Organoerbium compounds containing dendritic ligands

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The reactions of $Er[N(SiMe_3)_2]_3$ with phenylethynyl dendrons of the first and second generations gave complexes of erbium with dendritic ligands, $Er[C\equiv CC_6H_3(C\equiv CPh)_2\text{-}3,5]_3$ and $Er\{C\equiv CC_6H_3[C\equiv CC_6H_3(C\equiv CPh)_2\text{-}3,5]_2\text{-}3,5\}_3$.

Key words: dendrimers, organoerbium compounds, erbium, phenylethynyl dendrons.

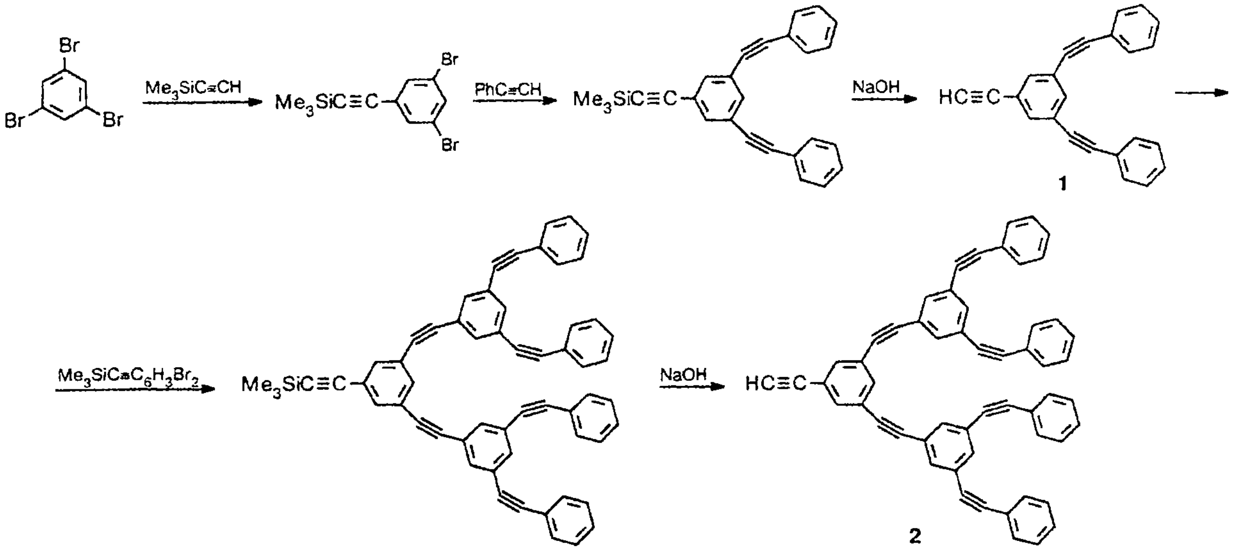
Presently, the synthesis and studies of organometallic dendritic compounds attract particular attention due to their unique structures and properties. A great number of these compounds, which contain atoms of transition and main-group elements in terminal groups, in macrochain units, or in the center of the dendritic molecule as the original nucleus, were prepared. Almost all of these compounds were synthesized according to a multistage divergent scheme.[1-5] A convergent method was used primarily for preparing organic dendrimers (dendrons).[6] Organic dendrimers can be considered as promising ligands in organometallic chemistry. In this work, we report for the first time the synthesis of organolanthanide dendritic compounds. We used a convergent method for the synthesis. At the final stage of the synthesis, dendrons are attached to the metal atom, which acts as the original nucleus of the dendritic molecule formed.

Results and Discussion

It is known that silylamide derivatives of lanthanides, $Ln[N(SiMe_3)_2]_3$, react readily with compounds that contain an active hydrogen atom (RH) to form hexamethyldisilazane and the corresponding complex LnR_3.[7] In particular, phenylethynyl complexes $Ln(C\equiv CPh)_3$ (Ln = Pr, Sm, Eu, Gd, Tb, Er, or Yb) were prepared according to this approach.[8] We used this reaction for preparing dendritic phenylethynyl compounds of erbium.

