

# A Multifunctional Substituted Cyclooctatetraene as a Ligand in Organosamarium Chemistry

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Received April 12, 1999

The reactivity of the multifunctionalized cyclooctatetraene  $\text{Li}_2(1,4\text{-R}_2\text{C}_8\text{H}_6)$  ( $\text{R} = o$ -(dimethylsilyl)-*N,N*-dimethylaniline) is reported. To obtain this ligand in large quantities, a new, safe, and convenient method for the preparation of cyclooctatetraene was developed. The ionic complex  $[\text{Li}(\text{diglyme})_2][\{1,4\text{-R}_2\text{C}_8\text{H}_6\}_2\text{Sm}_2(\mu\text{-Cl})_3]$  was synthesized by the reaction of the ligand with  $\text{SmCl}_3$  and characterized by single-crystal X-ray diffraction. The anion of the new complex is an unique example of a dimeric organolanthanide complex which is  $\mu_2$ -bridged by three chlorine atoms. In the solid state the donor functionality does not coordinate to the samarium center. As shown by spin lattice relaxation experiments, there is a coordination of one amino group to the samarium atom in solution. Density functional theory (DFT) calculations show that this coordination might in principle be in an intramolecular fashion. Reaction of  $\text{Li}_2(1,4\text{-R}_2\text{C}_8\text{H}_6)$  with  $[(\text{C}_8\text{H}_8)\text{SmI}(\text{THF})_2]$  does not lead to a mixed-sandwich complex. By a ligand rearrangement the nonfunctionalized complex  $[\text{Li}(\text{THF})_3\{\mu\text{-}(\eta^2\text{:}\eta^8\text{-C}_8\text{H}_8)\}\text{Sm}(\text{C}_8\text{H}_8)]$  was isolated and characterized by single-crystal X-ray diffraction analysis.

## Introduction

The coordination chemistry of cyclopentadienyl ligands that contain an additional coordination site appended to the ring periphery by a covalent bridge has seen an enormous amount of interest since Bercaw and Shapiro replaced one ring ligand with a *tert*-butylamido group in the classic *ansa*-metallocene.<sup>1</sup> Today, group 4 metal complexes containing an amidocyclopentadienyl ligand have considerable importance as homogeneous polymerization catalysts in the presence of methylalumoxane.<sup>2</sup> In addition to the complexes used for catalytic applications, a huge number of main-group and transition-metal complexes containing the cyclopentadienyl ligand (or its derivatives) are also known<sup>3</sup> in which at least one additional coordination site is tethered via a bridge to the five-membered ring such as  $\text{BR}_2$ ,<sup>4</sup>  $-\text{CH}=\text{CH}_2$ ,<sup>5</sup>  $\text{NR}$ ,<sup>1,2,6</sup>  $\text{NR}_2$ ,<sup>7</sup>  $\text{PR}_2$ ,<sup>8</sup>  $\text{O}$ ,<sup>9</sup>  $\text{OR}$ ,<sup>10</sup> and  $\text{SR}$ .<sup>11</sup>

There are a number of advantages for bi- or multifunctional ligands. First, the additional donor tethered to the ligand could stabilize the binding of the entire ligand framework by forming an additional bond to the metal center, thus preventing decomposition reactions. Second, if the additional donor is a weakly coordinating donor, it will be possible to design semilabile ligands.

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Third, it is known that functional groups tethered to a cyclopentadienyl have a significant impact on the catalytic activity of group 3 and group 4 metallocenes.<sup>2,3a</sup>

The concept of bi- or multifunctional ligands is mainly based on cyclopentadienyl or its derivatives. Recently, we have begun to study the properties of cyclooctatetraene sandwich complexes that contain additional coordination sites tethered via a bridge to the periphery of the eight-membered rings.<sup>12</sup> The new ligand 1,4-bis- $[\sigma$ -(dimethylsilyl)-*N,N*-dimethylaniline]cyclooctatetraenide dianion and the preparation of organolanthanide sandwich complexes  $[\text{Li}(\text{diglyme})_2]^+[\text{Ln}(1,4\text{-R}_2\text{C}_8\text{H}_6)_2]^-$  (Ln = Nd, Sm; R =  $\sigma$ -(dimethylsilyl)-*N,N*-dimethylaniline) were reported by us.<sup>12</sup> To the best of our knowledge, they are the first examples of structurally characterized cyclooctatetraene complexes with a donor functionality attached to the eight-membered ring. Only two bis( $\eta^8$ -cyclooctatetraene)uranium complexes (uranocenes),  $\text{U}(\text{C}_8\text{H}_7\text{R})$  (R =  $-\text{CH}_2\text{NMe}_2$ ,  $-(\text{CH}_2)_3\text{NMe}_2$ ), which could not be characterized by single-crystal X-ray studies, have been reported by Streitwieser.<sup>13</sup> In this contribution, we report on the synthesis of a half-sandwich complex by using the new donor-functionalized cyclooctatetraene ligand system. Additionally, a new method for the preparation of cyclooctatetraene is given.

## Experimental Section

**General Considerations.** All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual-manifold Schlenk line, interfaced to a high-vacuum ( $10^{-4}$  Torr) line, or in an argon-filled Braun Atmospheres glovebox. Ether solvents (tetrahydrofuran and ethyl ether) were predried over Na wire and distilled under nitrogen from Na/K alloy benzophenone ketyl. Hydrocarbon solvents (toluene and pentane) were distilled under nitrogen from Na wire. All solvents for vacuum line manipulations were stored in vacuo over Na/K alloy in resealable flasks. Deuterated solvents were obtained from Aldrich (all 99 atom % D) and were degassed, dried, and stored in vacuo over Na/K alloy in resealable flasks. NMR spectra were recorded on a Bruker AC 250 instrument. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. IR spectra were performed on a Bruker IFS 28; mass spectra were recorded at 70 eV on Varian MAT 711. Elemental analyses were performed at the microanalytical laboratory of the Institute of Inorganic Chemistry in Karlsruhe. Dilithium 1,4-bis- $[\sigma$ -(dimethylsilyl)-*N,N*-dimethylaniline]cyclooctatetraenide (THF adduct) (**1**)<sup>12</sup> and  $[(\text{C}_8\text{H}_8)\text{Sm}(\text{THF})_2]$ <sup>14</sup> were prepared by literature procedures.

**Preparation of Cyclooctatetraene.** To a solution of 35 mL (300 mmol) of cyclooctadiene in 100 mL of pentane was slowly added 563 mL of a 1.6 M (900 mmol) *n*BuLi solution in hexane at 0 °C. Then, 135 mL (900 mmol) tetramethylethylenediamine was added to the solution. The mixture was stirred for 2 days. The solution turned red, and after 1 day orange crystals precipitated. Next, 80 g (300 mmol) of solid  $\text{HgCl}_2$  was slowly added at 0 °C. The organic layer was then washed with 5 M HCl (3  $\times$  25 mL) and 50 mL of water. Finally, the remaining mixture was distilled at normal pressure. Yield: 14.0 g (45%). <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ , 250 MHz, 25 °C):  $\delta$  5.79 (s).

