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**Preparation of Organometallic Hydroxides and their
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Research Report

Preparation of Organometallic Hydroxides and their Reactions with Lanthanide Compounds

Herbert W. Roesky ^[a]

Keywords

Organometallic Hydroxides; Organometallic Oxides; Lanthanides; Aluminum; Gallium; Germanium.

Abstract

The preparation of soluble organometallic hydroxides is a key step in the preparation of organometallic oxides containing the heterobimetallic M–O–M' unit. Compounds of composition LMOH where M is a Main Group metal (Ca, Sr, Al, Ga, Ge, Sn) and transition metal (Zr, Hf) are summarized. The reactions of Cp₃Ln (Ln = Yb, Dy, Er, Sm) with several hydroxides to yield compounds with the skeletons M(μ -O)Ln and M(μ -OH)Ln are reported. The application of the latter compounds in ϵ -caprolactone polymerization is discussed. An unforeseen formation of a chlorine-centered cluster of composition [(Me₃Si)₂NC(NCy)₂SmCl₂]₅(THF)₂ is reported.

Introduction

Heterobi- and heteropoly-metallic compounds are of great interest ranging from advanced materials to efficient catalysts. The compounds with different metals have often modified the properties of the individual metal atoms, a feature that is difficult to achieve otherwise. For example, two metal atoms with a given property when combined together in a compound can apply synergetically to an entirely new behavior. For that reason the combination of two different metals in one compound in a desired proximity is very important. Two different metals are believed to be better than one in catalysis because of the cooperative effect between two metal centers. In addition, these systems might function as both catalyst and cocatalyst in the same complex [1–3]. Our approach in this field to arrange two different metals in close proximity to each other was the generation of compounds containing an oxygen bridge between two different metals of composition M–O–M'. An early experiment using alkoxides of different metals such as Ti(OR)₄ and Zr(OR)₄ to

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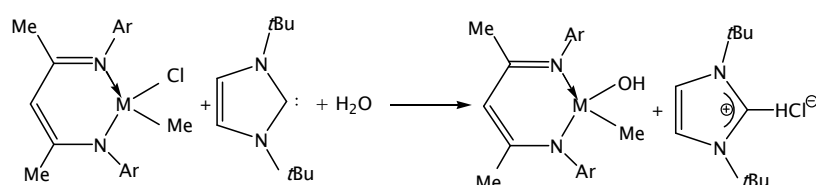
prepare heterobimetallic Ti–O–Zr compounds failed, due to the different rates of hydrolysis of these compounds in the presence of water. In this case it leads to the deposition of anatase rather than to a compound with a Ti–O–Zr bond. The synthetic strategy which we developed is the preparation of well-defined organometallic hydroxides and their reactions with various metallic substrates [4].

Results and Discussion

Organometallic Hydroxides

a) Organometallic hydroxides of Group 13

Organometallic hydroxides are a class of compounds which have been prepared mainly by serendipity especially while looking for something else entirely unrelated. Therefore organometallic hydroxides are considered by chemists as compounds which have been prepared under conditions not carefully accomplished, with the result that the chemistry of organometallic hydroxides has been neglected [5, 6]. In contrast to this historic development we became interested in preparing organometallic hydroxides as precursors to assemble heterobimetallic oxides with the M–O–M' arrangement. The synthesis of an aluminum hydroxide and the corresponding gallium congener supported by a β -diketiminato ligand is shown in Scheme 1 [7, 8]. The sterically demanding β -diketiminato ligand turned out to be the ligand of choice in this synthesis, as it not only provides the delicate electronic balance and electronic relief to the Lewis acidic metal center on the account of its electron rich nitrogen atoms, but the bulky 2,6-diisopropyl phenyl substituents on nitrogen atoms render also the necessary steric protection. The overall result is the prevention of self condensation, and thus the formation of oligomeric polynuclear non-soluble cage compounds.



