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Lanthanide Silanolates: Development of New Procedures for the Modification of Silicones with Rare-earth Metals

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The reactions of LnI_3 (Ln = La, Ce, Er, Yb) with sodium silanolate ($NaOSiMe_3$) in THF at room temperature yield lanthanide silanolates $Ln(OSiMe_3)_3$ which seem to be oligomers with μ-$OSiMe_3$ ligands. Reaction of CeI_3 with potassium siliconate, $KO[Me_{1.96}Ph_{0.04}SiO]_{20.75}K$, yields a netted polymer $[Me_{61.59}Ph_{1.29}Si_{31.44}O_{39.02}Ce]_x$. An analogous procedure which involves reaction of LnI_3 (Ln = Ln, Er) with $KO[Me_{1.96}Ph_{0.04}SiO]_{50.00}K$, and following treatment with $NaOSiMe_3$, results in the formation of soluble product $(Me_3SiO)_2LnO[Me_{1.96}Ph_{0.04}SiO]_{50.00}Ln(OSiMe_3)_2$.

Keywords: lanthanum; cerium; erbium; ytterbium; silanolates; silicones

INTRODUCTION

Silicones are of great importance for the industry and are used for the production of polymeric design materials, synthetic oils, rubbers, etc. because of their unusual mechanical and chemical properties.[1] The stabilization of such polymers towards thermal and thermo-oxidative destruction is a very important problem. Modern industry applies various additives to stabilize the silicones. Some of those involve compounds of iron, chromium, etc.[2] However, the best additives are compounds of rare-earth metals, especially cerium. Although silicones have low affinity for most organic and inorganic materials, the compounds of lanthanides form homogeneous mixtures with silicones. However, the effects of lanthanides have not been much studied. Even heterogeneous cerium additives turned out to result in extraordinary stabilization of silicones.[3]

Lanthanide silanolates which involve both Ln—O—Ln and Ln—O—Si fragments will probably have some affinity for silicones and, therefore, will form homogeneous mixtures. However, simple silanolates $Ln(OSiR_3)_3$ (Ln = Sc, Y, La, lanthanides) have not been synthesized so far.[4] Polymeric silanolates of lanthanides are known and have been synthesized by the treatment of erbium or gadolinium isopropylate with $Me_3SiOCOCH_3$ in boiling cyclohexane.[5] Another method is the treatment of acetates of corresponding rare-earth metals with $PhSiCl_3$[6–8] or Et_3SiCl.[9] The reaction with $PhSiCl_3$ yields polymers $[PhSiO_{1.35-1.01}Ln_{0.01-0.42}(OH)_{0.24-0.42}]_{7-26}$ with $M = 2000$–5000. Polymetallophenylsiloxanes are likely to involve metal fragments with eight oxygen atoms in the vicinity of lanthanide, e.g. as shown in Fig. 1.

The present work is aimed at the syntheses both of lanthanide silanolates $Ln(OSiMe_3)_3$, and of silanolates with well-characterized oligosiloxane substituents.

RESULTS AND DISCUSSION

The first attempt to synthesize $Ln(OSiMe_3)_3$ from anhydrous chlorides of lanthanum(III) or cerium(III) and $NaSiOMe_3$ in THF was not successful. Probably this resulted from both the low

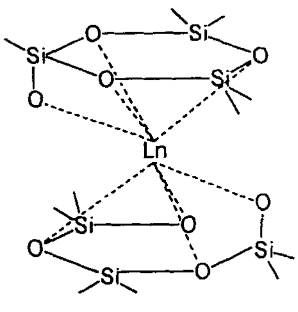

Figure 1

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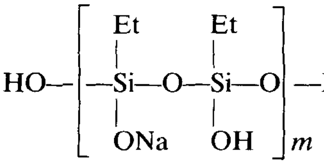
nucleophilicity of sodium silanolate and the high stability of chlorine bridging in anhydrous polymeric $LnCl_3$,[10] as well as the possibility of the formation of stable ate-complexes of lanthanides.[11] Analogous reactions with lanthanide(III) iodides (Eqn [1]) yield lanthanide silanolates **1–4**. The compounds were isolated in high yield and were found to be colored (besides the complex of lanthanum) solids which are very sensitive to moisture. The compounds melt with decomposition in the range 170–190 °C (see Experimental section). On the evidence of molecular weight measurements, the complexes **1–4** are oligomers with $OSiMe_3$ bridging. Molecular weight depends considerably on the concentration of **1–4** in toluene solution.

