

Studies on the Thermolysis of Ether-Stabilized $\text{Lu}(\text{CH}_2\text{SiMe}_3)_3$. Molecular Structure of $\text{Lu}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})(\text{diglyme})$

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Z. Naturforsch. **60b**, 533 – 537 (2005); received December 27, 2004

$\text{Lu}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ (**2**) decomposes slowly at room temperature with formation of Me_4Si . In order to understand the mechanism of this elimination process, $\text{Lu}(\text{CH}_2\text{SiMe}_3)_3([\text{D}_8]-\text{THF})_2$ (**1**), $\text{Lu}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})(\text{DME})$ (**3**), and $\text{Lu}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})(\text{diglyme})$ (**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.

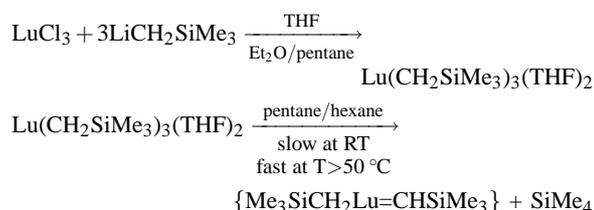
Key words: Lutetium Alkyls, Decomposition, X-Ray Structure, γ -H Elimination

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(iminodiphenylphosphorano)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 $\text{Ln}(\text{CH}_2\text{SiMe}_3)_3$ 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 Me_4Si to leave THF-free polymeric materials. These products are insoluble in organic solvents, but upon quenching with D_3O^+ gave rise to singly as



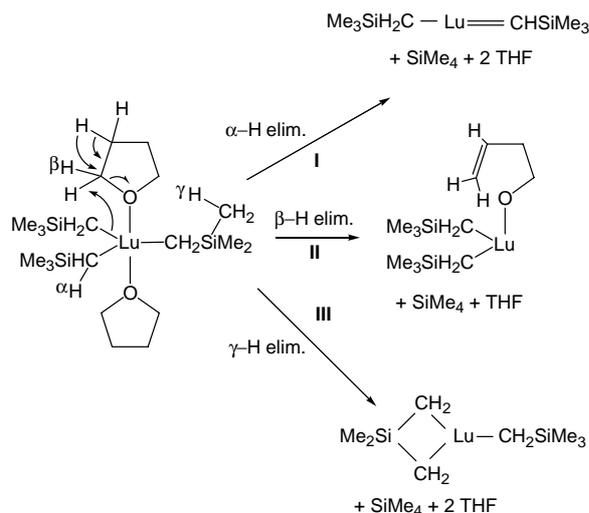
Scheme 1.

well as doubly deuterated Me_4Si . This fact was interpreted by assuming formation of lanthanide alkylidene complexes resulting from α -H-elimination of one of the Me_3SiCH_2 groups (Scheme 1) [9]. However, this mechanism was not sufficiently proven and the nature of the decomposition products was not studied any further.

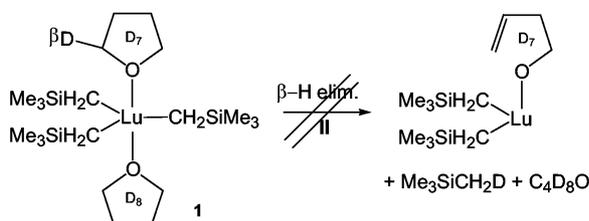
In order to support the proposed formation of $\text{Ln}=\text{C}$ species, we decided to reinvestigate the thermal decomposition of $\text{Lu}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ with the aim to delineate the elimination pathway in this particular case. In addition, we synthesized other ether adducts of $\text{Lu}(\text{CH}_2\text{SiMe}_3)_3$ and studied their chemical and thermal stability.

Results and Discussion

Three elimination pathways can be proposed for the thermal decomposition of $\text{Lu}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$



Scheme 2.



Scheme 3.

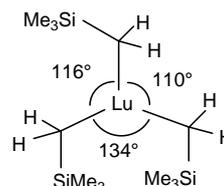
forming SiMe_4 : i) *via* α -H elimination from a $\text{Lu}-\text{SiCH}_2$ group (I), ii) *via* β -H elimination from a THF ligand (II), and iii) *via* γ -H elimination releasing a hydrogen from a SiCH_3 group (III) (Scheme 2).