M = Al, Ga

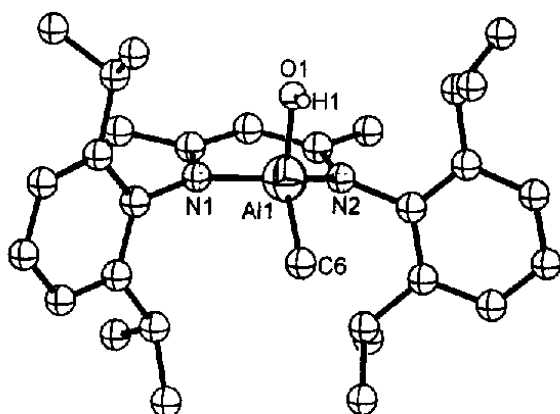
Al: 1

Ar = 2,6-*i*Pr₂C₆H₃

Ga: 2

Scheme 1: Preparation of monohydroxo complexes of aluminum and gallium

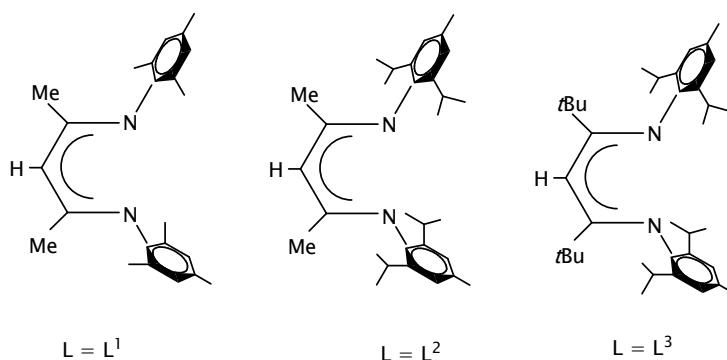
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5 The structure of $\text{LAl}(\text{Me})\text{OH}$ (**1**) ($\text{L} = \text{CH}(\text{NArCMe})_2$, $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$) is shown in
6 Figure 1 [7].
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31 Figure 1: Perspective view of the β -diketiminato methylaluminum hydroxide
32 (**1**)
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37 The aluminum monohydroxide $\text{LAl}(\text{Me})\text{OH}$ (**1**) is very stable and did not eliminate
38 methane to yield LAlO , even when heated above its melting point (192 °C).
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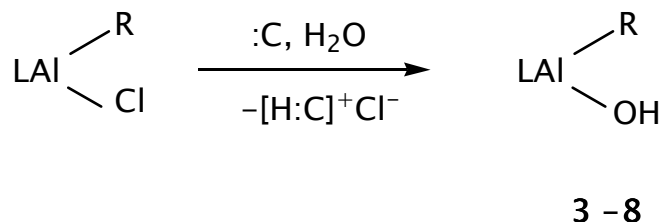
40 In the course of this project we prepared a number of derivatives of $\text{LAl}(\text{Me})\text{OH}$ (**1**)
41 by replacing the methyl group by other substituents to investigate the properties of
42 these aluminum hydroxides on a broader scale. In addition we used differently
43 substituted β -diketiminates (Scheme 2) for the preparation of the aluminum
44 precursors [9].
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Scheme 2: Differently substituted ligand L

In general, LH was converted by *n*BuLi to the LLi and then treated with EtAlCl₂ to yield LAI(Et)Cl. This procedure followed the preparation of LAI(Me)Cl. However, for the introduction of the C₆H₅, OEt and OSiMe₃ groups we prepared first LAICl₂ and treated this with the corresponding lithium salts.

The hydrolysis of LAIRCl in the presence of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (:C) as a HCl scavenger resulted in the formation of LAI(R)OH (Scheme 3).



