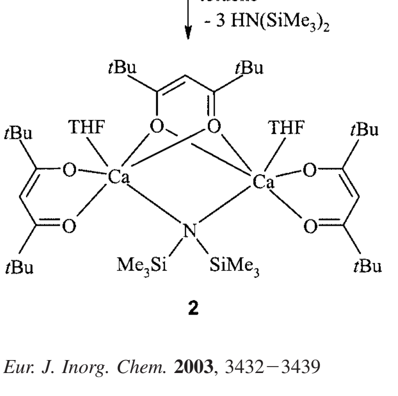
Synthesis

Until now the synthesis of β-diketonato complexes of calcium started from the alkoxides. However, the soluble and readily accessible {by transmetalation of $Sn[N(SiMe_3)_2]_2$} bis(tetrahydrofuran)calcium bis[bis(trimethylsilyl)-amide][10,11] is a more reactive metalation reagent. The equimolar reaction of $Ca[N(SiMe_3)_2]_2$ with Htmhd in tetrahydrofuran yielded the liquid, mononuclear complex tris-(tetrahydrofuran)(2,2,6,6-tetramethylheptane-3,5-dionato)-calcium bis(trimethylsilyl)amide (**1**) according to Equation (1) with a surprisingly low melting point of 4 °C. The prolonged exposure of this complex to vacuum gave a brown and nearly insoluble oil. The metalation of Htmhd with $[Ca\{N(SiMe_3)_2\}_2(THF)_2]$ in a stoichiometric ratio of 3:2 in toluene gave binuclear bis[(tetrahydrofuran)calcium]-tris(2,2,6,6-tetramethylheptane-3,5-dionato)bis(trimethylsilyl)amide (**2**) according to Equation (2) in good yield. This complex reacts in THF with alcohols such as methanol, ethanol and 2-propanol by substitution of the amide ligand by an alkoxide anion. However, recrystallization from toluene gave the homoleptic dismutation product $[Ca(tmhd)_2]_3$ and a mixture of alkoxide-rich complexes of yet unknown composition. However, the structure of **2** was maintained upon alcoholysis with sterically demanding alcohols such as 2,6-di(*tert*-butyl)phenol and 1-phenylethanol, and compounds of the type $[(THF)Ca]_2(tmhd)_3OR$ were isolated.



1)

1



(2)

2

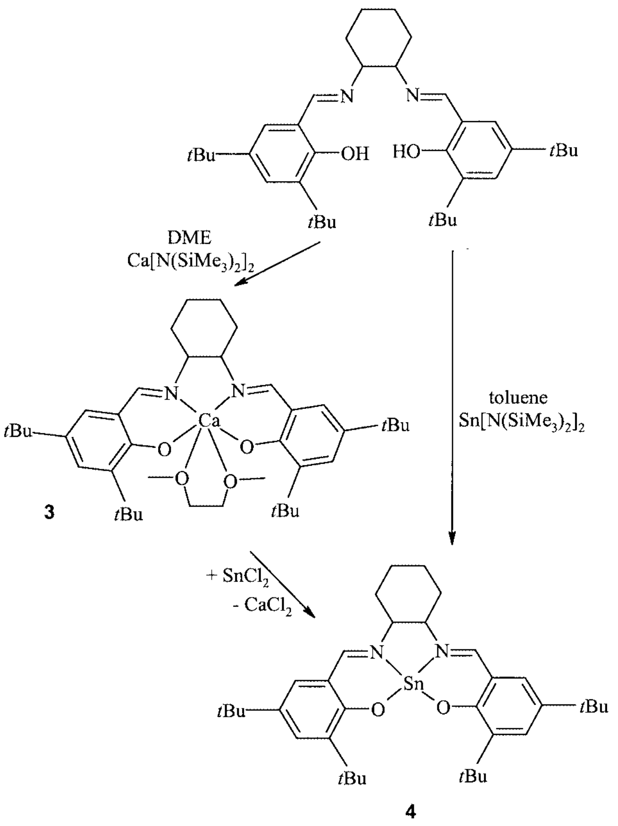
The different coordination spheres of the nitrogen atoms of the bis(trimethylsilyl)amido ligands is clearly shown by the $^{29}Si\{^1H\}$ NMR chemical shifts.[12] For **1** the $N(SiMe_3)_2$ substituent with a triply coordinated nitrogen atom shows a chemical shift of $\delta = -15.9$ ppm which is a characteristic value for a terminally bonded amido group. The low-field shifted $^{29}Si\{^1H\}$ NMR resonance of **2** at $\delta = -8.0$ ppm proves the bridging position of the bis(trimethylsilyl)amido ligand. Similar characteristic shifts have been found for the calcium bis[bis(trimethylsilyl)amides].[12]