It is well known that the CH-acidity of O-CH₂-protons in coordinated THF is higher than in free THF, therefore decomposition of $\text{Lu}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ can in principle proceed *via* activation of such a proton. In order to study this possibility we synthesized $\text{Lu}(\text{CH}_2\text{SiMe}_3)_3([\text{D}_8]\text{-THF})_2$ (**1**) and thermolyzed it in hexane at elevated temperatures (Scheme 3). No formation of $\text{Me}_3\text{SiCH}_2\text{D}$ 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 $\text{Lu}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ (**2**) either *via* α -H- or γ -H-elimination should yield Me_4Si and organolutetium compounds. After D_3O^+ quenching these residues are expected to form $\text{Me}_3\text{SiCH}_2\text{D}$ and $\text{Me}_3\text{SiCHD}_2$ as deuterolysis products of $\text{Me}_3\text{SiCH}_2\text{Lu}=\text{CHSiMe}_3$ in the case of α -H elimination, and $\text{Me}_3\text{SiCH}_2\text{D}$ and $\text{Me}_2\text{Si}(\text{CH}_2\text{D})_2$ gener-

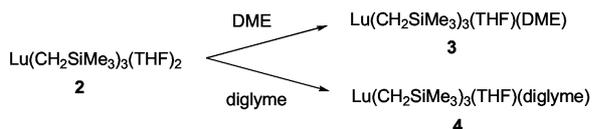
ated by deuterolysis of $\text{Me}_3\text{SiCH}_2\text{Lu}(\mu\text{-CH}_2)_2\text{SiMe}_2$ in the case of γ -H elimination. Heating of **2** in hexane to 60 °C for 4 days gave an extremely air-sensitive yellowish product which turns white immediately when exposed to air. Hydrolysis of this product with D_3PO_4 in $[\text{D}_6]$ -benzene did not result in the formation of any $\text{Me}_3\text{SiCHD}_2$. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum the 1 : 1 : 1 : 1 : 1 quintet of $\text{Me}_3\text{SiCHD}_2$ was not observed but two 1 : 1 : 1 triplets appeared with $^1J_{\text{C-D}}$ coupling constants of 18 Hz which can be assigned to the deuterolysis product $\text{Me}_2\text{Si}(\text{CH}_2\text{D})_2$, proving the fact that γ -H elimination of Me_4Si is the predominant decomposition pathway of **2**.

X-ray structural investigations of $\text{Lu}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ (**2**) proved the molecule to have a trigonal bipyramidal structure with the Me_3SiCH_2 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 Me_3SiCH_2 ligands are distributed unsymmetrically with C-Lu-C angles of 110.00, 116.16, and 133.74°. Two Me_3Si groups face each other, impeding any α -elimination of Me_4Si (Fig. 1) [11].

Fig. 1. View along the O-Lu-O axis to the LuC_3 plane in $\text{Lu}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ (**2**).

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 $\text{Lu}(\text{CH}_2\text{SiMe}_3)_3$ using chelating ligands like DME and diglyme. However, alkylation of LuCl_3 with $\text{LiCH}_2\text{SiMe}_3$ in DME/pentane under reaction conditions used for the synthesis of **2** did not yield DME-solvated $\text{Lu}(\text{CH}_2\text{SiMe}_3)_3$, but gave only viscous insoluble materials. Probably “ate”-complexes analogous to $[\text{Li}(\text{TMEDA})_2]^+[\text{Lu}(\text{CH}_2\text{SiMe}_3)_4]^-$ 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),



Scheme 4.

as demonstrated by the ¹H and ¹³C 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(CH₂SiMe₃)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 °C as colorless needles. The diglyme ligand is coordinated to lutetium only *via* two oxygen atoms leaving a dangling CH₂CH₂OMe arm (Fig. 2).