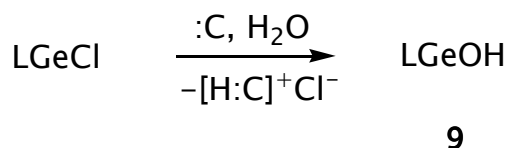
L = L ¹ ,	R = Et	3
L = L ² ,	R = Et	4
L = L ¹ ,	R = Ph	5
L = L ² ,	R = Ph	6
L = L ² ,	R = OEt	7
L = L ²	R = OSiMe ₃	8

Scheme 3: Preparation of compounds of composition LAI(R)OH

Compounds **3** – **8** were formed in low yield compared to $\text{LAl}(\text{Me})\text{OH}$ (**1**). Moreover, they turned out to be less stable than **1** so that reactions with Cp_3Ln ($\text{Ln} =$ lanthanides) were not successful. We observed no reactions at lower temperature and decomposition products at higher temperatures.

b) Organometallic hydroxides of Group 14

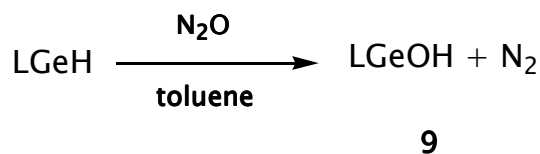
We were especially interested in the preparation of hydroxides with low valent Group 14 elements. The reaction of LGeCl ($\text{L} = \text{HC}(\text{CMeNAr})_2$, $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$) with water in the presence of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene ($:\text{C}$) resulted in the formation of LGeOH (**9**) [10] (Scheme 4).



Scheme 4: Preparation of LGeOH (**9**)

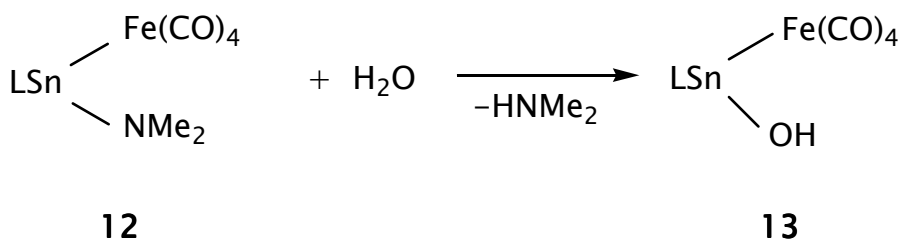
The coordination geometry of **9** around the germanium center is distorted tetrahedral. The germanium atom in **9** is attached to two nitrogen atoms of the ligand L and one hydroxyl group. The fourth coordination site is occupied by a lone pair of electrons. The latter assumption is supported by the presence of intermolecular interaction as evident from the short $\text{OH}\cdots\text{Ge}$ distance of 3.064 Å between the hydrogen of the hydroxyl group and the germanium atom of an adjacent molecule leading to the existence of **9** as a dimer. The LGeOH does not rearrange to the corresponding structure of composition $\text{LGe}=\text{O}(\text{H})$ [10]. This is quite in contrast to $\text{RC}(\text{OH})$ which turned out to be very unstable.

More recently we found that the reaction of LGeH with nitrous oxide (N_2O) proceeds under the formation of LGeOH (**9**) in almost quantitative yield under insertion of the oxygen into the Ge-H bond (Scheme 5) [11].



Scheme 5: Alternative preparation of LGeOH (**9**)

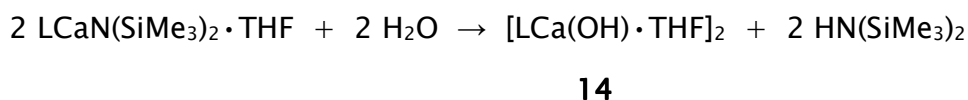
This alternative route to **9** does not need the N-heterocyclic carbene which was used for the preparation of **9** when starting from LGeCl .



Scheme 7: Preparation of the first well-characterized stannylenehydroxide complex **13**

c) Organometallic hydroxides of Group 2

A hydrocarbon soluble substituted calcium hydroxide of composition $[\text{LCa}(\text{OH}) \cdot \text{THF}]_2$ (**14**) was prepared from $\text{LCa}(\text{SiMe}_3)_2 \cdot \text{THF}$ and water (Scheme 8).



$\text{L} = \text{HC}(\text{CMeNAr})_2$, $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$

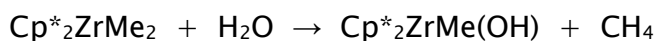
Scheme 8: Preparation of hydrocarbon-soluble calcium hydroxide

Compound **14** is remarkably stable against ligand exchange and formation of $\text{Ca}(\text{OH})_2$ [14].