In order to investigate the reactive coordination sites of the calcium-containing complexes the molecular structures of **1** and **2** were determined (see below). We have already shown that **2** shows catalytic activity in anionic ring opening polymerization of cyclic esters.[13]

Another possibility to enhance the reactivity of organocalcium compounds is to embed the calcium center in an unusual coordination sphere. Vacant coordination sites at the Lewis-acid metal center lead immediately to coordination of Lewis bases such as ethers or to a dimerization of the calcium-containing compound. Therefore, the unusual coordination sphere has to be fixed by employing a multidentate ligand which shows very restricted flexibility and enforces a non-octahedral coordination sphere of the calcium atom.

In order to investigate the coordination sphere the Jacobsen ligand[14] was chosen due to its nearly square-planar tetradentate N_2O_2 coordination site and its dianionic charge to ensure a stable complex with *tert*-butyl groups at the periphery to ensure solubility in common organic solvents such as ethers. The metalation of the Jacobsen reagent with calcium bis[bis(trimethylsilyl)amide] in 1,2-dimethoxyethane (DME) yielded (1,2-dimethoxyethane-*O*,*O′*)calcium (*R*,*R*)-(−)-*N*,*N′*-bis[3,5-di(*tert*-butyl)salicylate]-1,2-cyclohexenediimine (**3**) according to Equation (3).

In order to investigate the suitability of the calcium complex **3** for metathesis reactions a well-known tin(II) complex was prepared. Compound **3** was reacted with tin dichloride to give nearly quantitatively the corresponding yellow tin(II) (*R*,*R*)-(−)-*N*,*N′*-bis[3,5-di(*tert*-butyl)salicylate]-1,2-cyclohexenediimine (**4**) according to Equation (3). The $^{119}Sn\{^1H\}$ NMR chemical shift of $\delta = -536.0$ ppm is similar to the published value ($\delta = -524.5$ ppm[15]). This compound was prepared earlier by metalation of the Jacobsen reagent with $Sn[N(SiMe_3)_2]_2$, however, only the oxidation product with 3,5-di(*tert*-butyl)-1,2-benzoquinone[15] and the addition products to metal carbonyl fragments[16] were characterized by X-ray crystallography. The metal centers of organometallic tin(II) compounds usually display coordination numbers of two and three. Monomeric molecules such as $Sn[N(SiMe_3)_2]_2$ are bent due to the lone pair at the metal center.[17] The dimeric molecules can either form a tin-tin bond in a trans-bent fashion, as for example observed for $[Sn\{CH(SiMe_3)_2\}_2]_2$,[18] or can exhibit a Sn_2X_2 cycle, as for example in $[RSn(\mu\text{-}Cl)_2SnR][R = N(SiMe_3)_2, N(CMe_2CH_2)_2CH_2]$.[19] In all compounds with a triply coordinated tin(II) atom the metal atoms show a strongly pyramidal coordination sphere because stannanediyls of the type SnR_2 are Lewis acids as well as Lewis bases.[20] Due to the geometry of the Jacobsen ligand the formation of a distorted tetragonal pyramid has to be expected, as found for a similar complex.[21] The molecular structure of **4** was determined by X-ray crystallography.



(3)

Molecular Structures

Due to their low melting point single crystals of **1** have to be handled at temperatures below −20 °C during isolation from the mother liquor and mounting on the diffractometer. The molecular structure of **1** and the numbering scheme is represented in Figure 1. Selected structural parameters are summarized in Table 1. The calcium center is in a distorted octahedral environment with a meridional arrangement of the three anionic donors.

The Ca−O distances of the anionic diketonate ligand are approximately 12 pm smaller than those of the THF molecules. The Ca−N bond length of 237.7 pm is rather large in comparison to Ca−N bonds of terminally bonded bis(trimethylsilyl)amido substituents in $[Ca\{N(SiMe_3)_2\}_2(THF)_2]$ (230 pm[11]) and $[Ca\{N(SiMe_3)_2\}_2(DME)]$ (227 pm[22]).