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**Preparation of  $[\text{Li}(\text{diglyme})_2]^+[(1,4\text{-R}_2\text{C}_8\text{H}_6)_2\text{Sm}_2(\mu\text{-Cl})_3]^-$  (R =  $\sigma$ -(Dimethylsilyl)-*N,N*-dimethylaniline **2**).** THF (20 mL) was condensed at  $-196$  °C onto a mixture of 308 mg (1.2 mmol) of  $\text{SmCl}_3$  and 473 mg (1 mmol) of **1**. Then the mixture was stirred for 12 h at room temperature. The solvent was evaporated in vacuo, and ether (10 mL) was condensed onto the mixture. Then, the violet solution was filtered and the solvent removed under vacuum. Finally, 80 mg of the remaining solid was dissolved in 4 mL of ether and 15 mL of pentane that contained 1 mL of diglyme was layered on top. After 2 days purple needle-shaped crystals were obtained. Yield: 230 mg (28%). <sup>1</sup>H NMR ( $d_8$ -THF, 250 MHz, 25 °C):  $\delta$  0.12 (s, 6 H,  $\text{CH}_3\text{Si}$ ), 0.26 (s, 3 H,  $\text{CH}_3\text{Si}$ ), 0.38 (s, 3 H,  $\text{CH}_3\text{Si}$ ), 2.59 (s, 6 H,  $\text{CH}_3\text{N}$ ), 2.85 (s, 6 H,  $\text{CH}_3\text{N}$ ), 2.96 (s, 3 H,  $\text{CH}_3\text{N}$ ), 6.69–7.53 (m, 8 H, Ph), 9.99 (br, 2 H, COT), 10.62 (br, 2 H, COT), 11.44 (br, 2 H, COT). <sup>13</sup>C{<sup>1</sup>H} NMR ( $d_8$ -THF, 62.9 MHz, 25 °C):  $\delta$  1.2 ( $\text{CH}_3\text{Si}$ ), 2.2 ( $\text{CH}_3\text{Si}$ ), 2.3 ( $\text{CH}_3\text{Si}$ ), 46.2 ( $\text{CH}_3\text{N}$ ), 47.1 ( $\text{CH}_3\text{N}$ ), 47.2 ( $\text{CH}_3\text{N}$ ), 84.7 (COT), 85.7 (COT), 87.8 (COT), 88.0 (COT), 95.5 (COT), 95.9 (COT), 121.2 (Ph), 124.5 (Ph), 129.9 (Ph), 137.2 (Ph), 141.5 (Ph), 161.6 (Ph). <sup>29</sup>Si NMR ( $d_8$ -THF, 49.7 MHz, 25 °C):  $\delta$  11.5. Anal. Calcd for  $\text{C}_{68}\text{H}_{102}\text{Cl}_3\text{-LiN}_4\text{O}_6\text{Si}_4\text{Sm}_2$ : C, 51.11; H, 6.43; N, 3.51. Found: C, 50.79; H, 6.08; N, 3.72.

**Preparation of  $[\text{Li}(\text{THF})_3\{\mu\text{-}(\eta^2\text{-}\eta^8\text{-C}_8\text{H}_8)\}\text{Sm}(\text{C}_8\text{H}_8)]$  (**3**).** THF (20 mL) was added at 0 °C onto a mixture of 562 mg (1.0 mmol) of  $[(\text{C}_8\text{H}_8)\text{Sm}(\text{THF})_2]$  and 617 mg (1.0 mmol) of **1**. Then the mixture was stirred for 24 h at room temperature. The solvent was evaporated in vacuo, and 20 mL of ether was added onto the residue. Then, the violet solution was filtered and onto 4 mL of the solution 4 mL of ether and 8 mL of hexane were layered on top. After 4–6 days red-brown crystals were obtained. Yield: 200 mg (34%). <sup>1</sup>H NMR ( $d_8$ -THF, 250 MHz, 25 °C):  $\delta$  13.2.

**X-ray Crystallographic Studies of **2**.** Crystals of  $\text{C}_{73}\text{H}_{112}\text{-Cl}_3\text{LiN}_4\text{O}_6\text{Si}_4\text{Sm}_2$  (**2**) were grown from a THF/pentane/diglyme solution. A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to the  $-73$  °C cold  $\text{N}_2$  stream of a STOE IPDS diffractometer. Subsequent computations were carried out on a SGI Power Challenge.

Systematic absences and successful refinement of the proposed structure showed **2** to crystallize in the space group  $C2/c$  (No. 15). The structure was solved by the Patterson method (SHELXS-86<sup>15</sup>) and refined by full-matrix least-squares methods using the program SHELXL-93.<sup>16</sup> The atoms were refined anisotropically, except for C29–C37 and O. The hydrogen atom positions were calculated in ideal geometry and were not refined. The final cycle of full-matrix least-squares refinement was based on 18 521 reflections measured, of which 5231 were independent reflections and 3919 were considered observed ( $I > 2.0\sigma(I)$ ), and 655 variable parameters and converged with  $R1 = 0.0462$  and  $wR2 = 0.1207$ . The maximum and minimum peaks on the final difference Fourier map were 1.174 and  $-0.770$  e/Å<sup>3</sup>, respectively. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication (No. CCDC-125066). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax, +44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

**X-ray Crystallographic Studies of **3**.** Crystals of  $\text{C}_{28}\text{H}_{40}\text{-LiO}_3\text{Sm}$  (**3**) were grown from a pentane/THF (1:1) solution. A suitable crystal was covered with mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to the  $-70$  °C cold  $\text{N}_2$  stream of an STOE STADI/IV diffractometer. Subsequent computations were carried out on a SGI Power Challenge.

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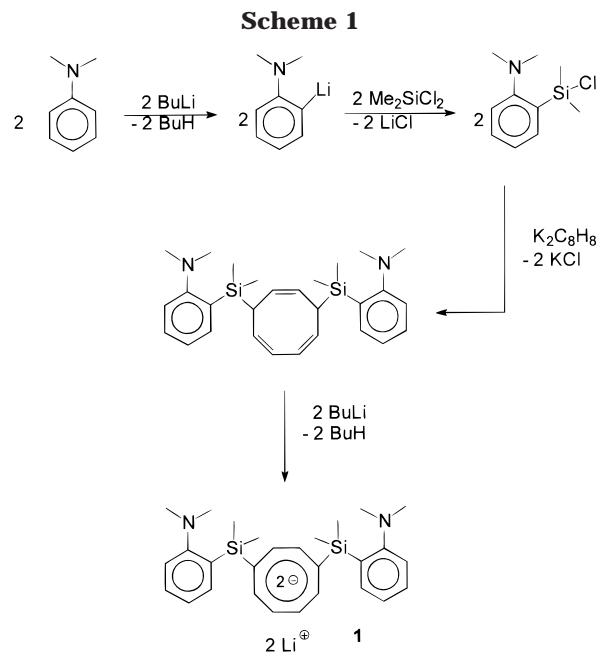
Lattice parameters were determined for 30 angle reflections set in the range  $15.0^\circ < 2\theta < 24.0^\circ$ . Systematic absences and successful refinement of the proposed structure showed **3** to crystallize in the space group  $P2_1/m$  (No. 11). Intensities of two standard reflections were measured every 2 h of X-ray exposure and showed no significant variations. An empirical absorption correction based on  $\psi$ -scan data was applied to **3**. The structure was solved by the Patterson method (SHELXS-86<sup>15</sup>) and refined by full-matrix least-squares methods using the program SHELXL-93.<sup>16</sup> All non-hydrogen atoms were refined anisotropically, except for C9–C14. The hydrogen atom positions were calculated in ideal geometry and were not refined. The final cycle of full-matrix least-squares refinement was based on 2314 reflections measured, of which 2314 were independent reflections and 1971 were considered observed ( $I > 2.0\sigma(I)$ ), and 137 variable parameters and converged with  $R1 = 0.0419$  and  $wR2 = 0.0934$ . The maximum and minimum peaks on the final difference Fourier map were 0.953 and  $-0.745 \text{ e}/\text{\AA}^3$ , respectively. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication (No. CCDC-125067). See the previous section for contact information for the CCDC.