$$LnI_3 + 3\,NaOSiMe_3 \xrightarrow[\text{2. toluene, }-\text{NaI}]{\text{1. THF, 20 °C}} \underset{\mathbf{1\text{–}4}}{Ln(OSiMe_3)_3} \qquad [1]$$

Ln = La (**1**), Ce (**2**), Er (**3**), Yb (**4**)

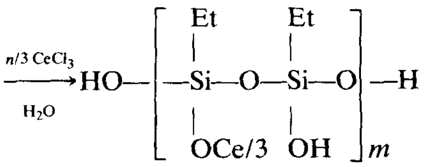
The complexes **1–4** were found to be easily soluble in hydrocarbons and moderately in commercially available methyl- and methylphenylsilicones at room temperature. However, their solubility in the latter liquids increase considerably at 150 °C.

We hoped that lanthanide silanolates, which involve oligomeric siloxane fragments, would have high solubility in silicone oils. The treatment of commercially available sodium siliconate **5** with an aqueous solution of $CeCl_3$ turned out to yield the corresponding cerium siliconate **6** (Eqn [2]). This polymer is likely to have a netted structure and is insoluble both in common solvents and in silicones.



$$HO\text{—}\left[\text{—}\overset{\displaystyle Et}{\underset{\displaystyle ONa}{Si}}\text{—}O\text{—}\overset{\displaystyle Et}{\underset{\displaystyle OH}{Si}}\text{—}O\right]_m\text{—}H$$

5



$$\xrightarrow[H_2O]{n/3\,CeCl_3} HO\text{—}\left[\text{—}\overset{\displaystyle Et}{\underset{\displaystyle OCe/3}{Si}}\text{—}O\text{—}\overset{\displaystyle Et}{\underset{\displaystyle OH}{Si}}\text{—}O\right]_m\text{—}H \qquad [2]$$

6

The molecular weight of potassium siliconate **7**, which has been synthesized by the reaction of Eqn [3], depends on the ratio D_4: KOH.

$$nD_4 + 2\,KOH \xrightarrow[\text{115 °C, 3 h}]{A_3(\text{mol 5\%})} \underset{\mathbf{7}}{KO[Me_{1.96}Ph_{0.04}SiO]_{4.15n}K} \qquad [3]$$

where $D_4 = [\text{—}Me_2SiO\text{—}]_4$, $A_3 = [\text{—}PhMeSiO\text{—}]_3$

The treatment of potassium siliconate **7** ($n = 5$) with CeI_3 in THF leads to the formation of netted cerium siliconate **8** (Eqn [4]) which is insoluble in silicones also.

$$KO[Me_{1.96}Ph_{0.04}SiO]_{20.75}K \xrightarrow[\text{THF, 20 °C}]{CeI_3} \underset{\mathbf{8}}{[Me_{61.59}Ph_{1.29}Si_{31.44}O_{39.02}Ce]_x} \qquad [4]$$

The modification of this procedure, i.e. when the reaction of 1 equivalent of LnI_3 (Ln = Ce, Er) with 0.5 equivalent of potassium siliconate **7** ($n = 12.05$) is followed by the treatment with 2 equivalents of $NaOSiMe_3$, was found to result in the formation of linear products **9**, **10** (Eqn [5]). This synthetic route yields soluble lanthanide silanolates which involve an oligomeric siloxane chain with a determined molecular weight. On the evidence of molecular weight determination the lanthanide silanolates **9**, **10** are monomers in toluene solution. The vicinity of the lanthanide atoms is likely to occur with the participation of both silanolate oxygen atoms and those of the siloxane chain.

$$2\,LnI_3 \xrightarrow[\text{2. 4 NaOSiMe}_3\text{, THF, 20 °C}]{\text{1. KO[Me}_{1.96}\text{Ph}_{0.04}\text{SiO]}_{50.00}\text{K, THF, 0 °C}}$$

$$\underset{\mathbf{9\text{–}10}}{(Me_3SiO)_2LnO[Me_{1.96}Ph_{0.04}SiO]_{50.00}Ln(OSiMe_3)_2} \qquad [5]$$

Ln = Ce (**9**), Er (**10**)

Thus, convenient synthetic routes for the preparation of both simple lanthanide silanolates $Ln(OSiMe_3)_3$ and silanolates of rare-earth metals containing determined oligomeric siloxane fragments were developed. The compounds are prospective additives to silicone materials to stabilize them towards thermal and thermo-oxidative destruction.

