Inorganic Chemistry
Article
pubs.acs.org/IC

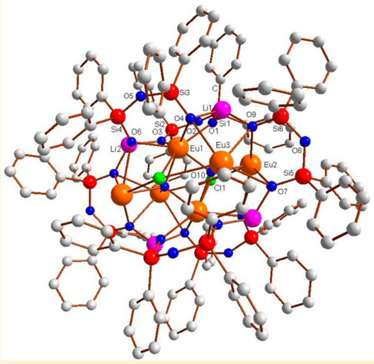
# Heterometallic Europium Disiloxanediolates: Synthesis, Structural Diversity, and Photoluminescence Properties

Janek Rausch,[†] Volker Lorenz,[†] Cristian G. Hrib,[†] Vanessa Frettlöh,[‡] Matthias Adlung,[‡] Claudia Wickleder,[‡] Liane Hilfert,[†] Peter G. Jones,[§] and Frank T. Edelmann*,[†]

[†]Chemisches Institut der Otto-von-Guericke-Universität Magdeburg, Universitätsplatz 2, 39106 Magdeburg, Germany
[‡]Naturwissenschaftlich-Technische Fakultät, Universität Siegen, Adolf-Reichwein-Straße, 57068 Siegen, Germany
[§]Institut für Anorganische und Analytische Chemie der TU Braunschweig, Hagenring 30, 38106 Braunschweig, Germany

*Supporting Information*

**ABSTRACT:** This contribution presents a full account of a structurally diverse class of heterometallic europium disiloxanediolates. The synthetic protocol involves *in situ* metalation of (HO)$SiPh_2OSiPh_2$(OH) (**1**) with either $^n$BuLi or $KN(SiMe_3)_2$ followed by treatment with $EuCl_3$ in suitable solvents such as 1,2-dimethoxyethane (DME) or tetrahydrofuran (THF). Reaction of $EuCl_3$ with 2 equiv of (LiO)$SiPh_2OSiPh_2$(OLi) in DME afforded the $Eu^{III}$ bis(disiloxanediolate) "ate" complex $[\{(Ph_2SiO)_2O\}\{Li(DME)\}_3]EuCl_2$ (**2**), which upon attempted reduction with Zn gave the tris(disiloxanediolate) $[\{(Ph_2SiO)_2O\}_3\{Li(DME)\}_3]Eu$ (**3**). Treatment of $EuCl_3$ with (LiO)$SiPh_2OSiPh_2$(OLi) in a molar ratio of 1:2 yielded both the ate complex $[\{(Ph_2SiO)_2O\}_3Li\{Li(THF)_2\}\{Li(THF)\}]EuCl{\cdot}Li(THF)_3$ (**4**) and the LiCl-free europium(III) complex $[\{(Ph_2SiO)_2O\}_2\{Li(THF)_2\}_2]EuCl$ (**5**). Compound **5** was found to exhibit a brilliant red triboluminescence. When (KO)$SiPh_2OSiPh_2$(OK) was used as starting material in a 3:1 reaction with $EuCl_3$, the $Eu^{III}$ tris(disiloxanediolate) $[\{(Ph_2SiO)_2O\}_3\{K(DME)\}_3]Eu$ (**6**) was isolated. Attempted ligand transfer between **5** and $(DAD^{Dipp})_2Ba(DME)$ ($DAD^{Dipp}$ = *N*,*N*′-bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene) afforded the unique mixed-valent $Eu^{III}/Eu^{II}$ disiloxanediolate cluster $[(Ph_2SiO)_2O]_6Eu^{II}_4Eu^{III}_2Li_4O_2Cl_2$ (**7**). All new complexes were structurally characterized by X-ray diffraction. Photoluminescence studies were carried out for complex **5** showing an excellent color quality, due to the strong $^5D_0{\to}^7F_2$ transition, but a weak antenna effect.



## INTRODUCTION

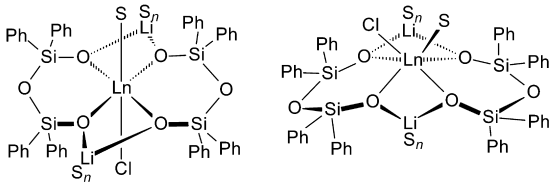
The chemistry of well-defined metal siloxides (metallasiloxanes) comprising the M−O−Si functionality continues to attract considerable interest due to the diverse potential applications of that functionality.[1] Not only are metal siloxides excellent molecular models for silica-supported heterogeneous metal catalysts[2] but they also serve as useful precursors for new materials,[3] nanoparticles,[4] well-defined surface species,[5] and homogeneous catalysts.[6] Moreover, it is well-established that siloxide ligands can support highly reactive metal complexes in low oxidation states (e.g., Co(I), Ti(III), Sm(II), U(III), etc.).[7] Suitable silanol precursors range from simple triorganosilanols, $R_3SiOH$,[1,8] through silanediols, $R_2Si(OH)_2$,[9] *α*,*ω*-oligosiloxanediols, $HO(R_2SiO)_nH$,[10] and silanetriols, $RSi(OH)_3$,[11] to more complex systems such as trisilanols, for example, $MeSi(R_2SiOH)_3$,[12] and incompletely condensed polyhedral oligosilsesquioxanes (POSS), for example, $R_7Si_7O_9(OH)_3$.[1,13]

A seemingly simple, though particularly useful and versatile precursor for a large variety of metal siloxides is the readily accessible 1,1,3,3-tetraphenyl-disiloxane-1,3-diol, (HO)$SiPh_2OSiPh_2$(OH) (**1**), which forms stable complexes with virtually every metallic element across the periodic table ranging from lithium to uranium.[1,14] Lanthanide disiloxanediolates derived from **1** already form a well-investigated class of compounds.[1q] The most prominent types of lanthanide disiloxanediolates are heterometallic bis-ligand complexes of the type $[\{(Ph_2SiO)_2O\}\{Li(S)_n\}]_2LnCl(S)$ (Ln = Sc, Y, Pr, Nd, Sm, Gd, Ho, Er, Yb, Lu; S (solvent) = $Et_2O$, tetrahydrofuran (THF), 1,2-dimethoxyethane (DME)); $n$ = 1, 2). In these complexes, two formally monoanionic $[\{(Ph_2SiO)_2O\}\{Li(S)_n\}]^-$ units form a twelve-membered $Si_4O_6Li_2$ inorganic ring system. These Si−O-based inorganic ring ligands have been well-established to effectively shield one side of even the largest lanthanide ions. While the smaller ions like $Sc^{3+}$, $Y^{3+}$, or $Lu^{3+}$ fit into the center of the $Si_4O_6Li_2$ ring (Scheme 1, **A**, *trans*-form), the larger ions such as $Pr^{3+}$ or $Nd^{3+}$ are significantly displaced from the center of the twelve-membered rings (Scheme 1, **B** (*cis*-form)).[1q,15]

A small number of homoleptic tris(disiloxanediolates) of the type $[\{(Ph_2SiO)_2O\}\{Li(solvent)_n\}]_3Ln$ (Ln = Nd, Eu) have also been prepared.[1q,15] The only europium disiloxanediolate complex reported thus far was the homoleptic, heterobimetallic species $[\{(Ph_2SiO)_2O\}\{Li(Et_2O)\}]_3Eu$.[15a,b] This compound

**Received:** July 30, 2014
**Published:** October 20, 2014

**Scheme 1. Schematic Representation of the *trans* and *cis* Forms of Heterometallic Lanthanide Bis(disiloxanediolate) Complexes**

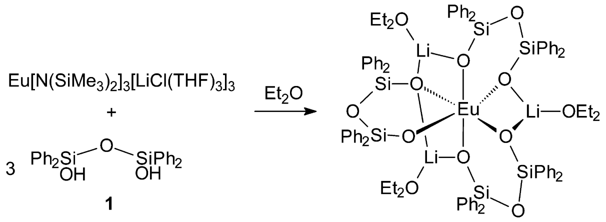


**A** (*trans*)
Ln = Sc, Y, Lu; S = THF, DME; n = 1, 2

**B** (*cis*)
Ln = Pr, Nd, Sm, Gd, Ho, Er, Yb
S = THF, DME; n = 1, 2

was made in moderate yield (41%) by treatment of the heterobimetallic silylamide precursor [(Me$_3$Si)$_2$N]$_3$Eu[($\mu$-Cl)-Li(THF)$_3$]$_3$[16] with 3 equiv of (HO)SiPh$_2$OSiPh$_2$(OH) (**1**) according to Scheme 2.[15a,b] This “silylamide route”, developed by Anwander and co-workers, allows a salt-free preparation of such complexes.[17] In addition to this *tris*(disiloxanediolate) derivative, no europium species comprising two or three disiloxanediolate ligands has been described in the previous literature.

**Scheme 2. Synthesis of the Homoleptic Europium(III) Tris(disiloxanediolate) Complex [{(Ph$_2$SiO)$_2$O}{Li(Et$_2$O)}]$_3$Eu[15a,b]**



In view of the tremendous practical importance of europium luminescence,[18,19] we decided to carry out respective studies of europium disiloxanediolate complexes. In this paper we present first results for compound **5**, which exhibits a remarkable triboluminescence behavior. The results of more detailed studies including the investigation of the antenna effect will be presented elsewhere.

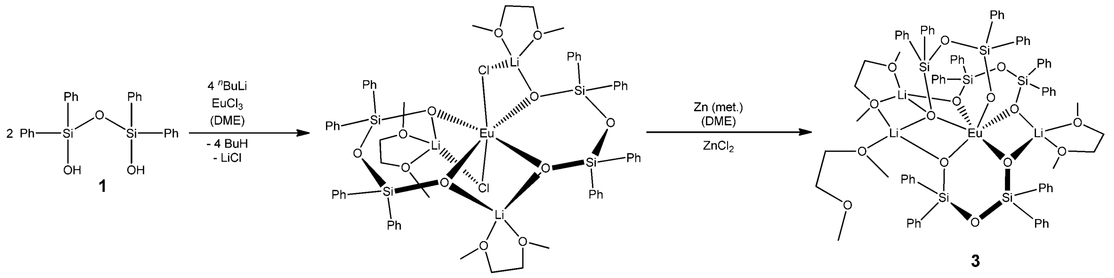
## ■ RESULTS AND DISCUSSION

**Syntheses and Structures.** We began our study by investigating synthetic routes leading to europium(III) bis(disiloxanediolate) complexes that retained a potentially reactive chloro functionality. *In situ* deprotonation of disiloxanediol **1** using 2 equiv of *n*-butyllithium in DME afforded a solution of (LiO)SiPh$_2$OSiPh$_2$(OLi), which was subsequently treated with anhydrous EuCl$_3$ in a molar ratio of 2:1. Separation of the LiCl byproduct followed by crystallization from DME afforded the europium(III) bis(disiloxanediolate) “ate” complex [{(Ph$_2$SiO)$_2$O}$_2${Li(DME)}$_3$]EuCl$_2$ (**2**) in the form of colorless, needlelike crystals in 68% isolated yield (Scheme 3).

Despite the presence of paramagnetic Eu$^{3+}$, NMR data ($^1$H, $^{13}$C, $^{29}$Si) could be obtained for compound **2**. However, it should be pointed out at this stage that full characterization of lanthanide disiloxanediolates derived from **1** heavily relies on single-crystal X-ray diffraction studies. Meaningful mass spectra could not be obtained for any of the new compounds reported here. This can be traced back to a combination of high molar weights in the range of $M_r$ = 1339 (**2**)−3518 (**7**) with a high degree of ionic bonding in these molecules. The $^1$H and $^{13}$C NMR spectra of **2** (and all other compounds reported here) only revealed the presence of disiloxanediolate ligands (only phenyl protons) and coordinated solvent in the molecule. After all, the usual combination of spectroscopic methods and elemental analyses largely failed to provide sufficiently detailed information about the structures of these europium disiloxanediolates. Fortunately, all new compounds prepared in the course of the present study could be structurally characterized by single-crystal X-ray diffraction. Table 1 summarizes the crystallographic data for **2**−**7**. The molecular structures of **2**−**7** as well as core structural representations are illustrated in Figures 1−6.