The starting phenylethynyl dendrons of the first (**1**) and second (**2**) generations were prepared according to a convergent procedure, which has been developed previ-

Scheme 1



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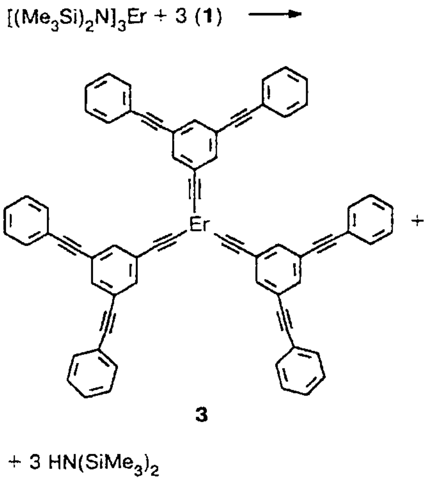
ously for phenylethynyl dendrons containing peripheral 3,5-di-*tert*-butylphenyl groups[9] (Scheme 1).

Cross-coupling of phenylacetylene with 3,5-dibromophenyl-1-trimethylsilylacetylene catalyzed by organopalladium compounds was carried out in evacuated vessels with the aim of eliminating side reactions (dimerization and resinification of phenylacetylene, monomers, and the resulting dendrons), which are catalyzed by molecular oxygen. We have found that in this case the use of CuI_2, which is a usual cocatalyst of the reaction, resulted in complication of the reaction. When the reaction was carried out in the absence of CuI_2, the yields of the dendrons of the first and second generations were increased to 76 and 52%, respectively.

According to the data of computer simulation, dendrons are rigid planar molecules.

The reaction of $[(Me_3Si)_2N]_3Er$ with 3 equivalents of dendron **1** occurred readily at ~20 °C and afforded dendrimer **3** in 75% yield. In the volatile products, silazane was found in approximately quantitative yield.



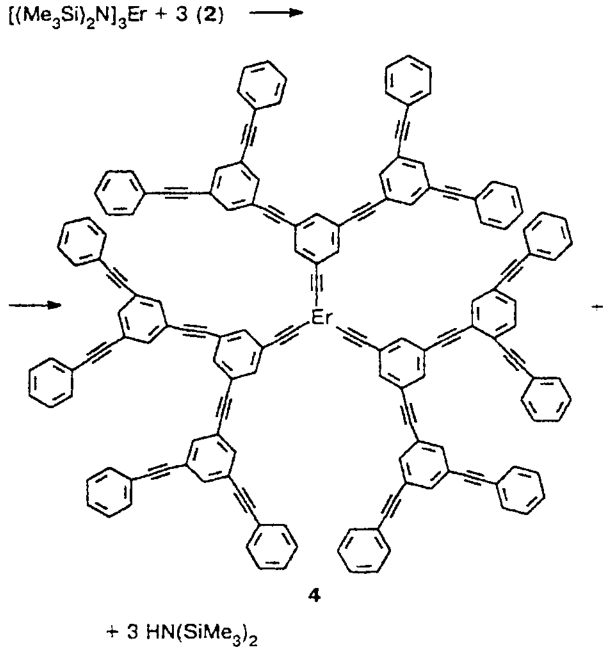
$[(Me_3Si)_2N]_3Er + 3\ (\mathbf{1}) \longrightarrow$

3

$+\ 3\ HN(SiMe_3)_2$

The reaction of erbium amide with the dendron of the second generation **2** was carried out analogously to give dendrimer **4** in 84% yield (Scheme 2).

