Organometallic Chemistry

Study of reactions of some halides, cyclopentadienyl dichlorides, and bis(cyclopentadienyl) chlorides of lanthanides with *trans*-stilbene adducts with alkali metals $[PhCHCHPh]^{\cdot -}M^+$ (M = Li, Na)

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Reaction of $SmI_2(THF)_2$ with metallic lithium and *trans*-stilbene in 1 : 2 : 2 ratio in DME gives the stilbene complex of divalent samarium $(PhCHCHPh)Sm(DME)_2$. This complex reacts with hydrogen in THF to give $SmH_2(THF)_2$ and 1,2-diphenylethane. The reaction with $(Me_3Si)_2NH$ gives the amide $[(Me_3Si)_2N]_2Sm(DME)_2$ and the reaction with triphenylgermane yields $Ph_3GeGePh_3$. Reaction of $CpLuCl_2(THF)_2$ with 2 equivalents of $[PhCHCHPh]^{\cdot -}$ Na^+ in DME results in the dimerization of stilbene fragments to give an *ate*-complex $\{Cp_2Lu[\mu\text{-}CH(Ph)CH(Ph)CH(Ph)CH(Ph)]\}Na(DME)_3$. In the reaction of Cp_2GdCl with $[PhCHCHPh]^{\cdot -}Na^+$, the known complex $Cp_3Gd(THF)$ was isolated as the only lanthanide-containing product.

Key words: lanthanides, stilbene, complex, reactivity.

A broad range of lanthanide complexes with neutral and anionic π-donor ligands have been prepared and described by now.[1] However, the series of compounds containing substituted olefins (both neutral and charged) is still limited.

The binuclear complexes $(Cp^*{}_2Sm)_2(\mu\text{-}\eta^2{:}\eta^4\text{-}PhCHCHPh)$ and $(Cp^*{}_2Sm)_2(\mu\text{-}\eta^2{:}\eta^4\text{-}PhCHCH_2)$ were prepared by the reaction of $Cp^*{}_2Sm$ ($Cp^* = C_5Me_5$) with *cis*-stilbene and styrene, respectively.[2] The structure and magnetic moments of these complexes pointed to partial or complete oxidation of samarium to the trivalent state and formation of Sm—C σ-bonds with the bridging ligand. However, both complexes are readily destroyed on treatment with THF with regeneration of *trans*-stilbene or styrene and the tetrahydrofuranate of the initial samarocene $Cp^*{}_2Sm(THF)_2$, *i.e.*, they exhibit the properties of labile coordination compounds. The sandwich complex $[Na(THF)_6][Y(Ph_2CCPh_2)_2]$ was recently synthesized[3] by the reaction of YCl_3 with the disodium derivative of tetraphenylethylene. The central metal atom in this compound is bound not only to the ethylene C atoms but also to the *ipso*- and *ortho*-C atoms of the

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benzene rings. A complex of divalent ytterbium with the stilbene dianion $(PhCHCHPh)Yb(THF)_2$ was prepared in our previous study[4] by the reaction of $YbI_2(THF)$ with (PhCHCHPh)Na. This compound is highly reactive with respect to a wide range of reagents; thus it can be used to synthesize other derivatives of di- and trivalent ytterbium.

It can be seen from the above examples that lanthanide complexes with substituted olefins are convenient subjects regarding the study of both the nature of the metal—π-donor ligand interaction and features of their reactivity.

The purpose of this work is to study reactions of some rare-earth metal halides with radical anion complexes of *trans*-stilbene $[PhCHCHPh]^{\cdot -}M^+$ (M = Li, Na) and to study the properties of the resulting compounds.

Results and Discussion

The reaction of samarium iodide $SmI_2(THF)_2$ with metallic lithium and *trans*-stilbene (molar ratio $SmI_2(THF)_2$: Li : PhCHCHPh = 1 : 2 : 2) in DME gives crystalline complex **1** in 63% yield.

$$SmI_2(THF)_2 + 2\ Li + 2\ \textit{trans}\text{-}PhCH{=}CHPh \xrightarrow{DME} \underset{\mathbf{1}}{(PhCHCHPh)Sm(DME)_2}$$