**Methods of the Theoretical Investigations.** The density functional theory (DFT)<sup>17</sup> investigations were carried out by employing the program system TURBOMOLE<sup>18</sup> using the efficient RIDFT program<sup>19,20</sup> with the Becke–Perdew (B-P) functional<sup>21</sup> and the grid size m5. The RIDFT program has been developed on the basis of the DFT program,<sup>22</sup> approximating the coulomb part of the two-electron interactions. Basis sets were of SV(P) quality (SV(P) = split valence plus polarization for all non-hydrogen atoms, split valence for hydrogen atoms),<sup>23</sup> the Sm atom being treated with an effective core potential (ECP). The latter serves as approximation for inner electrons considering relativistic effects. Since f electrons are not supposed to play any significant role in the ionic Sm(III)–ligand interaction, an ECP-51, containing all five f electrons, was employed.<sup>24</sup>

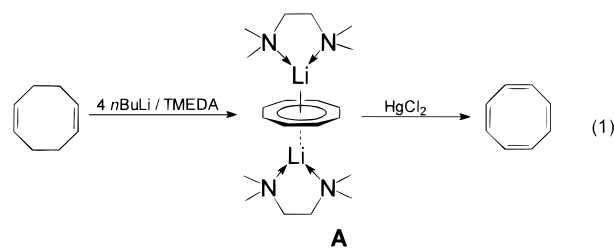
## Results and Discussion

A new synthesis of cyclooctatetraene will be discussed, followed by the synthesis and structural characterization of a new functionalized monocyclooctatetraene samarium and a nonfunctionalized bis(cyclooctatetraene)samarium complex.

**Synthesis of Cyclooctatetraene.** Recently, we reported the synthesis of the ligand dilithium 1,4-bis[(*o*-dimethylsilyl)-*N,N*-dimethylaniline]cyclooctatetraene (**1**) starting from cyclooctatetraene (COT) (Scheme 1).<sup>12</sup> To avoid elimination reactions, the key step of the ligand synthesis is the incorporation of a silicon atom into the side chain in the  $\alpha$ -position to the eight-membered ring. Unfortunately, COT is getting more and more expensive since the production of COT by the



Reppe synthesis (high-pressure tetramerization of acetylene) was canceled by industry. Acetylene under high pressure can be dangerous, and expensive equipment is needed to perform the Reppe synthesis in laboratory scale. Therefore, we developed a safe and convenient one-pot synthesis of cyclooctatetraene by combining some literature procedures.<sup>25–27</sup> The new synthesis is more efficient than any other known method in laboratory scale.<sup>28</sup> As reported by Wilke<sup>25</sup> and Cloke,<sup>26</sup> 1,5-cyclooctadiene can be reduced to the cyclooctatetraene dianion (**A**) with *n*-butyllithium/*N,N,N,N*-tetramethylethylenediamine (TMEDA). **A** can then be readily oxidized in situ with  $\text{HgCl}_2$  to afford COT in 45% yield (eq 1).<sup>29</sup> The intermediate **A** turned out not to be useful for further derivatizations because the TMEDA could not be completely removed from the reaction products.



**Metal Complex.** The synthesis of the organosamarium complex  $[\text{Li}(\text{diglyme})_2][\{1,4\text{-R}_2\text{C}_8\text{H}_6\}_2\text{Sm}(\mu\text{-Cl})_3]$  (**2**) (Scheme 2) was performed by transmetalation of **1** with anhydrous samarium trichloride. After extraction with diethyl ether and crystallization from diethyl ether/pentane (1:5) the ionic compound **2** crystallizes in

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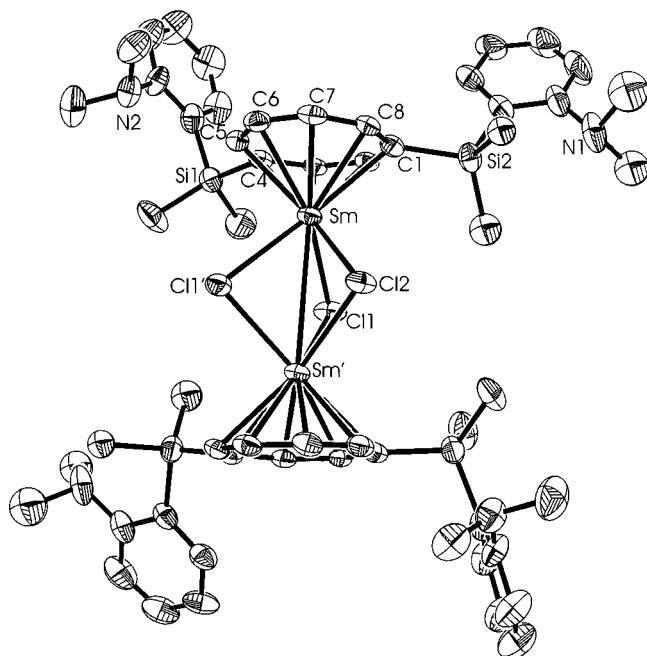
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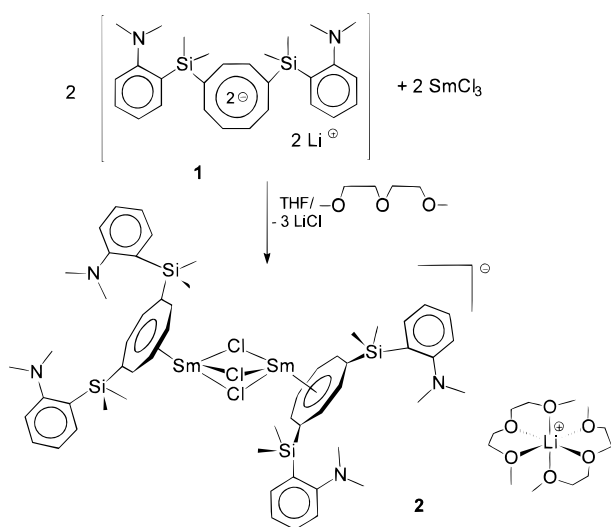
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**Figure 1.** Perspective ORTEP view of the molecular structure of the anion of **2**. Thermal ellipsoids are drawn to encompass 30% probability.

the presence of diglyme as purple needles (Figure 1). Data collection details and selected bond lengths and angles are given in Tables 1 and 2, respectively.