The distortion of the octahedral coordination sphere of the calcium atom is caused by the bite of the β-diketonate ligand, with an O1···O2 distance of 278.8 pm, which gives an O1−Ca1−O2 angle of only 74.2°. The anionic charge is delocalized within the planar diketonate fragment. Therefore, average C−O and C−C bond lengths of 128 and 139 pm, respectively, are observed.

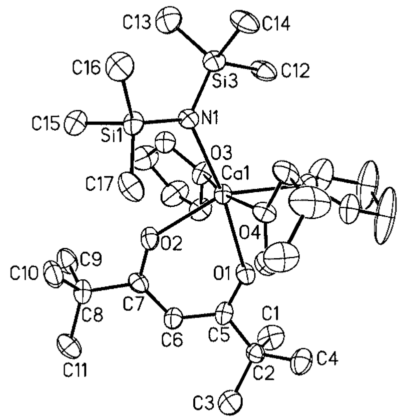


Figure 1. Molecular structure of **1**; the ellipsoids represent a probability of 40%; the hydrogen atoms are omitted for clarity; selected bond lengths (pm) of the coordination sphere of calcium: Ca1−O1 232.0(6), Ca1−O2 230.1(6), Ca1−O3 243.5(6), Ca1−O4 239.8(6), Ca1−O5 247.0(6), Ca1−N1 237.7(6); bond angles (°): O1−Ca1−O2 74.2(2), O1−Ca1−O3 94.6(2), O1−Ca1−O4 84.1(2), O1−Ca1−O5 77.1(2), O1−Ca1−N1 165.4(2), O2−Ca1−O3 82.6(2), O2−Ca1−O4 108.8(2), O2−Ca1−O5 147.4(2), O2−Ca1−N1 97.3(2), O3−Ca1−O4 167.5(2), O3−Ca1−O5 84.7(2), O3−Ca1−N1 96.1(2), O4−Ca1−O4 82.9(2), O4−Ca1−N1 87.6(2), O5−Ca1−N1 113.9(2)

Table 1. Selected structural parameters of the compounds **3** (M = Ca) and **4** (M = Sn)

	3	4 (molecule A)	4 (molecule B)
M−O1	218.8(2)	209.6(4)	210.7(5)
M−O2	219.4(2)	211.9(4)	212.3(5)
M−O3	244.2(2)	−	−
M−O4	245.2(2)	−	−
M−N1	247.0(3)	235.0(4)	232.5(5)
M−N2	240.2(3)	236.1(5)	238.0(5)
O1−M−O2	104.46(7)	80.4(2)	79.9(2)
O1−M−O3	89.97(9)	−	−
O1−M−O4	140.98(9)	−	−
O1−M−N1	75.83(9)	76.6(2)	78.0(2)
O1−M−N2	133.13(9)	110.5(2)	118.9(2)
O2−M−O3	149.90(8)	−	−
O2−M−O4	87.11(9)	−	−
O2−M−N1	123.79(9)	129.2(2)	120.7(2)
O2−M−N2	74.79(9)	78.4(2)	76.2(2)
N1−M−O3	85.03(8)	−	−
N1−M−O4	128.20(9)	−	−
N1−M−N2	67.64(8)	68.6(2)	68.3(2)
N2−M−O3	114.21(9)	−	−
N2−M−O4	85.73(9)	−	−
O3−M−O4	65.98(7)	−	−

The molecular structure of **2** and the numbering scheme are represented in Figure 2. In this dinuclear molecule the calcium atoms are in distorted octahedral environments. The molecule contains two octahedra connected by a common face. The bridging ligands are the bis(trimethylsilyl)amido and one of the β-diketonato substituents, which