An X-ray analysis of **2** (Figure 1) revealed the presence of the desired europium(III) bis(disiloxanediolate) complex, although in the form of an ate complex containing added lithium chloride. The formation of ate complexes is a common phenomenon in (organo)lanthanide chemistry.[20] Often this results from the retention and complexation of alkali metal halides formed during a metathetical reaction. This is a common way of increasing the coordination number around the central lanthanide ion. Typical examples are the bent metallocene ate complexes of the type Cp*$_2$Ln($\mu$-Cl)$_2$(THF)$_2$ (Cp* = pentamethylcyclopentadienyl), which result from addition of LiCl and THF to monomeric “Cp*$_2$LnCl”, whereby the formal coordination number around Ln is increased from 7 to 8.[20] The europium(III) complex **2** differs from all previously described lanthanide bis-disiloxanediolates depicted in Scheme 1 in that the cyclic Si$_4$O$_6$Li$_2$ coordination around Eu is opened up on one side through the ate complex formation with LiCl. Each of the two involved lithium ions is bonded to a disiloxanediolate oxygen atom and a chloride ligand that is bridging Eu and Li. In both cases, the tetrahedral coordination around Li is completed by a chelating DME ligand. The third Li(DME) unit is coordinated in the usual

**Scheme 3. Synthesis of the Europium(III) Disiloxanediolates [{(Ph$_2$SiO)$_2$O}$_2${Li(DME)}$_3$]EuCl$_2$ (2) and [{(Ph$_2$SiO)$_2$O}$_3${Li(DME)}$_3$]Eu (3).**



**1** **2** **3**

Table 1. Crystallographic Data for 2−7

| complex | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|
| empirical formula | $C_{60}H_{70}Cl_2EuLi_3O_{12}Si_4$ | $C_{84}H_{91}EuLi_3O_{15}Si_6$ | $C_{96}H_{108}ClEuLi_4O_{15}Si_6\cdot THF$ | $C_{72}H_{88}ClEuLi_2O_{12}Si_4$ | $C_{84}H_{90}EuK_3O_{15}Si_6$ | $C_{144}H_{120}Cl_2Eu_6Li_4O_{20}Si_{12}$ |
| $a$ (Å) | 10.932(2) | 14.538(3) | 14.559(3) | 10.768(2) | 25.334(5) | 14.3252(8) |
| $b$ (Å) | 47.919(10) | 22.675(5) | 20.423(4) | 16.011(3) | 14.541(3) | 16.9100(8) |
| $c$ (Å) | 13.137(3) | 24.963(5) | 33.688(7) | 21.244(4) | 25.145(5) | 17.9276(8) |
| $\alpha$ (deg) | 90 | 90 | 90 | 90 | 90 | 85.008(4) |
| $\beta$ (deg) | 111.22(3) | 94.64(3) | 90 | 101.91(3) | 111.92(3) | 86.407(4) |
| $\gamma$ (deg) | 90 | 90 | 90 | 90 | 90 | 74.361(4) |
| $V$ (Å$^3$) | 6415(2) | 8202(3) | 10017(3) | 3584.0(12) | 8593(3) | 4162.7(4) |
| $Z$ | 4 | 4 | 4 | 2 | 4 | 1 |
| forumula weight | 1339.20 | 1681.89 | 1885.53 + 72.11 | 1459.07 | 1777.36 | 3517.90 |
| space group | $P2_1/n$ | $P2_1/n$ | $P2_12_12_1$ | $Pn$ | $Cc$ | $P\overline{1}$ |
| $T$ (°C) | 143(2) K | 153(2) | 143(2) | 133(2) | 143(2) | 100(2) |
| $\lambda$ (Å) | 0.710 73 | 0.710 73 | 0.710 73 | 0.710 73 | 0.710 73 | 154.184 |
| $D_{calcd}$ (g cm$^{-3}$) | 1.387 | 1.362 | 1.250 | 1.285 | 1.374 | 1.403 |
| $\mu$ (mm$^{-1}$) | 1.193 | 0.916 | 0.783 | 1.033 | 1.020 | 17.471 |
| $F$(000) | 2752 | 3484 | 3920 | 1436 | 3672 | 1736 |
| data/restraints/ parameters | 11 651/0/746 | 16 753/137/1051 | 24 877/0/1109 | 14 935/2/780 | 22 900/716/1267 | 17 244/6/847 |
| goodness-of-fit on $F^2$ | 0.908 | 0.981 | 0.993 | 1.043 | 0.927 | 0.839 |
| $R(F_o$ or $F_o^2)$ | 0.0377 | 0.0344 | 0.0586 | 0.0511 | 0.0393 | 0.0417 |
| $R_w(F_o$ or $F_o^2)$ | 0.0852 | 0.0867 | 0.1467 | 0.1390 | 0.0701 | 0.0971 |

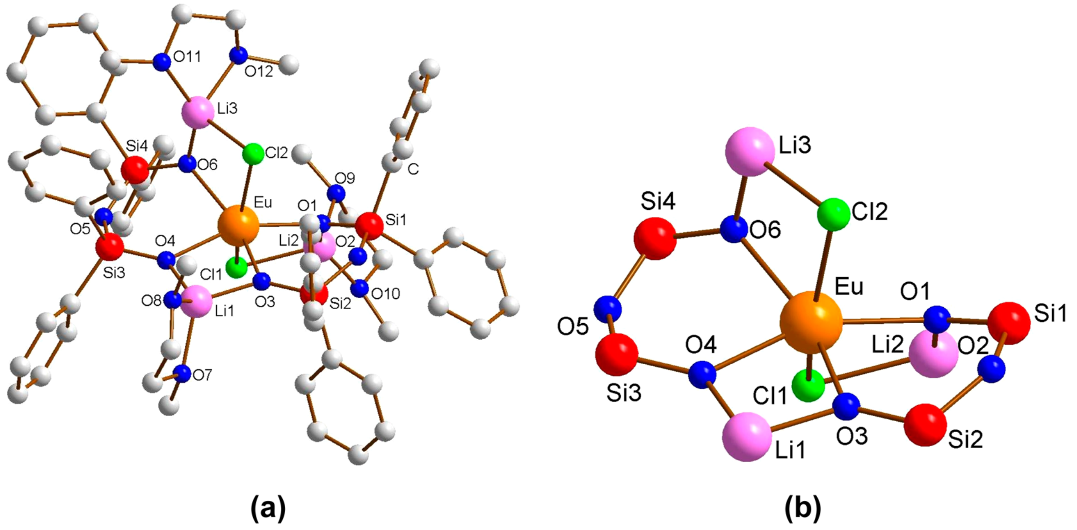


**Figure 1.** (a) Molecular structure of $[\{(Ph_2SiO)_2O\}_2\{Li(DME)\}_3]EuCl_2$ (**2**). For clarity, hydrogen atoms are omitted. (b) Core structural representation of complex **2**. Selected bond lengths (Å) and angles (deg): Eu−O(1) 2.328(3), Eu−O(3) 2.277(2), Eu−O(4) 2.281(3), Eu−O(6) 2.328(2), Eu−Cl(1) 2.7240(14), Eu−Cl(2) 2.7250(13), Li(1)−O(3) 1.909(7), Li(1)−O(4) 1.903(6), Li(1)−O(7) 1.994(7), Li(1)−O(8) 2.005(7), Li(2)−O(1) 1.869(7), Li(2)−O(9) 1.995(8), Li(2)−O(10) 1.984(8), Li(2)−Cl(1) 2.314(8), Li(3)−O(6) 1.985(7), Li(3)−O(11) 1.925(8), Li(3)−O(12) 1.987(8), O(1)−Eu−O(3) 111.42(7), O(1)−Eu−O(4) 156.47(9), O(1)−Eu−O(6) 117.32(9), O(1)−Eu−Cl(1) 77.66(6), O(1)−Eu−Cl(2) 91.46(7), O(3)−Eu−O(4) 74.80(9), O(3)−Eu−(O6) 153.04(9), O(3)−Eu−Cl(1) 111.42(7), O(3)−Eu−Cl(2) 87.06(7), O(4)−Eu−O(6) 84.62(9), O(4)−Eu−Cl(1) 96.04(7), O(4)−Eu−Cl(2) 101.28(7), O(6)−Eu−Cl(1) 87.85(7), O(6)−Eu−Cl(2) 79.98(7), Cl(1)−Eu−Cl(2) 157.53(3).

manner to two disiloxanediolate oxygen atoms. The coordination geometry around the central $Eu^{3+}$ ion can be best described as distorted octahedral. The solution structure appears to be highly fluxional in solution as the $^{29}Si$ NMR spectrum of **2** displays only a single resonance at $\delta$ −19.7 ppm.

With the first europium(III) bis-disiloxanediolate complex in hand, the reduction of compound **2** to the first *divalent* europium disiloxanediolate species was attempted. Metallic zinc is well-known to be a suitable reagent to achieve $Eu^{3+}/Eu^{2+}$ reduction.[21] A DME solution of **2** was stirred for one week in the presence of excess Zn turnings. The reaction vessel was periodically placed in an ultrasonic bath to reactivate the metal surface, which became covered by a white solid ($ZnCl_2$) during the course of the reaction. Filtration and subsequent crystallization of the product **3** (Scheme 3) from DME/*n*-pentane afforded colorless crystals in relatively low isolated yield (30%). The insoluble material also contained part of the europium, which might account for the low isolated yield. From the supernatant solution (after isolation of **3**), only some free $(HO)SiPh_2OSiPh_2(OH)$ (**1**) and the tetramer $(Ph_2SiO)_4$[1c] could be isolated. Once again, IR and NMR data turned out to be more or less uninformative. Single crystals of **3**

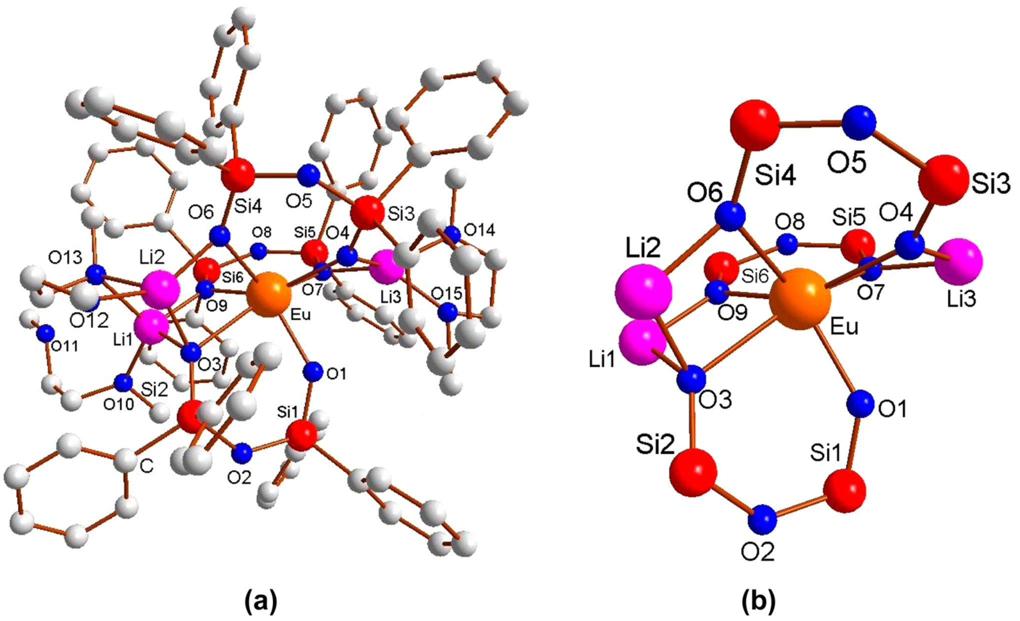


**Figure 2.** (a) Molecular structure of $[\{(Ph_2SiO)_2O\}_3\{Li(DME)\}_3]Eu$ (**3**). For clarity, hydrogen atoms are omitted. (b) Core structural representation of complex **3**. Selected bond lengths (Å) and angles (deg): Eu−O(1) 2.2023(18), Eu−O(3) 2.4767(17), Eu−O(4) 2.3081(19), Eu−O(6) 2.3442(18), Eu−O(7) 2.301(2), Eu−O(9) 2.3372(18), Li(1)−O(3) 1.941(5), Li(1)−O(9) 1.910(5), Li(1)−O(10) 1.914(5), Li(2)−O(3) 1.923(5), Li(2)−O(6) 1.873(5), Li(2)−O(12) 1.966(5), Li(2)−O(13) 2.170(5), Li(3)−O(4) 1.954(8), Li(3)−O(7) 1.953(7), Li(3)−O(14) 2.041(8), Li(3)−O(15) 2.119(9), O(1)−Eu−O(3) 82.07(6), O(1)−Eu−O(4) 84.78(7), O(1)−Eu−O(6) 134.01(7), O(1)−Eu−O(7) 88.79(7), O(1)−Eu−O(9) 117.50(7), O(3)−Eu−O(4) 131.28(6), O(3)−Eu−O(6) 73.86(6), O(3)−Eu−O(7) 151.61(7), O(3)−Eu−O(9) 75.23(6), O(4)−Eu−O(6) 82.72(7), O(4)−Eu−O(7) 73.94(7), O(4)−Eu−O(9) 149.62(7), O(6)−Eu−O(7) 128.94(7), O(6)−Eu−O(9) 93.65(7), O(7)−Eu−O(9) 85.53(7).

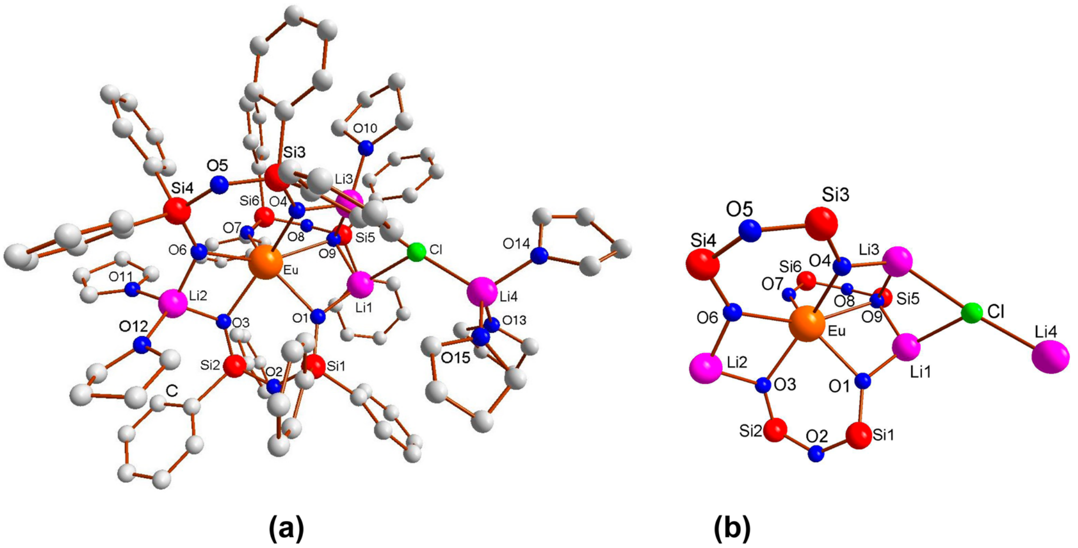


**Figure 3.** (a) Molecular structure of $[\{(Ph_2SiO)_2O\}_3Li\{Li(THF)_2\}\{Li(THF)\}]EuCl\cdot Li(THF)_3$ (**4**). For clarity, hydrogen atoms are omitted. (b) Core structural representation of complex **4**. Selected bond lengths (Å) and angles (deg): Eu−O(1) 2.450(3), Eu−O(3) 2.406(3), Eu−O(4) 2.431(3), Eu−O(6) 2.391(3), Eu−O(7) 2.293(3), Eu−O(9) 2.603(3), Li(1)−O(1) 1.816(9), Li(1)−O(9) 1.919(9), Li(1)−Cl 2.323(8), Li(2)−O(3) 1.897(11), Li(2)−O(6) 1.914(10), Li(2)−O(11) 1.976(9), Li(2)−O(12) 1.959(13), Li(3)−O(4) 1.924(10), Li(3)−O(9) 1.998(10), Li(3)−O(10) 1.891(10), Li(3)−Cl 2.603(9), Li(4)−O(13) 1.958(13), Li(4)−O(14) 1.928(11), Li(4)−O(15) 1.915(11), Li(4)−Cl 2.320(10), O(1)−Eu−O(3) 80.94(11), O(1)−Eu−O(4) 94.05(11), O(1)−Eu−O(6) 125.05(11), O(1)−Eu−O(7) 131.44(13), O(1)−Eu−O(9) 70.06(10), O(3)−Eu−O(4) 145.74(11), O(3)−Eu−O(6) 72.45(12), O(3)−Eu−O(7) 95.00(11), O(3)−Eu−O(9) 134.91(12), O(4)−Eu−O(6) 83.48(11), O(4)−Eu−O(7) 112.76(12), O(4)−Eu−O(9) 72.01(11), O(6)−Eu−O(7) 98.61(13), O(6)−Eu−O(9) 152.63(11), O(7)−Eu−O(9) 80.46(11).

suitable for X-ray diffraction were obtained by recrystallization from DME/*n*-pentane at room temperature.

