

Deoligomerization by Cocomplexation: Syntheses and Structures of Aluminum–Calcium Alkoxides and Aryloxides

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Received October 4, 2005

Reactions of oligomeric "Ca(dbbfo)₂" and Ca₉(CH₃OCH₂CH₂O)₁₈(CH₃OCH₂CH₂OH)₂ with Al(CH₃)₃ in toluene gave tetranuclear heterobimetallic [Ca(μ-dbbfo){(μ-dbbfo)(μ-CH₃)Al(CH₃)₂}₂] (71%) and polymeric Ca{(μ-CH₃OCH₂CH₂O)-(μ-CH₃)Al(CH₃)₂}₂ (86%). The latter can be obtained as monomeric THF adduct Ca{(μ-CH₃OCH₂CH₂O)Al(CH₃)₃}₂·(THF)₂ (78%) when a mixture of solvents is used. The results, including an initial L-lactide polymerization test, are discussed in the context of calcium alkoxo cluster degradation in solution.

Introduction

Heavier alkaline-earth-metal alkoxides¹ are seeing increasing use as precursors for materials of numerous applications. They are, for instance, highly desirable for the preparation of high-purity oxides that are in great demand in electronic materials production.² In turn, heterometallic alkoxides³ are precursors to numerous ceramic materials. Calcium alkoxides are also becoming important in the area of new biomaterials. The examples include the synthesis of polylactides which are very attractive from medicinal and pharmaceutical perspective.⁴ Moreover, calcium alkoxides are used as catalysts in the production of environmentally friendly lubricants⁵ or as bioactive sol–gel glasses.⁶ They are also of major importance in synthetic organic chemistry.⁷

Numerous homo- and heteroleptic calcium alkoxides and aryloxides have been synthesized and structurally characterized to date.⁸ Unfortunately, small alcohol derivatives often form large aggregates.^{9,10} For instance, the homoleptic calcium 2-methoxyethoxide contains nine calcium atoms.¹⁰ Such properties hinder application to make them unattractive for MOCVD or as well-defined catalysts. The synthesis of calcium alkoxides of low nuclearity is not trivial and usually requires bulky ligands. The use of 2,6-diphenylphenolates allows us to obtain formally tricoordinating species with weak interactions of the calcium atom with phenyl substituents.¹¹ Another rational synthetic route to such species involves Lewis acid blocking of the alkoxo oxygens, the bridging ability of which are responsible for the aggregation. A solid foundation for the strategy is the assumption that alkoxo-bridged oligomers degrade in solution to low-nuclearity species.⁹

In this communication, we report the syntheses and partial characterization of a series of heterobimetallic aluminum–calcium compounds.

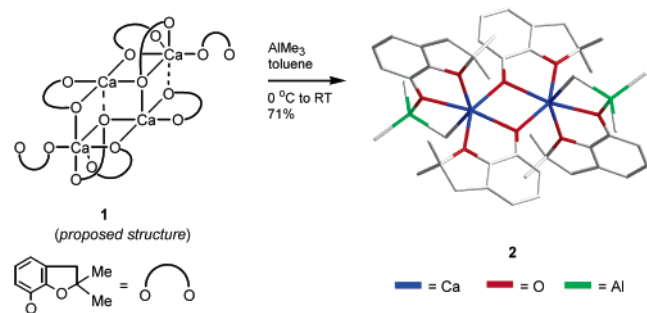
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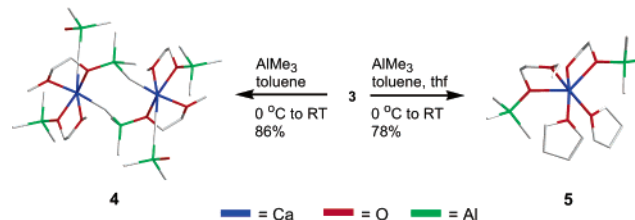
Table 1. Crystallographic Data for **2**, **4**, and **5**