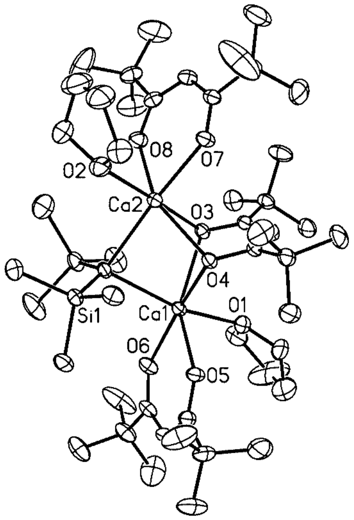


Figure 2. Molecular structure of **2**; the ellipsoids represent a probability of 40%; the hydrogen atoms are omitted for clarity; selected bond lengths (pm): Ca1−N 246.5(2), Ca1−O1 243.7(2), Ca1−O3 248.1(2), Ca1−O4 243.7(2), Ca1−O5 226.4(2), Ca1−O6 229.2(2), Ca2−N 251.2(2), Ca2−O2 241.8(2), Ca2−O3 244.8(2), Ca2−O4 239.7(2), Ca2−O7 231.5(2), Ca2−O8 225.9(2), Ca1···Ca2 337.46(7)

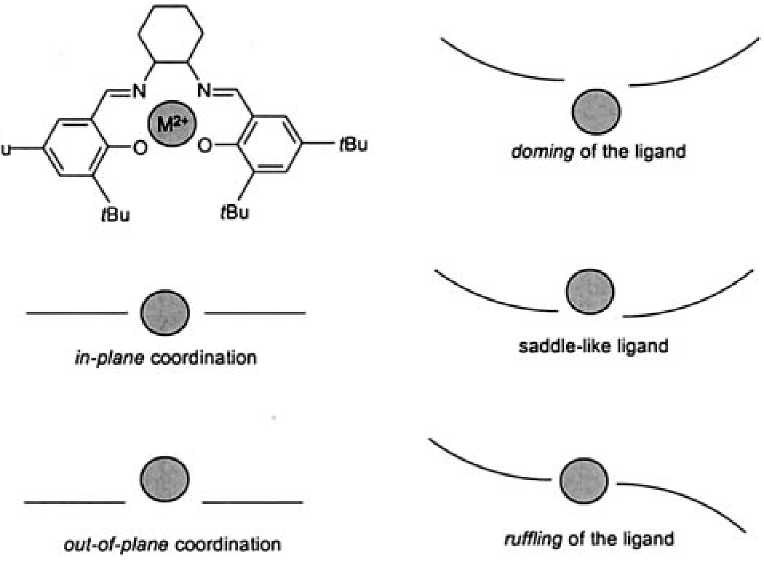
leads to coordination numbers of four for the nitrogen atom and three for the bridging oxygen atoms O3 and O4.

The Ca−N bonds, with an average length of 249 pm, are extraordinarily long. Likewise, the bridging Ca−O bonds have an average length of 244 pm, which is even slightly larger than the distance between the metal centers and the THF molecules. The terminally bonded β-diketonate ligands display much shorter Ca−O bonds, with an average value of 228 pm. These Ca−O distances are the smallest due to the electrostatic attraction and the small coordination numbers of the oxygen atoms. The N−Si distances, with a mean value of 172 pm, are in the expected region found for other calcium bis[bis(trimethylsilyl)amides] and do not support an ionic picture where extremely short N−Si bonds are to be expected, as, for example, for barium bis[bis(trimethylsilyl)amide].[12]

For multidentate ligands with a fixed arrangement of the Lewis donors several possibilities of coordination behaviour are possible (Scheme 1). Depending on the ratio of the radii of the metal atoms and the coordination gap an in-plane or out-of-plane coordination is realized. Furthermore, doming of the ligand is often observed, with the metal atom on the outside, or a saddle-like arrangement, with the metal on the inside of the ligand. Sometimes a twisting or ruffling of the multidentate base is also observed. To enhance the reactivity, a doming of the ligand with the metal center bonded from the outside is necessary.

The Jacobsen ligand retains its stereochemical centers and therefore centrosymmetric space groups have been excluded during the structure determination and refinement procedures of the calcium complex **3**. The geometry of the unit cell and the reflection conditions lead to the acentric orthorhombic space group $P2_{1}2_{1}2_{1}$. Surprisingly, other authors have found centrosymmetric space groups for solid-state structures of complexes of the Jacobsen ligand with divalent metals such as zinc,[23] even though the synthesis was performed with a stereochemically pure starting material.

The molecular structure of the calcium compound **3** with the Jacobsen ligand is shown in Figure 3. Here also the alkaline-earth metal center displays a coordination number of six, although the calcium atom is in an unusual distorted trigonal prismatic environment. The Ca−O distances of 219 pm to the alkoxide groups are extremely small due to the anionic charge, whereas in **2** the anionic charge on the oxygen atoms is reduced because it is delocalized within the β-diketonate fragment. In Figure 3 the doming of the Jacobsen ligand can clearly be seen.



