Studies on the Thermolysis of Ether-Stabilized Lu(CH₂SiMe₃)₃, Molecular Structure of Lu(CH₂SiMe₃)₃(THF)(diglyme)

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Lu(CH₂SiMe₃)₃(THF)₂ (2) decomposes slowly at room temperature with formation of Me₄Si. In order to understand the mechanism of this elimination process, Lu(CH₂SiMe₃)₃([D₈]-THF)₂ (1), Lu(CH₂SiMe₃)₃(THF)(DME) (3), and Lu(CH₂SiMe₃)₃(THF)(diglyme) (4) were prepared. The results of ¹H NMR spectroscopic studies of the decomposition in solution exclude an α- as well as a β-H elimination mechanism and point towards a γ-H elimination. The molecular structure of 4 has been determined by single crystal X-ray diffraction.

Key words: Lutetium Alkyls, Decomposition, X-Ray Structure, γ-H Elimination

Introduction

Until recently chemical bonding in coordination and organometallic compounds of the lanthanides has been considered as purely ionic with the metal d orbitals not involved in covalent σ- or π-bonds [1]. However, some experimental observations cannot be understood on this simple basis. Very recently the first examples of imido complexes of the lanthanides have been described [2 – 4], in which the 5d metal acceptor orbitals appear to play a significant role in stabilizing π-donation from imido groups to a lanthanide (Sm) center [5].

Related lanthanide alkylidene complexes are less well known. In examples containing either neutral simple imidazol-2-ylidene [5 – 7] or bis(imidophenyl-phosphorano)methylidene ligands [7], the carbenoid carbon atoms are stabilized by directly bound heteroatoms, and the Ln-C bonds cannot be considered to have true metallaalkene character.

In 1978 we synthesized THF adducts of homoleptic alkyl complexes Ln(CH₂SiMe₃)₃ of the late lanthanides Er, Tm, and Lu (Scheme 1) [8 – 10] and studied their thermal decomposition. We found that these complexes are rather unstable and decompose evolving Me₄Si to leave THF-free polymeric materials. These products are insoluble in organic solvents, but upon quenching with D₂O gave rise to singly as well as doubly deuterated Me₄Si. This fact was interpreted by assuming formation of lanthanide alkylidene complexes resulting from α-H-elimination of one of the Me₃SiCH₂ groups (Scheme 1) [9]. However, this mechanism was not sufficiently proven and the nature of the decomposition products was not studied any further.

In order to support the proposed formation of Ln=C species, we decided to reinvestigate the thermal decomposition of Lu(CH₂SiMe₃)₃(THF)₂ with the aim to delineate the elimination pathway in this particular case. In addition, we synthesized other ether adducts of Lu(CH₂SiMe₃)₃ and studied their chemical and thermal stability.

Results and Discussion

Three elimination pathways can be proposed for the thermal decomposition of Lu(CH₂SiMe₃)₃(THF)₂

LuCl₃ + 3LiCH₂SiMe₃ \xrightarrow{\text{THF}} \text{Et₂O/pentane} \rightarrow \text{Lu(CH₂SiMe₃)₃(THF)₂}

Lu(CH₂SiMe₃)₃(THF)₂ \xrightarrow{\text{pentane/hexane}} \text{slow at RT} \rightarrow \text{fast at T>50 °C}

\{Me₃SiCH₂Lu=CHSiMe₃\} + SiMe₄

Scheme 1.
Studies on the Thermolysis of Ether-Stabilized Lu(CH₂SiMe₃)₃

forming SiMe₄: i) via α-H elimination from a Lu-SiCH₂ group (I), ii) via β-H elimination from a THF ligand (II), and iii) via γ-H elimination releasing a hydrogen from a SiCH₃ group (III) (Scheme 2).

It is well known that the CH-acidity of O-CH₂-protons in coordinated THF is higher than in free THF, therefore decomposition of Lu(CH₂SiMe₃)₃(THF)₂ can in principle proceed via activation of such a proton. In order to study this possibility we synthesized Lu(CH₂SiMe₃)₃([D₈]-THF)₂ (1) and thermolyzed it in hexane at elevated temperatures (Scheme 3). No formation of Me₃SiCH₂D was observed by NMR and GC-MS analysis of the products in solution. Based on these results a β-H-elimination mechanism can be ruled out.