complex	2	4	5
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
cryst syst	monoclinic	monoclinic	monoclinic
chemical formula	$C_{46}H_{62}Al_2Ca_2O_8$	$C_{15.5}H_{35.5}Al_2CaO_4$	$C_{20}H_{48}Al_2CaO_6$
fw	877.08	379.98	478.62
a [Å]	9.307(2)	8.298(3)	10.340(3)
b [Å]	17.157(4)	15.842(4)	18.638(4)
c [Å]	15.298(4)	18.316(4)	15.377(4)
β [°]	103.70(4)	111.24(3)	109.32(3)
V [Å ³]	2373.3(10)	2244.2(11)	2796.5(13)
Z	2	4	4
ρ_{calcd} [g/cm ³]	1.227	1.125	1.137
μ [mm ⁻¹]	0.326	0.370	0.315
T [K]	100(2)	100(2)	100(2)
$F(000)$	936	826	1048
cryst size, [mm ³]	$0.2 \times 0.2 \times 0.15$	$0.4 \times 0.3 \times 0.04$	$0.3 \times 0.2 \times 0.06$
range for data collection, [°]	3.13–27.98	3.51–28.00	3.01–28.00
index ranges (h, k, l)	–12–11, 0–22, 0–20	–10–10, –19–20, –22–24	0–13, 0–24, –20–19
reflins for cell measurement	1821	3761	2436
reflins collected	5330	14263	6637
independent reflins	5330	5191	6637
R_{int}	0.00	0.0400	0.00
reflins [$I > 2\sigma(I)$]	2332	3670	5693
params	293	265	330
absorption correction $T_{\text{min}}/T_{\text{max}}$	none	none	none
R indices (all data)	$R1 = 0.0600$ $wR2 = 0.0728$	$R1 = 0.0595$ $wR2 = 0.1149$	$R1 = 0.0422$ $wR2 = 0.0932$
GOF	0.822	1.112	1.128
$\Delta\sigma$ (max; min), [e/Å ³]	0.302; –0.318	0.768; –0.345	0.604; –0.579

Scheme 1. Synthesis of **2**

Results and Discussion

As shown in Scheme 1, oligomeric “Ca(dbbfo)₂” (**1**)¹² was combined at 0 °C with Al(CH₃)₃ in toluene. Workup gave neutral heterobimetallic dimer [Ca(μ -dbbfo){(μ -dbbfo)(μ -CH₃)Al(CH₃)₂}]₂ (**2**) as moisture-sensitive colorless crystals in 71% overall yield. Due to the lack of the neutral alcohol molecules in the metal coordination sphere of **1**, the Al(CH₃)₃ simply coordinates to alkoxo oxygens to yield an adduct. Similar reaction of barium analogue Ba(dbbfo)₂(dbbfoH)₂·3dbbfoH with Al(CH₃)₃ led to methyl group elimination and formation of Ba{(μ -dbbfo)₂Al(CH₃)₂}]₂ with two aluminum-buckled tetracoordinating ligands.¹⁶

Scheme 2. Synthesis of **4** and **5**

Similar low-temperature reaction of previously described Ca₉(CH₃OCH₂CH₂O)₁₈(CH₃OCH₂CH₂OH)₂^{10,17} (**3**) with an excess of Al(CH₃)₃ gave colorless crystalline Ca{(μ -CH₃-OCH₂CH₂O)(μ -CH₃)Al(CH₃)₂}]₂ (**4**) with a 1:2 calcium-to-aluminum ratio as evidenced by EA. The ¹H NMR spectrum showed a set of proton signals characteristic for 2-methoxyethoxide and a single resonance at –0.35 ppm from the methyl groups of an aluminum fragment. The analogous reaction ceased with THF addition and did not lead to donor-induced cleavage¹⁸ of an Al–O(alkoxo) bond to form low-coordinated calcium alkoxide.

Instead, THF molecules coordinate to the calcium center to form six-coordinated Ca{(μ -CH₃OCH₂CH₂O)Al(CH₃)₃}]₂-(THF)₂ (**5**) as shown in Scheme 2.