Scheme 1. Coordination behaviour of potentially multidentate ligands with reference to the flexibility of compounds **3** (M^{2+} = Ca·DME) and **4** (M^{2+} = Sn)

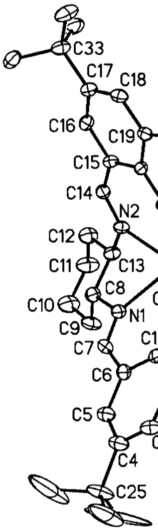


Figure 3. Molecular structure of **3**; the ellipsoids show a probability of 40%; the hydrogen atoms are omitted for clarity

The square-planar fragment is slightly distorted, as can be seen from the widening of the O1−Ca1−O2 angle (104.5°), whereas the other (endocyclic) angles are much smaller (O1−Ca1−N1 75.8°, N1−Ca1−N2 67.6°, N2−Ca1−O2 74.8°). However, the smallest angle is observed to the bidentate DME ligand. The calcium atom is larger than the O_2N_2 gap, and therefore it is located above the plane containing O1, O2, N1, and N2. Furthermore, the Jacobsen ligand is not planar but arched. Nevertheless, the nitrogen atoms are coordinated in a trigonal planar manner by two carbon atoms and the alkaline earth metal dication. The Ca1−O1−C1 and Ca1−O2−C20 fragments are bent (average 142.2°). The cyclohexane backbone shows the favoured chair conformation with a slightly elongated C8−C13 bond (154.3 pm) compared to the other C−C bonds of the cyclohexane moiety (average value of 152 pm).

The distances between the calcium center and the oxygen atoms of the DME molecule are approximately 25 pm longer than those to the alkoxide anions. In solution exchange reactions with solvent molecules are observed. Dissolving **3** in tetrahydrofuran immediately leads to the THF adduct, which can be isolated as a powder after standard workup procedures. Another coordination sphere of this molecule which contains monodentate Lewis bases has to expected. Atwood and co-workers[24] found a heptacoordinate calcium center for [Ca(*t*Bu-salen)(HOEt)(THF)$_2$] with a distorted pentagonal bipyramidal coordination. The use of a bidentate ligand is necessary to enforce the trigonal prismatic environment of the alkaline-earth metal atom. This easily exchangeable DME molecule offers the possibility of creating a coordination vacancy for the initial step of the polymerization reaction namely the coordination of the cyclic ester such as lactide or ε-caprolactone. Detailed studies of the polymerization process are under investigation and will be published elsewhere.

Compound **4** (M.p. 291−293 °C) crystallizes in the acentric orthorhombic space group $P2_12_12_1$ with two crystallographically independent molecules which are distinguished by the letters A and B. The molecular structure of molecule A is shown in Figure 4. Both the molecules show nearly identical structural parameters. Therefore, the discussion of this structure is limited to molecule A; however, in Table 1 selected bond lengths and angles of both molecules are listed together with the data of the calcium complex **3**.

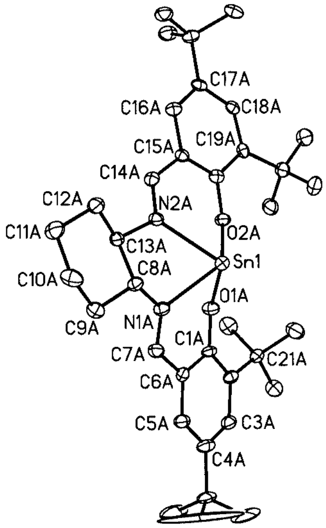


Figure 4. Molecular structure of **4**; the ellipsoids show a probability of 40%; the hydrogen atoms are omitted for clarity