### Scheme 2



The cationic part is a lithium ion which is coordinated by two diglyme molecules. In the single-crystal X-ray structure the diglyme molecules are disordered. The anionic part is a unique example of a dimeric organolanthanide complex which is  $\mu_2$ -bridged by three chlorine atoms. The chlorine atoms are almost symmetrically located between the two samarium atoms. Two of these chlorine atoms (Cl1 and Cl1') are somewhat shifted toward one samarium atom (Cl1–Sm = 2.782(2) Å and Cl1–Sm' = 2.822(2) Å), whereas the third chlorine atom is located on the crystallographic  $C_2$  axis midway between two samarium ions (Cl2–Sm = 2.788(2) Å). The Sm–Cl–Sm' angles are in the close range 85.71(5)–86.26(7)°. One of the rare examples of a

**Table 1. Crystallographic Details for [Li(diglyme)<sub>2</sub>]<sup>+</sup>[(1,4-R<sub>2</sub>C<sub>8</sub>H<sub>6</sub>)<sub>2</sub>Sm<sub>2</sub>( $\mu$ -Cl)<sub>3</sub>]<sup>-</sup> (R = *o*-(Dimethylsilyl)-*N,N*-dimethylaniline) (2·(pentane)) and [Li(THF)<sub>3</sub>( $\mu$ - $\eta^2$ : $\eta^8$ -C<sub>8</sub>H<sub>8</sub>)<sub>2</sub>Sm(C<sub>8</sub>H<sub>8</sub>)] (3)**

	<b>2</b>	<b>3</b>
formula	C <sub>73</sub> H <sub>112</sub> Cl <sub>3</sub> LiN <sub>4</sub> O <sub>6</sub> Si <sub>4</sub> Sm <sub>2</sub>	C <sub>28</sub> H <sub>40</sub> LiO <sub>3</sub> Sm
fw	1668.02	581.89
space group (No.)	<i>C2/c</i> (15)	<i>P2<sub>1</sub>/m</i> (11)
<i>a</i> , Å	19.298(3)	8.9420(3)
<i>b</i> , Å	14.883(3)	13.8180(3)
<i>c</i> , Å	30.799(5)	11.3750(4)
$\beta$ , °	108.260(17)	110.68(2)
<i>V</i> , Å <sup>3</sup>	8400(2)	1314.9(1)
<i>Z</i>	4	2
<i>T</i> , °C	-70	-70
radiation ( $\lambda$ , Å)	Mo K $\alpha$ (0.710 69)	Mo K $\alpha$ (0.710 69)
$\rho$ (calcd), g/cm <sup>3</sup>	1.319	1.470
R1 <sup>a</sup>	0.0462	0.0419
wR2 <sup>b</sup>	0.1207	0.0934

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$$

**Table 2. Selected Bond Lengths (Å) and Angles (deg) in [Li(diglyme)<sub>2</sub>]<sup>+</sup>[(1,4-R<sub>2</sub>C<sub>8</sub>H<sub>6</sub>)<sub>2</sub>Sm<sub>2</sub>( $\mu$ -Cl)<sub>3</sub>]<sup>-</sup> (R = *o*-(Dimethylsilyl)-*N,N*-dimethylaniline) (2·(pentane))**

C1–Sm	2.648(7)	C1–Si2	1.895(7)
C2–Sm	2.603(6)	C4–Si1	1.888(7)
C3–Sm	2.595(7)	Cl1–Sm	2.782(2)
C4–Sm	2.624(7)	Cl1–Sm'	2.822(2)
C5–Sm	2.590(8)	Cl2–Sm'	2.788(2)
C6–Sm	2.625(7)	Cl2–Sm	2.780(2)
C7–Sm	2.629(7)	Sm–Cl1'	2.822(2)
C8–Sm	2.635(6)	Sm–Sm'	3.812(1)
Si1–C4–Sm	132.2(4)	Cl1–Sm–Cl2	78.74(5)
Si2–C1–Sm	129.7(4)	Cl1–Sm–Sm'	47.59(4)
Sm–Cl1–Sm'	85.71(5)	Cl2–Sm–Sm'	46.87(3)
Sm–Cl2–Sm'	86.26(7)	C1–Sm–Cl1	98.85(16)
Cl1–Sm–Cl1'	77.85(7)	C1–Sm–Cl2	108.32(16)

inorganic lanthanide compound with three  $\mu_2$ -bridged chlorine atoms is the [Cl<sub>3</sub>Nd( $\mu$ -Cl)<sub>3</sub>NdCl<sub>3</sub>]<sup>3-</sup> anion.<sup>29</sup> However, in the neodymium anion two chlorine atoms are located about 0.50 Å closer to one metal center than to the other one. The third one is also located midway between the two metal ions. The disubstituted cyclooctatetraene ring of **2** is  $\eta^8$ -coordinated to the samarium atom. The Sm–C<sub>ring</sub> distances are in the range between 2.590(8) and 2.648(7) Å. Comparable bond distances were observed for [(C<sub>8</sub>H<sub>8</sub>)Sm( $\mu_2$ -SePh)(THF)]<sub>2</sub> (Sm–C<sub>ring</sub> = 2.61(1)–2.70(1) Å)<sup>14,30</sup> and [(C<sub>8</sub>H<sub>8</sub>)SmI(hmpa)<sub>3</sub>] (hmpa = hexamethylphosphoric triamide; Sm–C<sub>ring</sub> = 2.64(2)–2.69(3) Å).<sup>31</sup> The silicon atoms are almost tetrahedrally coordinated, having bond angles C–Si1–C in the range of 105.0(6) and 115.0(8)°. The amino group of the aniline ring points away from the samarium atom. There is neither an intramolecular nor an intermolecular interaction. Obviously, **2** crystallizes preferably in an ionic form, in which the third chlorine atom occupies a free coordination site at the samarium atom. Additionally, 1 equiv of (disordered) pentane cocrystallizes with **2**. Attempts to isolate the neutral form of **2** failed.

**2** was also characterized in solution by <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectroscopy. In comparison to the dilithiated

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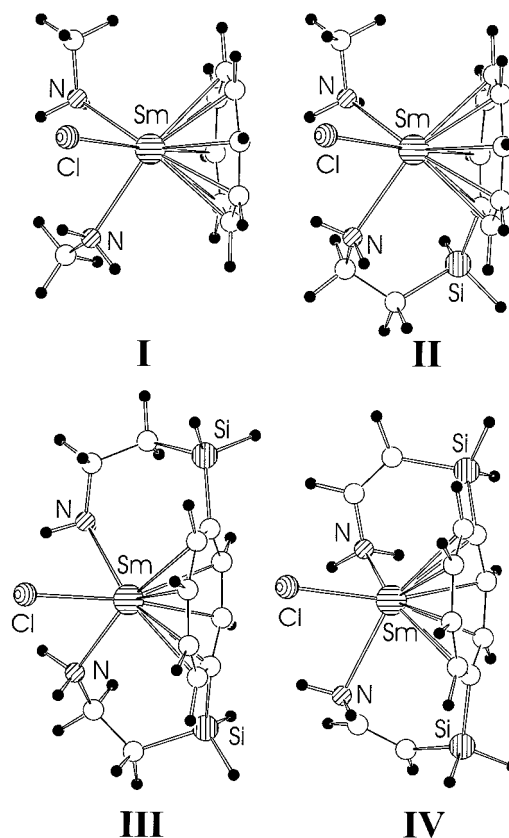
(30) Mashima, K.; Nakayama, Y.; Kanehisa, N.; Kai, Y.; Nakamura, A. *J. Chem. Soc., Chem. Commun.* **1993**, 1847–1849.