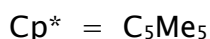
Controlled hydrolysis of $\text{LSrN}(\text{SiMe}_3)_2 \cdot \text{THF}$ leads to the hydrocarbon-soluble strontium hydroxide $\text{LSr}(\text{THF})(\mu\text{-OH})_2\text{Sr}(\text{THF})_2\text{L}$ (**15**). From the two strontium atoms of **15** one is coordinate to a single THF while the other one is coordinate to two THF molecules [15].

d) Organometallic hydroxides of Group 4

The controlled hydrolysis of $\text{Cp}^*_2\text{ZrMe}_2$ with one equivalent of water at $-30\text{ }^\circ\text{C}$ resulted in the formation of $\text{Cp}^*_2\text{ZrMe}(\text{OH})$ (**16**) in high yield with elimination of methane (Scheme 9).

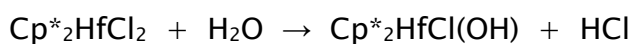


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Scheme 9: Preparation of Cp*₂ZrMe(OH) (**16**)

Compound **16** is a crystalline compound and was characterized by single crystal X-ray structural analysis [16]. Compound **16** is soluble in *n*-hexane, toluene, ether, tetrahydrofuran, and dichloromethane. The corresponding Cp*₂HfCl(OH) (**17**) was only prepared in situ using Cp*₂HfCl₂ and equivalent amounts of water [17].

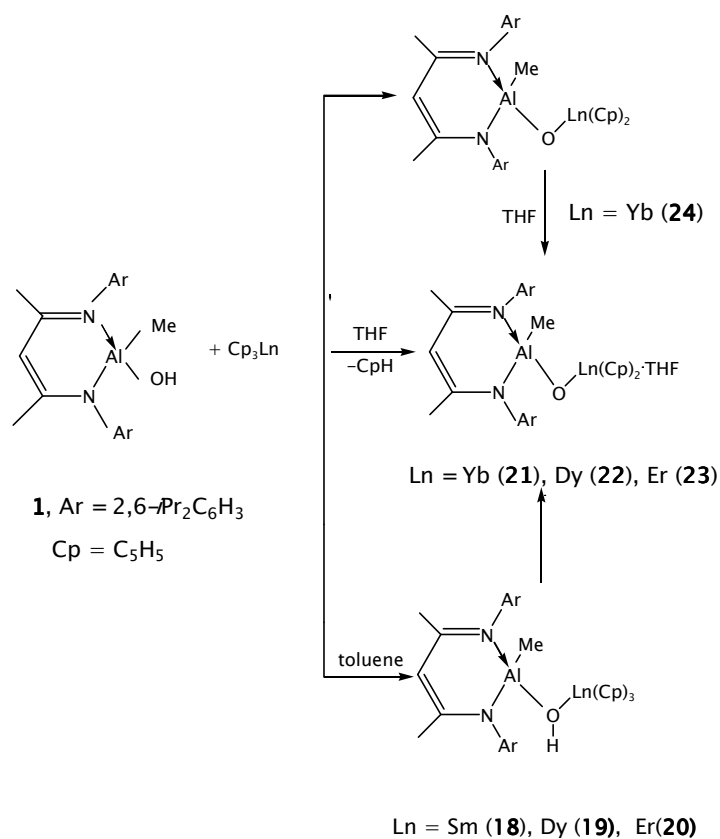


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Scheme 10: Synthesis of Cp*₂HfCl(OH) (**17**)