The tin atom is bonded above the N_2O_2 plane with Sn−O bond lengths of 209.6 and 211.9 pm which are larger than in tin(II) bis[2,6-di(*tert*-butyl)phenolate] (200.3 and 204.4 pm[25]) and tin(II) bis[2,6-di(*tert*-butyl)-4-methylphenolate] (200.8 pm[26]). In dimeric Sn(O*t*Bu)$_2$, with a central Sn_2O_2 ring, endocyclic and exocyclic Sn−O bonds of 214.7 (average) and 200.9 pm, respectively, were found.[27] The Sn−N distances are coordinative bonds with large values of 235.0 and 236.1 pm. The Sn−O−C angles display an average value of 127°. The oxidation of tin(II) to tin(IV) leads to a drastic contraction of the bonding parameters, even though the enhancement of the coordination number to six is realized in an octahedral environment of the tin(IV) atom.[15] Also, the Sn−N bonds show a smaller average length of 218.3 pm, with the Sn−O bonds having average values of 201.8 pm. The Jacobsen ligands of **2** and **3** display nearly the same orientation and structural features. This observation shows that an inflexible ligand can enforce unusual coordination spheres at the metal atoms, namely a trigonal prism for the calcium center and the tin(II) atom being the apex of a distorted square pyramid.

Perspective

The catalytic reactivity of **2** was tested towards the polymerization of lactide and ε-caprolactone in THF solution. A fast gel formation as a sign of polymerization was observed. The polymeric materials show high molecular weights of approximately 1.67 × 10^5 g·mol^{-1} and a broad mass distribution. The substitution of the bis(trimethylsilyl)-

amide by an alkoxide substituent, or the polymerization in the presence of an alcohol, leads to a living polymerization. The preparative details of the ring-opening polymerization and the concept that labile anionic ligands support the catalytic activity of this polymerization reaction will be presented in detail elsewhere. The preformed coordination gap by enforcing a trigonal prismatic coordination sphere at the calcium atom as realized in **3** is also a promising working hypothesis. Usually an octahedral environment of the alkaline earth metal atoms is preferred, and therefore the 1,2-dimethoxyethane ligand is immediately substituted by monodentate ligands, which is the first step in the polymerization process. On the other hand, the liquid complex **1** also loses neutral coligands very easily at room temperature during handling under an inert gas atmosphere or in hydrocarbons; a brown, nearly insoluble oil forms which separates from solution. Therefore, it is not recommended to use this calcium compound as an initiator or catalyst for the anionic polymerization of lactones and lactides. In a short communication Chisholm[28] has reported calcium compounds with four-coordinate calcium centers which can be used as catalysts for the ring-opening polymerization of lactides.

The advantage of the catalytically active complexes **2** and **3** in comparison to the already investigated calcium bis[bis(trimethylsilyl)amide][6,29] lies in the reduced sensitivity towards air and moisture and, therefore, an easier handling outside of a glove box seems to be possible during the polymerization experiments. Preliminary experiments support the expectation that these compounds are valuable initiators for the anionic polymerization of lactones and other cyclic ester.

Experimental Section

General Remarks: All experiments and manipulations were carried out under an atmosphere of argon. Reactions were performed using standard Schlenk techniques and dried, thoroughly deoxygenated solvents. Calcium bis[bis(trimethylsilyl)amide] was prepared according to a literature procedure.[10,11] NMR spectra were recorded on Jeol spectrometers GSX270 and EX400. A Nicolet 520 FT-IR spectrophotometer was used to record the IR spectra; solid substances were measured in nujol between KBr plates (vs very strong, s strong, m medium strong, w weak, vw very weak, sh shoulder).

Tris(tetrahydrofuran)(2,2,6,6-tetramethylheptane-3,5-dionato)calcium Bis(trimethylsilyl)amide (1): A solution of [Ca{N(SiMe$_3$)$_2$}$_2$(THF)$_2$] (2.40 g, 4.76 mmol) in 20 mL of THF was cooled to 0 °C. Then 2,2,6,6-tetramethylheptane-dione (0.99 mL, 4.76 mmol) was added. After stirring for an additional hour the solution was warmed to room temperature and the volume reduced to a few milliliters. After cooling to approximately −20 °C 1.74 g of colorless crystals of **1** (yield 66%) were collected. M.p. 4 °C. ^{1}H NMR ([D$_6$]benzene/THF mixture): δ = 0.19 (SiMe$_3$), 1.13 (*t*Bu), 5.68 (CH), 1.51 and 3.57 (THF) ppm. ^{13}C{^{1}H} NMR ([D$_6$]benzene/THF mixture): δ = 5.42 (SiMe$_3$), 28.46 (C*Me$_3$*), 40.69 (*C*Me$_3$), 89.00 (CH), 199.29 (CO), 25.40 and 67.65 (THF) ppm. ^{29}Si{^{1}H} NMR ([D$_6$]benzene/THF mixture): δ = −15.9 (NSi$_2$) ppm. IR: $\tilde{\nu}$ = 1693 m, 1660 s, 1562 w, 1538 m, 1505 s, 1480 w, 1450 w, 1417 s, 1390 m, 1360 m, 1250 m, 1224 w, 1183 w, 1131 w, 956 w, 932 m, 881 w, 867 m, 841 m, 794 w, 479 w, 403 w. C$_{25}$H$_{45}$CaNO$_4$Si$_2$ (527.95) [bis(THF) complex due to loss of THF during handling and combustion]: calcd. C 57.76, H 8.72, N 2.69; found C 57.48, H 8.71, N 2.69.