(31) Mashima, K.; Fukumoto, H.; Nakayama, Y.; Tani, K.; Nakamura, A. *Polyhedron* **1998**, *17*, 1065–1071.

compound **1** the  $^{29}\text{Si}$  NMR chemical resonance ( $\delta$  11.5)<sup>12</sup> is shifted to higher field. Due to the paramagnetic influence of the samarium atom, the three  $^1\text{H}$  NMR resonances of the eight-membered ring are broadened and low-field shifted ( $\delta$  9.99, 10.62, and 11.44). Spin lattice relaxation experiments ( $T_1$ ) were performed for the protons of complex **2**. These experiments were carried out in order to probe the proximity of the dimethylamino group to the paramagnetic  $\text{Sm}^{\text{III}}$  center.<sup>32</sup> Static or transitory  $\text{Sm}-\text{N}$  interactions should result in efficient electron–nuclear dipolar relaxation ( $\sim 1/r^6$ )<sup>33</sup> of the  $\text{Me}_2\text{N}$  spin system. The  $T_1$  results indicate an increase followed by a decrease in  $T_1$  along only one of the two pendant chains as the  $\text{Me}_2\text{N}$  group is approached. This suggests that either an inter- or an intramolecular coordination of one  $\text{Me}_2\text{N}$  takes place in solution, whereas the other  $\text{Me}_2\text{N}$  group (also with a small decrease in  $T_1$ ) seems to be more remote from the metal center. These observations were also confirmed by VT experiments in which the groups with short  $T_1$  relaxation times show a strong temperature-dependent chemical shift. The  $^1\text{H}$  NMR spectrum additionally shows two signals for the  $\text{Me}_2\text{N}$  group with the shorter  $T_1$  values indicating a strong coordination of this group to the samarium center, whereas the other group shows only one signal.

For an explanation of the observed coordination behavior in solution, we were interested whether it is in principle possible for the 1,4- $\text{R}_2\text{C}_8\text{H}_6$  ligand ( $\text{R} = \alpha$ -(dimethylsilyl)- $N,N$ -dimethylaniline), or similar  $-\text{CH}_2\text{CH}_2-$  saturated ligands, to intramolecularly coordinate to the metal center via the eight-membered ring and the amino group at the same time. Therefore, quantum chemical investigations were carried out by employing the density functional theory (DFT) method (see Experimental Section). To reduce the computational effort, we chose three hypothetical derivatives **I–III** of the also computed model compound **IV** (Figure 2) instead of **2** and corresponding derivatives for the structure optimizations: **I**,  $\text{SmCl}(\text{NH}_2\text{CH}_3)_2\text{C}_8\text{H}_8$ ; **II**,  $\text{SmCl}(\text{NH}_2\text{CH}_3)(\text{NH}_2\text{CH}_2\text{CH}_2\text{SiH}_2)\text{C}_8\text{H}_7$ ; **III**,  $\text{SmCl}(\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SiH}_2)_2\text{C}_8\text{H}_6$ ; **IV**,  $\text{SmCl}(\text{NH}_2\text{CHCHSiH}_2)_2\text{C}_8\text{H}_6$ . All calculated compounds feature the desired  $2(\text{NH}_2\text{R}) + \text{COT} + \text{Cl}$  coordination toward the Sm atom and contain no  $\text{Sm}-\text{N}-\text{C}-\text{C}-\text{Si}-\text{COT}$  bridge (**I**), one  $-\text{CH}_2\text{CH}_2-$  saturated bridge (**II**), two saturated bridges (**III**), or two  $-\text{CH}=\text{CH}-$  unsaturated bridges (**IV**). Thus, we were able to find out how many bridges and which types of bridges are possible and favored in the investigated complex system. In Table 3, total energies and some selected structural parameters of **I–IV** are listed.

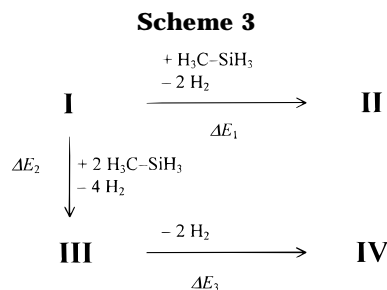
DFT was found to give good bond lengths. The calculated  $\text{Sm}-\text{C}_{\text{COT}}$  bond lengths (all in a narrow range: 2.673–2.726 Å; see Table 3) deviated from those measured in compounds **2** and **3** (2.590–2.648 and 2.647–2.697 Å) by a maximum of 0.08 Å. The calculated  $\text{Sm}-\text{N}$  bond lengths (2.665–2.725 Å) deviate from those measured in further  $\text{Sm}-\text{N}$  complexes (e.g.  $[(\text{C}_5\text{Me}_5)_2(\text{THF})-\text{Sm}(\mu_2-\eta^2-\text{PhN}-\text{NHPH})]$ , 2.610 Å;  $[(\text{C}_5\text{H}_5)_3\text{SmNC}_5\text{H}_5]$ , 2.656 Å)<sup>34,35</sup> by a maximum of ca. 0.10 Å. However, it



**Figure 2.** Molecular structures of the calculated complexes **I–IV** as they result from the DFT structure optimizations.

should be noted that the DFT method does not consider dispersion effects explicitly. Thus, longer bonds compared to the experimental values are expected, especially for heavy atoms.

Using the total energies  $E$ , including those of the “missing link” molecules  $\text{H}_3\text{C}-\text{SiH}_3$  and  $\text{H}_2$  (Table 3), it is possible to calculate the relative energies  $\Delta E_1$ ,  $\Delta E_2$ , and  $\Delta E_3$  ( $\Delta E_j = \sum E_{j,\text{product}} - \sum E_{j,\text{reactant}}$ ), which can be viewed as reaction energies for the three formal isodesmic reactions of one molecule to another via homolytic bond breaking and formation (Scheme 3).  $\Delta E_1$  is the



energy difference through the formal formation of one  $-\text{CH}_2\text{CH}_2-$  containing bridge (formal conversion of **I** to **II**). The hypothetical formation of two simultaneously existing bridges of that type is denoted  $\Delta E_2$  (formal conversion of **I** to **III**). Finally, the energy difference through the formal substitution of  $-\text{CH}=\text{CH}-$  contain-