Assembling of Heterobimetallic Oxides

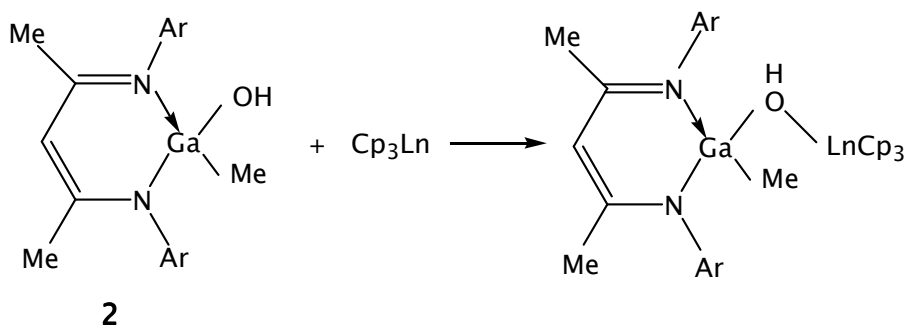
A few organometallic hydroxides of Group 13 and 14 turned out to be useful precursors for the preparation of oxygen bridged Main Group f-element systems. The majority of the prepared hydroxides did not react at room temperature and decomposed at elevated temperatures. However, reaction of LAIme(OH) (**1**) with a series of Cp₃Ln (Ln = lanthanide) showed selective reactivity and complexes of composition LAIme(μ-OH)LnCp₃ [Ln = Sm **18**, Dy **19**, Er **20**], LAIme(μ-O)LnCp₂(THF) [Ln = Yb **21**, Dy **22**, Er **23**] and LAIme(μ-O)YbCp₂ **24** were obtained in good yield (Scheme 11) [18].



Scheme 11: Preparation of Al–O–Ln compounds

The formation of the Al–O–Ln unit is a multi step process. First the adduct $\text{LAlMe}(\mu\text{-OH})\text{LnCp}_3$ is formed which at elevated temperatures eliminates CpH to generate the Al–O–Ln moiety (Scheme 11) [18]. The compounds have been characterized by single crystal X-ray structural analysis.

$\text{LGaMe}(\text{OH})$ (**2**) was prepared by the same method like that for $\text{LAlMe}(\text{OH})$ (**1**) using LGaMeCl and water in the presence of a N-heterocyclic carbene [8]. The reaction of **2** with Cp_3Ln leads to the products $\text{LGaMe}(\mu\text{-OH})\text{LnCp}_3$ [Ln = Sm **25**, Nd **26**, Yb **27**] (Scheme 12) [19].



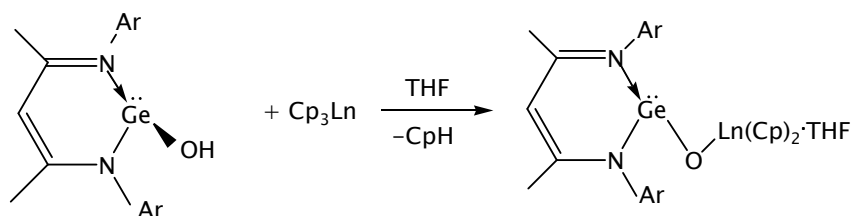
Ar = 2,6-*i*Pr₂C₆H₃

Ln = Sm (**25**), Nd (**26**), Yb (**27**)

Scheme 12: Synthesis of compounds with the Ga-(OH)-Ln skeleton

The less acidic nature of **2** in comparison to that of **1** does not lead to products under elimination of CpH. Compounds **25** and **26** have been characterized by single crystal X-ray structures [19].

Another successful example is the preparation of the monomeric heterobimetallic oxide of composition LGe-O-Cp₂Ln·THF with a Ge(II)-O-Ln skeleton. The synthesized compounds of composition LGe(μ -O)Ln(Cp)₂·THF (Ln = Yb **28**, Y **29**) are shown in Scheme 13 [20].



Ar = 2,6-*i*Pr₂C₆H₃

Ln = Yb (**28**), Y (**29**)

Scheme 13: Germanium(II) oxides of ytterbium and yttrium

Compounds **28** and **29** have been characterized by single crystal structural analysis. Presently these are the only examples containing the Ge(II)-O-Ln linkage reported in literature. The N-Ge-N bond angles of **28** and **29** are found to be less than 90° which may be attributed to the stereochemically active lone pair of

electrons on the germanium demanding higher angular volume for its accommodation [20].