Bis[(tetrahydrofuran)calcium] Tris(2,2,6,6-tetramethylheptane-3,5-dionate) Bis(trimethylsilyl)amide (2): A solution of [Ca{N(SiMe$_3$)$_2$}$_2$(THF)$_2$] (4.41 g, 8.74 mmol) in 50 mL of toluene was cooled to 0 °C and then 2,2,6,6-tetramethylheptane-3,5-dione (1.82 mL, 8.74 mmol) was added. After warming to room temperature the solution was stirred for an additional 12 hours. All volatile materials were removed under vacuum and the residue redissolved in 50 mL of *n*-pentane. The remaining solid materials were removed and the volume of the solution reduced to 10 mL. At −30 °C 3.25 g of colorless crystals of **2** (yield 80%) precipitated. Dec. 74 °C (without melting). ^{1}H NMR ([D$_6$]benzene): δ = 0.53 (SiMe$_3$), 1.26 (*t*Bu), 5.89 (CH), 1.37 and 3.63 (THF) ppm. ^{13}C{^{1}H} NMR ([D$_6$]benzene): δ = 5.12 (SiMe$_3$), 28.63 (C*Me$_3$*), 41.11 (*C*Me$_3$), 91.24 (CH), 200.84 (CO), 28.63 and 68.09 (THF) ppm. ^{29}Si{^{1}H} NMR ([D$_6$]benzene): δ = −8.0 (NSi$_2$) ppm. IR: $\tilde{\nu}$ = 1693 m, 1660 s, 1562 w, 1537 m, 1505 s, 1450 w, 1419 s, 1390 m, 1360 m, 1249 w, 1224 w, 1183 w, 1131 w, 933 m, 867 m, 843 w, 793 w, 479 w. C$_{47}$H$_{91}$Ca$_2$NO$_8$Si$_2$ (934.57): calcd. C 60.40, H 9.80, N 1.50; found C 60.38, H 9.81, N 1.41.

(1,2-Dimethoxyethane-*O,O′*)calcium (*R,R*)-(−)-*N,N′*-bis[3,5-di(*tert*-butyl)salicylate]-1,2-cyclohexenediimine (3): A solution of Htmhd (1.08 g, 1.98 mmol) in 10 mL of toluene was added to a solution of (1,2-dimethoxyethane-*O,O′*)calcium bis[bis(trimethylsilyl)amide] (1.07 g, 1.98 mmol) in 10 mL of toluene. The yellow solution was stirred for one day at room temperature and then all volatile materials were removed under vacuum. The yellow residue was redissolved in a few milliliters of toluene. At 5 °C 0.82 g of yellow plates of **3** (1.2 mmol, 61%) precipitated. M.p. 255−257 °C. ^{1}H NMR ([D$_6$]benzene): δ = 8.04 (s, 2 H, CH=N), 7.71 (s, H, aryl), 7.24 (s, 2 H, aryl), 3.05 (s, 6 H, DME), 2.96−2.78 (m, 6 H, DME, CH), 1.84 (s, 18 H, *t*Bu), 1.61 (s, 4 H, CH$_2$), 1.49 (s, 18 H, *t*Bu), 1.24−1.12 (m, 4 H, CH$_2$) ppm. ^{13}C{^{1}H} NMR ([D$_6$]benzene): δ = 168.1, 166.3 (CH=N), 139.9, 132.3, 129.9, 128.3, 126.3, 122.0 (aryl), 70.4 (DME), 69.5 (CH), 59.5(DME), 35.8, 33.8 (*C*Me$_3$), 31.9 (C*Me$_3$*), 31.4, 30.9 (CH$_2$), 29.9 (C*Me$_3$*), 29.5, 25.4 (CH$_2$) ppm. IR: $\tilde{\nu}$ = 1633 vs, 1615 vs, 1523 vs, 1479 vs, 1462 vs, 1439 vs, 1412 vs, 1398 vs, 1380 vs, 1361 vs, 1348 vs, 1334 vs, 1313 m, 1276 s, 1257 vs, 1230 s, 1199 s, 1158 vs, 1128 w, 1114 m, 1101 m, 1067 vs, 1030 m, 1023 m, 984 w, 974 w, 953 w, 927 w, 915 w, 882 s, 866 s, 857 m, 836 m, 810 w, 794 s, 743 m, 729 w, 637 w, 520 m, 475 w, 440 s, 421 w, 380 w, 336 w, 307 w.