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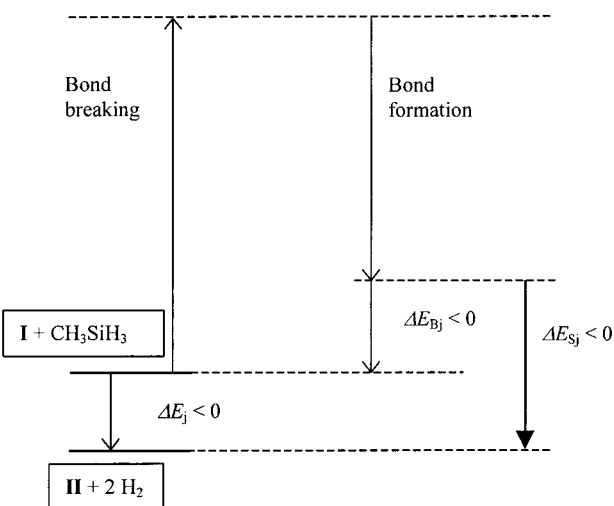
**Table 3. Total Energies  $E$  (au)<sup>a</sup> and Selected Bond Lengths (Å) and Angles (deg) for the Calculated Compounds I–IV as Well as for the “Missing Link” Molecules  $H_3C-SiH_3$  and  $H_2$** 

	$E$	$d(\text{Sm}-\text{N})$	$d(\text{Sm}-\text{Cl})$	$d(\text{Sm}-\text{C}_{\text{cot}})$	$\angle\text{N}-\text{C}-\text{C}$	$\angle\text{C}-\text{C}-\text{Si}$	$\angle\text{H}-\text{C}-(\text{C},\text{Si}), \angle\text{H}-\text{C}-\text{N}$
<b>I</b>	-996.047 938	2.667, 2.670	2.961	2.685–2.713			108.5–113.8 <sup>d</sup>
<b>II</b>	-1 324.825 939	2.665, <sup>b</sup> 2.680 <sup>c</sup>	2.681	2.673–2.726	112.6	118.4	105.0–110.3
<b>III</b>	-1 653.554 078	2.684, 2.700	2.687	2.682–2.712	113.6, 112.3	117.3, 117.3	105.8–110.6
<b>IV</b>	-1 651.197 272	2.725, 2.753	2.658	2.681–2.718	124.4, 125.1	124.1, 126.6	117.5–121.7
H	-1.169 958						
$\text{CH}_3-\text{SiH}_3$	-331.104 356						110.9, 110.8 <sup>e</sup>

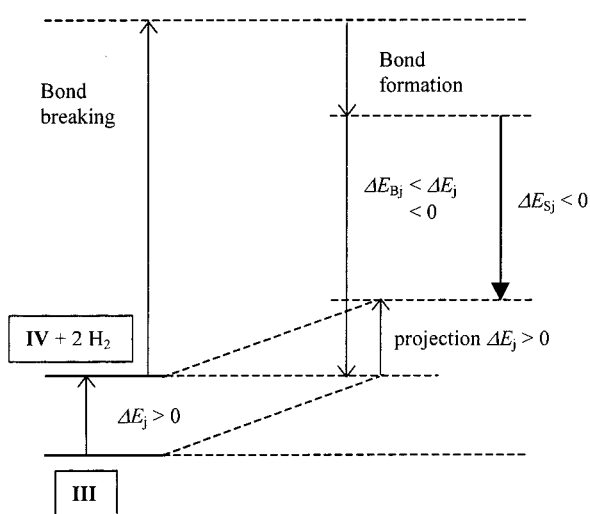
<sup>a</sup> 1 au = 1 hartree (H) = 628.1 kcal/mol. <sup>b</sup> Free  $\text{NH}_2\text{R}$ . <sup>c</sup> Bridging  $\text{NH}_2\text{R}$ . <sup>d</sup>  $\angle\text{N}-\text{C}-\text{H}$ . <sup>e</sup>  $\angle\text{Si}-\text{C}-\text{H}$ .

**Scheme 4**

Type 1,  $\Delta E_j < 0$ ,  $\Delta E_{\text{Bj}} < 0$ .



Type 2,  $\Delta E_j > 0$ ,  $\Delta E_{\text{Bj}} < \Delta E_j < 0$ .



ing bridges for  $-\text{CH}_2\text{CH}_2-$  containing bridges is  $\Delta E_3$  (formal conversion of **III** to **IV**).

$\Delta E_1$ ,  $\Delta E_2$ , and  $\Delta E_3$  implicitly contain the energy loss or gain through bond breaking and formation in all reactants and products during these formal reactions. Assuming that only, or at least mainly, the formal broken or formed bonds are involved, consideration of the respective binding energy values (see footnote in Table 4) shows a loss of binding energy on the product

**Table 4. Total Energy Differences  $\Delta E_j$  ( $j = 1-3$ ) for the Formal Formation of Different Numbers of Coordinating  $\text{COT-Si-C-C-N-Sm}$  Bridges<sup>a</sup> Starting with **I**, or for the Formal Substitution of the  $-\text{CH}=\text{CH}-$  Containing Bridges in **IV** for the  $-\text{CH}_2\text{CH}_2-$  Containing Bridges in **III**, the Differences  $\Delta E_{\text{Bj}}$ <sup>b,c</sup> of the Binding Energies of the Concerned  $\text{C}-\text{H}$ ,  $\text{Si}-\text{H}$ ,  $\text{C}-\text{C}$ ,  $\text{Si}-\text{C}$ ,  $\text{H}-\text{H}$ , and  $\text{C}=\text{C}$   $\pi$  Bonds, and the Stabilization Energies  $\Delta E_{\text{Sj}}$ <sup>d</sup>**

$j$	formal react <sup>a</sup>	$\Delta E_j$ (au) <sup>e</sup> [kcal/mol]	$\Delta E_{\text{Bj}}$ <sup>b,c</sup> (kcal/mol)	$\Delta E_{\text{Sj}}$ <sup>d</sup> (kcal/mol)
1 <sup>f</sup>	<b>I</b> → <b>II</b>	-0.013 561 [-8.5]	-23.2	-31.7
2 <sup>g</sup>	<b>I</b> → <b>III</b>	0.011 370 [14.3]	-46.4	-32.1
3 <sup>h</sup>	<b>III</b> → <b>IV</b>	0.016 890 [10.6]	-69.8	-59.2