For most of the products, X-ray-quality crystals were obtained. The crystal structures of **2**, **4**, and **5** were determined as described in Table 1. Compound **2** crystallizes as a centrosymmetric dimer, and its ORTEP view is presented in Figure 1.

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(17) Ca₉(OCH₂CH₂OMe)(HOCH₂CH₂OMe)₂ was obtained as described but with the use of toluene instead of hexanes. The non-optimized yield was 81%.

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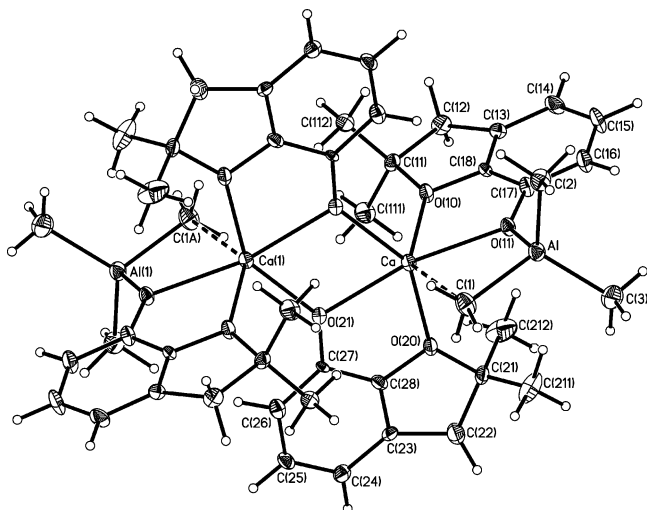


Figure 1. ORTEP view of dimeric **2**.

Both calcium atoms in **2** are octahedrally coordinated by five oxygen atoms of two bridging and one nonbridging phenoxides.

The last coordination site is occupied by the γ -agostic methyl group of $\text{Al}(\text{CH}_3)_3$, which binds to phenoxo oxygen of nonbridging dbbfo. Coordination through the methyl group of $\text{Al}(\text{CH}_3)_3$ is well known and shows carbanionic character of the alkyl group.¹⁹ $\text{Al}(\text{CH}_3)_3$ acts both as a Lewis acid and as a neutral base interacting through a methyl group. All ether oxygens from furan rings are coordinated to calcium atoms. The Ca–O–Ca bridge is unsymmetrical with Ca–O(phenoxo) distances of 2.250(2) and 2.313(2) Å. The Ca–O(phenoxo) distance from the Ca–O(11)–Al bridge is 2.323(2) Å. The Ca–O(11)–Al bond angle of 106.27(11)° is much larger than that of Al–C(1)–Ca (89.51(17)°), which makes the Ca–C(1)–Al–O(11) core an irregular rhombohedron (O(11) is 0.2195 Å out of the plane defined by Ca, C(1), and Al). A similar coordination mode of $\text{Al}(\text{CH}_3)_3$ was observed, e.g., in monomeric $(\text{ArO})\text{M}[(\mu\text{-OAr})(\mu\text{-CH}_3)\text{Al}(\text{CH}_3)_2]$ (ArO = 2,6-*i*-Pr₂C₆H₃O; M = Y,²⁰ Sm,²¹ and La²²).

The hydrogen atoms of the $\text{Al}(\text{CH}_3)_3$ moiety were refined. There are no distinct differences between C–H distances in the agostic C(1) and nonagostic C(2) and C(3) methyl groups. The geometry around five-coordinated C(1) is a distorted trigonal bipyramid with one hydrogen and one calcium atom in the apical positions and with the Ca–C(1)–H(axial) bond angle of 164(2)°. There is only slightly noticeable elongation of the Al–C(1) bond distance (1.988(4) Å) of the agostic methyl group compared to nonagostic Al–C(2) (1.939(4) Å) and Al–C(3) (1.954(4) Å). This elongation is bigger in the recently published cationic $[\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{janeN}_3)(\mu\text{-CH}_3)_2\text{Al}(\text{CH}_3)_2][\text{BAr}^F_4]$ (2.081(2) and 2.075(2) vs 1.963(3)