Complex **1** is readily soluble in THF and sparingly soluble in DME; it is extremely sensitive to oxygen and air moisture. The IR spectrum of **1** contains bands at 700 and 760 cm^{-1} (C—H) and 1600 cm^{-1} (C—C of the benzene rings), in addition to the band of coordinated DME (1050 cm^{-1}). The pronounced change in the ratio of the intensities of the bands corresponding to the C—H and C—C vibrations in the spectrum of **1** with respect to this ratio in the spectrum of the starting *trans*-stilbene points to substantial participation of the benzene rings in the metal—ligand interaction. Magnetic measurements showed that the magnetic moment of **1** is 3.7 μ_B, which is in good agreement with the values observed for compounds of divalent samarium.[5] Hydrolysis of **1** affords 1,2-diphenylethane. Thus the description of the structure of compound **1** as a complex of divalent samarium with the stilbene dianion does not contradict experimental data.

Complex **1** reacts with hydrogen in THF at room temperature under atmospheric pressure. The reaction gives 1,2-diphenylethane and divalent samarium hydride **2**, which precipitates as a red-brown amorphous powder upon the addition of hexane to the tetrahydrofuran solution.

$$\underset{\mathbf{1}}{(PhCHCHPh)Sm(DME)_2} + H_2 \xrightarrow{THF} \underset{\mathbf{2}}{SmH_2(THF)_2} + PhCH_2CH_2Ph$$

Recently,[6] we prepared this compound by hydrogenation of naphthalenesamarium $C_{10}H_8Sm(THF)_3$ with hydrogen under comparable conditions. The physicochemical characteristics of samples synthesized in this study and those prepared previously[6] coincide.

The reaction of **1** with hexamethyldisilazane in DME proceeds rather easily, giving rise to the divalent samarium amide $[(Me_3Si)_2N]_2Sm(DME)_2$ and *trans*-stilbene.

$$\underset{\mathbf{1}}{(PhCHCHPh)Sm(DME)_2} + 2\ (Me_3Si)_2NH \xrightarrow{DME} [(Me_3Si)_2N]_2Sm(DME)_2 + PhCHCHPh + H_2$$

The physicochemical characteristics of the complex are identical with those reported previously[7] for this compound synthesized by transmetallation of $[(Me_3Si)_2N]_2Hg$ on treatment with metallic samarium.

An attempt to use complex **1** as the starting compound for the synthesis of germyl samarium derivatives failed. The reaction of this complex with Ph_3GeH yields digermane $Ph_3GeGePh_3$ instead of the expected complex $[(Ph_3Ge)_2Sm(DME)_x]$, which would be similar to the known Eu^{II} and Yb^{II} analogs (see Refs. 8 and 9, respectively).

It was found that complex **1** is an efficient catalyst of block polymerization of styrene; however, it is inert with respect to propylene.

The reactions of $LaCl_3$, LaI_3, $NdCl_3$, NdI_3, and $LuCl_3$ with 3 equiv. of $[PhCHCHPh]^{\cdot -}M^+$ (M = Li, Na) in THF or DME result in the formation of dark-colored solutions and in the precipitation of NaCl (when lanthanide chlorides are used); however, we could not isolate stilbene derivatives of Ln^{III} in a pure state.

The reaction of $CpLuCl_2(THF)_3$ with $[PhCHCHPh]^{\cdot -}Na^+$ in a molar ratio of 1 : 2 in DME gives rise to *ate*-complex **3** (in 47% yield) rather than to a mixed cyclopentadienyl stilbene complex of lutetium. This product is formed as a result of several reactions, namely, dimerization of stilbene radical anions, resulting in the 1,2,3,4-tetraphenylbutane dianion and redistribution of the cyclopentadienyl rings between two half-sandwich CpLu fragments leading to a Cp_2Lu group.

$$CpLuCl_2(THF)_3 + 2\ (PhCHCHPh)Na \xrightarrow[-2\ NaCl]{DME} \underset{\mathbf{3}}{\{Cp_2Lu[\mu\text{-}CH(Ph)CH(Ph)CH(Ph)CH(Ph)]\}Na(DME)_3}$$

It should be noted that disproportionation of $CpLnX_2$ molecules has also been observed previously for metals of both the beginning and the end of the lanthanides series.[4,10,11]

Complex **3** is a bright yellow diamagnetic crystalline substance sensitive to moisture and oxygen, sparingly soluble in THF, DME, and pyridine, and insoluble in aromatic and aliphatic hydrocarbons. Its IR spectrum contains an array of absorption bands typical of the cyclopentadienyl ligand (780, 1020 cm^{-1}) and molecules of coordinated DME (1080 cm^{-1}). Unlike the spectrum of the starting *trans*-stilbene, in the spectrum of complex 3, the bands corresponding to the C—C (1600 cm^{-1}) and C—H (700 and 770 cm^{-1}) vibrations of monosubstituted benzene rings are split and represented by the following set of bands: 1590 and 1580, 695 and 710, and 750 and 770 cm^{-1}.

