Molecular hydrides of samarium and europium $LnH_2(THF)_2$ (Ln = Sm or Eu): synthesis and properties

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The molecular hydrides $Ln^{II}H_2(THF)_2$ (Ln = Sm or Eu) were prepared by hydrogenolysis of the naphthalene complexes of divalent samarium and europium $C_{10}H_8Ln(THF)_2$ (Ln = Sm or Eu, respectively) as well as of the stilbene derivative of samarium(II) $(PhCHCHPh)Sm(DME)_2$ in THF at room temperature under atmospheric pressure. The resulting complexes were characterized by the data of microanalysis, IR spectroscopy, and magnetic susceptibility. Chemical properties of the complexes were studied.

Key words: samarium, europium, lanthanides, hydride, complex, hydrogenolysis.

Hydride complexes of lanthanides have attracted the attention of researchers for more than 10 years. This interest stems largely from their high reactivity and catalytic activity in a number of reactions with the participation of unsaturated substrates, *viz.*, in hydrogenation, polymerization, hydrosilylation, hydroamination, cyclization, and hydroboration.[1—3]

As of now, bi- and mononuclear hydride complexes of virtually all lanthanides, including organobimetallic complexes, with different structures and compositions have been synthesized. However, the range of these compounds is limited to derivatives containing substituted or unsubstituted stabilizing cyclopentadienyl ligands along with the catalytically active Ln—H group.[1] The only exception is divalent ytterbium hydride $[YbH_2(THF)_x]_n$ (x = 1 or 2) prepared by us previously.[4,5] This hydride exhibits high activity in catalytic hydrogenation of alkenes and acetylenes as well as in stoichiometric reduction of trialkylbromosilanes and germanes yielding the corresponding derivatives R_3EH (E = Si or Ge).[6]

The aim of this work is to synthesize molecular hydrides of divalent samarium and europium, which do not contain π-bonded carbocyclic ligands and, consequently, which have the maximum unsaturated coordination sphere of the metal atom, as well as to study their activity in polymerization of α-olefins.

Results and Discussion

Previously, it has been found[4,5] that the reaction of the ytterbium naphthalene complex $C_{10}H_8Yb(THF)_2$ with hydrogen proceeds readily at room temperature under atmospheric pressure to form the hydride $[YbH_2(THF)_x]_n$ in good yield. We also synthesized hydrides of divalent samarium and europium by hydrogenolysis of the corresponding naphthalene (**1** and **2**) and stilbene (**3**) complexes of Ln^{2+}.

It was found that complexes **1** and **2**, like the ytterbium analog, react with H_2 in a THF medium at room temperature under atmospheric pressure to form samarium hydride tetrahydrofuranate (**4**) in 60% yield and europium hydride tetrahydrofuranate (**5**) in 20% yield, respectively.

$$\underset{\mathbf{1,\,2}}{C_{10}H_8Ln(THF)_2} + H_2 \xrightarrow{THF} \underset{\mathbf{4,\,5}}{LnH_2(THF)_2} + C_{10}H_8$$

Ln = Sm (**1**, **4**), Eu (**2**, **5**)

Complex **4** can also be prepared in 69% yield by the reaction of samarium stilbene complex **3**[7] with H_2 under analogous conditions. However, in the case under consideration, stilbene was hydrogenated to dibenzyl

$$\underset{\mathbf{3}}{(PhCHCHPh)Sm(DME)_2} + H_2 \xrightarrow{THF}$$

$$\longrightarrow \underset{\mathbf{4}}{SmH_2(THF)_2} + PhCH_2CH_2Ph$$

unlike the reactions of the naphthalene derivatives, which gave naphthalene upon hydrogenolysis of the initial compounds.

Both reactions were accompanied by gradual dissolution of initial compounds **1**—**3**, which are insoluble in organic media, to yield intensely colored solutions from which the corresponding dihydrides were isolated as amorphous dark-red (Sm) or orange (Eu) powders upon slow diffusion of hexane. In the case of europium, a THF-insoluble hydride complex (apparently, of the poly-

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meric nature $[\mathrm{EuH_2(THF)}]_n$) also formed in a yield of up to 60%. Complexes **4** and **5** are very sensitive to atmospheric oxygen and moisture. Upon storage *in vacuo* at room temperature, these complexes slowly decompose with elimination of H_2, thus losing solubility.

