Neutral “Cp-Free” Silyl-Lanthanide(II) Complexes: Synthesis, Structure, and Bonding Analysis

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INTRODUCTION

Complexes with the metal in the oxidation state 3+ bearing Cp or substituted Cp ligands are dominating the organometallic chemistry of the rare-earth elements. For a long time only three lanthanide elements, samarium, europium, and ytterbium, were readily accessible. However, in the meantime the number of elements has increased substantially, and quite recently Evans et al. were successful in completing the series of crystalline examples of divalent molecular complexes of all lanthanides.3–6 This enabled for the first time a comparison of all lanthanides in a single uniform coordination environment and postulation of the electronic ground state.6 The results show conclusively single uniform coordination environment and postulation of the exception of some divalent silylene complexes reported by Bochkarev and co-workers.12

Although numerous examples of d-block metal-silyl compounds exist, examples of rare-earth metal-silyl compounds are still scarce or entirely unknown for some elements. The few reported samarium silyl compounds, which have also been characterized by X-ray diffraction analysis, feature Sm with Cp* ligands almost exclusively in oxidation state 3+7–9 with the exception of some divalent silylene complexes reported by Evans and co-workers9 and our group.10 The reaction of Cp*Yb(η2-O2) with (Me3Si)3SiLi was shown to result in the formation of Cp*Yb(SiMe3)3(THF)2 accompanied by elimination of Cp*Li.12 Reacting Cp*Yb(SiMe3)3(THF)2 with excess (Me3Si)3SiLi led to the formation of some 30% of [(Me3Si)3Si]2Yb(THF)4, which could not be isolated.12 The reaction of Cp*2Ln(THF)2 (Ln = Sm, Eu, Yb) with PhSiH3/KH, which yields metalla complexes of the type K-[Cp*2Ln(THF)2]13 also seems to involve silyl anions. The respective Eu and Yb complexes could be successfully characterized using single crystal X-ray diffraction analysis. In addition Bechkarev and co-workers reported the synthesis of neutral Cp-free (Ph3Si)2Yb(THF)4 by direct treatment of elemental ytterbium with Ph3SiCl in THF.14 Divalent rare-earth amides, particularly silylamides [LnII-(N(SiMe3))2], have also received some attention.15–18 A few of these compounds do not contain cyclopentadienyl ligands on the metal and are therefore interesting for the exploration of catalytic processes such as hydrosilylation19 or enantioselective hydroamination20 and polymerization of polar monomers like methyl methacrylate and lactones.21 Recently, Evans et al. could show reactions of N2, CO, and CO2 with [(Me3Si)2N]Ln complexes, where N2 is reduced to (N═N)2− and (N2)3− and CO and CO2 are reduced to the rare (CO)1− and (CO2)2− radicals.22 Despite the lack of direct Ln−Si bonds, β-agostic interactions play an important role in lanthanide complexes

ABSTRACT: Complexes featuring lanthanide silicon bonds represent a research area still in its infancy. Herein, we report a series of Cp-free lanthanide (+II) complexes bearing σ-bonded silyl ligands. By reactions of LnI2 (Ln = Yb, Eu, Sm) either with a 1,4-oligosilanyl dianion [K-Si(SiMe3)2SiMe2Si(SiMe3)2-K] (1) or with 2 (Me3Si)3SiK (3) the corresponding neutral metalla complexes of all lanthanides in a single uniform coordination environment and postulation of the electronic ground state.6 The results show conclusively single uniform coordination environment and postulation of the exception of some divalent silylene complexes reported by Bochkarev and co-workers.12

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that contain the N(SiMe2H)2 group. Several types of agostic lanthanide hydridosilylamido complexes have been prepared employing [N(SiMe2H)2] and [THF]32,33 and with the use of density functional theory (DFT) calculations their role as ligands was examined. In a recent example, Niemeyer reacted divalent [YbII{N(SiMe3)2}2] with (Me3Si)2Si to afford K[(Me3Si)2Si]3Yb31[N-(SiMe3)]2.28,29 In sharp contrast, reaction of the respective trivalent [YbIII{N(SiMe3)2}3] with KSi(SiMe3)3 led to methyl deprotonation of a trimethylsilyl group rather than to Si−Yb bond formation.28,29