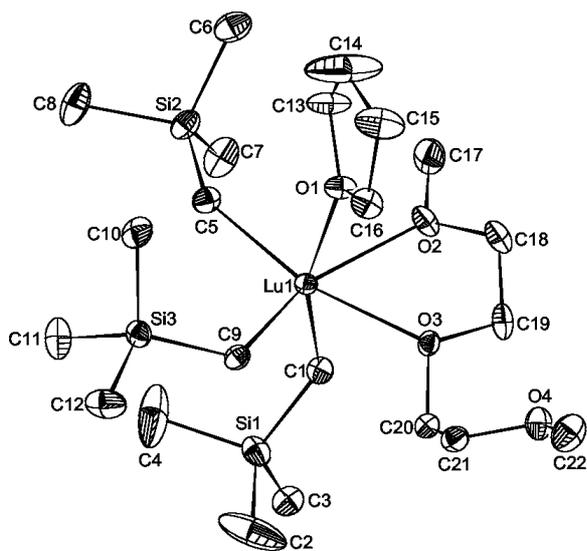


Fig. 2. ORTEP [14] drawing and numbering scheme of the molecular structure of **4** (30% probability thermal ellipsoids); all hydrogen atoms have been omitted for clarity; selected bond lengths (Å) and angles (°): Lu–C(1) 2.375(6), Lu–C(5) 2.347(6), Lu–C(9) 2.375(6), Lu–O(1) 2.432(4), Lu–O(2) 2.407(4), Lu–O(3) 2.450(4), C(1)–Lu–C(5) 98.7(2), C(1)–Lu–C(9) 106.2(2), C(1)–Lu–O(2) 85.44(18), C(1)–Lu–O(3) 87.07(18), C(5)–Lu–C(9) 103.1(2), C(5)–Lu–O(1) 91.47(19), C(5)–Lu–O(2) 101.45(19), C(9)–Lu–O(1) 88.23(18), C(9)–Lu–O(3) 86.70(17), O(1)–Lu–O(2) 75.43(15), O(1)–Lu–O(3) 79.54(14), O(2)–Lu–O(3) 66.75(13).

The molecular structure of **4** shows the lutetium atom in a distorted *fac*-octahedral coordination very similar to that found in Sm(CH₂SiMe₃)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 Me₃Si 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(CH₂SiMe₃)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 Ln(CH₂SiMe₃)₃ ether adducts. The remaining γ -H elimination pathway, yielding Me₄Si and Me₃SiCH₂Lu(μ -CH₂)₂SiMe₂, 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. LuCl₃ [16] and LiCH₂SiMe₃ [17] as well as Lu(CH₂SiMe₃)₃([D₈]-THF)₂ (**1**) and Lu(CH₂SiMe₃)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 xylenolorange after digestion in 60% HClO₄ at pH 6 to 7 [18].

Lu(CH₂SiMe₃)₃([D₈]-THF)₂ (**1**) [8]

¹H NMR ([D₆]-benzene, 200 MHz): δ = 0.18 (s, 27 H, CH₃Si), –1.02 (s, 6 H, CH₂). –¹³C{¹H} NMR ([D₆]-benzene, 50 MHz): δ = 4.5 (CH₃Si), 24.7 (CH₂).

Lu(CH₂SiMe₃)₃(THF)₂ (**2**) [8]

¹H NMR ([D₆]-benzene, 200 MHz): δ = –0.99 (s, 6 H, LuCH₂), 0.19 (s, 27 H, CH₃Si), 1.35 (m, 8 H, THF), 3.94

(m, 8 H, THF). – ¹³C{¹H} NMR ([D₆]-benzene, 50 MHz): δ = 4.7 (CH₃Si), 25.1 (LuCH₂), 41.7 (THF), 71.0 (THF).

Lu(CH₂SiMe₃)₃(THF)(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 first to 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**. – ¹H NMR ([D₆]-benzene, 400 MHz): δ = –0.68 (s, 6 H, LuCH₂), 0.35 (s, 27 H, SiCH₃), 1.33 [m, 4 H, β-CH₂(THF)], 2.73 [s_{br}, 4 H, OCH₂(DME)], 3.08 [s_{br}, 6 H, OCH₃(DME)], 3.63 [s_{br}, 4 H, α-CH₂(THF)]. – ¹³C{¹H} NMR ([D₆]-benzene, 100.64 MHz): δ = 4.7 (CH₃Si), 25.2 (LuCH₂), 42.3 [β-CH₂(THF)], 61.0 [CH₂(DME)], 69.5 [α-CH₂(THF)], 70.8 [CH₃(DME)]. – C₂₀H₅₁LuO₃Si₃ (598.85): calcd. C 40.11, H 8.58, Lu 29.22; found C 40.58, H 8.09, Lu 29.43.