<sup>a</sup> See text and Figure 2. <sup>b</sup>  $\Delta E_{\text{Bj}} = \sum E_{\text{Bj,product}} - \sum E_{\text{Bj,reactant}}$ ; note that (unlike  $\Delta E_j$ ,  $\Delta E_{\text{Sj}}$ )  $\Delta E_{\text{Bj}} < 0$  means destabilization. <sup>c</sup> Binding energies were calculated using the same method as for the compounds **I**–**IV** (see Experimental Section) considering the following total energies  $E$  (au)<sup>e</sup> and isodesmic reactions:  $E(\text{H})$ , -0.498947;  $E(\text{C})$ , -37.806 215;  $E(\text{Si})$ , -289.306 521;  $E(\text{H}_2)$ , -1.169 958;  $E(\text{CH}_4)$ , -40.474 663;  $E(\text{SiH}_4)$ , -291.811 730;  $E(\text{CH}_3-\text{CH}_3)$ , -79.754 316;  $E(\text{CH}_3-\text{SiH}_3)$ , -331.104 356;  $E(\text{CH}_2=\text{CH}_2)$ , -78.528 698.  $\text{C}-\text{H}$  and  $\text{Si}-\text{H}$  binding energies resulted from the reaction energies of the atomization of  $\text{C}_2\text{H}_6$  or  $\text{SiH}_4$  with respect to atomic energies of  $\text{H}$  and  $\text{C}$  or  $\text{Si}$ ; using these values, the reaction energies of the hydration of  $\text{C}_2\text{H}_6$  or  $\text{CH}_3\text{SiH}_3$ , respectively, lead to the  $\text{C}-\text{C}$  and  $\text{C}-\text{Si}$  binding energies. Finally, the saturation of  $\text{C}_2\text{H}_4$  by  $\text{H}_2$  served to calculate the  $\text{C}=\text{C}$   $\pi$  binding energy. Compared to literature values,<sup>36</sup> the calculated binding energies show acceptable deviations of 2.7–6.1 kcal/mol. Calculated binding energies (kcal/mol):  $\text{H}-\text{H}$ , 108.1;  $\text{C}-\text{H}$ , 105.6;  $\text{Si}-\text{H}$ , 80.0;  $\text{C}-\text{C}$ , 87.4;  $\text{Si}-\text{C}$ , 70.0;  $\text{C}=\text{C}$ , 68.2. Assumptions:  $E_{\text{B}}(\text{C}^{\pi}-\text{H}) = E_{\text{B}}(\text{C}^{\sigma}-\text{H})$ ;  $E_{\text{B}}(\text{C}^{\pi}-\text{Si}) = E_{\text{B}}(\text{C}^{\sigma}-\text{Si})$ . <sup>d</sup>  $\Delta E_{\text{Sj}} = \Delta E_j + \Delta E_{\text{Bj}}$  ((energy gained on ring closing) - (energy needed/gained by reaction) - (energy needed for bond breaking) + (energy gained by bond formation)). Qualitative Born–Haber cycle processes explaining  $\Delta E_{\text{Sj}}$  are shown in Scheme 4. <sup>e</sup> 1 au = 1 hartree (H) = 628.1 kcal/mol. <sup>f</sup>  $\Delta E_1 = E_{\text{II}} - E_{\text{I}} - [E(\text{H}_3\text{C}-\text{SiH}_3) - 2E(\text{H}_2)]$ . <sup>g</sup>  $\Delta E_2 = [E_{\text{III}} - E_{\text{I}}] - [2E(\text{H}_3\text{C}-\text{SiH}_3) - 4E(\text{H}_2)]$ . <sup>h</sup>  $\Delta E_3 = [E_{\text{IV}} - E_{\text{III}}] - 2E(\text{H}_2)$ .

side for all mentioned reactions: with  $\Delta E_{\text{Bj}} = \sum E_{\text{Bj,product}} - \sum E_{\text{Bj,reactant}}$ , the three values for  $\Delta E_{\text{B1}}$ ,  $\Delta E_{\text{B2}}$ , and  $\Delta E_{\text{B3}}$  are negative. This thus leads to an exothermic correction for the “pure ring closing” reactions (without the involved bonds), given through the stabilization energies  $\Delta E_{\text{S1}}$ ,  $\Delta E_{\text{S2}}$ , and  $\Delta E_{\text{S3}}$  with  $\Delta E_{\text{Sj}} = \Delta E_j + \Delta E_{\text{Bj}}$  ((energy gained on ring closing) = (energy needed/gained by reaction) - (energy needed for bond breaking) + (energy gained by bond formation)). Qualitative Born–Haber cycle processes explaining  $\Delta E_{\text{Sj}}$  are shown in Scheme 4. However, it should be noted that not only the explicitly changed bonds but also all structural changes contribute to the energy differences. As consideration of this will hardly be possible without the use of further approximations and as the development of the bonds and angles (see Table 3) will not cause significant energy differences, we concentrated only on the mentioned values. All energy differences are given in Table 4.

It can be seen from the  $\Delta E_{\text{Sj}}$  values that the formation of bridges is always favored in the investigated Sm

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complex system. Interestingly, the unsaturated, more rigid bridge seems to better fit for the ring closing. The formation of two  $-\text{CH}_2\text{CH}_2-$  saturated bridges (**III**) leads only to about the same stabilization (cf. two bridges) as the formation of one bridge of that type (**II**). In contrast, starting from the disfavored compound **III**, the transition to a doubly  $-\text{CH}=\text{CH}-$  unsaturated bridging system **IV** leads to another enormous stabilization.

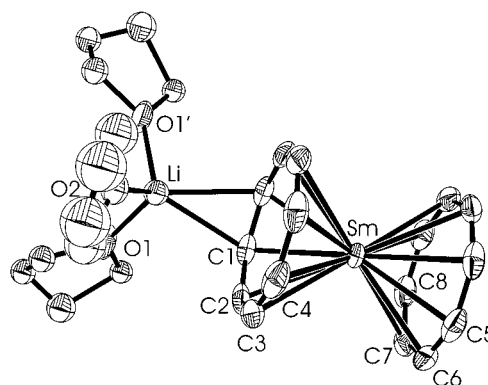
From the structural parameters (Table 3) one gets also the information that ring closing does not collide with the structural restraints: besides significantly tightened  $\text{Sm}-\text{C1}$  bonds (up to 0.30 Å) and nearly unchanged  $\text{Sm}-\text{C}_{\text{COT}}$  distances, the  $\text{Sm}-\text{N}$  bond lengths become only up to 0.08 Å larger on going from **I** to **IV** and remain in the range of known  $\text{Sm}-\text{N}$  distances.<sup>34,35</sup> The angles along  $\text{N}-\text{C}-\text{C}-\text{Si}$  in **II**, **III**, and **IV**, respectively, do not show unacceptable deviations from the desired  $109.5^\circ$  (saturated) or  $120^\circ$  (unsaturated) values, which is in agreement with nonbridged **I** or free  $\text{CH}_3-\text{SiH}_3$ .

These results let us suggest that the experimentally used ligand, containing the  $-\text{CH}=\text{CH}-$  related phenyl group in the bridges, might in principle coordinate to the Sm center in an intramolecular fashion. It is even more likely to completely coordinate with both amino groups than a similar ligand featuring saturated  $-\text{CH}_2-\text{CH}_2-$  groups in it would be. Thus, the observation of **2** (Figure 1) instead of an  $2(\text{NMe}_2\text{R}) + \text{COT} + \text{Cl}$  coordinated  $\{1,4-\text{R}_2\text{C}_8\text{H}_6\}\text{Sm}(\mu-\text{Cl})$  complex cannot be explained by steric or energetic problems. Possibly, the isolated dimer is a kinetically controlled product. Accordingly, we do not exclude the coordination in solution found in the NMR experiments to be intramolecular.