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2**^a

Ca–O(10)	2.383(2)	Ca–O(21)	2.313(2)
Ca–O(11)	2.323(2)	Ca–O(21)'	2.250(2)
Ca–O(20)	2.396(3)	Ca–C(1)	2.701(4)
Al–C(1)	1.988(4)	Al–C(3)	1.939(5)
Al–C(2)	1.954(4)	Al–O(11)	1.836(2)
O(10)–Ca–O(11)	71.26(8)	O(11)–Ca–C(1)	68.05(11)
O(10)–Ca–O(20)	90.30(8)	O(20)–Ca–O(21)	71.85(8)
O(10)–Ca–O(21)	110.50(8)	O(20)–Ca–O(21)'	145.91(8)
O(10)–Ca–O(21)'	95.53(9)	O(20)–Ca–C(1)	98.30(12)
O(10)–Ca–C(1)	139.08(11)	O(21)–Ca–O(21)'	74.66(9)
O(11)–Ca–O(20)	96.51(8)	O(21)–Ca–C(1)	110.21(11)
O(11)–Ca–O(21)	168.07(8)	O(21)#1–Ca–C(1)	98.97(12)
O(11)–Ca–O(21)'	117.18(8)		
C(1)–Al–C(2)	112.1(2)	C(2)–Al–C(3)	114.8(2)
C(1)–Al–C(3)	112.6(2)	C(2)–Al–O(11)	107.65(16)
C(1)–Al–O(11)	95.35(15)	C(3)–Al–O(11)	112.65(18)

^a Symmetry transformations used to generate equivalent atoms: (') $-x + 1, -y, -z$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **4**^a

Ca–O(10)	2.3714(19)	Ca–O(21)	2.2958(19)
Ca–O(11)	2.300(2)	Ca–C(1)'	2.835(3)
Ca–O(20)	2.3673(19)	Ca–C(4)''	2.843(3)
Al(1)–C(1)	2.011(3)	Al(2)–C(4)	2.003(3)
Al(1)–C(2)	1.968(3)	Al(2)–C(5)	1.973(3)
Al(1)–C(3)	1.969(4)	Al(2)–C(6)	1.977(3)
Al(1)–O(11)	1.824(2)	Al(2)–O(21)	1.818(2)
O(10)–Ca–O(11)	71.70(7)	O(11)–Ca–C(4)''	81.53(8)
O(10)–Ca–O(20)	92.18(7)	O(20)–Ca–O(21)	71.36(7)
O(10)–Ca–O(21)	87.98(7)	O(20)–Ca–C(1)'	94.15(9)
O(10)–Ca–C(1)'	166.00(8)	O(20)–Ca–C(4)''	167.33(8)
O(10)–Ca–C(4)''	91.54(8)	O(21)–Ca–C(1)'	82.24(8)
O(11)–Ca–O(20)	88.16(7)	O(21)–Ca–C(4)''	120.89(8)
O(11)–Ca–O(21)	150.73(7)	C(1)#1–Ca–C(4)'	84.97(10)
O(11)–Ca–C(1)'	120.94(8)		
C(1)–Al(1)–C(2)	109.73(15)	C(4)–Al(2)–C(5)	110.49(15)
C(1)–Al(1)–C(3)	110.81(18)	C(4)–Al(2)–C(6)	110.23(16)
C(1)–Al(1)–O(11)	101.86(11)	C(4)–Al(2)–O(21)	101.81(11)
C(2)–Al(1)–C(3)	113.86(18)	C(5)–Al(2)–C(6)	114.97(15)
C(2)–Al(1)–O(11)	109.22(13)	C(5)–Al(2)–O(21)	108.26(13)
C(3)–Al(1)–O(11)	110.68(14)	C(6)–Al(2)–O(21)	110.27(13)