Unfortunately, due to the poor quality of the crystals of 3, the results of the X-ray diffraction experiment do not allow one to discuss the bond lengths and angles; nevertheless, they provide information on the composition and the geometry of the molecule. The X-ray diffraction study showed that the lutetium atom in the anion of this compound coordinates two cyclopentadienyl rings according to the η^5-type and the 2σ-bonded 1,2,3,4-tetraphenylbutane ligand (Fig. 1). The cation consists of a sodium ion surrounded by three DME molecules. The presence of the tetraphenylbutane ligand in compound 3 and the general structure of this complex are also confirmed by the result of hydrolysis, which gives 1,2,3,4-tetraphenylbutane in quantitative yield.

Previously,[12] the reaction of an excess of PhC≡CPh with the naphthalene complex $CpLuC_{10}H_8(THF)_2$ also involved the formation of a carbon—carbon bond, resulting in the bridging 1,2,3,4-tetraphenylbut-2-ene ligand linking two CpLu moieties.

The results of studies of compound 3 by ^{1}H and ^{13}C NMR spectroscopy also confirm the composition and structure proposed. The protons of the benzene rings are observed as five groups of signals in the ^{1}H NMR spectrum, while each type of C atoms gives two signals in the ^{13}C NMR spectrum. This indicates the presence of pairs of nonequivalent phenyl groups and methine carbon atoms of the tetraphenylbutane dianion, which is due to the concentration of the negative charge on the terminal carbon atoms involved in the binding to the lutetium atom. Since the ^{1}H NMR signals of the *ortho*-protons of the phenyl groups are not shifted upfield, it is reasonable to conclude that in this compound, unlike the complex $[Na(THF)_6][Y(Ph_2CCPh_2)_2]$,[3] the *ortho*-C atoms of the terminal phenyl groups are not involved in the coordination.

Compound 3 exhibits moderate activity as a catalyst of styrene polymerization (the degree of conversion over a period of 24 h at room temperature does not exceed 25%) and does not exhibit any activity in the case of propylene.

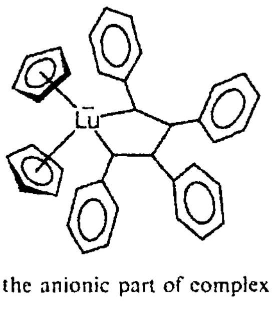

Fig. 1. Structure of the anionic part of complex 3.

Cyclopentadienyldichlorolanthanides $CpLaCl_2(THF)_3$, $CpNdCl_2(THF)_3$, $CpSmCl_2(THF)_3$, $Cp^*SmCl_2(THF)_3$, and $Cp^*LuCl_2(THF)_3$ also react with stilbenesodium in DME; however, in none of these cases, were we able to isolate the lanthanide-containing reaction products in a pure state.

The reaction of Cp_2GdCl with stilbenesodium in THF affords a complex mixture of organogadolinium compounds; one of them is the complex $Cp_3Gd(THF)$, which was isolated in 17% yield.

$$Cp_2GdCl(THF) + [PhCHCHPh]^{\cdot -}Na^+ \xrightarrow[-NaCl]{THF}$$

$$\longrightarrow Cp_3Gd(THF) + \ldots$$

Experimental

The synthesis was carried out under conditions excluding contact with oxygen and air moisture using standard Schlenk equipment. THF, hexane, and toluene were dried over sodium benzophenone ketyl, thoroughly degassed, and recondensed *in vacuo* into a reaction tube directly prior to use. Styrene was dried over 5A molecular sieves. Propylene was purified by passing successively through a column with copper on Kieselguhr, two columns with 3A molecular sieves, and a trap filled with tris-*iso*-butylaluminum. The purified gas was condensed in a trap cooled with liquid nitrogen and recondensed into the reactor *in vacuo*.

IR spectra were recorded on a Specord M-80 instrument; the samples were prepared as suspensions in Vaseline oil between KBr glasses.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-200 instrument. The chemical shifts are given in ppm relative to the known chemical shifts of the residual protons of deuterated solvents.