Decomposition of Lu(CH₂SiMe₃)₀(THF)₂ (2) either via α-H- or γ-H-elimination should yield Me₃Si and organolutetium compounds. After D₂O⁺ quenching these residues are expected to form Me₃SiCH₂D and Me₃SiCHD₂ as deuteriolysis products of Me₃SiCH₂Lu=CHSiMe₃ in the case of α-H elimination, and Me₁SiCH₂D and Me₂Si(CHD)₂ in the case of β-H elimination of Me₃SiCH₂Lu(μ-CH₂)₂SiMe₂ in the case of γ-H elimination. Heating of 2 in hexane to 60 °C for 4 days gave an extremely air-sensitive yellowish product which turns white immediately when exposed to air. Hydrolysis of this product with D₂PO₄ in [D₆]-benzene did not result in the formation of any Me₃SiCHD₂. In the ¹³C{¹H} NMR spectrum the 1:1:1:1:1 quintet of Me₃SiCHD₂ was not observed but two 1:1:1 triplets appeared with ¹JC-D coupling constants of 18 Hz which can be assigned to the deuteriolysis product Me₂Si(CHD)₂, proving the fact that γ-H elimination of Me₄Si is the predominant decomposition pathway of 2.

X-ray structural investigations of Lu(CH₂SiMe₃)₃(THF)₂ (2) proved the molecule to have a trigonal bipyramidal structure with the Me₃SiCH₂ ligands in equatorial and the THF ligands in apical positions. The angle O-Lu-O of 177.73° indicates only a minor deviation from the ideal linear arrangement. On the other hand, the three Me₃SiCH₂ ligands are distributed unsymmetrically with C-Lu-C angles of 110.00, 116.16, and 133.74°. Two Me₃Si groups face each other, impeding any α-elimination of Me₄Si (Fig. 1) [11].

In order to facilitate α-H elimination as a decomposition pathway we decided to preorganize the cis-configuration of the alkyl groups in the coordination sphere of the Lu center by synthesizing other ether adducts of Lu(CH₂SiMe₃)₃ using chelating ligands like DME and diglyme. However, alkylation of LuCl₃ with LiCH₂SiMe₃ in DME/pentane under reaction conditions used for the synthesis of 2 did not yield DME-solvated Lu(CH₂SiMe₃)₃, but gave only viscous insoluble materials. Probably "ate"-complexes analogous to [Li(TMEDA)₂][Lu(CH₂SiMe₃)₄] are formed in these reactions as in the presence of TMEDA [9, 10].

Substitution of THF ligands in 2 by DME resulted in an increase of the coordination number of Lu to six and formation of the lutetium complex 3 bearing one THF and one chelating DME ligand (Scheme 4),...
as demonstrated by the $^1$H and $^{13}$C NMR spectra of the product 3. Unfortunately its crystal structure could not be refined satisfactorily because of disorder of the coordinated THF and DME molecules [12]. It appears that in contrast to the direct synthesis of Lu(CH$_2$SiMe$_3$)$_3$(12-crown-4) from 2 and 12-crown-4, recently described [13], substitution of only one THF by DME has occurred. A further displacement of coordinated THF by DME could not be accomplished.

The reaction of 2 with diglyme proceeds similarly (Scheme 4), yielding the octahedrally coordinated mixed THF/diglyme lutetium complex 4. The product crystallizes from pentane at $-10^\circ$C as colourless needles. The diglyme ligand is coordinated to lutetium only via two oxygen atoms leaving a dangling CH$_2$CH$_2$OMe arm (Fig. 2).

The molecular structure of 4 shows the lutetium atom in a distorted fac-octahedral coordination very similar to that found in Sm(CH$_2$SiMe$_3$)$_3$(THF)$_3$ [11]. Most angles at the lutetium atom deviate strongly from linearity or from 90°. The smallest angle O(2)-Lu-O(3) (66.75°) is a result of the geometry of the diglyme molecule. The sterical demand of the Me$_3$Si groups bonded to C(5) and C(9) causes a widening of the angles C(5)-Lu-C(9) (103.1°) and C(5)-Lu-O(2) (101.45°), but nevertheless an almost planar coordination of C(5), C(9), O(3) and O(2) around the lutetium atom results, including a small C(9)-Lu-O(3) angle of 86.70°. Owing to the small difference in the atomic radii of samarium and lutetium [15], the Ln-C bond lengths are generally the same in 4 and Sm(CH$_2$SiMe$_3$)$_3$(THF)$_3$ [11]. They are also equal in the distorted trigonal bipyramidal complex 2 and in the fac-octahedral molecule 4.

In contrast to 2, the two mixed adducts 3 and 4 are thermally robust complexes. 4 shows only little decomposition after heating for 2 days in heptane to 70–90°C. This observation undoubtedly confirms that α-H elimination is clearly not a favourable process in the thermal decomposition of Lu(CH$_2$SiMe$_3$)$_3$ ether adducts. The remaining γ-H elimination pathway, yielding Me$_4$Si and Me$_3$SiCH$_2$Lu(µ-CH$_2$)$_2$SiMe$_2$, has to be confirmed or excluded by further investigations.

**Experimental Section**

All experiments were performed in an atmosphere of dry, oxygen-free nitrogen using Schlenk techniques and solvents dried over sodium/benzophenone and distilled prior to use. LuCl$_3$ [16] and LiCH$_2$SiMe$_3$ [17] as well as Lu(CH$_2$SiMe$_3$)$_3$([D$_8$]-THF)$_2$ (1) and Lu(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (2) [8] were synthesized according to literature methods. NMR spectra were recorded using Bruker ARX 200 and 400 spectrometers. Lu was determined complexometrically against xyleneorange after digestion in 60% HClO$_4$ at pH 6 to 7 [18].