Scheme 2



$[(Me_3Si)_2N]_3Er + 3\ (\mathbf{2}) \longrightarrow$

4

$+\ 3\ HN(SiMe_3)_2$

It should be noted that the reaction of the reagents taken in a molar ratio of 1 : 2 or 1 : 1 gave no asymmetrical complexes. Air-unstable compounds **3** and **4** are soluble in THF, DME, and toluene and are poorly soluble in hexane. When heated above 330 °C, these compounds decomposed without melting. The IR spectra of complexes **3** and **4** are identical, which indicates that their structures are similar. These spectra contain a series of bands typical of terminal monosubstituted aromatic rings (ν 720 and 750 cm^{-1}) and bands, which characterize the C—H bond of the trisubstituted benzene ring (at 650, 740, and 840 cm^{-1}). The stretching vibrations of the C≡C bond in the Er—C≡C fragment are observed at 2040 cm^{-1}. Apparently, this spectrum does not show the absorption band of the C≡C bond between the benzene rings, which is observed in the case of the initial ligands at 2200 cm^{-1}, because of the symmetry. Hydrolysis of complex **3** in toluene gave dendron **1** in 86% yield. Hydrolysis in THF afforded a complex mixture of products among which we failed to detect dendron **1**. In the case of dendrimer **4**, hydrolysis both in toluene and THF gave a mixture of phenylethynyl derivatives, which was difficult to separate and which did not contain the expected dendron **2**. The IR spectrum of this mixture shows all bands typical of the initial ligand, except for the band typical of the C—H bond in the C≡C—H group. An analogous spectrum was observed for a mixture of products of hydrolysis of dendrimer **3** in THF.

The magnetic moments of the resulting compounds **3** and **4** (9.6 μ_B) correspond to the values typical of organic compounds of trivalent erbium (9.6 μ_B).[10]

Taking into account the large size of dendrons **1** and **2**, one could expect that dendritic erbium compounds obtained on the basis of these dendrons would exhibit enhanced stability with respect to atmospheric oxygen and moisture. However, it appeared that these complexes, like other organolanthanide derivatives, are sensitive to air. Apparently, planar phenylethynyl dendrons, in spite of their large size, do not provide sufficient shielding of the central Er atom.

Experimental

All reactions were carried out in evacuated tubes under conditions which excluded exposure to atmospheric oxygen and moisture. The solvents were purified according to standard procedures and were distilled into a reaction tube before use. Chromatographic analysis was performed on a Tsvet-104 gas chromatograph (3-m column, 10% PEG-20M on Chromaton N-AW) and on a Milikhrom-1A liquid chromatograph (a 64×2-mm steel column, SGX (5-μm) was used as the adsorbent, and hexane was used as the eluent). The erbium content was determined chelatometrically. The IR spectra were recorded on a Perkin—Elmer 577 instrument as Nujol mulls. Magnetic moments were measured according to a known procedure.[11]

1,3,5-Tribromobenzene was prepared according to a standard procedure by diazotization of 2,4,6-tribromoaniline, which was obtained by bromination of aniline. The ($\mathrm{Me_3SiC{\equiv}CC_6H_3Br_2}$) monomer and erbium tris[bis(trimethylsilyl)amide] were prepared according to known procedures.[9,12]

3,5-Bis(phenylethynyl)phenylacetylene, 3,5-$(\mathrm{PhC{\equiv}C})_2\mathrm{C_6H_3C{\equiv}CH}$, (1). $\mathrm{PhC{\equiv}CH}$ (6.3 mL, 0.06 mol) was added to a solution of $\mathrm{Me_3SiCC{\equiv}CC_6H_3Br_2}$ (9.52 g, 0.03 mol), $\mathrm{Pd(dba)_2}$ (0.33 g, 0.0006 mol), and $\mathrm{PPh_3}$ (1.07 g, 0.004 mol) in $\mathrm{Et_3N}$ (20 mL). The reaction mixture was stirred at 40—50 °C for 170 h. The resulting solution was separated from the precipitate by filtration. The solvent was removed *in vacuo*. Column chromatography on $\mathrm{Al_2O_3}$ (hexane as the eluent) gave $\mathrm{Me_3SiC{\equiv}CC_6H_3(C{\equiv}CPh)_2}$ in a yield of 6.62 g (76%). IR, ν/cm^{-1}: 2200, 2140 ($\mathrm{SiMe_3}$), 1240 ($\mathrm{SiMe_3}$), 840, 750, 740, 720, 650. The compound obtained was dissolved in EtOH (30 mL), and a 30% NaOH solution in EtOH (10 mL) was added. The reaction mixture was stirred for 10 min. Then water (200 mL) was added, the mixture was extracted with hexane (3×20 mL), and the extract was washed with water and dried with $\mathrm{MgSO_4}$. The solvent was evaporated, and compound **1** was obtained in a yield of 6.6 g (75.7% with respect to the starting $\mathrm{Me_3SiC{\equiv}CC_6H_3Br_2}$) as a flocculent amorphous yellow powder. IR, ν/cm^{-1}: 3260, 2200, 840, 750, 740, 720, 650. According to the data of liquid chromatography, the product contained 7% of phenylethynyl compounds devoid of the terminal acetylenic bond.