^a Symmetry transformations used to generate equivalent atoms: (') $-x, -y - 1, -z$; (') $-x + 1, -y - 1, -z$.

and 1.981(3) Å),²³ in $(\text{ArO})\text{Sm}[(\mu\text{-OAr})(\mu\text{-CH}_3)\text{Al}(\text{CH}_3)_2]_2^{21}$ (2.060(5) Å vs 1.945(5) and 1.960(5) Å), or in $\text{Cp}_2\text{Zr}(\mu\text{-}\eta^1\text{:}\eta^2\text{-C}_6\text{H}_4)(\mu\text{-CH}_3)\text{Al}(\text{CH}_3)_2$ (2.101(5) Å vs 1.966(5) and 1.952(5) Å).²⁴ The average Al–C distance for the terminal methyl groups in $\text{Al}_2(\text{CH}_3)_6$ is 1.97 Å.²⁵

The Ca–C(1) bond distance of 2.701(4) Å is much shorter than Ca–CH₃ in $[(\eta\text{-C}_5\text{Me}_5)_2\text{Ca}(\mu\text{-CH}_3)_2\text{Al}(\text{CH}_3)(\text{THF})]^{26}$ (2.948(7) and 2.999(7) Å), but it is longer than the Ca–C σ -bond distances in $\text{Ca}[\text{C}(\text{Si}(\text{CH}_3)_3)_3]_2$ (2.459(9) Å),²⁷ $(\text{DMAT})_2\text{Ca}(\text{THF})_2$ (2.618(3) Å; DMAT = 2-NMe₂- α -(CH₃)₃SiBz), $(p\text{-Bu}^t\text{Bz})_2\text{Ca}(\text{THF})_4$ (2.592(3) and 2.602(3) Å) or in $(\text{Bz})_2\text{Ca}(\text{THF})_4$ (2.595(5), 2.587(6), 2.574(6), and 2.568(5) Å).²⁸

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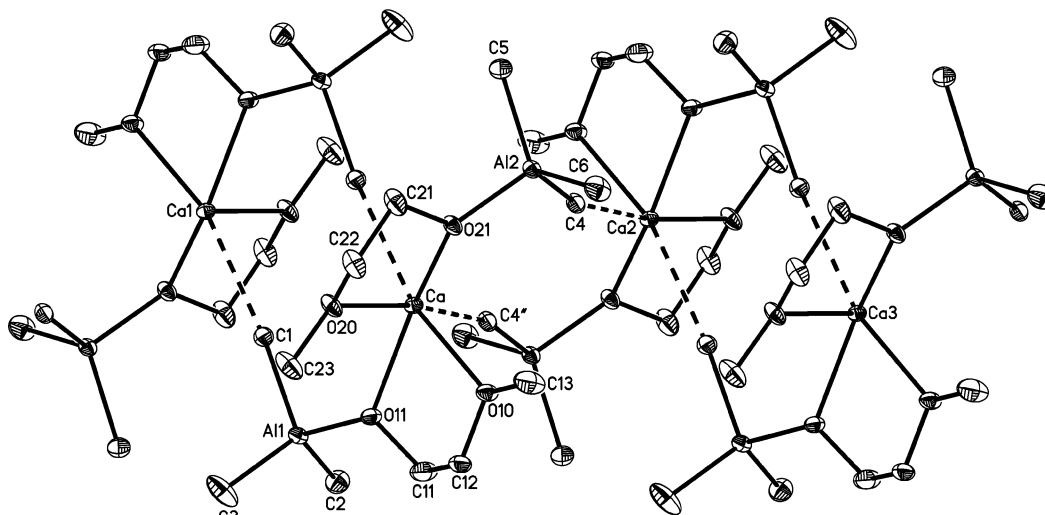


Figure 2. ORTEP views of polymeric **4**.