The crystal structure determination of **3** revealed the unexpected presence of a europium(III) tris(disiloxanediolate) complex of the composition $[\{(Ph_2SiO)_2O\}_3\{Li(DME)\}_3]Eu$ (Figure 2). This product is a DME-solvated analogue of the previously reported homoleptic species $[\{(Ph_2SiO)_2O\}\{Li(Et_2O)\}]_3Eu$ (cf. Scheme 2).[15a,b] In both heterobimetallic tris(disiloxanediolates) the central $Eu^{3+}$ ion is surrounded by three formally monoanionic $[\{(Ph_2SiO)_2O\}\{Li(S)\}]^-$ units (S = $Et_2O$, DME (**3**)). Once again, this results in a distorted octahedral coordination geometry around the central $Eu^{3+}$ ion.

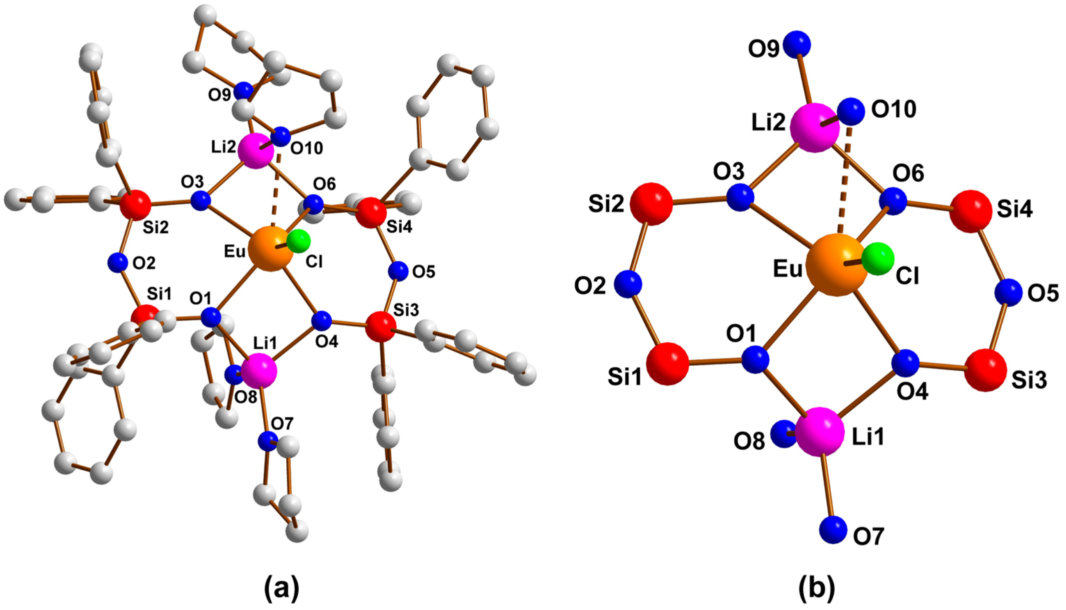


**Figure 4.** (a) Molecular structure of $[\{(Ph_2SiO)_2O\}_2\{Li(THF)_2\}_2]EuCl$ (**5**). For clarity, hydrogen atoms are omitted. (b) Core structural representation of complex **5**. Selected bond lengths (Å) and angles (deg): Eu–O(1) 2.246(4), Eu–O(3) 2.279(4), Eu–O(4) 2.257(4), Eu–O(6) 2.286(4), Eu–Cl 2.6288(16), Li(1)–O(1) 2.005(12), Li(1)–O(4) 1.975(13), Li(1)–O(7) 1.924(13), Li(1)–O(8) 1.962(11), Li(2)–O(3) 1.937(11), Li(2)–O(6) 1.934(11), Li(2)–O(9) 1.909.(12), Li(2)–O(10) 2.108(11), O(1)–Eu–O(3) 85.78(14), O(1)–Eu–O(4) 77.55(15), O(1)–Eu–O(6) 135.18(14), O(1)–Eu–Cl 98.81(10), O(3)–Eu–O(4) 135.40(14), O(3)–Eu–O(6) 77.97(15), O(3)–Eu–Cl 123.11(11), O(4)–Eu–O(6) 85.36(15), O(4)–Eu–Cl 100.36(11), O(6)–Eu–Cl 125.09(11).

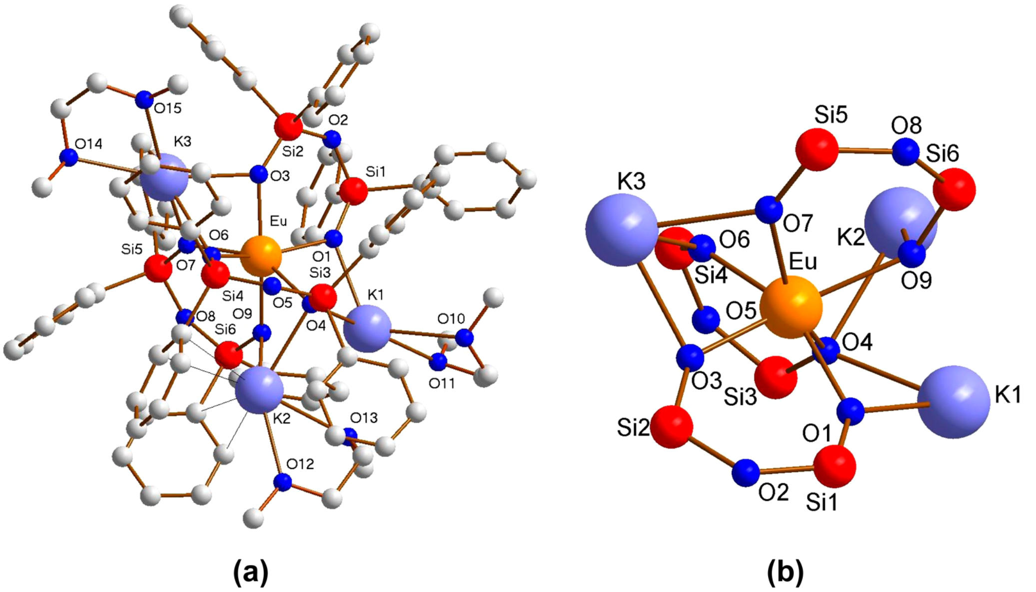


**Figure 5.** Molecular structure of $[\{(Ph_2SiO)_2O\}_3\{K(DME)\}_3]Eu$ (**6**). For clarity, hydrogen atoms are omitted. (b) Core structural representation of complex **6**. Selected bond lengths (Å) and angles (deg): Eu–O(1) 2.302(3), Eu–O(3) 2.258(2), Eu–O(4) 2.357(2), Eu–O(6) 2.296(3), Eu–O(7) 2.283(3), Eu–O(9) 2.376(3), K(1)–O(1) 2.648(3), K(1)–O(4) 2.687(3), K(1)–O(10) 2.916(11), K(1)–O(11) 2.649(9), K(2)–O(4) 2.754(3), K(2)–O(9) 2.713(3), K(2)–O(12) 2.677(3), K(2)–O(13) 2.990(3), K(3)–O(3) 2.606(3), K(3)–O(6) 2.689(3), K(3)–O(7) 2.689(3), K(3)–O(14) 2.715(6), K(3)–O(15) 2.739(8), O(1)–Eu–O(3) 83.60(10), O(1)–Eu–O(4) 85.59(9), O(1)–Eu–O(6) 152.78(9), O(1)–Eu–O(7) 119.71(11), O(1)–Eu–O(9) 86.35(11), O(3)–Eu–O(4) 118.03(12), O(3)–Eu–O(6) 82.21(11), O(3)–Eu–O(7) 84.52(11), O(3)–Eu–O(9) 159.40(9), O(4)–Eu–O(6) 80.80(9), O(4)–Eu–O(7) 149.07(10), O(4)–Eu–O(9) 78.90(9), O(6)–Eu–O(7) 81.86(12), O(6)–Eu–O(9) 113.69(12), O(7)–Eu–O(9) 84.91(11).

As in $[\{(Ph_2SiO)_2O\}\{Li(Et_2O)\}]_3Eu$, the molecule of **3** comprises three inorganic $EuSi_2O_3$ heterocyclic ring systems. Structural differences between $[\{(Ph_2SiO)_2O\}\{Li(Et_2O)\}]_3Eu$ and **3** arise from the presence of bidentate DME ligands in the latter. As shown in Scheme 2, the lithium ions in the diethyl ether adduct $[\{(Ph_2SiO)_2O\}\{Li(Et_2O)\}]_3Eu$ are only tricoordinate with one diethyl ether ligand completing the coordination sphere around each Li. Four oxygen atoms are coordinated to one Li (tricoordination around O), while one oxygen is engaged in two Li–O bonds (tetracoordination around O). The remaining oxygen is not bonded to lithium and remains dicoordinate. As in $[\{(Ph_2SiO)_2O\}\{Li(Et_2O)\}]_3Eu$ (Scheme 2) the structural core