Lu(CH₂SiMe₃)₃(THF)(diglyme) (4)

4 was synthesized analogously to **3** from **2** (520 mg, 0.9 mmol) and diglyme (1 ml) in hexane (50 ml). Yield 575 mg (> 99%) of colorless crystals. – ¹H NMR ([D₆]-benzene, 400 MHz): δ = –0.70 (s, 6 H, LuCH₂), 0.40 (s, 27 H, (SiCH₃)), 1.41 [m, 4 H, β-CH₂(THF)], 2.76 [s_{br}, 4 H, OCH₂(diglyme)], 3.11 [s_{br}, 10 H, CH₃OCH₂(diglyme)], 3.61 [m, 4 H, α-CH₂(THF)]. – ¹³C{¹H} NMR ([D₆]-benzene, 100.64 MHz): δ = 4.8 (SiCH₃), 25.6 (LuCH₂), 41.0 [β-CH₂(THF)], 60.6 [CH₂(diglyme)], 68.6 [α-CH₂(THF)], 69.6 [CH₃(diglyme)]. – C₂₂H₅₅LuO₄Si₃ (642.90): calcd. 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 different hexanes, a small amount of pentane, Me₄Si and [D₈]-THF. Me₃SiCH₂D 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

slight vacuum and allowed to stand in an oil bath at 60 °C for 4 d. The yellowish precipitate was filtered, washed two times with hexane and dried *in vacuo* at 80 °C. Then [D₆]-benzene (5 ml) was added and a solution of P₄O₁₀ (1 g) in D₂O (10 ml) was added dropwise *via* a septum. After completion of the exothermic reaction, the mixture was cooled to 10 °C and the upper [D₆]-benzene layer was slowly syringed to a Schlenk flask containing Na₂SO₄ (1 g) and equipped with a presealed NMR-tube. After standing for 1 h, the solution was slowly decanted into the NMR tube, which was immediately sealed off. – ¹³C{¹H} NMR ([D₆]-benzene, 50 MHz): δ = –0.45 (t, ¹J_{CD} = 18 Hz, CH₂D), –0.43 (t, ¹J_{CD} = 18 Hz, CH₂D), –0.16 (s, CH₃), –0.12 (s, CH₃).

Crystallography

Data were collected on a Siemens SMART CCD diffractometer (graphite monochromated Mo-K_α radiation, λ = 0.71073 Å) with area-detector by use of ω scans at 173 K. The structure was solved by direct methods and refined on F² using all reflections with SHELX-97 [19]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 0.08 Å². The idealised methyl-groups were allowed to rotate about their X-C bond. SADABS [20] was used to perform area-detector scaling and absorption corrections.

Crystal data and structure refinement details:

C₂₂H₅₅LuO₄Si₃, *M* = 642.90, monoclinic, *a* = 19.8966(3), *b* = 18.3186(3), *c* = 19.4804(2) Å, β = 112.748°, *V* = 6547.88 Å³, space group *C2/c* (no. 15), *Z* = 8, μ = 3.146 mm^{–1}, *D*_{calcd.} = 1.304 g cm^{–3}, θ range 1.57–25.00 deg; 19996 reflections measured, 5762 unique (*R*_{int} = 0.0773). *GOF* on *F*² 1.041. The final residuals *R*_{*F*} (*wR*_{*F*}²) were 0.0419 (0.0746) [*I* > 2σ(*I*)].

Crystallographic data for the structure of **4** have been deposited with the Cambridge Crystallographic Data Centre, CCDC-245414. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (Graduiertenkolleg “Synthetische, mechanistische und reaktionstechnische Aspekte von Metallkatalysatoren” and SPP “Lanthanoidspezifische Funktionalitäten in Molekül und Material”) and the Fonds der Chemischen Industrie.

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