The IR spectra of compounds **4** and **5** have a broad band at 1250 cm^{-1} along with absorption bands of coordinated THF molecules (at 860 and 1050 cm^{-1}). For the ytterbium derivative $[\mathrm{YbH_2(THF)}_x]_n$, this broad band was assigned[4] to vibrations of the Ln—H bond based on the shift in the spectra of its deuterium analog. Magnetic measurements demonstrated that the magnetic moments of complexes **4** and **5** at room temperature are 3.5 and 7.6 μ_B, respectively, which correlate well with the values generally observed for divalent samarium and europium derivatives.[8]

To confirm the presence of active hydride hydrogen in compounds **4** and **5**, we studied the reduction of triethylbromogermane by these complexes.

$$\underset{\mathbf{4,\,5}}{\mathrm{LnH_2(THF)_2}} + 2\,\mathrm{Et_3GeBr} \xrightarrow{\mathrm{THF}} \mathrm{Et_3GeH} + \mathrm{Et_3GeGeEt_3} + \mathrm{LnBr_2(THF)_2}$$

Ln = Sm (**4**), Eu (**5**)

It appeared that dihydrides **4** and **5** readily react with $\mathrm{Et_3GeBr}$ in a THF medium at room temperature and the latter is reduced to $\mathrm{Et_3GeH}$ in 79 and 77% yields, respectively. Small amounts of hexaethyldigermane (10% for Sm and 2% for Eu) were also detected among the reaction products. In both reactions, the corresponding dibromides $\mathrm{LnBr_2(THF)_2}$ were obtained in virtually quantitative yields.

Studies of the catalytic activity of complexes **4** and **5** as well as of the $[\mathrm{YbH_2(THF)}_x]_n$ complex in polymerization of α-olefins demonstrated that all three compounds are inactive toward propylene at room temperature both under atmospheric pressure and under high pressure (the propylene pressure of 20 atm). However, these compounds exhibit high activity in styrene polymerization. The molecular weight (M_w) of the resulting polymer noticeably increases in the series Sm (150 000), Yb (350 000), and Eu (1 000 000).

Experimental

The syntheses were performed under conditions precluding exposure to atmospheric oxygen and moisture using the standard Schlenk technique. The reagents and solvents were commercial products (Ekros). Hexane, THF, and toluene were dried over sodium benzophenone ketyl (which was prepared from metallic sodium and benzophenone), thoroughly degassed, and condensed *in vacuo* into a reaction tube immediately before run. Styrene was dried over 5A molecular sieves. Propylene was dried by passing through a column with copper on kiselguhr and two column with 3A molecular sieves. Then the propylene was passed through a trap filled with tris(isobutyl)aluminum, condensed into a trap with liquid nitrogen, and refrozen *in vacuo*. Polymerization of propylene was carried out under high pressure in a steel autoclave equipped with a manometer. The molecular weight of polystyrene was measured according to a known procedure.[9]

The IR spectra were recorded on a Specord M80 instrument; the samples were prepared as Nujol mulls and placed between KBr plates. The ^{1}H NMR spectra were obtained on a Gemini-300 instrument; the chemical shifts were measured relative to the known signals of the residual protons of deuterated solvents. The organic products were analyzed on a Milikhrom-1A microcolumn liquid chromatograph (UV detector with the variable wavelength (λ = 250 nm), steel 64×2-mm column, Separon S6X (15 μm) as the adsorbent, a hexane—THF mixture as the eluent, 200 : 1 (by volume), the rate of the eluent 200 μm min^{-1}). The volatile organic products were analyzed on a Tsvet-530 instrument (katharometer as the detector; steel 2 m × 3 mm-column packed with 5% SE-30 on Chromaton N-AW; helium as the carrier gas). The magnetic measurements were carried out according to a procedure reported previously.[10]

The complexes $\mathrm{C_{10}H_8Ln(THF)_2}$ (Ln = Sm (**1**) or Eu (**2**)[11]) and $\mathrm{(PhCHCHPh)Sm(DME)_2}$ (**3**)[7] were prepared according to procedures reported previously.