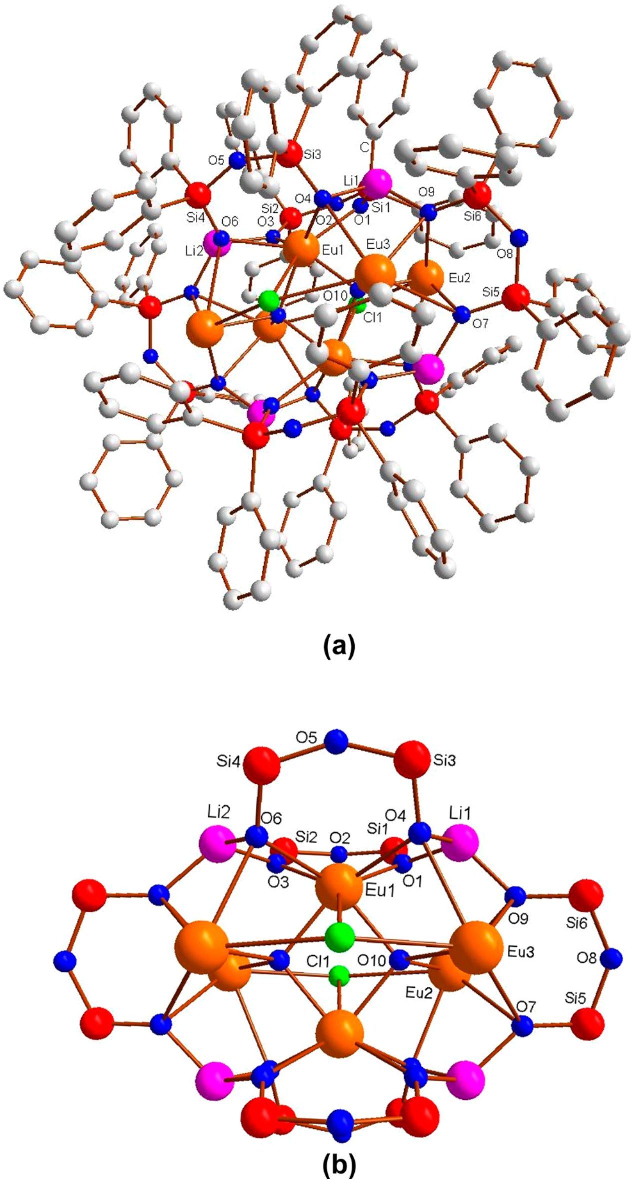


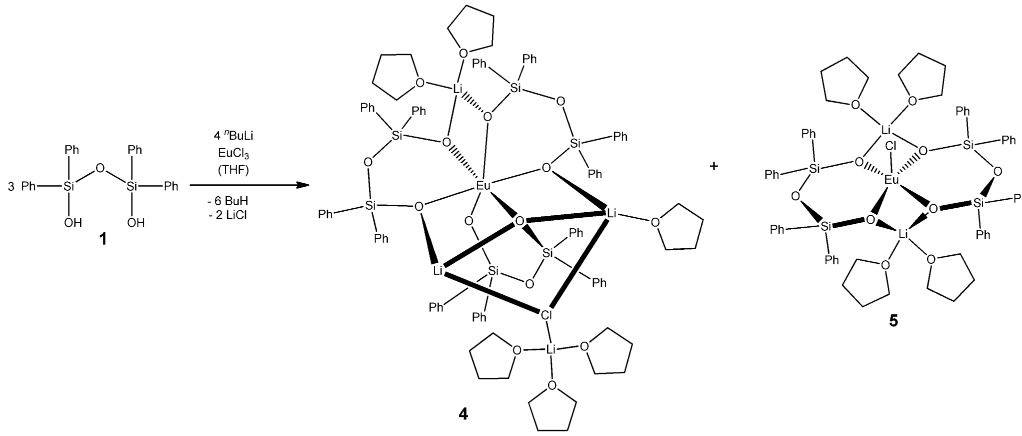
**Figure 6.** Molecular structure of $[(Ph_2SiO)_2O]_6Eu^{II}_4Eu^{III}_2Li_4O_2Cl_2$ (**7**). For clarity, hydrogen atoms are omitted. (b) Core structural representation of complex **7**. Selected bond lengths (Å) and angles (deg): Eu(1)−O(1) 2.400(3), Eu(1)−O(3) 2.406(3), Eu(1)−O(4) 2.443(3), Eu(1)−O(6) 2.451(3), Eu(1)−O(10) 2.232(3), Eu(1)−Cl(1)#1 3.2320(14), Eu(2)−O(6)#1 2.830(3), Eu(2)−O(7) 2.278(3), Eu(2)−O(9) 2.905(3), Eu(2)−O(10) 2.411(3), Eu(2)−Cl(1) 3.0262(13), Eu(3)−O(4) 2.751(3), Eu(3)−O(7) 2.825(3), Eu(3)−O(9) 2.783(3), Eu(3)−O(10) 2.430(3), Eu(3)−Cl(1)#1 3.0483(13), Li(1)−O(1) 1.899(9), Li(1)−O(4) 1.899(9), Li(1)−O(9) 1.853(9), Li(2)−O(3) 1.890(10), Li(2)−O(6) 1.911(10), Li(2)−O(7)#1 1.839(9).

of **3** is not centrosymmetric (cf. Figure 2b). Figure 2 also shows that in **3** all three lithium ions and DME ligands are coordinated in a different fashion. One Li(DME) unit (Li3) bridges two disiloxanediolate ligands via oxygen in the usual manner.[1q,15] Li2 is coordinated by a chelating DME ligand, but one MeO oxygen atom of the latter also bridges Li1 and Li2. The third DME ligand is coordinated to Li1 in an unusual monodentate fashion with one dangling methoxyethyl group. This way a distorted tetrahedral coordination environment is achieved around each of the three lithium ions. Certainly the high degree of asymmetry in the molecular structure of **3** can be traced back to severe steric congestion as can be clearly seen in Figure 2a in comparison with the significantly less crowded structure of **2** (Figure 1a). High steric crowding in **3** is also assumed to be the reason for the presence of a rare monodentate DME ligand.[22] For the same reason, the lithium ions in $[\{(Ph_2SiO)_2O\}\{Li(Et_2O)\}]_3Eu$ are only tricoordinate through addition of only one diethyl ether ligand.[15a,b]

In another experiment, the reaction of anhydrous $EuCl_3$ with 2 equiv of *in situ*-generated $(LiO)SiPh_2OSiPh_2(OLi)$ was carried out in THF solution to study the influence of the reaction medium on the product formation. In this case a product mixture of bis- and tris(disiloxanediolate) complexes was obtained, which could be separated by fractional crystallization from the concentrated reaction mixture. The molecular structures of both products were authenticated through X-ray diffraction studies. As a result, the less soluble product turned out to be the europium(III) tris(disiloxanediolate) ate complex $[\{(Ph_2SiO)_2O\}_3Li\{Li(THF)_2\}\{Li(THF)\}]EuCl\cdot Li(THF)_3$ (**4**, 24% yield), while the more soluble product was shown to be the LiCl-free europium(III) bis(disiloxanediolate) $[\{(Ph_2SiO)_2O\}_2\{Li(THF)_2\}_2]EuCl$ (**5**, 61% yield) (Scheme 4). The reaction of anhydrous $EuCl_3$ with 2 equiv of *in situ*-generated $(LiO)SiPh_2OSiPh_2(OLi)$ according to Scheme 4 appears to be the best way to obtain both **4** and **5** as pure, crystalline materials in synthetically useful quantities. The same reaction in a 1:1 molar ratio resulted only in unseparable mixtures, while a 1:3 reaction provided only slightly higher yields of **4** still admixed with large amounts of **5** and some free $(HO)SiPh_2OSiPh_2(OH)$ (**1**), which made the separation of **4** and **5** by fractional crystallization more difficult.

The europium(III) tris(disiloxanediolate) complex $[\{(Ph_2SiO)_2O\}_3Li\{Li(THF)_2\}\{Li(THF)\}]EuCl\cdot Li(THF)_3$ (**4**) was isolated in the form of colorless, cubelike crystals by crystallization from the concentrated reaction mixture after separation of the LiCl byproduct. A single-crystal X-ray analysis (Table 1, Figure 3) revealed the presence of a third variation of the europium(III) tris(disiloxanediolate) motif. The central europium is coordinated in a distorted octahedral fashion by six siloxide oxygen atoms of the disiloxanediolate ligands. Three lithium ions (Li1, Li2, Li3) each bridge two neighboring siloxide oxygen atoms of different disiloxanediolate ligands, thereby forming three nearly planar four-membered $EuO_2Li$ rings. The tetrahedral coordination sphere around Li2 is completed by two THF ligands. A novel structural feature of complex **4** is that it is an ate complex formed by incorporation of 1 equiv of LiCl. The Cl atom bridges Li1 and Li3 to give a four-membered $OLi_2Cl$ ring. Additional bonding to Li4 results in a flat trigonal-pyramidal coordination around chlorine. The normal tetrahedral coordination geometry around Li4 is achieved through addition of three THF ligands. This part of the molecule closely resembles the well-investigated lanthanide silylamide-derived ate complexes $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ (Ln = Y, La, Nd, Sm, Eu, Yb).[16,22] These compounds are formed by reactions of anhydrous lanthanide(III) chlorides with 3 equiv of lithium bis(trimethylsilyl)amide, $LiN(SiMe_3)_2$, in THF, followed by recrystallization from toluene. Sublimation of the ate complexes afforded the corresponding homoleptic tricoordinate silylamide complexes $[(Me_3Si)_2N]_3Ln$.[16] In the $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ intermediates, which have been shown to be promising homogeneous catalysts,[22] there is a nearly linear Ln−Cl−Li linkage, and the tetrahedral coordination sphere is also completed by three THF ligands as in **4**.

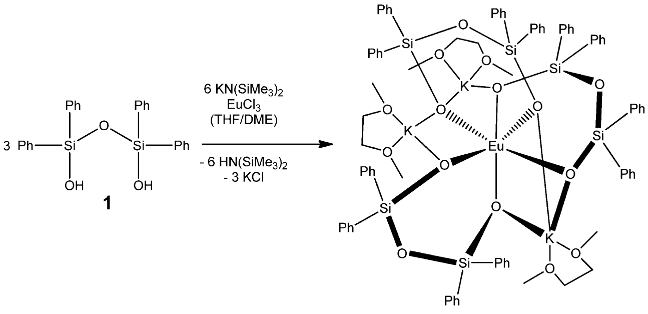
Scheme 4. Formation of [{$(Ph_2SiO)_2O$}$_3$Li{Li$(THF)_2$}{Li(THF)}]EuCl·Li$(THF)_3$ (4) and [{$(Ph_2SiO)_2O$}$_2${Li$(THF)_2$}$_2$]EuCl (5)



The less-soluble product formed in the reaction shown in Scheme 4 was the europium(III) bis(disiloxanediolate) derivative [{$(Ph_2SiO)_2O$}$_2${Li$(THF)_2$}$_2$]EuCl (**5**), which was isolated in the form of colorless crystals in 61% yield. The molecular structure of this product was again established by single-crystal X-ray diffraction (Table 1, Figure 4). The X-ray analysis revealed the presence of a simple symmetric bis(disiloxanediolate) of trivalent europium of the composition [{$(Ph_2SiO)_2O$}$_2${Li$(THF)_2$}$_2$]EuCl. This complex is closely related to the *cisoid* form B shown in Scheme 1, although in this case there is no additional solvent coordinated to the central $Eu^{3+}$ ion. Thus, at the first glance, the central europium appeared to be only five-coordinate, which would be an unusually low coordination number for europium. However, a closer examination of the X-ray structural data revealed that there is a weak but significant interaction between Eu and an oxygen of one of the THF ligands coordinated to Li2 (Eu−O10 2.801(6) Å. Taking this bridging THF ligand into account, the coordination geometry around europium in **5** can be best described as distorted trigonal prismatic (Figure 4). As can be also seen in Figure 4, the europium is significantly displaced from the center of the 12-membered $Si_4O_6Li_2$ inorganic ring system formed by two lithium disiloxanediolate units. Here the use of the intermediate size $Eu^{3+}$ ion leads to a structural variety of lanthanide bis(disiloxanediolates), which has been previously reported only for [{$(Ph_2SiO)_2O$}$_2${Li$(THF)_2$}$_2$]HoCl·2THF and [{$(Ph_2SiO)_2O$}$_2${Li$(THF)_2$}$_2$]ErCl·2THF,[23] although these two derivatives crystallize with two molecules of THF in the unit cell, whereas **5** is unsolvated. Two lithium disiloxanediolate units are connected to form a 12-membered $Si_4O_6Li_2$ metallacycle to which the lanthanide ion is coordinated in an out-of-plane fashion. The other structural details of **5** are unexceptional with the $Eu-O_{silox}$ distances being in the narrow range of 2.246(4) (O1)−2.268(4) (O6) Å. With 2.6288(16) Å the Eu−Cl bond length is only slightly shorter than those reported for adducts of europium trichloride, for example, Eu−Cl 2.637 Å in $EuCl_3(THF)_4$[24a] and Eu−Cl 2.654 Å in $EuCl_3(pyridine)_4$.[24b]

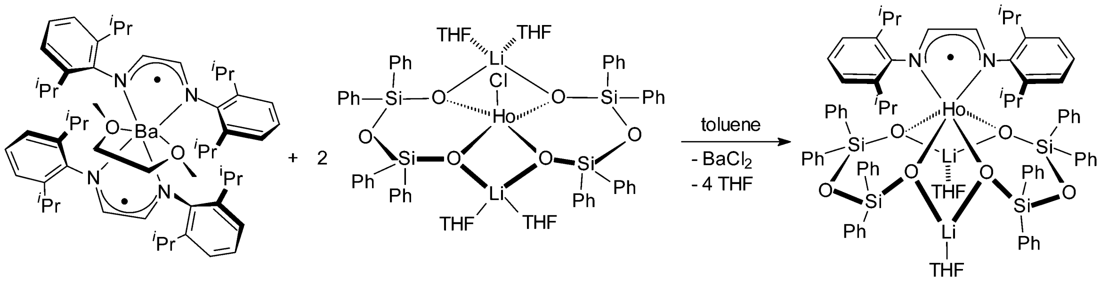
The reaction illustrated in Scheme 5 was carried out with the aim of studying the influence of the alkali metal on the structures of the resulting heterometallic europium disiloxanediolates. That is, lithium was replaced by potassium. In this experiment, 1,1,3,3-tetraphenyl-disiloxane-1,3-diol, $(HO)SiPh_2OSiPh_2(OH)$ (**1**) was deprotonated with $KN(SiMe_3)_2$ in THF, and the resulting $(KO)SiPh_2OSiPh_2(OK)$ intermediate was treated with anhydrous europium(III) trichloride in a molar ratio of 3:1. Workup followed by crystallization from THF/DME produced the colorless heterometallic (Eu/K) tris(disiloxanediolate) complex **6** in moderate yield (31%) (Scheme 5).