EXPERIMENTAL

Tetrahydrofuran for synthesis was purified by distillation over $LiAlH_4$. Hydrocarbon solvents were distilled and stored over calcium hydride. Turnings of lanthanum, cerium, erbium and ytterbium (99.5% pure) (Giredmet, Russia) were used as received. Molecular weights of the compounds were measured in toluene solution with a vapor pressure osmometer (Knaver). Lanthanide content was assayed by titration (EDTA, Xyleon Orange).

$LaI_3(THF)_3$

A mixture of 6.31 g (45.4 mmol) of lanthanum turnings with 30.00 g (65.9 mmol) of HgI_2 in 500 ml of THF was boiled for 15 h until the test on HgI_2 (TLC: Silufol UV 254, acetone) was negative. The reaction mixture was decanted from the mercury drop and then evaporated to *ca* 50 ml. After cooling to 0 °C for one day, white crystals were separated by filtration and dried. Yield 29.7 g (92%) of $LaI_3(THF)_3$.

Analysis: calcd for $C_{12}H_{24}I_3LO_3$: C, 19.57; H, 3.26; La, 18.89. Found: C, 19.81; H, 3.40; La, 18.59%.

$CeI_3(THF)_3$

The reaction was carried out similarly to the preparation of $LaI_3(THF)_3$, starting from 4.22 g (30.1 mmol) of cerium turnings and 19.86 g (43.6 mmol) of HgI_2 in 300 ml of THF for four days at room temperature. Yield 18.4 g (86%) of $CeI_3(THF)_3$.

Analysis: calcd for $C_{12}H_{24}CeI_3O_3$: C, 19.54; H, 3.26; Ce, 19.00. Found: C, 19.68; H, 3.35; Ce, 18.71%.

$ErI_3(THF)_3$

The reaction was carried out similarly to the preparation of $LaI_3(THF)_3$, starting from 8.25 g (49.5 mmol) of erbium turnings and 32.70 g (71.8 mmol) of HgI_2 in 500 ml of THF for 20 h at 66 °C. Yield 34.7 g (95%) of $ErI_3(THF)_3$.

Analysis: calcd for $C_{12}H_{24}ErI_3O_3$: C, 18.85; H, 3.14; Er, 21.86. Found: C, 18.70; H, 3.10; Er, 21.94%.

$YbI_3(THF)_3$

The reaction was carried out similarly to the preparation of $LaI_3(THF)_3$, starting from 4.58 g (26.5 mmol) of ytterbium turnings and 18.08 g (39.7 mmol) of HgI_2 in 300 ml of THF for 20 h at 66 °C. Yield 19.0 g (93%) of $YbI_3(THF)_3$.

Analysis: calcd for $C_{12}H_{24}I_3O_3Yb$: C, 18.70; H, 3.12; Yb, 22.47. Found: C, 18.61: H, 3.05; Yb, 24.64%.

$NaOSiMe_3$

A solution of 88.5 ml (72.0 g, 0.80 mol) of Me_3SiOH in 100 ml of THF was added dropwise to a suspension of 24.0 g (0.95 mol) of 95% NaH in 350 ml of THF over a period of 1.5 h at ambient temperature. The mixture was stirred for 2 h. The solution was decanted from excess NaH and evaporated to dryness. Yield 82.4 g (92%) of colorless crystals of $NaOSiMe_3$.

Analysis: calcd for C_3H_9NaOSi: C, 32.14; H, 8.04. Found: C, 32.17; H, 8.00%.

$La(OSiMe_3)_3$ (1)

$NaOSiMe_3$ (3.10 g; 27.7 mmol) was added to a suspension of 6.80 g (9.2 mmol) of $LaI_3(THF)_3$ in 100 ml of THF. The mixture was stirred at room temperature for 3 h. The solution was evaporated to dryness and the residue was extracted with 3 × 10 ml of hexane to remove the impurities of $NaOSiMe_3$, and then was extracted with 2 × 30 ml of toluene. The toluene solution was evaporated to dryness and the solid was dried *in vacuo* at 40–50 °C. Yield 2.85 g (76%) of colorless solid **1** with m.p. 173–176 °C (dec.).