Starting from **1** and  $[(\text{C}_8\text{H}_8)\text{SmI}(\text{THF})_2]$ ,<sup>14</sup> we also tried to prepare mixed-sandwich complexes of composition  $[\text{Li}(\text{diglyme})_2]^+[\text{Sm}(1,4-\text{R}_2\text{C}_8\text{H}_6)_2]^-$  ( $\text{R} = o$ -(dimethylsilyl)-*N,N*-dimethylaniline).<sup>12</sup> By crystallization of the reaction mixture the desired product was not obtained. Even under different reaction conditions only the rearranged homoleptic product  $[\text{Li}(\text{THF})_3\{\mu-(\eta^2:\eta^8-\text{C}_8\text{H}_8)\}\text{Sm}(\text{C}_8\text{H}_8)]$  (**3**) was isolated by crystallization. As shown by an NMR-scale reaction an equilibrium between **3**, the mixed-sandwich compound, and  $\text{Li}^+[\text{Sm}(1,4-\text{R}_2\text{C}_8\text{H}_6)_2]^-$  ( $\text{R} = o$ -(dimethylsilyl)-*N,N*-dimethylaniline)<sup>12</sup> exists in solution, from which **3** crystallizes preferably. The signal due to the protons of the eight-membered ring in **3** shows, as expected, one broad resonance which has a marked downfield shift ( $\delta$  13.2) compared to  $\text{K}[\text{Sm}(\text{C}_8\text{H}_8)_2]$  ( $\delta$  -11.4)<sup>37</sup> but is in the same range as the anion in  $[(\text{C}_8\text{H}_8)\text{Sm}(\text{hmpa})_3][(\text{C}_8\text{H}_8)_2\text{Sm}]$  ( $\delta$  13.5).<sup>31</sup>

The molecular structure of **3** (Figure 3) was probed further by single-crystal X-ray diffraction. Data collection details and selected bond lengths and angles are given in Tables 1 and 5, respectively.

The molecular structure of **3** formally consists of a  $[\text{Li}(\text{THF})_3]^+$  cation and a  $[(\text{C}_8\text{H}_8)_2\text{Sm}]^-$  anion in which the lithium atom is  $\eta^2$ -coordinated to two carbon atoms (C1 and C1') of one COT ring. A comparable  $\eta^2$  coordination mode was observed for  $[(\text{C}_8\text{H}_8)\text{Nd}(\text{THF})_2\{\mu-(\eta^2:\eta^8-\text{C}_8\text{H}_8)\}\text{Nd}(\text{C}_8\text{H}_8)]$ <sup>38</sup> and  $[\text{Li}(\text{THF})_2\{\mu-(\eta^2:\eta^8-\text{C}_8\text{H}_8)\}\text{Sm}-\{\text{CH}(\text{SiMe}_3)_2\}_2]$ .<sup>39</sup> The  $\text{Li}-\text{C}$  bond distances (2.42(2) Å)



**Figure 3.** Perspective ORTEP view of the molecular structure of **3**. Thermal ellipsoids are drawn to encompass 30% probability.

**Table 5. Selected Bond Lengths (Å) and Angles (deg) in  $[\text{Li}(\text{THF})_3\{\mu-(\eta^2:\eta^8-\text{C}_8\text{H}_8)\}\text{Sm}(\text{C}_8\text{H}_8)]$  (**3**)**

$\text{Sm}-\text{C1}$	2.689(6)	$\text{Sm}-\text{C}(\text{av})$	2.676(7)
$\text{Sm}-\text{C2}$	2.692(7)	$\text{Li}-\text{O1}$	1.940(12)
$\text{Sm}-\text{C3}$	2.695(8)	$\text{C1}-\text{C1}'$	1.39(2)
$\text{Sm}-\text{C4}$	2.697(7)	$\text{C1}-\text{C2}$	1.369(11)
$\text{Sm}-\text{C5}$	2.647(7)	$\text{C2}-\text{C3}$	1.404(12)
$\text{Sm}-\text{C7}$	2.666(7)	$\text{Li}-\text{C1}$	2.42(2)
$\text{Sm}-\text{C8}$	2.666(7)	$\text{Li}-\text{O2}$	1.90(2)
$\text{C1}-\text{Sm}-\text{C1}'$	30.0(3)	$\text{O1}-\text{Li}-\text{O1}'$	102.9(9)
$\text{C5}-\text{Sm}-\text{C1}$	149.6(3)	$\text{O1}-\text{Li}-\text{O2}$	103.5(7)
$\text{C6}-\text{Sm}-\text{C1}$	122.0(3)	$\text{O1}-\text{Li}-\text{C1}$	98.8(5)
$\text{C7}-\text{Sm}-\text{C1}$	101.1(2)	$\text{O2}-\text{Li}-\text{C1}$	117.5(8)
$\text{C8}-\text{Sm}-\text{C1}$	93.6(2)	$\text{O2}-\text{Li}-\text{C1}'$	117.5(8)

are comparable to the bond distances observed for  $[\text{Li}(\text{THF})_2\{\mu-(\eta^2:\eta^8-\text{C}_8\text{H}_8)\}\text{Sm}\{\text{CH}(\text{SiMe}_3)_2\}_2]$  (2.384(8) and 2.395(8) Å).<sup>39</sup> Due to the coordination of the lithium atom no significant deviation of the  $\text{Sm}-\text{C1}$  bond length (2.676(7) Å) compared to the other  $\text{Sm}-\text{C}$  bond distances can be observed. Additionally, no difference within the  $\text{C}-\text{C}$  distances of the eight-membered ring can be seen. Both COT rings are coplanar and are coordinated to the samarium atom in a  $\eta^8$  fashion. **3** features a mirror plane along Sm, Li, and O2. Recently the structure of  $[\text{Li}(\text{THF})_4][(\text{C}_8\text{H}_8)_2\text{Sm}]\cdot 2\text{THF}$  was reported,<sup>40</sup> which is more or less the same compound as **3**. Even though both compounds are very similar, the rearrangement condition described above exclusively leads to **3**. In comparison to **3**, in  $[\text{Li}(\text{THF})_4][(\text{C}_8\text{H}_8)_2\text{Sm}]\cdot 2\text{THF}$  the lithium atom is not coordinated to a COT ring. Instead, a fourth THF molecule is coordinated on to the lithium atom.

**Summary.** A new type of complex containing a multifunctional cyclooctatetraene and the triple  $\mu_2$ -chloro-bridged  $[\text{Li}(\text{diglyme})_2][\{1,4-\text{R}_2\text{C}_8\text{H}_6\}_2\text{Sm}_2(\mu-\text{Cl})_3]$  was obtained. Whereas in the solid state no interaction of the  $\text{Me}_2\text{N}$  group of the ligand with the samarium center was observed,  $T_1$   $^1\text{H}$  NMR experiments show a coordination of one  $\text{Me}_2\text{N}$  group in solution. Density functional theory (DFT) calculations show that this coordination might in principle be in an intermolecular fashion. Reaction of **1** with  $[(\text{C}_8\text{H}_8)\text{SmI}(\text{THF})_2]$  does not

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lead to a mixed-sandwich complex. By a ligand rearrangement the nonfunctionalized complex  $[\text{Li}(\text{THF})_3\{\mu-(\eta^2:\eta^8\text{-C}_8\text{H}_8)\}\text{Sm}(\text{C}_8\text{H}_8)]$  was isolated and characterized by single-crystal X-ray diffraction.

**Acknowledgment.** This work was supported by the Deutsche Forschungsgemeinschaft (Habilitation fellowship for P.W.R.), the Fonds der Chemischen Industrie and the State of Baden-Württemberg (Margarete-von-Wrangell fellowship for S.D.). Additionally, generous support from Prof. Dr. D. Fenske and Prof. Dr. R.

Ahlrichs is gratefully acknowledged. We are very indebted to S. Elliott for valuable help with the manuscript.

**Supporting Information Available:** X-ray experimental details, including tables of positional and anisotropic displacement parameters and bond lengths and angles and additional views of the structures of **2** and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM990259U