Scheme 5. Preparation of the Homoleptic $Eu^{III}$ Tris(disiloxanediolate) [{$(Ph_2SiO)_2O$}$_3${K(DME)}$_3$]Eu (6)

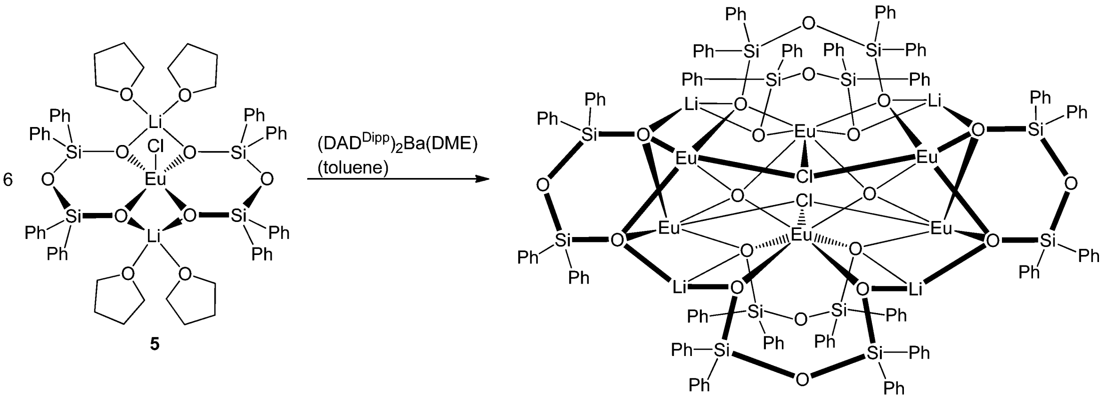


Again, compound **6** could be characterized by the standard set of elemental analysis and spectroscopic data (IR; $^1H$, $^{13}C$, and $^{29}Si$ NMR), but a single-crystal X-ray diffraction study was essential to unambiguously assign the molecular structure of **6** (Table 1, Figure 5). The X-ray analysis revealed the presence of the homoleptic $Eu^{III}$ tris(disiloxanediolate) [{$(Ph_2SiO)_2O$}$_3${K(DME)}$_3$]Eu (**6**). Surprisingly, the use of the larger potassium ion instead of lithium in this case had no major influence on the molecular structure of the homoleptic tris(disiloxanediolate) product. A comparison of **6** (Scheme 5) with the homoleptic, heterometallic (Eu/Li) europium tris(disiloxanediolate) [{$(Ph_2SiO)_2O$}{Li$(Et_2O)$}]$_3$Eu shown in Scheme 2 revealed a close structural similarity. In both cases, the siloxide oxygen atoms of the chelating disiloxanediolate ligands are bridged in the same manner by the alkali metals, only that the tricoordinate $Li(OEt_2)$ units in [{$(Ph_2SiO)_2O$}{Li$(Et_2O)$}]$_3$Eu are replaced by tetracoordinate K(DME) units in **6**. The only significant structural difference concerns the potassium ion K3 in the molecular structure of **6**. In this molecule, both K1 and K2 comprise the same distorted tetrahedral $KO_4$ coordination geometry by being coordinated to two siloxide oxygens and a chelating DME. In contrast, K3 is five-coordinated by carrying a chelating DME ligand and simultaneously bridging three siloxide oxygen atoms (Figure 5). Similar to compound **2**, the structure of **6** in solution appears to be highly fluxional because in the $^{29}Si$

Scheme 6. Synthesis of the Holmium Bis(disiloxanediolate) Complex $[\{(Ph_2SiO)_2O\}_2\{Li(THF)_2\}_2]Ho(DAD^{Dipp})$



Scheme 7. Formation of the Mixed-Valent $Eu^{III}/Eu^{II}$ Disiloxanediolate Cluster $[(Ph_2SiO)_2O]_6Eu^{II}_4Eu^{III}_2Li_4O_2Cl_2$ (7).



**5**

**7**

NMR spectrum only a single resonance at δ −24.3 ppm was observed.

Notably, the trivalent europium disiloxanediolate complexes **2**−**6** can be safely handled in dry air for short periods of time (hours) but are easily susceptible to hydrolysis.

Recently we reported the synthesis and structural characterization of a unique lanthanide bis(disiloxandiolate) complex comprising the radical anion of a bulky diazadiene as additional ligand. The barium reagent $(DAD^{Dipp})_2Ba(DME)$ contains the bulky diazadiene ligand *N*,*N*′-bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene ($DAD^{Dipp}$) in its radical-anionic form. The barium complex was then successfully employed to transfer the $DAD^{Dipp}$ radical anion ligand onto holmium in the holmium bis(disiloxanediolate) complex $[\{(Ph_2SiO)_2O\}_2\{Li(THF)_2\}_2]$-HoCl[23] as illustrated in Scheme 6.[25] The successful isolation of the product, $[\{(Ph_2SiO)_2O\}_2\{Li(THF)_2\}_2]Ho(DAD^{Dipp})$, was facilitated by the virtual insolubility of the barium chloride byproduct in toluene. With this synthesis, transfer of a DAD radical anion ligand from an alkaline earth metal to a rare-earth metal had been achieved for the first time.

As shown above, the new compound $[\{(Ph_2SiO)_2O\}_2\{Li(THF)_2\}_2]EuCl$ (**5**) is the europium analogue of $[\{(Ph_2SiO)_2O\}_2\{Li(THF)_2\}_2]HoCl$.[23] Thus we attempted to prepare the analogous europium complex $[\{(Ph_2SiO)_2O\}_2\{Li(THF)_2\}_2]Eu(DAD^{Dipp})$ by following the route outlined in Scheme 6. As described for the Ho derivative, the reaction was carried out in toluene solution in a molar ratio of 2:1 (Eu/Ba). Almost immediately the black−red color of the radical anion complex $(DAD^{Dipp})_2Ba(DME)$ disappeared, and a white precipitate of $BaCl_2$ appeared. However, the reaction took an entirely different and unexpected course. The orange color of the resulting solution already indicated the presence of divalent europium. Filtration followed by crystallization from toluene afforded small orange crystals, which were shown by X-ray crystallography to be the unusual mixed-valent $Eu^{III}/Eu^{II}$ disiloxanediolate cluster $[(Ph_2SiO)_2O]_6Eu^{II}_4Eu^{III}_2Li_4O_2Cl_2$ as illustrated in Scheme 7.

After having established the molecular structure of **7**, the isolated yield was determined to be 61%. Although details of the formation of **7** are unclear, it can be assumed that the strongly reducing radical anion reagent $(DAD^{Dipp})_2Ba(DME)$ reduces part of the trivalent europium to the divalent state. In accordance with this assumption, the free diazadiene $DAD^{Dipp}$ was found in the concentrated mother liquid. The X-ray analysis (Table 1, Figure 6) revealed the presence of a huge molecule having the composition $[(Ph_2SiO)_2O]_6Eu^{II}_4Eu^{III}_2Li_4O_2Cl_2$ and a molar mass of $M_r$ = 3517.96. The formation of this neutral cluster with balanced ionic charges can only be explained by the presence of four $Eu^{2+}$ ions. This accounts for the unusual orange color of **7**, whereas all of the europium(III) disiloxanediolates **2**−**6** are colorless. The presence of divalent europium in **7** also accounts for the fact that, unlike the trivalent complexes **2**−**6**, this species is rather air-sensitive. Both crystals and solutions of **7** are rapidly decolorized upon contact with air. The fact that complex **7** shows an intense orange color while the other compounds are colorless can be explained by the existence of an intervalence charge transfer (IVCT) excited state due to the presence of europium ions in different oxidation states. The overall structure is centrosymmetric with the six europium atoms forming a distorted octahedron. Together with the two chlorine atoms in the equatorial plane, the octahedral cluster core is expanded to a hexagonal bipyramid. The central core is further held together by two oxide ions (O10 and O10#1). Each of these oxide ions is tetrahedrally surrounded by four europium atoms. Six bridging disiloxanediolate ligands provide an organic periphery around the cluster core, which explains the high solubility of the cluster

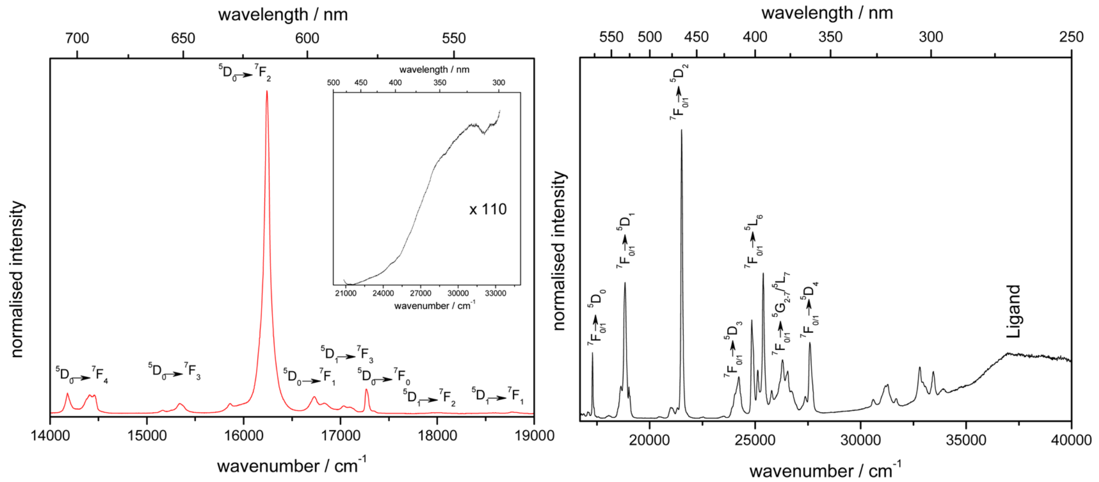


**Figure 7.** Room-temperature emission spectrum excited at 37 740 $cm^{-1}$ (265 nm) (left) and excitation spectrum detected at 16 240 $cm^{-1}$ (617 nm) (right) of $[\{(Ph_2SiO)_2O\}_2\{Li(THF)_2\}_2]EuCl$ (**5**). (inset) The weak emission of the ligand at higher energies.

even in toluene. While the cluster **7** is unique in lanthanide disiloxanediolate chemistry, note that previous literature holds various examples of, for example, hexa- and octanuclear europium complexes, most of which contain $\mu_6$-oxo and $\mu_3$-hydroxo ligands.[26] Mixed-valent $Ln^{II}/Ln^{III}$ complexes of samarium, europium, and ytterbium are also not without precedent. The formation of such compounds has frequently been observed, for example, in the chemistry of alkoxides and aryloxides of these metals.[27]

**Luminescence Studies.** None of the compounds **2**−**7** showed significant visible emission upon irradiation with UV light of 254 or 365 nm. However, it was found that upon fracturing of larger crystals, the europium(III) bis(disiloxanediolate) $[\{(Ph_2SiO)_2O\}_2\{Li(THF)_2\}_2]EuCl$ (**5**) exhibited a brilliant red triboluminescence; therefore, we present first results of its photoluminescence properties here. Previous examples of lanthanide complexes, for which red triboluminescence has been reported, include, for example, the triethylammonium[28a] and piperidinium salts[28b] of the tetrakis(dibenzoylmethanato)europate anion, $[Eu\{CH(COPh)_2\}_4]^-$, hexakis(antipyrine)terbium triiodide,[28b] and $[Tb(H_2O)_6Cl_2]Cl$.[28b] The optical emission and excitation spectra for crystals of hexakis(antipyrine)terbium triiodide and -triperchlorate have also been reported.[28c]

Characteristic $Eu^{3+}$ f−f emission bands could be detected upon excitation of the ligands (21 505 $cm^{-1}$, 465 nm), as well as excitation of Eu ions directly (37 740 $cm^{-1}$, 265 nm) (Figure 7, left). They can mostly be assigned to transitions starting from the $^5D_0$ state to the $^7F_J$ ground state manifold. The most intensive emission band originates from the induced electric dipole transition $^5D_0 \rightarrow ^7F_2$, while the magnetic dipole-allowed transition, $^5D_0 \rightarrow ^7F_1$, is of moderate intensity. The occurrence of the $^5D_0 \rightarrow ^7F_0$ transition indicates the absence of an inversion center[29] in agreement with the results of the crystal structure determination. It should be mentioned here that the by far most intense, narrow $^5D_0 \rightarrow ^7F_2$ transition causes a brilliant red emission of the compound.

Because of the low point symmetry ($C_1$) of the $Eu^{3+}$ ions in **5**, the emission bands of the $^5D_0 \rightarrow ^7F_J$ ($J$ = 1, 2, 3, and 4) transitions should split into 3, 5, 7, and 9 peaks, respectively.[29] In fact, we observed much less crystal field-assisted transitions than expected. This can be explained by several reasons. Mainly, some transitions may be very close in energy, which cannot be resolved in room-temperature measurements. However, the observation of only two peaks for both $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions is remarkable; in general they are split even at room temperature. Therefore it can be assumed that the local symmetry is slightly distorted and, thus, pseudo $C_{2v}$ or $C_{4v}$.[30,31] This fact will be investigated in detail in future low-temperature measurements.

In addition, weak emission bands starting from the $^5D_1$ level, which is populated at room temperature, into the $^7F_J$ states could be observed. However, in general these transitions are quenched by multiphonon processes or by cross relaxation. However, in the present case, this observation can be explained by the long distance of about 13.6 Å between two Europium atoms, which prohibits an efficient cross relaxation. Ligand excitation at 465 nm leads also to weak ligand emission starting at ∼21 700 $cm^{-1}$ and peaking at 31 000 $cm^{-1}$ (inset in Figure 7, left). The weakness of this band illustrates that excitation followed by relaxation of the ligands leads rather to Eu f−f emission and, thus, to ligand−Eu transfer than to ligand emission.

In the excitation spectrum several narrow bands and a rather weak, broad band peaking at ∼37 500 $cm^{-1}$ could be observed (Figure 7 right). The narrow peaks can be assigned to the transition from the $^7F_0$ and $^7F_1$ ground states into the excited f-states of $Eu^{3+}$ ions as assigned in Figure 7. The broad band originates most probably to excitation of the ligands and not to the charge-transfer (CT) transition of the ligands to Eu ions, because a respective emission is observed (inset in Figure 7, left). While CT transitions of $Eu^{3+}$ ions leads in general to Eu f−f emission exclusively, ligand excitation shows at least partly ligand emissions. The allowed ligand excitation band is rather low compared to the forbidden $Eu^{3+}$ f−f excitation peaks. This indicates that although the ligand excitation leads rather to Eu emission than to direct ligand emission, quenching of the ligand emission is the dominant process, so that Eu emission can be induced more efficiently by direct Eu excitation.

Lifetime measurements of **5** were performed at room temperature by detecting the $Eu^{3+}$ $5D_0 \rightarrow ^7F_J$ emission with excitation of the ligands and the $Eu^{3+}$ ions directly. All photoluminescence decay curves are biexponential (Supporting Information, Figure S13). For ligand excitation we observed longer lifetimes ($\tau_1$ = 255 $\mu s$/$\tau_2$ = 807 $\mu s$) than for direct $Eu^{3+}$ excitation ($\tau_1$ = 140 $\mu s$/$\tau_2$ = 702 $\mu s$). For ligand excitations two lifetimes are in general observed due to energy transfer and Eubased emission processes. The biexponential decay for direct Eu excitation cannot, however, be assigned on the current stage. Moreover, it is remarkable that only complex **5** shows luminescence at room temperature. Obviously the emission of the other compounds is mostly quenched by vibronic-assisted radiationless transitions. This behavior cannot be easily understood from the crystal structures, and more detailed investigations of all compounds, mainly temperature-dependent luminescence measurements, are necessary to clear this point. Respective investigations will be done in the future.