Analysis: calcd for $C_9H_{27}LaO_3Si_3$: C, 26.60; H, 6.65; La, 34.24. Found: C, 26.90; H, 6.81; La, 34.03%.

$Ce(OSiMe_3)_3$ (2)

The reaction was carried out similarly to the preparation of **1**, starting from 4.26 g (5.8 mmol) of $CeI_3(THF)_3$ and 1.94 g (17.3 mmol) of $NaOSiMe_3$ in 70 ml of THF. Yield 1.55 g (66%) of yellowish solid **2** with m.p. 175–179 °C (dec).

Analysis: calcd for $C_9H_{27}CeO_3Si_3$: C, 26.54; H, 6.63; Ce, 34.40. Found: C, 27.02; H, 6.89; Ce, 33.91%.

$Er(OSiMe_3)_3$ (3)

The reaction was carried out similarly to the preparation of **1**, starting from 7.54 g (9.9 mmol) of $ErI_3(THF)_3$ and 3.32 g (29.6 mmol) of $NaOSiMe_3$ in 100 ml of THF. Yield 4.30 g (83%) of pink solid **3** with m.p. 193–197 °C (dec).

Analysis: calcd for $C_9H_{27}ErO_3Si_3$: C, 24.71; H, 6.18; Er, 38.22. Found: C, 25.40; H, 6.39; Er, 37.53%.

$Yb(OsMe_3)_3$ (4)

The reaction was carried out similarly to the preparation of **1**, starting from 6.40 g (8.3 mmol) of $YbI_3(THF)_3$ and 2.79 g (24.9 mmol) of $NaOSiMe_3$ in 100 ml of THF. Yield 2.96 g (81%) of orange solid **4** with m.p. 189–192 °C (dec).

Analysis: calcd for $C_9H_{27}O_3Si_3Yb$: C, 24.55; H, 6.14; Yb, 39.32. Found: C, 24.79; H, 6.40; Yb, 39.11%.

$KO[Me_{1.96}Ph_{0.04}SiO]_{50.00}K$

Tablets of KOH (10.8 g; 0.19 mol) were ground in *ca* 50 ml of octamethylcyclosiloxane (D_4) under dry argon at room temperature. The suspension was transferred into a reaction vessel. The residue of D_4 [in total 350 g (1.15 mol) of D_4 was used] and 27 g (65 mmol) of trimethyltriphenylcyclosiloxane (A_3) were added. This reaction mixture was stirred at 115 °C for 3 h. This procedure yielded a transparent colorless viscous oil of potassium oligosiliconate.

Compound 9

$KO[Me_{1.96}Ph_{0.04}SiO]_{50.00}K$ (32.6 g; 8 mmol) in 100 ml of THF was added to a suspension of 11.8 g (16 mmol) of $CeI_3(THF)_3$ in 200 ml of THF at 0 °C. This mixture was stirred at 0 °C for 1 h, and then a solution of 3.58 g (32 mmol) of $NaOSiMe_3$ in 70 ml of THF was added. The reaction mixture was stirred at 0 °C for 3 h, and then THF was evaporated *in vacuo*. The viscous oil was dissolved in 300 ml of hexane, and this mixture was filtered (G3). The solution was evaporated, and the residue was dried *in vacuo* at 60–70 °C for one day. This procedure yielded 33.6 g (94%) of viscous yellowish oil **9** with $M = 4720$.

Analysis: calcd for $C_{122}H_{340}Ce_2O_{55}Si_{54}$: C, 32.67; H, 7.64; Ce, 6.25; Si, 33.82. Found: C, 33.51; H, 8.08; Ce, 5.77; Si, 34.20%.

Compound 10

The reaction was carried out similarly to the preparation of **9**, starting from 40.8 g (10 mmol) of $KO[Me_{1.96}Ph_{0.04}SiO]_{50.00}K$, 15.3 g (20 mmol) of $ErI_2(THF)_3$, and 4.48 g (40 mmol) of $NaOSiMe_3$. Yield of 43.9 g (97%) of viscous pink oil **10** with $M = 4800$.

Analysis: calcd for $C_{122}H_{34}0Er_2O_{55}Si_{54}$: C, 32.28; H, 7.55; Er, 7.37; Si, 33.41. Found: C, 30.73; H, 8.14; Er, 6.07; Si, 34.92%.

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