Application of Heterobimetallic Oxides

Compounds of composition $\text{LAlMe}(\mu\text{-O})\text{ZrRCp}_2$ where R is CH_3 or chlorine exhibit the highest activity in ethylene polymerization. The activity was observed (activity = g polyethylene/mol·cat·h) in the order of 10^6 [7]. According to DFT calculation the bridging oxygen lowers the electron density at the metal centers of these complexes with the consequence that they increase their electrophilicity. This results in a remarkable decrease in the amount of the cocatalyst and increase in activity. The polymerization experiments with ethylene were carried out with a variety of different M–O–M' systems such as $\text{LAlMe}(\mu\text{-O})\text{TiMe}_2\text{Cp}$ [21], $\text{LAlMe}(\mu\text{-O})\text{HfMeCp}_2$ [22], $\text{Cp}^*_2\text{ZrMe}(\mu\text{-O})\text{TiMe}_2\text{Cp}^*$ [23].

The ring opening polymerization of ϵ -caprolactone was realized with some of the lanthanide complexes **18** – **24** given in Scheme 11. These complexes exhibit catalyst activity with almost quantitative yield and polydispersities (M_w/M_n) in the order of 1.5 to 2.3 at ambient temperature in THF or toluene (see Table 1).

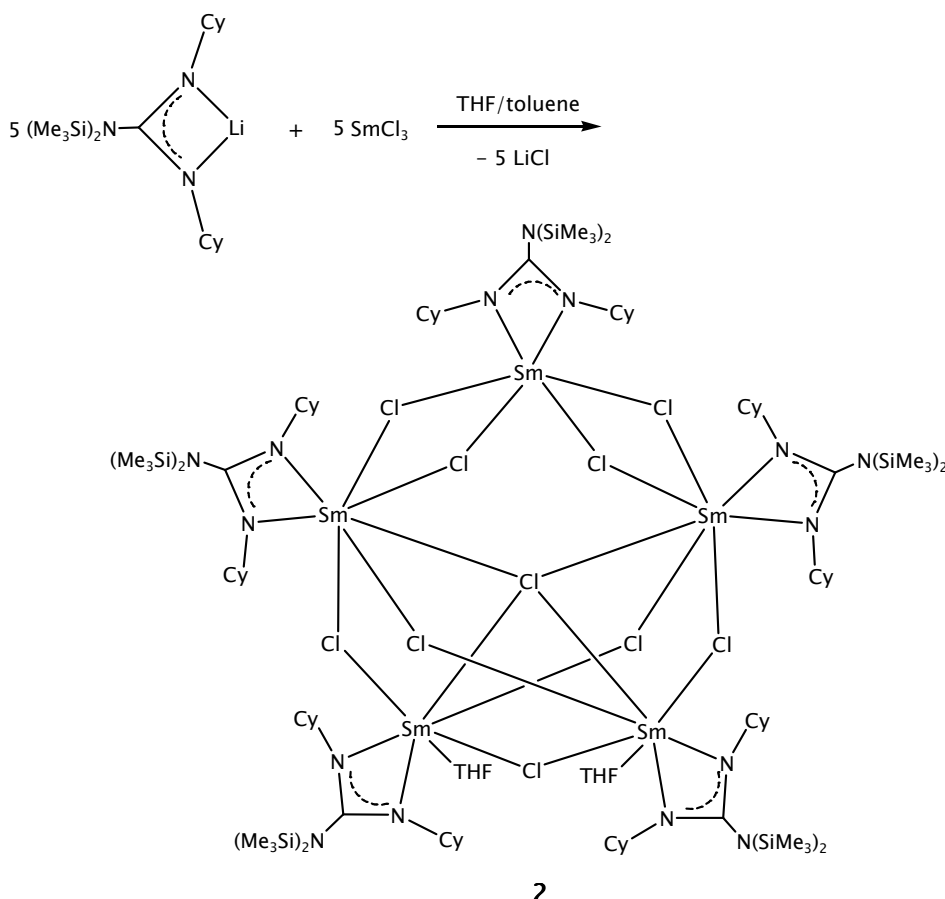
Table 1: Polymerization of ϵ -caprolactone^a