3,5-Bis[3,5-bis(phenylethynyl)phenylethynyl]phenylacetylene, 3,5-$\{3,5\text{-}(\mathrm{PhC{\equiv}C})_2\mathrm{C_6H_3C{\equiv}C}\}_2\mathrm{C_6H_3C{\equiv}CH}$, (2). The reaction of $\mathrm{Me_3SiC{\equiv}CC_6H_3Br_2}$ (3.1 g, 0.009 mol) with 3,5-$(\mathrm{PhC{\equiv}C})_2\mathrm{C_6H_3C{\equiv}CH}$ (6.3 g, 0.02 mol) under the conditions described above afforded dendron **2** as a flocculent amorphous yellow-brown powder in a yield of 3.3 g (50.4% with respect to the starting $\mathrm{Me_3SiC{\equiv}CC_6H_3Br_2}$). IR, ν/cm^{-1}: 3280, 2240, 840, 750, 740, 720, 650. According to the data of liquid chromatography, the product contained 9% of phenylethynyl compounds devoid of the terminal acetylenic bond.

Tris[3,5-bis(phenylethynyl)phenylethynyl]erbium, $\mathrm{Er[C{\equiv}CC_6H_3(C{\equiv}CPh)_2]_3}$, (3). A solution of dendron **1** (1.21 g, 4.0 mmol) in toluene (10 mL) was added to a solution of $\mathrm{Er[N(SiMe_3)_2]_3}$ (0.86 g, 1.3 mmol) in toluene (15 mL). The color of the solution gradually changed from pale-pink to dark-brown. The mixture was kept at ~20 °C for 45 min. The solvent and volatile products were removed by *in vacuo*. According to the data of GLC, the hexamethyldisilazane content of the volatile products was 99%. The solid residue was washed with cold ether and reprecipitated from toluene with hexane. Complex **3** was obtained as an amorphous dark-brown powder, which decomposed above 330 °C, in a yield of 1.065 g (75%). Found: Er, 15.1%. $\mathrm{C_{72}H_{39}Er}$. Calculated: Er, 15.61%. IR, ν/cm^{-1}: 2040, 840, 750, 740, 720, 650. The magnetic moment (293 K): μ_{eff} = 9.6 μ_B. After hydrolysis in toluene, compound **1** was isolated from the organic layer in 86% yield.

Tris{3,5-bis[3,5-bis(phenylethynyl)phenylethynyl]phenylethynyl}erbium, $\mathrm{Er\{C{\equiv}CC_6H_3[C{\equiv}CC_6H_3(C{\equiv}CPh)_2]_2\}_3}$, (4). A solution of dendron **2** (1.04 g, 1.5 mmol) in toluene (15 mL) was added to a solution of $\mathrm{Er[N(SiMe_3)_2]_3}$ (0.32 g, 0.5 mmol) in toluene (10 mL). The color of the solution changed from pale-pink to dark-brown. The mixture was kept at ~20 °C for 45 min. The solvent and volatile products were removed *in vacuo*. The solid residue was washed with cold ether, dissolved in toluene, and precipitated with hexane. Compound **4** was obtained as an amorphous dark-brown powder, which decomposed above 330 °C, in a yield of 0.94 g (84%). Found: Er, 7.40%. $\mathrm{C_{168}H_{87}Er}$. Calculated: Er, 7.36%. IR, ν/cm^{-1}: 2040, 840, 750, 740, 720, 650. The magnetic moment (293 K): μ_{eff} = 9.6 μ_B.

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