## CONCLUSIONS

In summarizing the work reported here, the chemistry of europium disiloxanediolate complexes has been greatly expanded by the synthesis and structural characterization of six new derivatives of this class of metallasiloxanes. The results underline the astonishing versatility of the tetraphenyl-1,3-disiloxanediolate dianionic ligand. Heterometallic bis- and tris(disiloxanediolates) have been prepared using straightforward synthetic protocols, and the influence of solvent and the nature of the alkali metal (Li vs K) have been studied. An unexpected reaction between $[\{(Ph_2SiO)_2O\}_2\{Li(THF)_2\}_2]EuCl$ (**5**) and the diazadiene radical anion complex $(DAD^{Dipp})_2Ba(DME)$ afforded the unprecedented mixed-valent $Eu^{III}/Eu^{II}$ disiloxanediolate cluster $[(Ph_2SiO)_2O]_6Eu^{II}{}_4Eu^{III}{}_2Li_4O_2Cl_2$ (**7**). All new compounds have been structurally authenticated by single-crystal X-ray diffraction. While none of the new compounds showed luminescence under UV light, a brilliant red triboluminescence was discovered for the $Eu^{3+}$ bis(disiloxanediolate) complex $[\{(Ph_2SiO)_2O\}_2\{Li(THF)_2\}_2]EuCl$ (**5**).

## EXPERIMENTAL SECTION

**General Procedures.** All operations were performed with rigorous exclusion of air and water in oven-dried or flame-dried glassware under an inert atmosphere of dry argon or dry nitrogen, employing standard Schlenk, high-vacuum, and glovebox techniques (MBraun MBLab; <1 ppm $O_2$, <1 ppm $H_2O$). THF, DME, toluene, and *n*-pentane were dried over sodium/benzophenone and freshly distilled under nitrogen atmosphere prior to use. All glassware was oven-dried at 120 °C for at least 24 h, assembled while hot, and cooled under high vacuum prior to use. The starting materials, $(HO)SiPh_2OSiPh_2(OH)$ (**1**),[32] anhydrous $EuCl_3$,[33] and $(DAD^{Dipp})_2Ba(DME)$[25] were prepared according to published procedures. *n*-Butyllithium (1.6 M solution in *n*-hexane) and $KN(SiMe_3)_2$ were purchased from Aldrich and used as received. The NMR spectra were recorded in THF-$d_8$ solutions on a Bruker DPX 600 ($^1$H: 600.1 MHz; $^{13}$C: 150.9 MHz; $^{29}$Si: 79.5 MHz) or a Bruker DPX 400 ($^1$H: 400.1 MHz; $^{13}$C: 100.6 MHz) spectrometer. $^1$H, $^{13}$C, and $^{29}$Si shifts are referenced to internal solvent resonances and reported in parts per million relative to tetramethylsilane, $Si(CH_3)_4$. IR (KBr) spectra were measured using a Perkin-Elmer FT-IR 2000 spectrometer. Microanalyses of the compounds were performed using a Vario El cube (Elementaranalysensysteme GmbH) apparatus.

**X-Ray Diffraction Analyses.** All new compounds prepared in the course of the present study have been structurally characterized by single-crystal X-ray diffraction. Table 1 summarizes the crystallographic data for **2**−**7**. The intensity data of **2**−**6** were collected on a Stoe IPDS 2T diffractometer with Mo K$\alpha$ radiation. The data were collected with the Stoe XAREA[34] program using $\omega$-scans. The space groups were determined with the XRED32[34] program. The intensity data of **7** were registered on an Oxford Diffraction Nova A diffractometer using mirror-focused Cu K$\alpha$ radiation. Absorption corrections were applied using the multiscan method. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods on $F^2$ using SHELXL-97.[35]

**Photoluminescence and Lifetime Measurements.** Photoluminescence measurements on solid-state samples of **5** at room temperature were performed with the aid of a Fluorolog3 spectrofluorometer Fl3−22 (Horiba Jobin Yvon) equipped with double Czerny−Turner monochromators, a 450 W xenon lamp, a 75 W flash lamp, and a photomultiplier R928 (Hamamatsu). Emission spectra were corrected for the photomultiplier sensitivity, and excitation spectra were corrected for the intensity of the excitation source.

*Synthesis of* $[\{(Ph_2SiO)_2O\}_2\{Li(DME)\}_3]EuCl_2$ *(**2**).* $(Ph_2SiOH)_2O$ (**1**, 10.0 mmol, 4.10 g) was dissolved in DME (125 mL), and *n*-butyllithium (12.4 mL of a 1.6 M solution in *n*-hexane) was added at 0 °C. The reaction mixture was stirred overnight at room temperature, and anhydrous $EuCl_3$ (1.29 g, 5.0 mmol) was added, followed by stirring for another 24 h. The volume of the solution was reduced to ∼50 mL, and the precipitated LiCl was removed by filtration. After concentrating the filtrate to a total volume of ca. 15 mL, colorless needles of **2** (4.69 g, 68%) were isolated upon standing at room temperature. Anal. Calcd. for $C_{60}H_{70}Cl_2EuLi_3O_{12}Si_4$ ($M_r$ = 1339.20): C, 53.72; H, 5.28. Found: C, 53.19; H, 5.23%. mp > 151 °C (dec). IR (KBr) $\nu_{max}$ (cm$^{-1}$): 3131 (w), 3066 (m, $\nu_{C-H}$), 3046 (m, $\nu_{C-H}$), 2999 (m, $\nu_{C-H}$), 2935 (m), 2833 (w), 2342 (vw), 1965 (vw), 1892 (vw), 1835 (vw), 1775 (vw), 1656 (vw), 1619 (vw), 1589 (w, $\nu_{C=C}$), 1568 (w), 1474 (w), 1451 (m), 1428 (s), 1366 (w), 1273 (w), 1244 (w), 1194 (m, $\nu_{Si-C}$), 1119 (vs, $\nu_{Si-O}$, $\nu_{C-O}$), 1082 (vs), 1033 (s), 1009 (vs), 962 (vs), 873 (m), 837 (w), 748 (s), 702 (vs), 682 (m), 620 (vw), 535 (vs), 506 (s), 478 (s). $^1$H NMR (400.1 MHz, THF-$d_8$, 294.4 K): $\delta$ 7.23−6.64 (m, 40H, Ph), 3.14 (s, 12H, DME), 3.00 (s, 18H, DME). $^{13}$C NMR (100.6 MHz, THF-$d_8$, 294.4 K): $\delta$ 133.6 (*ipso*-C), 128.0, 127.0, 126.6 (Ph), 72.0, 58.4 (DME). $^{29}$Si NMR (79.5 MHz, THF-$d_8$, 294.4 K): $\delta$ −19.7.

*Synthesis of* $[\{(Ph_2SiO)_2O\}_3\{Li(DME)\}_3]Eu$ *(**3**).* The compound $[\{(Ph_2SiO)_2O\}_2\{Li(DME)\}_3]EuCl_2$ (**2**, 3.4 mmol, 4.7 g) was dissolved in DME (130 mL), and excess zinc (turnings, 0.13 g) was added. The mixture was stirred for one week. During this time an ultrasonic bath was used periodically to activate the Zn metal surface. Unreacted Zn and a white solid ($ZnCl_2$), which precipitated during the reaction, were removed by filtration. The volume of solution was reduced to a volume of ∼10 mL, and 2.5 mL of *n*-pentane were added. Colorless crystals of **3** (1.7 g, 30%) were isolated at room temperature. Anal. Calcd. for $C_{84}H_{90}EuLi_3O_{15}Si_6$ ($M_r$ = 1680.90): C, 60.02; H, 5.40. Found: C, 59.86; H, 5.26%. mp > 223 °C (dec). IR (KBr) $\nu_{max}$ (cm$^{-1}$): 3066 (m, $\nu_{C-H}$), 3045 (m, $\nu_{C-H}$), 2999 (m, $\nu_{C-H}$), 2932 (m), 2539 (w), 1961 (vw), 1891 (vw), 1827 (vw), 1776 (vw), 1637 (m), 1607 (m), 1590 (m, $\nu_{C=C}$), 1474 (w), 1451 (m), 1428 (m), 1368 (w), 1343 (w), 1306 (w), 1245 (m), 1193 (w, $\nu_{Si-C}$), 1182 (w, $\nu_{Si-C}$), 1156 (m), 1120 (vs, $\nu_{Si-O}$, $\nu_{C-O}$), 1084 (s), 1064 (m), 1033 (s), 1006 (vs), 971 (vs), 875 (w), 850 (w), 743 (m), 702 (vs), 683 (w), 621 (vw), 530 (s), 487 (m), 406 (vw). $^1$H NMR (400.1 MHz, THF-$d_8$, 298.0 K): $\delta$ 9.56 (s, 12H, Ph), 7.86−7.01 (m, 48H, Ph), 3.43 (s, 12H, DME), 3.28 (s, 18H, DME). $^{13}$C NMR (100.6 MHz, THF-$d_8$, 295 K): $\delta$ 142.7 (*ipso*-C), 138.0, 135.6, 135.4.0, 134.0, 128.9, 128.7, 128.4, 127.6, 127.4, 127.0 (Ph), 72.6, 58.8 (DME). $^{29}$Si NMR (79.5 MHz, THF-$d_8$, 294.5 K): $\delta$ −39.7.

*Synthesis of* $[\{(Ph_2SiO)_2O\}_3Li\{Li(THF)_2\}\{Li(THF)\}]EuCl\cdot Li(THF)_3$ *(**4**) and* $[\{(Ph_2SiO)_2O\}_2\{Li(THF)_2\}_2]EuCl$ *(**5**).* $(Ph_2SiOH)_2O$ (**1**, 10.0 mmol, 4.10 g) was dissolved in THF (125 mL), and *n*-butyllithium (12.4 mL of a 1.6 M solution in *n*-hexane) was added at 0 °C. The reaction mixture was stirred overnight at room temperature, and anhydrous $EuCl_3$ (1.29 g, 5.0 mmol) was added, followed by stirring for another 24 h. Lithium chloride was separated by filtration, and the brown filtrate was reduced to a total volume of ∼10 mL. Colorless cuboids of **4** (2.26 g, 24%) were isolated at room temperature. The solution was then allowed to stand at room temperature for a few days to afford colorless crystals of **5** (4.01 g, 61%).

For **4**: Anal. Calcd. for $C_{96}H_{108}ClEuLi_4O_{15}Si_6$ ($M_r$ = 1885.53): C, 61.15; H, 5.77. Found: C, 60.88; H, 5.70%. mp 98−100 °C (dec). IR (KBr) $\nu_{max}$ (cm$^{-1}$): 3134 (w), 3067 (m, $\nu_{C-H}$), 3046 (m, $\nu_{C-H}$), 2997 (m, $\nu_{C-H}$), 2957 (m), 2929 (m), 2876 (m), 1959 (w), 1892 (w), 1827 (w), 1774 (w), 1656 (w), 1590 (m, $\nu_{C=C}$), 1568 (w), 1487 (w), 1459 (w), 1428 (s), 1376 (w), 1306 (m), 1262 (m), 1185 (m, $\nu_{Si-C}$), 1118 (vs, $\nu_{Si-O}$, $\nu_{C-O}$), 1046 (vs), 974 (vs), 742 (s), 701 (vs), 683 (m), 620 (w), 534 (vs), 492 (s). $^1$H NMR (600.1 MHz, THF-$d_8$, 298.0 K): $\delta$ 7.98−6.91 (m, 60H, Ph), 3.50 (t, 24H, THF), 1.51 (m, 24H, THF). $^{13}$C NMR (100.6

MHz, THF-$d_8$, 294.9 K): $\delta$ 142.5 (*ipso*-C), 135.9, 128.7, 127.8 (Ph), 68.3, 26.3 (THF). $^{29}$Si NMR (79.5 MHz, THF-$d_8$, 294.4 K): $\delta$ −49.3.

For **5**: Anal. Calcd. for $C_{64}H_{72}ClEuLi_2O_{10}Si_4$ ($M_r$ = 1314.85): C, 58.46; H, 5.52. Found: C, 58.19; H, 5.23%. mp > 122 °C (dec). IR (KBr) $\nu_{max}$ (cm$^{-1}$): 3134 (w), 3087 (w), 3067 (m, $\nu_{C\text{-}H}$), 3046 (m, $\nu_{C\text{-}H}$), 3018 (m, $\nu_{C\text{-}H}$), 2999 (m, $\nu_{C\text{-}H}$), 2977 (m), 2878 (m), 2698 (w), 2616 (w), 2314 (vw), 1964 (w), 1894 (w), 1832 (w), 1776 (w), 1666 (w), 1618 (w), 1590 (w, $\nu_{C=C}$), 1568 (w), 1486 (w), 1459 (w), 1448 (w), 1428 (s), 1371 (w), 1306 (w), 1263 (w), 1185 (w, $\nu_{Si\text{-}C}$), 1120 (vs, $\nu_{Si\text{-}O}$, $\nu_{C\text{-}O}$), 1036 (vs), 1019 (vs), 995 (vs), 958 (vs), 892 (s), 742 (s), 714 (vs), 701 (vs), 683 (m), 620 (w), 527 (vs), 490 (s). $^1$H (400.1 MHz, THF-$d_8$, 294.5 K): $\delta$ 7.64−6.2 (m, 40H, Ph), 3.67 (s, 16H, THF), 1.79 (m, 16H, THF). $^{13}$C NMR (100.6 MHz, THF-$d_8$, 294.9 K): $\delta$ 137.8 (*ipso*-C), 133.8, 128.3, 126.9 (Ph), 68.1, 26.2 (THF). $^{29}$Si NMR (79.5 MHz, THF-$d_8$, 295.0 K): $\delta$ −22.0.