Compound	Solvent	T(°C)	Time (h)	Yield (%)	M_n	M_w/M_n
$\text{LAlMe}(\mu\text{-O})\text{YbCp}_2(\text{THF})$ (21)	THF	22	3	96	51766	1.6
$\text{LAlMe}(\mu\text{-O})\text{YbCp}_2(\text{THF})$ (21)	toluene	70	0.5	95	18556	2.3
$\text{LAlMe}(\mu\text{-O})\text{YbCp}_2(\text{THF})$ (21)	THF	70	0.5	96	24172	2.1
$\text{LAlMe}(\mu\text{-O})\text{DyCp}_2(\text{THF})$ (22)	THF	22	3	95	61345	1.7
$\text{LAlMe}(\mu\text{-O})\text{DyCp}_2(\text{THF})$ (22)	THF	70	0.5	96	33256	1.7
$\text{LAlMe}(\mu\text{-O})\text{YbCp}_2$ (24)	toluene	22	5	94	21807	1.5
$\text{LAlMe}(\mu\text{-O})\text{YbCp}_2$ (24)	toluene	70	0.5	95	17718	1.8
$\text{LAlMe}(\mu\text{-OH})\text{DyCp}_3$ (19)	toluene	22	5	95	20934	1.6
$\text{LAlMe}(\mu\text{-OH})\text{DyCp}_3$ (19)	toluene	70	0.5	97	39690	1.7

^a Cat. = [0.01 mol/L]; caprolactone/cat. = 100

Unforeseen Result in Lanthanide Chemistry

To our surprise the preparation of $[(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\text{SmCl}_2]_5(\text{THF})_2$ (**25**) from anhydrous SmCl_3 and $(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\text{Li}$ in a mixture of THF and toluene resulted in the chlorine-centered cluster (Scheme 14) [24]. The cluster crystallizes in the triclinic space group $P\bar{1}$. The single crystal X-ray structure confirmed that no Li ions are incorporated in the cluster. This is a unique assembly of substituted samarium chlorides.



Scheme 14: Preparation of $[(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\text{SmCl}_2]_5$ (**25** · 2THF)

The molecular structure of the cluster is shown in Figure 2. The Cy groups on the nitrogen atoms are omitted for clarity.