Dihydrosamariumbis(tetrahydrofuran) (4). *A.* A suspension of complex **1** (0.7 g, 1.65 mmol) in THF (10 mL) was stirred under H_2 (~20 °C, 1 atm) for 5 days. The precipitate was gradually dissolved, and the reaction mixture turned red-brown. The solution was filtered and then hexane (5 mL) was added. The precipitate of compound **4** that formed was separated from the mother liquor and dried *in vacuo*. Complex **4** was obtained as a red-brown powder in a yield of 0.32 g (60%). Found (%): C, 31.98; H, 5.66; Sm, 50.22. $\mathrm{C_8H_{18}O_2Sm}$. Calculated (%): C, 32.40; H, 6.07; Sm, 50.72. $\mathrm{C_{10}H_8}$ (0.18 g, 84%) was detected in the solution by HPLC.

B. A suspension of complex **3** (0.9 g, 1.76 mmol) in THF (15 mL) was stirred under H_2 for 5 days. The red-brown solution that formed was filtered. After the addition of hexane (5 mL) to the reaction mixture, complex **4** was obtained in a yield of 0.36 g (69%). Dibenzyl (0.25 g, 79%) was determined in the mother liquor by HPLC.

Dihydroeuropiumbis(tetrahydrofuran) (5). A suspension of complex **2** (1.82 g, 4.29 mmol) in THF (15 mL) was stirred under H_2 for 3 days. The orange solution that formed was filtered. After the addition of hexane (5 mL) to the reaction mixture, complex **5** was obtained in a yield of 0.26 g (20%). Found (%): C, 31.78; H, 5.61; Eu, 50.85. $\mathrm{C_8H_{18}O_2Eu}$. Calculated (%): C, 32.23; H, 6.03; Eu, 50.98. $\mathrm{C_{10}H_8}$ (0.4 g, 73%) was determined in the mother liquor by HPLC.

Reaction of compound 4 with $\mathbf{Et_3GeBr}$. A solution of $\mathrm{Et_3GeBr}$[12] (0.37 g, 1.54 mmol) in THF (2 mL) was added to a solution of complex **4** (0.23 g, 0.77 mmol) in THF (3 mL) at ~20 °C. The reaction mixture turned colorless and a precipitate of $\mathrm{SmBr_2(THF)_2}$ (0.27 g, 78%) was formed. $\mathrm{Et_3GeH}$ (0.20 g, 79%) and $\mathrm{Et_3GeGeEt_3}$ (0.02 g, 10%) were determined in the solution by HPLC.

Reaction of compound 5 with $\mathbf{Et_3GeBr}$. A solution of $\mathrm{Et_3GeBr}$ (0.64 g, 2.68 mmol) in THF (2 mL) was added to a solution of complex **5** (0.4 g, 1.34 mmol) in THF (3 mL). The color of the reaction mixture changed from orange to pale-yellow and a precipitate of $\mathrm{EuBr_2(THF)_2}$ (0.60 g, 98%) formed. $\mathrm{Et_3GeH}$ (0.33 g, 77%) and $\mathrm{Et_3GeGeEt_3}$ (0.01 g, 2%) were determined in the solution by HPLC.

Styrene polymerization. Styrene (2.7 g, 3 mL), a weighed sample of a catalyst (3—5 wt.%), and toluene (10 mL) were placed into an evacuated tube. The reaction mixture was stirred at ~20 °C for 1 day. The solvent was removed under reduced pressure. The polymer was precipitated from THF with methanol and dried *in vacuo*.

Propylene polymerization. A weighed sample of a catalyst (3—5 wt.%) was placed into an evacuated tube. Then toluene (10 mL) was added and the calculated amount of dry propylene was condensed. The reaction mixture was stirred at ~20 °C for 1 day and methanol (0.5 mL) was added to neutralize the catalyst. Then the products of catalyst decomposition were separated on a glass filter. Methanol (30 mL) was added to the filtrate. No precipitate was formed, which was indicative of the absence of the polymer in the solution.

Propylene polymerization under high pressure. A weighed sample of a catalyst (3—5 wt.%) in a thin-walled tube was placed into an evacuated steel autoclave. Then toluene (10 mL) was added and the calculated amount of dry propylene was condensed. The reaction mixture was kept at ~20 °C for 1 day and methanol (0.5 mL) was added to neutralize the catalyst. Then the products of catalyst decomposition were separated on a glass filter. Methanol (30 mL) was added to the filtrate. No precipitate was formed, which was indicative of the absence of the polymer in the solution.

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