*Synthesis of* $[\{(Ph_2SiO)_2O\}_3\{K(DME)\}_3]Eu$ (**6**). $(Ph_2SiOH)_2O$ (**1**, 5.0 mmol, 2.1 g) was dissolved in THF (100 mL), and $KN(SiMe_3)_2$ (10.0 mmol, 1.99 g) was added at room temperature. The yellow reaction mixture was stirred for 4 h, and anhydrous $EuCl_3$ (0.69 g, 2.7 mmol) was added, followed by stirring for 24 h. A white precipitate of KCl was removed by filtration, the yellow solution was reduced to a total volume of ca. 10, and 20 mL of DME was added. The reaction mixture was then stirred at 40 °C for another 2 h. After the mixture stood for 12 h, again a white solid (KCl) was separated, and the solution was reduced to a total volume of ∼10 mL. Colorless crystals of **6** (1.5 g, 31%) were isolated at room temperature. Anal. Calcd. for $C_{84}H_{90}EuK_3O_{15}Si_6$ ($M_r$ = 1777.27): C, 56.76; H, 5.10. Found: C, 57.01; H, 5.49%. mp > 113 °C (dec). IR (KBr) $\nu_{max}$ (cm$^{-1}$): 3132 (w), 3066 (m, $\nu_{C\text{-}H}$), 3046 (m, $\nu_{C\text{-}H}$), 2998 (m, $\nu_{C\text{-}H}$), 2954 (m), 2896 (w), 2826 (w), 2583 (w), 2314 (vw), 1648 (w), 1589 (m, $\nu_{C=C}$), 1567 (w), 1484 (w), 1451 (w), 1428 (s), 1367 (w), 1308 (m), 1251 (s), 1187 (m, $\nu_{Si\text{-}C}$), 1119 (vs, $\nu_{Si\text{-}O}$, $\nu_{C\text{-}O}$), 1088 (s), 1032 (s), 984 (vs), 842 (s), 743 (s), 701 (vs), 620 (w), 523 (vs), 483 (m), 411 (w). $^1$H NMR (600.1 MHz, THF-$d_8$, 293.1 K): $\delta$ 7.57−7.12 (m, 60H, Ph), 3.42 (s, 12, DME), 3.26 (s, 18H, DME). $^{13}$C NMR (150.9 MHz, THF-$d_8$, 293.0 K): $\delta$ 134.8 (*ipso*-C), 130.5, 128.3, 127.9 (Ph), 72.7, 58.9 (THF). $^{29}$Si NMR (79.5 MHz, THF-$d_8$, 293.3 K): $\delta$ −24.3.

*Synthesis of* $[(Ph_2SiO)_2O]_6Eu^{II}{}_4Eu^{III}{}_2Li_4O_2Cl_2$ (**7**). $[\{(Ph_2SiO)_2O\}_2\{Li(THF)_2\}_2]EuCl$ (**5**) (0.66 g, 0.50 mmol) was added to a stirred solution of 0.24 g (0.25 mmol) of $(DAD^{DIPP})_2Ba(DME)$ in 40 mL of toluene. The reaction mixture was stirred overnight, an off-white precipitate was removed by filtration, and the volume of the orange solution was reduced stepwise to a total volume of less than 5 mL. Small orange crystals of $[(Ph_2SiO)_2O]_6Eu^{II}{}_4Eu^{III}{}_2Li_4O_2Cl_2$ (0.18 g, 61%) formed during one week at room temperature. The original off-white precipitate (50 mg) analyzed for a nearly quantitative formation of $BaCl_2$, while the oxidation product $DAD^{DIPP}$ was detected in the concentrated mother liquid by NMR spectroscopy. Anal. Calcd. for $C_{144}H_{120}Cl_2Eu_6Li_4O_{20}Si_{12}$ ($M_r$ = 3517.96): C, 49.16; H, 3.44; Cl, 2.02. Found: C, 48.77; H, 3.86; Cl, 1.73%. mp > 106 °C (mp). IR (KBr) $\nu_{max}$ (cm$^{-1}$): 3067 (m, $\nu_{C\text{-}H}$), 3046 (m, $\nu_{C\text{-}H}$), 2999 (m, $\nu_{C\text{-}H}$), 2963 (s), 2930 (m), 2871 (m), 2536 (w), 2347 (w), 1961 (w), 1895 (w), 1829 (w), 1637 (s), 1591 (m, $\nu_{C=C}$), 1568 (m), 1458 (m), 1428 (s), 1384 (m), 1368 (w), 1343 (w), 1328 (w), 1307(w), 1256 (m), 1182 (m, $\nu_{Si\text{-}C}$), 1156 (m), 1119 (vs, $\nu_{Si\text{-}O}$, $\nu_{C\text{-}O}$), 1083 (m), 1033(s), 1017 (s), 974 (vs), 876 (w), 859 (w), 797 (w), 743 (m), 712 (s), 703 (s), 683 (w), 664 (vw), 621 (vw), 531 (s), 41 (m). NMR data could not be obtained for **7** due to the paramagnetic character of europium.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

X-ray crystallographic data of **2**−**7** in CIF format. Full X-ray structural data (tabulated), the perspective views for **2**−**7**, and luminescence decay curves for **5**. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 1012111−1012116 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via ccdc.cam.ac.uk/products/csd/request.

## ■ AUTHOR INFORMATION

### Corresponding Author

*Phone: (+49)-391-6758327. Fax: (+49)-391-6712933. E-mail: frank.edelmann@ovgu.de.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

Financial support by the Otto-von-Guericke-Universität Magdeburg is gratefully acknowledged.

## ■ DEDICATION

Dedicated to Professor Klaus Jacob on the occasion of his 75th birthday.

## ■ REFERENCES

(1) For reviews on metal siloxides, see: (a) Chisholm, M. H. *Chemtracts: Inorg. Chem.* **1992**, *4*, 273−301. (b) Wolczanski, P. T. *Polyhedron* **1995**, *14*, 3335−3362. (c) Murugavel, R.; Voigt, A.; Walawalkar, M. G.; Roesky, H. W. *Chem. Rev.* **1996**, *96*, 2205−2236. (d) King, L.; Sullivan, A. C. *Coord. Chem. Rev.* **1999**, *189*, 19−57. (e) Lorenz, V.; Fischer, A.; Gießmann, S.; Gilje, J. W.; Gun'ko, Y.; Jacob, K.; Edelmann, F. T. *Coord. Chem. Rev.* **2000**, *206*−*207*, 321−368. (f) Abbenhuis, H. C. L. *Chem.—Eur. J.* **2000**, *6*, 25−32. (g) Marciniec, B.; Maciejewski, H. *Coord. Chem. Rev.* **2001**, *223*, 301−335. (h) Duchateau, R. *Chem. Rev.* **2002**, *102*, 3525−3542. (i) Hanssen, R. W. J. M.; van Santen, R. A.; Abbenhuis, H. C. L. *Eur. J. Inorg. Chem.* **2004**, 675−683. (j) Chandrasekhar, V.; Boomishankar, R.; Nagendran, S. *Chem. Rev.* **2004**, *104*, 5847−5910. (k) Marciniec, B. *Coord. Chem. Rev.* **2005**, *249*, 2374−2390. (l) Lorenz, V.; Edelmann, F. T. *Adv. Organomet. Chem.* **2005**, *53*, 101−153. (m) Veith. *Adv. Organomet. Chem.* **2006**, *54*, 49−72. (n) Levitskii, M. M.; Zavin, B. G.; Bilyachenko, A. N. *Russ. Chem. Rev.* **2007**, *76*, 847−866. (o) Boyle, T. J.; Ottley, L. A. M. *Chem. Rev.* **2008**, *108*, 1896. (p) Levitskii, M. M.; Smirnov, V. V.; Zavin, B. G.; Bilyachenko, A. N.; Rabkina, A. Y. *Kinet. Catal.* **2009**, *50*, 490−507. (q) Lorenz, V.; Edelmann, A.; Gießmann, S.; Hrib, C. G.; Blaurock, S.; Edelmann, F. T. *Z. Anorg. Allg. Chem.* **2010**, *636*, 2172−2191. (r) Krempner, C. *Eur. J. Inorg. Chem.* **2011**, 1689−1698.

(2) (a) Murugavel, R.; Walawalkar, M.; Prabusankar, G.; Davis, P. *Organometallics* **2001**, *20*, 2639−2642. (b) Fandos, R.; Otero, A.; Rodriguez, A.; Ruiz, M. J.; Terreros, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 2884−2887. (c) Fujdala, K. L.; Brutchey, R. L.; Tilley, T. D. *Top. Organomet. Chem.* **2005**, *16*, 69−115. (d) Jarupatrakorn, J.; Coles, M. P.; Tilley, T. D. *Chem. Mater.* **2005**, *17*, 1818−1828.

(3) (a) Drieß, M.; Merz, K.; Schönen, R.; Rabe, S.; Kruis, F. E.; Roy, A.; Birkner, A. *C. R. Chim.* **2003**, *6*, 273−281. (b) Murugavel, R.; Walawalkar, M. G.; Dan, M.; Roesky, H. W.; Rao, C. N. R. *Acc. Chem. Res.* **2004**, *37*, 763−774. (c) Hubert-Pfalzgraf, L. G.; Touati, N.; Pasko, S. V.; Vaissermann, J.; Abrutis, A. *Polyhedron* **2005**, *24*, 3066−3073. (d) Abrutis, A.; Hubert-Pfalzgraf, L. G.; Pasko, S.; Touati, N.; Kazlauskiene, V. *Vacuum* **2006**, *81*, 13−17. (e) Ehle, S.; Brüser, V.; Lorenz, V.; Hrib, C. G.; Saulich, K.; Müller, S.; Quade, A.; Edelmann, F. T. *Eur. J. Inorg. Chem.* **2013**, 1451−1457.

(4) Veith, M.; Freres, J.; König, P.; Schütt, O.; Huch, V.; Blin, J. *Eur. J. Inorg. Chem.* **2005**, 3699−3710.

(5) (a) Roveda, C.; Church, T. L.; Alper, H.; Scott, S. L. *Chem. Mater.* **2000**, *12*, 857−8672. (b) Holland, A. W.; Li, G.; Shahin, A. M.; Long, G. J.; Bell, A. T.; Tilley, T. D. *J. Catal.* **2005**, *235*, 150−163. (c) Gauvin, R. M.; Dlevoye, L.; Hassan, R. A.; Keldenich, J.; Mortreux, A. *Inorg. Chem.* **2007**, *46*, 1062−1070. (d) *Modern Surface Organometallic Chemistry;* Basset, J.-M., Psaro, R., Roberto, D., Ugo, R, Eds.; Wiley-VCH, Weinheim, Germany, 2009. (e) Michel, O.; König, S.; Törnroos, K. W.; Maichle-Mössmer, C.; Anwander, R. *Chem.—Eur. J.* **2011**, *17*, 11857−11867. (f) Marciniec, B.; Rogalski, S.; Potrzebowski, M. J.; Pietraszuk, C. *ChemCatChem* **2011**, *3*, 904−910. (g) Le Roux, E.; Liang, Y.; Törnroos, K. W.; Nief, F.; Anwander, R. *Organometallics* **2012**, *31*, 6526−6537. (h) Cordeiro, P. J.; Guillo, P.; Spanjers, C. S.; Chang, J. W.; Lipschutz,

M. I.; Fasulo, M. E.; Rioux, R. M.; Tilley, T. D. *ACS Catalysis* **2013**, *3*, 2269−2279. (i) Laurent, P.; Veyre, L.; Thieuleux, C.; Donet, S.; Copéret. *Dalton Trans.* **2013**, *42*, 238−248.

(6) (a) Kownacki, I.; Marciniec, B.; Szubert, K.; Kubicki, M. *Organometallics* **2005**, *24*, 6179−6183. (b) Mieczynska, E.; Trzeciak, A. M.; Ziolkowski, J. J.; Kownacki, I.; Marciniec, B. *J. Mol. Catal. A: Chem.* **2005**, *237*, 246−253. (c) Bruno, S. M.; Monteiro, B.; Balula, M. S.; Lourenco, C.; Valente, A. A.; Pillinger, M.; Ribeiro-Claro, P.; Goncalves, I. S. *Molecules* **2006**, *11*, 298−308. (d) Kownacki, I.; Marciniec, B.; Macina, A.; Rubinsztajn, S.; Lamb, D. *Appl. Catal., A: General* **2007**, *317*, 53−57.

(7) (a) Kownacki, I.; Kubickim, M.; Marciniec, B. *Polyhedron* **2001**, *20*, 3015−3018. (b) Lugmair, C. G.; Tilley, T. D. *Z. Naturforsch., B: Chem. Sci.* **2004**, *59*, 1540−1547. (c) Nishiura, M.; Hou, Z.; Wakatsuki, Y. *Organometallics* **2004**, *23*, 1359−1368. (d) Mougel, V.; Camp, C.; Pécaut, J.; Copéret, C.; Maron, L.; Kefalidis, C. E.; Mazzanti, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 12280−12284. (e) Camp, C.; Kefalidis, C. E.; Pécaut, J.; Maron, L.; Mazzanti, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 12646−12650.