The organic products were analyzed using a Milichrom 1A microcolumn liquid chromatograph (UV detector with variable wavelength, λ = 250 nm, a 64×2 mm steel column, adsorbent Separon S6X (15 μm), elution with hexane—THF, 200 : 1 (v/v), eluent flow rate 200 μL min^{-1}). The volatile organic products were analyzed on a Tsvet-530 instrument (detection by katharometer, a 2 m×3 mm steel column, 5% SE-30 Chromaton N-AW, helium as the carrier gas).

Magnetic measurements were carried out by the known procedure.[13] The content of lanthanide in the complexes was determined by complexometry.

1,2-Diphenylethane-1,2-diidesamarium bis(1,2-dimethoxyethanate), (PhCHCHPh)Sm(DME)$_2$ (1). *trans*-Stilbene (0.64 g, 3.55 mmol), metallic lithium (0.025 g, 3.57 mg-at.), $SmI_2(THF)_2$ (0.98 g, 1.78 mmol), and 10 mL of DME were placed in a tube. The reaction mixture was stirred for 24 h at –20 °C. The resulting dark-brown crystals were filtered off, washed with DME, and dried *in vacuo* at –20 °C to give 0.58 g (63.8%) of compound 1. Found (%): C, 51.33; H, 5.88; Sm, 29.38. $C_{22}H_{32}O_4Sm$. Calculated (%): C, 51.74; H, 6.26; Sm, 29.45. μ_{eff} = 3.7 μ_B (293 K). IR, ν/cm^{-1}: 1600 (C—C arom.); 1050 (C—O, DME); 700, 760 (C—H arom.).

Hydrolysis of complex 1. 5% HCl (3 mL) was added to complex 1 (0.28 g) in 5 mL of toluene. The organic layer was separated and analyzed. Found 0.09 g (91%) of 1,2-diphenylethane and 0.09 g (92%) of DME.

Reaction of complex 1 with hydrogen. A suspension of complex 1 (0.9 g, 1.76 mmol) in 15 mL of THF was stirred for 5 days in the atmosphere of H_2. The resulting red-brown solution was filtered. The addition of hexane (5 mL) to the reaction mixture gave 0.36 g (69%) of complex **2**. Found (%): C, 31.98; H, 5.66; Sm, 50.22. $C_8H_{18}O_2Sm$. Calculated (%): C, 32.40; H, 6.07; Sm, 50.72. According to HPLC analysis, the mother liquor contained 0.25 g (79%) of 1,2-diphenylethane.

Reaction of complex 1 with hexamethyldisilazane. $(Me_3Si)_2NH$ (3.3 mL, 15.94 mmol) in 20 mL of DME was added with vigorous stirring to a suspension of complex **1** (4.07 g, 7.97 mmol) in 30 mL of DME and the mixture was stirred for 6 h. The reaction was accompanied by hydrogen evolution and the reaction mixture acquired a dark-violet color. After completion of the reaction, the solution was filtered, the solvent was removed *in vacuo*, and the residue was washed with hexane and recrystallized from DME to give 3.1 g (60%) of dark-violet crystals of $[(Me_3Si)_2N]_2Sm(DME)_2$. Found (%): C, 39.12; H, 9.95; Sm, 24.48. $C_{20}H_{56}O_2N_2Si_4Sm$. Calculated (%): C, 38.80; H, 9.11; Sm, 24.29. According to HPLC analysis, the hexane extracts contained 1.31 g (92%) of stilbene.

Reaction of complex 1 with triphenylgermane. A solution of Ph_3GeH (0.67 g, 2.16 mmol) in 10 mL of THF was added to a suspension of complex **1** (0.55 g, 1.08 mmol) in 25 mL of THF. The reaction mixture was stirred for 12 h at ~20 °C; the mixture turned red and a small amount of hydrogen evolved. After completion of the reaction, the solution was filtered and concentrated to half its volume to give white crystals of $Ph_3GeGePh_3$ (0.56 g, 86%). The melting point of the product and that of a mixture with an authentic hexaphenyldigermane were 340—342 °C. After separation of the $Ph_3GeGePh_3$ precipitate, the solvent was removed from the solution under reduced pressure. The residue was washed with hexane. According to HPLC analysis, the hexane extracts contained 0.18 g (95%) of 1,2-diphenylethane. No individual samarium-containing products were isolated.