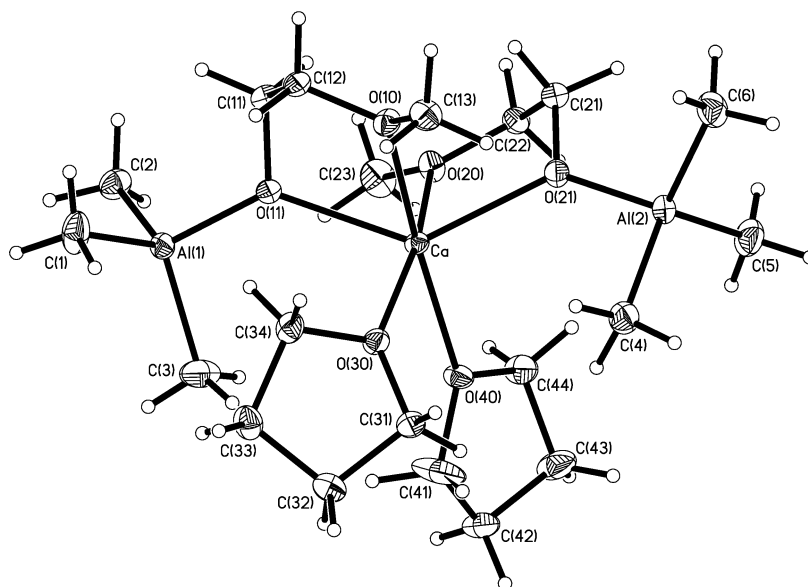


Figure 3. ORTEP view of dimeric **5**.

Compounds **4** and **5** show also six-coordinated spheres. Compound **4** crystallizes as polymer composed of centrosymmetric dimeric units, as presented in Figure 2. Each unit has two bridging (μ -CH₃)Al(CH₃)₂ groups that allow it to form a tetrametallaoctacyclic ring. A similar ring was found in the aluminum–calcium dimer reported by Hanusa.²⁶

Analogous (μ -CH₃)Al(CH₃)₃ bridges bind the macrocycles to form a polymer. The calcium atom in **4** is surrounded by two alkoxo and two etheric oxygens of 2-methoxyethoxides. The Ca–O(11) and Ca–O(21) distances of 2.300(2) and 2.2958(19) Å are typical.^{10,11,29} The last two *cis*-positioned coordination sites are occupied by carbon atoms from agostic methyl groups of the Al(CH₃)₃ units. The distorted trigonal bipyramids around five-coordinated carbons in **4** are different from that in **2** containing calcium and aluminum atoms in the apical positions.

The Ca–C–Al bond angles are 167.70(15)° and 167.01(16)°. The elongation of the Al–C bond distances of the agostic methyl groups (2.011(3) and 2.003(3) Å) is even less distinct than in **2** (nonagostic Al–C distances are 1.968(3), 1.969(4), 1.973(3), and 1.977(3) Å). The Ca–C distances of 2.835(3) and 2.843(3) Å are much longer than in **2** and comparable to that of [(η -C₅Me₅)₂Ca(μ -CH₃)₂Al(CH₃)(THF)].²⁶ Coordination of calcium to two alkyl groups allows it to reach a higher coordination number, which is typically between 6 and 8. For example, Cp₂Ca(THF)₂ when reacted with Al(CH₃)₃ in toluene loses THF molecules but enables intermolecular contacts with Cp ligands from adjacent molecules to also yield polymeric [Cp₂Ca]_n.³⁰

The coordination of the calcium atom in monomeric **5** is octahedral, as presented in Figure 3. It is surrounded by six oxygens from two bidentate ligands and two THF molecules located in *cis* positions. The coordination mode of the

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Table 4. Selected Bond Lengths (Å) and Angles (deg) for **5**