(8) (a) Lickiss, P. D. *Adv. Inorg. Chem.* **1995**, *42*, 147−262. (b) Edwards, D. A.; Harker, R. M.; Mahon, M. F.; Molloy, K. C. *J. Chem. Soc., Dalton. Trans.* **1997**, 3509−3515. (c) Veith, M.; Mathur, C.; Huch, V. *J. Chem. Soc., Dalton Trans.* **1997**, 995−999. (d) Jarupatrakprn, J.; Tilley, T. D. *Dalton Trans.* **2004**, 2808−2813. (e) Sydora, O. L.; Wolczanski, P. T.; Lobkovsky, E. B.; Buda, C.; Cundari, T. R. *Inorg. Chem.* **2005**, *44*, 2606−2618. (f) Rosenfeld, D. C.; Wolczanski, P. T.; Barakat, K. A.; Buda, C.; Cundari, T. R. *J. Am. Chem. Soc.* **2005**, *127*, 8262−8263. (g) Sydora, O. L.; Kuiper, D. S.; Wolczanski, P. T.; Lobkovsky, E. B.; Dinescu, A.; Cundari, T. R. *Inorg. Chem.* **2006**, *45*, 2008−2021. (h) Rosenfeld, D. C.; Wolczanski, P. T.; Barakat, K. A.; Buda, C.; Cundari, T. R.; Schröder, F. C.; Lobkovsky, E. B. *Inorg. Chem.* **2007**, *46*, 9715−9735. (i) Conde, A.; Fandos, R.; Otero, A.; Rodriquez, A.; Terreros, P. *Eur. J. Inorg. Chem.* **2008**, 3062−3067. (j) Kuiper, D. S.; Wolczanski, P. T.; Lobkovsky, E. B.; Cundari, T. R. *J. Am. Chem. Soc.* **2008**, *130*, 12931−12943. (k) Marshak, M. P.; Nocera, D. G. *Inorg. Chem.* **2013**, *52*, 1173−1175.

(9) Su, K.; Tilley, T. D. *Chem. Mater.* **1997**, *9*, 588−595.

(10) (a) Oishi, M.; Kawakami, Y. *Org. Lett.* **1999**, *1*, 549−551. (b) Krempner, C.; Reinke, H.; Weichert, K.; Spannenberg, A. *Polyhedron* **2004**, *23*, 2475−2479. (c) Krempner, C.; Reinke, H.; Weichert, K. *Organometallics* **2007**, *26*, 1386−1392. (d) Krempner, C.; Reinke, H.; Weichert, K. *Polyhedron* **2007**, *26*, 3633−3637. (e) Weichert, K.; Carlson, B.; Reinke, H.; Krempner, C. *Dalton Trans.* **2010**, *39*, 115313−11515.

(11) (a) Winkhofer, N.; Roesky, H. W.; Noltemeyer, M.; Robinson, W. T. *Angew. Chem., Int. Ed.* **1992**, *31*, 599−601. (b) Jutzi, P.; Schneider, M.; Stammler, H.-G.; Neumann, B. *Organometallics* **1997**, *16*, 5377−5380. (c) Pietschnig, R.; Belaj, F.; Tirrée, J. J. *Organometallics* **2004**, *23*, 4897−4901. (d) Prabusankar, G.; Murugavel, R.; Butcher, R. J. *Organometallics* **2005**, *24*, 2124−2128. (e) Spirk, S.; Ehmann, H. M.; Kargl, R.; Hurkes, N.; Reischl, M.; Novak, J.; Resel, R.; Wu, M.; Pietschnig, R.; Ribitsch, V. *ACS Appl. Mater. Interfaces* **2010**, *2*, 2956−2962.

(12) (a) Krempner, C.; Kopf, J.; Mamat, C.; Reinke, H.; Spannenberg, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 5406−5408. (b) Jäger-Fiedler, U.; Köckerling, M.; Ludwig, R.; Wulf, A.; Krempner, C. *Angew. Chem., Int. Ed.* **2006**, *45*, 6755−6759. (c) Krempner, C.; Jäger-Fiedler, U.; Köckerling, M.; Reinke, H. *Organometallics* **2009**, *28*, 382−385.

(13) For selected recent references, see: (a) Feher, F. J.; Budzichowski, T. A. *Polyhedron* **1995**, *14*, 3239−3253. (b) Klunduk, M. C.; Maschmeyer, T.; Meurig Thomas, J.; Johnson, B. F. G. *Chem.—Eur. J.* **1999**, *5*, 1481−1485. (c) Duchateau, R.; Dijkstra, T. W.; van Santen, R. A.; Yap, G. P. A. *Chem.—Eur. J.* **2004**, *10*, 3979−3990. (d) Ohde, C.; Brandt, M.; Limberg, C.; Döbler, J.; Ziemer, B.; Sauer, J. *Dalton Trans.* **2008**, 326−331. (e) Salinier, V.; Niccolai, G. P.; Dufaud, V.; Basset, J.-M. *Adv. Synth. Catal.* **2009**, *351*, 2168−2177. (f) Ohde, C.; Limberg, C.; Schmidt, D.; Enders, M.; Demeshko, S.; Knispel, C. *Z. Anorg. Allg. Chem.* **2010**, *636*, 2315−2322.

(14) For selected references, see: (a) Motevalli, M.; Shah, D.; Shah, S. A. A.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1994**, 2427−2428. (b) Brisdon, B. J.; Mahon, M. F.; Rainford, C. C. *J. Chem. Soc., Dalton Trans.* **1998**, 3295−3300. (c) Evans, W. J.; Broomhall-Dillard, R. N. R.; Simon, D.; Ziller, J. W. *J. Coord. Chem.* **1999**, *46*, 347−354. (d) Fandos, R.; Gallego, B.; Otero, A.; Rodriguez, A.; Ruiz, M. J.; Terreros, P. *Dalton Trans.* **2007**, 871−877. (e) Prabhu, M. S. R.; Jami, A. K.; Baskar, V. *Organometallics* **2009**, *28*, 3953−3956. (f) Schax, F.; Limberg, C.; Mügge, C. *Eur. J. Inorg. Chem.* **2012**, 4661−4668.

(15) (a) Lorenz, V.; Fischer, A.; Jacon, K.; Brüser, W.; Gelbrich, T.; Jones, P. G.; Edelmann, F. T. *Chem. Commun.* **1998**, 2217−2218. (b) Lorenz, V.; Fischer, A.; Jacon, K.; Brüser, W.; Edelmann, F. T. *Chem.—Eur. J.* **2001**, *7*, 848−857. (c) Gießmann, S.; Blaurock, S.; Lorenz, V.; Edelmann, F. T. *Inorg. Chem.* **2007**, *46*, 10383−10389. (d) Gießmann, S.; Blaurock, S.; Lorenz, V.; Edelmann, F. T. *Inorg. Chem.* **2007**, *46*, 10956−10958. (e) Edelmann, A.; Blaurock, S.; Hrib, C.; Edelmann, F. T. *J. Organomet. Chem.* **2010**, *695*, 1026−1030.

(16) Bradley, D. C.; Gothra, J. S.; Hart, F. A. *J. Chem. Soc., Dalton Trans.* **1973**, 1021.

(17) (a) Anwander, R. *Top. Organomet. Chem.* **1999**, *2*, 1−61. (b) Eppinger, J.; Spiegler, M.; Hieringer, W.; Herrmann, W. A.; Anwander, R. *J. Am. Chem. Soc.* **2000**, *122*, 3080−3096.

(18) (a) Whan, R. E.; Crosby, G. A. *J. Mol. Spectrosc.* **1962**, *8*, 315−327. (b) Mao, J.-G. *Coord. Chem. Rev.* **2007**, *251*, 1493−1520. (c) Ma, Y.; Wang, Y. *Coord. Chem. Rev.* **2010**, *254*, 972−990. (d) Andrews, P. C.; Brown, D. H.; Fraser, B. H.; Gorham, N. T.; Junk, P. C.; Massi, M.; St Pierre, T. G.; Skelton, B. W.; Woodward, R. C. *Dalton. Trans.* **2010**, *39*, 11227−11234. (e) Hauser, C. P.; Thielemann, D. T.; Adlung, M.; Wickleder, C.; Roesky, P. W.; Weiss, C. K.; Landfester, K. *Macromol. Chem. Phys.* **2011**, *212*, 286−296. (f) Borges, A. S.; Dutra, J. D. L.; Freire, R. O.; Moura, R. T.; Da Silva, J. G.; Malta, O. L.; Araujo, M. H.; Brito, H. F. *Inorg. Chem.* **2012**, *51*, 12867−12878.

(19) (a) Bünzli, J.-C. G.; Piquet, C. *Chem. Soc. Rev.* **2005**, *34*, 1048−1077. (b) Shavaleev, N. M.; Eliseeva, S. V.; Scopelliti, R.; Bünzli, J.-C. G. *Chem.—Eur. J.* **2009**, *15*, 10790−10802. (c) Eliseeva, S. V.; Bünzli, J.-C. G. *Chem. Soc. Rev.* **2010**, *39*, 189−227. (d) Bünzli, J.-C. G.; Chauvin, A.-S.; Kim, H. K.; Deiters, E.; Eliseeva, S. V. *Coord. Chem. Rev.* **2010**, *254*, 2623−2633.

(20) Edelmann, F. T. In *Comprehensive Organometallic Chemistry III, Vol. 3, Complexes of Scandium, Yttrium and Lanthanide Elements;* Crabtree, R. H., Mingos, D. M. P., Eds., Elsevier: Oxford, U.K., 2006; p 1, and refernces cited therein.

(21) Cotton, S. *Lanthanide and Actinide Chemistry;* John Wiley & Sons, Ltd.: Chichester, U.K., 2006; p. 55.

(22) (a) Edelmann, F. T.; Steiner, A.; Stalke, D.; Gilje, J. W.; Jagner, S.; Håkansson, M. *Polyhedron* **1994**, *13*, 539−546. (b) Zhou, S.; Wang, S.; Yang, G.; Liu, X.; Sheng, E.; Zhang, K.; Cheng, L.; Huang, Z. *Polyhedron* **2003**, *22*, 1019−1024. (c) Li, Q.; Wang, S.; Zhou, S.; Yang, G.; Zhu, X.; Liu, Y. *J. Org. Chem.* **2007**, *72*, 6763−6767.

(23) Lorenz, V.; Edelmann, A.; Blaurock, S.; Hrib, C.; Edelmann, F. T. *C. R. Chim.* **2010**, *13*, 577−583.

(24) (a) Kong, D.-Y.; Wang, S.-W.; Zhu, Q.; Xie, Y.-Y.; Huang, X.-Y. *Jiegou Huaxue* **1998**, *17*, 61−64. (b) Hu, N.; Lin, Y.; Shen, Q.; Xing, Y.; Shi, E. *Huaxue Xuebao* **1986**, *44*, 388−391.

(25) Lorenz, V.; Hrib, C. G.; Grote, D.; Hilfert, L.; Krasnopolski, M.; Edelmann, F. T. *Organometallics* **2013**, *32*, 4636−4642.

(26) For selected recent references, see: (a) Pernin, C. G.; Ibers, J. A. *Inorg. Chem.* **1997**, *36*, 3802−3803. (b) Babai, A.; Mudring, A.-V. *Z. Anorg. Allg. Chem.* **2006**, *632*, 1956−1958. (c) Calvez, G.; Daiguebonne, C.; Guillou, O.; Pott, T.; Meleard, P.; Le Dret, F. *C. R. Chim.* **2010**, *13*, 715−730. (d) Sun, Y.-Q.; Mei, H.-X.; Zhang, H.-H.; Chen, Y.-P.; Sun, R.-Q. *J. Cluster Sci.* **2011**, *22*, 279−288. (e) Liao, S.; Yang, X.; Jones, R. A. *Cryst. Growth Des.* **2012**, *12*, 970−974. (f) Demel, J.; Kubat, P.; Millange, F.; Marrot, J.; Cisarova, I.; Lang, K. *Inorg. Chem.* **2013**, *52*, 2779−2786.

(27) For selected recent references, see: (a) Deacon, G. B.; Forsyth, C. M.; Junk, P. C.; Skelton, B. W.; White, A. H. *Chem.—Eur. J.* **1999**, *5*, 1452−1459. (b) Evans, W. J.; Greci, M. A.; Ziller, J. W. *Inorg. Chem.* **2000**, *39*, 3213−3220. (c) Guo, H.; Zhou, H.; Yao, Y.; Zhang, Y.; Shen, Q. *Dalton Trans.* **2007**, 3555−3561. (d) Deacon, G. B.; Junk, P. C.; Moxey, G. J. *Chem.—Asian J.* **2009**, *4*, 1309−1317. (e) Jiang, Y.; Zhu, X.;

Chen, M.; Wang, Y.; Yao, Y.; Wu, B.; Shen, Q. *Organometallics* **2014**, *33*, 1972−1976.

(28) (a) Sweeting, L. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 2652−2658. (b) Rheingold, A. L.; King, W. *Inorg. Chem.* **1989**, *28*, 1715−1719. (c) Berry, M. T.; Kirby, A. F.; Richardson, F. S. *Mol. Phys.* **1989**, *66*, 723−746.

(29) Tanner, P. A. *Chem. Soc. Rev.* **2013**, *42*, 5090.

(30) Rambabu, U.; Mathur, A.; Buddhudu, S. *Mater. Chem. Phys.* **1999**, *61*, 156.

(31) Hölsä, J. *Acta Chem. Scand.* **1991**, *45*, 583.

(32) Harris, G. I. *J. Chem. Soc.* **1963**, 5978.

(33) Freeman, J. H.; Smith, M. L. *J. Inorg. Nucl. Chem.* **1958**, *7*, 224.

(34) *XAREA (Including XRED32) Program for X-ray Crystal Data Collection;* Stoe: Darmstadt, Germany, 2002.

(35) (a) Sheldrick, G. M. *SHELXL-97 Program for Crystal Structure Refinement;* Universität Göttingen: Germany, 1997. (b) Sheldrick, G. M. *SHELXS-97 Program for Crystal Structure Solution;* Universität Göttingen: Germany, 1997.