Reaction of $CpLuCl_2(THF)_3$ with $[PhCHCHPh]^{\cdot-}Na^+$. $CpLuCl_2(THF)_3$ (0.53 g, 1.02 mmol) was added to a solution of stilbenesodium, prepared from *trans*-stilbene (0.36 g, 2.04 mmol) and sodium (0.046 g, 2.04 mg-at.), in 25 mL of DME and the mixture was stirred for 18 h at ~20 °C. The resulting yellow-brown solution was filtered, concentrated to half its initial volume, and allowed to stand at 10 °C. The resulting bright yellow crystals of **3** were washed with cold DME and dried *in vacuo* at ~20 °C to give 0.44 g (47%) of compound **3**. Found (%): C, 64.30; H, 6.67; Lu, 18.86. $C_{50}H_{64}LuNaO_6$. Calculated (%): C, 64.26; H, 6.84; Lu, 18.72. IR, ν/cm^{-1}: 1590, 1580 (C—C arom.); 1080 (C—O, DME); 1020 (C—H, Cp); 780 (C—H, Cp); 695, 710, 750, 770 (C—H arom.). ^{1}H NMR (pyridine-d_5), δ: 3.26 (s, 18 H, CH_3, DME); 3.48 (s, 12 H, $-CH_2-$, DME); 3.75—3.87 (m, 4 H, methine CH); 6.25 (s, 10 H, Cp); 6.42, 6.70 (both t, each 2 H, *p*-CH arom.); 7.02 (t, 4 H, *m*-CH arom.); 7.05—7.15 (m, 8 H, *m*- and *o*-CH arom.); 7.33 (d, 4 H, *o*-CH arom., J = 8 Hz). ^{13}C NMR, δ: 55.53 (methine); 58.23 (MeO); 61.36 (methine); 71.64 (CH_2); 110 (Cp); 113.42 (*o*-C arom.); 123.43 (*o*-C arom.); 126.64 (*m*-C arom.); 127.50 (*p*-C arom.); 127.67 (*p*-C arom.); 128.77 (*m*-C arom.); 151.36 (*ipso*-C arom.); 156.83 (*ipso*-C arom.).

Reaction of Cp_2GdCl with $[PhCHCHPh]^{\cdot-}Na^+$. A solution of stilbenesodium, prepared by the reaction of *trans*-stilbene (0.43 g, 2.38 mmol) and sodium (0.054 g, 2.34 mg-at.), was added with vigorous stirring at 0 °C to a solution of Cp_2GdCl (0.76 g, 2.35 mmol) in 25 mL of THF. The reaction mixture was stirred for 18 h at ~20 °C and filtered and the solvent was removed *in vacuo*. The orange oily residue was extracted with hexane. In hexane extracts, 0.4 g (95%) of stilbene was found. Slow diffusion of hexane (5 mL) to a solution of the residue in 15 mL of THF gave 0.17 g (17%) of $Cp_3Gd(THF)$ as colorless crystals. Found (%): C, 53.55; H, 4.99; Gd, 37.17. $C_{19}H_{23}OGd$. Calculated (%): C, 53.74; H, 5.46; Gd, 37.03. μ_{eff} = 8.0 μ_B (293 K). IR, ν/cm^{-1}: 1020, 860 (C—O, THF); 760, 700 (C—H arom.).

Block polymerization of styrene. Styrene (2.7 g, 3 mL) and a catalyst (3—5% (w/w)) were placed in an evacuated tube. The reaction mixture was stirred at ~20 °C for 24 h. Polymerization catalyzed by complex **1** was over in 5 min and resulted in complete monomer conversion. The polymer was dissolved in THF, 0.5 mL of methanol was added to decompose the catalyst, and the mixture was filtered through a Schott filter. To precipitate the polymer, 30 mL of methanol was added to the filtrate.

Polymerization of propylene. A catalyst (3—5% (w/w)) was placed in an evacuated tube, 10 mL of toluene was added, and a calculated amount of dry propylene was condensed into the tube. The reaction mixture was stirred for ~20 °C under atmospheric pressure of propylene for 24 h. Methanol (0.5 mL) was added to neutralize the catalyst and then the products of catalyst decomposition were separated on a Schott filter. Methanol (30 mL) was added to the filtrate. No polymer precipitation was observed.

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