Lu(CH$_2$SiMe$_3$)$_3$([D$_8$]-THF)$_2$ (1) [8]

$^1$H NMR ([D$_8$]-benzene, 200 MHz): δ = 0.18 (s, 27 H, CH$_3$Si), –1.02 (s, 6 H, CH$_2$). –$^{13}$C{[1H]} NMR ([D$_8$]-benzene, 50 MHz): δ = 4.5 (CH$_3$Si), 24.7 (CH$_2$).

Lu(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (2) [8]

$^1$H NMR ([D$_8$]-benzene, 200 MHz): δ = –0.99 (s, 6 H, LuCH$_2$), 0.19 (s, 27 H, CH$_3$Si), 1.35 (m, 8 H, THF), 3.94
(m, 8 H, THF). – $^{13}$C$^1$H NMR ([D$_6$]-benzene, 50 MHz): δ = 47.2 (CH$_3$Si), 25.1 (LuCH$_2$), 41.7 (THF), 71.0 (THF).

$\text{Lu(CH}_2\text{SiMe}_3)_3\text{(THF)}\text{(DME)}$ (3)

To a solution of 2 (290 mg, 0.5 mmol) in pentane (10 ml) a mixture of DME (1 ml, 10 mmol) and pentane (10 ml) was added via syringe. The reaction mixture was slowly cooled from 0 °C and then to −30 °C. A white crystalline material precipitated. The reaction vessel was cooled to −78 °C and the mother solution was decanted under nitrogen. The residue was dried under vacuum yielding 300 mg (100%) of colorless crystals of 3. – $^1$H NMR ([D$_6$]-benzene, 400 MHz): δ = −0.68 (s, 6 H, LuCH$_2$), 0.35 (s, 27 H, SiCH$_3$), 1.33 (m, 4 H, β-CH$_2$(THF)), 2.73 (sbr, 4 H, OCH$_2$(DME)), 3.08 (sbr, 6 H, OCH$_3$(DME)), 3.63 (sbr, 4 H, α-CH$_2$(THF)), – $^{13}$C$^1$H NMR ([D$_6$]-benzene, 100.64 MHz): δ = 49.7 (CH$_3$Si), 25.2 (LuCH$_2$), 42.3 (β-CH$_2$(THF)), 61.0 (CH$_2$(DME)), 69.5 (α-CH$_2$(THF)), 70.8 (CH$_3$(DME)), – C$_2$H$_5$LuO$_3$Si$_3$ (598.85): calcld. C 40.11, H 8.62, Lu 27.22; found C 40.32, H 8.51, Lu 27.12.

$\text{Lu(CH}_2\text{SiMe}_3)_3\text{(THF)}$ (diglyme) (4)

4 was synthesized analogously to 3 from 2 (520 mg, 0.9 mmol) and diglyme (1 ml) in hexane (50 ml). Yields 575 mg (> 99%) of colorless crystals. – $^1$H NMR ([D$_6$]-benzene, 400 MHz): δ = −0.70 (s, 6 H, LuCH$_2$), 0.40 (s, 27 H, SiCH$_3$), 1.43 (m, 4 H, β-CH$_2$(THF)), 2.76 (sbr, 4 H, OCH$_2$(diglyme)), 3.11 (sbr, 10 H, CH$_2$OCH$_2$(diglyme)), 3.61 (m, 4 H, α-CH$_2$(THF)), – $^{13}$C$^1$H NMR ([D$_6$]-benzene, 100.64 MHz): δ = 4.8 (SiCH$_3$), 25.6 (LuCH$_2$), 41.0 (β-CH$_2$(THF)), 60.6 (CH$_3$(diglyme)), 68.6 (α-CH$_2$(THF)), 69.6 (CH$_2$(diglyme)). – C$_2$H$_5$LuO$_3$Si$_3$ (642.90): calcld. C 41.10, H 8.62, Lu 27.22; found C 40.51, H 8.29, Lu 27.78.

Thermal decompositions of 1

Freshly recrystallized 1 (300 mg) was put in a 25 ml Schlenk vessel, dissolved in hexane (10 ml), exposed to a slight vacuum and allowed to stand in an oil bath at 60 °C for 4 d. Already after one night a yellow precipitate was formed, leaving the solution colorless and transparent. GC-MS analysis of the hexane solution showed three hexanes, a small amount of pentane, Me$_2$Si and [D$_6$]-THF. Me$_2$SiCH$_2$D could not be detected.

Thermal decomposition of 2

Freshly recrystallized 2 (500 mg) was put in a 50 ml Schlenk vessel, dissolved in hexane (25 ml), exposed to a
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