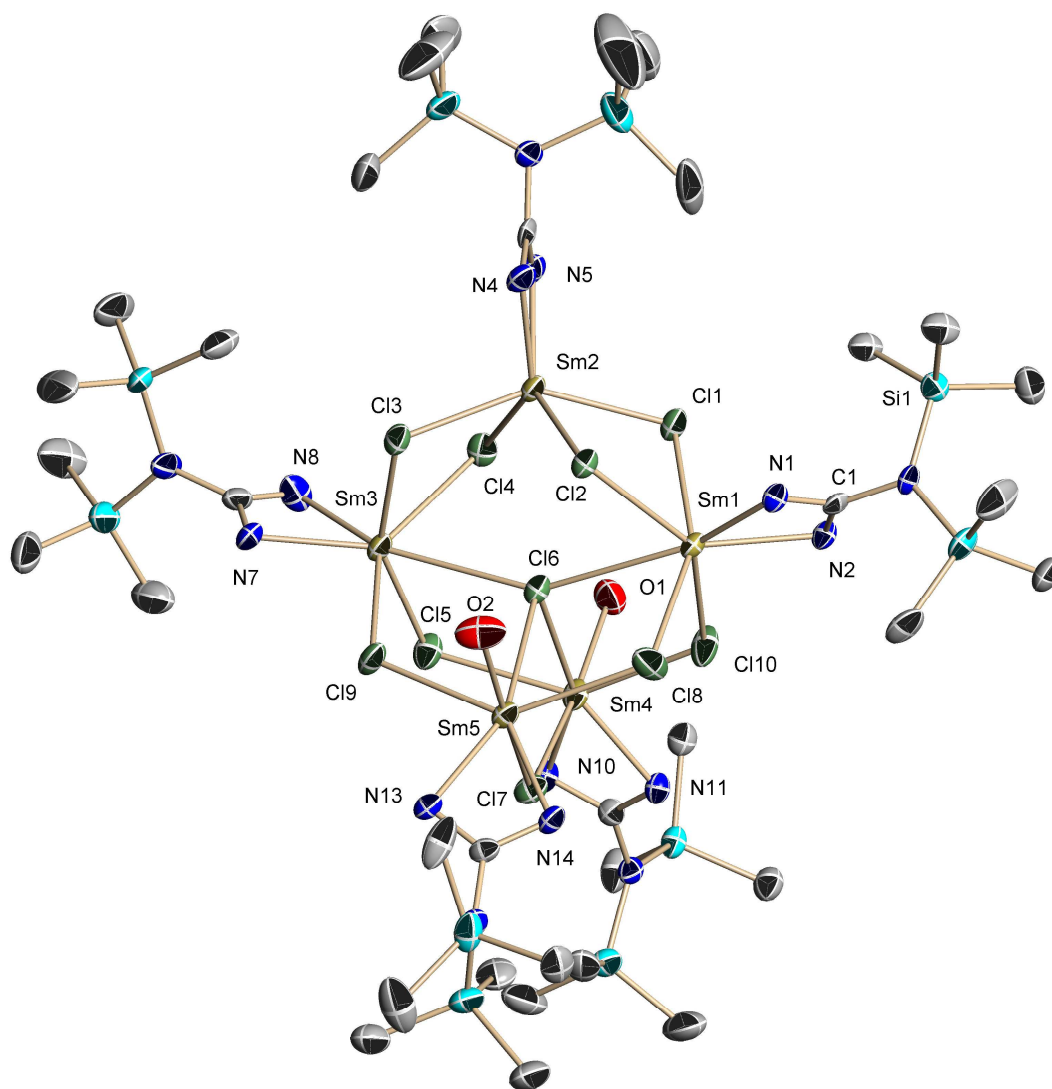
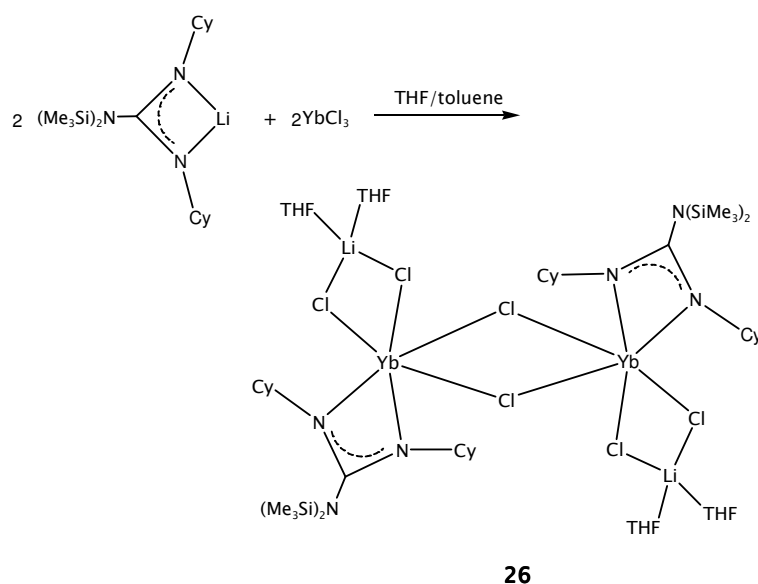


Figure 2: Molecular structure of $[(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\text{SmCl}_2]_5(\text{THF})_2$ ($25 \cdot 2\text{THF}$)

In contrast to the reaction with SmCl_3 the analogous reaction with YbCl_3 resulted in the expected dimer of composition $[(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\text{YbCl}_2]_2 \cdot (\text{LiCl})_2(\text{THF})_4$ with incorporated lithium chloride molecules (Scheme 15).



Scheme 15: Synthesis of $[(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy}_2)_2\text{YbCl}_2]_2$ (**26**)

Acknowledgment

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