Ca–O(10)	2.4128(12)	Ca–O(40)	2.3773(13)
Ca–O(20)	2.4049(13)	Ca–O(11)	2.3231(12)
Ca–O(30)	2.4024(14)	Ca–O(21)	2.3056(13)
Al(1)–C(1)	1.989(2)	Al(2)–C(4)	1.993(2)
Al(1)–C(2)	1.981(2)	Al(2)–C(5)	1.986(2)
Al(1)–C(3)	1.989(2)	Al(2)–C(6)	1.984(2)
Al(1)–O(11)	1.8299(13)	Al(2)–O(21)	1.8187(13)
O(10)–Ca–O(11)	70.43(4)	O(11)–Ca–O(40)	116.92(5)
O(10)–Ca–O(21)	83.38(5)	O(20)–Ca–O(21)	69.13(5)
O(10)–Ca–O(20)	104.23(5)	O(20)–Ca–O(30)	166.38(4)
O(10)–Ca–O(30)	84.22(5)	O(20)–Ca–O(40)	85.36(5)
O(10)–Ca–O(40)	169.17(4)	O(21)–Ca–O(30)	123.15(5)
O(11)–Ca–O(21)	133.00(4)	O(21)–Ca–O(40)	95.63(5)
O(11)–Ca–O(20)	80.15(5)	O(30)–Ca–O(40)	87.35(5)
O(11)–Ca–O(30)	92.98(5)		
C(1)–Al(1)–C(2)	110.67(9)	C(4)–Al(2)–C(5)	114.33(10)
C(1)–Al(1)–C(3)	114.36(11)	C(4)–Al(2)–C(6)	113.33(10)
C(1)–Al(1)–O(11)	106.98(9)	C(4)–Al(2)–O(21)	100.87(7)
C(2)–Al(1)–C(3)	112.16(10)	C(5)–Al(2)–C(6)	110.73(10)
C(2)–Al(1)–O(11)	109.06(8)	C(5)–Al(2)–O(21)	107.82(8)
C(3)–Al(1)–O(11)	103.08(8)	C(6)–Al(2)–O(21)	109.05(8)

chelating ligand is similar to that of **4**, and all the bond lengths and angles are within the typical range.

The results clearly show that the strategy of blocking the bridging alkoxo group to deoligomerize calcium alkoxides and obtain low-nuclearity species works effectively.

These results support the assumption that high-nuclearity metal alkoxides spontaneously degrade in solution to smaller, even monomeric, species.⁹ We assumed that these undercoordinated molecules should be active catalyst or initiators, e.g., in the lactide polymerization process. Indeed, the homopolymerization of L-lactide on high-molecular-weight $\text{Ca}_9(\text{CH}_3\text{OCH}_2\text{CH}_2\text{O})_{18}(\text{CH}_3\text{CH}_2\text{CH}_2\text{OH})_2$ at 1:15 calcium to

monomer (1:135 of **3** to monomer ratio) revealed a fast process. The conversion was complete within 2 min to give a homopolymer, as evidenced by ¹H NMR.³¹ Moreover, the spectra showed the ratio of CH₂ protons from the end group to methine protons of PLA to be 1:12–16 which stays close to the calcium-to-monomer ratio. This, in our opinion, supports the conclusion of polymerization occurring with participation of degraded species.

In conclusion, we have presented an easy and high-yield synthetic route to heterobimetallic aluminum–calcium alkoxides. We have demonstrated that the alkoxo group responsible for oligomerization of metal alkoxides can easily be blocked with metal organometallics to prevent agglomeration. The synthetic and L-lactide polymerization results confirm the already speculated destruction of alkoxo calcium clusters in solution with the formation of smaller species.^{9,32}

Acknowledgment. We thank the Polish State Committee for Scientific Research (Grant No. 3 T09A 158 26) for support of this research.

Supporting Information Available: Text and tables giving experimental and X-ray details; and crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC051710E

(31) The isolated PLA has a M_w of 8800 and PDI of 1.4. The ¹H NMR spectrum of PLA (see Supporting Information) shows the polymer terminated with 2-methoxyethoxy and hydroxyl groups.

(32) Evans, W. J.; Boyle, T. J.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 5084.