X-ray Structure Determinations of 1−4: Data were collected on a Siemens P4 diffractometer with a Siemens SMART-CCD area detector using oil-coated rapidly cooled single crystals.[30,31] Graphite monochromated Mo-K_α radiation (λ = 71.073 pm) was used. Crystallographic parameters, details of data collection and refinement procedures are summarized in Table 2. The structures were solved by direct methods and refined with the software packages SHELXL-93 and SHELXL-97.[33] Neutral scattering factors were taken from Cromer and Mann[34] and for the hydrogen atoms from Stewart et al.[35] The non-hydrogen atoms were refined anisotropically. The H-atoms were considered with a riding model under restriction of ideal symmetry at the corresponding carbon atoms or refined isotropically. Crystallographic details can be obtained from the Cambridge Crystallographic Data Centre quoting the CCDC numbers given in Table 2.[36] One of the *tert*-butyl groups of **3** and **4** shows a rotatory disordering which was not resolved by split-positions of the corresponding atoms because neither the *R*

Table 2. Crystallographic data of **3** and **5** as well as details of the structure solution and refinement procedures

Compound	**1**	**2**	**3**	**4**
Formula	$C_{29}H_{61}CaNO_5Si_2$	$C_{47}H_{91}Ca_2NO_8Si_2$	$C_{40}H_{62}CaN_2O_4$	$C_{36}H_{52}N_2O_2Sn$
Formula mass [$g \cdot mol^{-1}$]	600.05	934.554	675.00	663.485
T [K]	193(2)	200(2)	193(2)	193(2)
Space group[32]	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_12_12_1$ (No. 29)	$P2_12_12_1$ (No. 29)
a [pm]	976.8(1)	1270.91(2)	1353.97(9)	1080.78(5)
b [pm]	2082.7(2)	2432.61(4)	1568.33(9)	2347.7(1)
c [pm]	1818.9(2)	1865.35(2)	1944.9(1)	2676.3(2)
β [°]	93.129(2)	97.708	90	90
V [nm^3]	3.6949(7)	5.7149(1)	4.1299(4)	6.7907(7)
Z	4	4	4	8
$d_{calcd.}$ [$g \cdot cm^3$]	1.079	1.086	1.086	1.298
μ [mm^{-1}]	0.267	0.285	0.190	0.785
$F(000)$	1320	2048	1472	2784
Scan range [°]	$10.2 < 2\theta < 44.0$	$4.4 < 2\theta < 55.0$	$3.3 < 2\theta < 46.5$	$2.3 < 2\theta < 46.6$
Collected data	14049	64185	18551	30937
Unique data	4318	12758	5850	8668
Data with $I > 2\sigma(I)$	1452	7990	4910	7123
Parameters	356	541	518	771
Restraints	0	0	0	0
wR_2[a] (all data, on F^2)	0.2102	0.1759	0.1071	0.0970
wR_2 [a] [$I > 2\sigma(I)$]	0.1977	0.1421	0.1010	0.0907
R_1 [a] [$I > 2\sigma(I)$]	0.0914	0.0553	0.0416	0.0376
GOF[b] on F^2	0.681	1.057	1.046	1.035
Residual dens. [$e \cdot Å^{-3}$]	510/-350	597/-501	342/-328	712/-490
CCDC number	210028	210029	210030	210031

[a] $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$. [b] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

values nor the standard deviations of the molecular parameters were improved.

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[36] CCDC-210028, -210029, -210030 and -210031 (as given in Table 2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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