β-Agostic interactions are important not only in complexes with N(SiMe2H)2 groups but also in complexes like Yb[C(SiMe2H)3]2·THF30 or Yb[C(SiMe2H)3]2·TMEDA31 containing the C(SiMe2H)3 ligand. The short Yb−Si distances as well as the small Yb−C−Si angles in the crystal structure are in perfect concordance with the β-agostic Si−H−Yb interactions.30,31

We recently reported synthesis and characterization of some σ-bonded Cp2-lanthanide-silyl complexes (Ln = Tm, Ho, Gd, Tb, Ce) in the oxidation state 3+. Herein, the synthesis of Cp-free samarium-, europium-, and ytterbium-silyl complexes in the oxidation state 2+ are described in addition to a thorough investigation into their spectroscopic properties, X-ray diffraction studies, and the first systematic density functional theory (DFT) investigation for this class of complexes.

RESULTS AND DISCUSSION

Synthesis. Ytterbium(II), europium(II), and samarium(II) diiodides were investigated with regard to their reactivity with oligosilyl anions. The THF complexes LnI2(THF)2 [Ln = Yb (yellow), Eu (dark yellow), Sm (dark blue)] were prepared by reaction of small pieces of metal with 1,2-diiodoethane in THF34 or Yb[Me2Si-(Me3Si)2Si]2·THF34 with K[C(SiMe3)2]·TMEDA31 containing the C(SiMe3)2 ligand. The short Yb−Si distances as well as the small Yb−C−Si angles in the crystal structure are in perfect concordance with the β-agostic Si−H−Yb interactions.30,31

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Scheme 1. Preparation of Lanthanide Oligosilyl Complexes 2a–c

Scheme 2. Synthesis of Lanthanide Oligosilyl Complexes 4a–c

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With this success, we reasoned that the synthesis of analogous ytterbium complexes might be accomplished in a similar manner. Monitoring the reaction of 3 with YbI2(THF)2 by NMR spectroscopy showed after only 15 min complete consumption of starting material 3 and the formation of 4a along with substantial amounts of tetrakis(trimethylsilyl)silane and tris(trimethylsilyl)silane. In an analogous manner, reaction of YbI2(THF)2 with 1 showed formation of 2a, but again the generation of several side products was observed. These results are similar to what was previously described for titanium37 and yttrium38 complexes bearing tris(trimethylsilyl)silyl groups. The problem could be overcome by strict exclusion of light during the formation and storage of 2a and 4a. Exposure of 2a to ambient light over the duration of a week caused decomposition to 1,1,2,2-tetrasilanesilane and uncharacterizable insoluble metal species.

The synthesis of the europium compounds 2b and 4b turned out to be similar to the ytterbium complexes. Again, selective reactions with short reaction time were observed in toluene, and air and moisture sensitive crystalline compounds were obtained.

Reaction of LnI2 (Ln = Yb, Eu, or Sm) according to Scheme 2 with just 1 equiv of silyl anion 3 led in all our attempts only to products 4a–c, and no evidence for the formation of a monosilylated complex (Me3Si)3SiLnI was found.

The determination of yields of all compounds was somewhat hampered by some loss of THF during the isolation process due to the use of reduced pressure. For the diamagnetic Yb...
compound 2a the yield could however be determined NMR spectroscopically by using a defined amount of toluene as internal standard.

To get an estimate of the reactivity of the Si–Yb bond of 2a a reaction with Cp₂ZrCl₂ was carried out. The analogous reactions with the potassium or magnesium 1,4-disila-

dienes³⁴,⁴⁰,⁴¹ are known to give the respective zirconacyclopenta-
silanes (5).⁴⁰,⁴¹ The same course was also observed in the reaction of 2a with Cp₂ZrCl₂ (Scheme 3). This outcome certainly marks compound 2a as possessing a strong disilane character.

Scheme 3. Preparation of a Zirconacyclopentasilane 5 from Yb Complex 2a

NMR Spectroscopy. With respect to NMR spectroscopy, the diamagnetic ytterbium complexes 2a and 4a are the most interesting ones with respect to insight into the bonding situation. While for the europium complexes interesting ones with respect to insight into the bonding situation. While for the europium complexes 2b and 4b no meaningful NMR spectra could be obtained at all, the samarium complex 2c and 4c exhibited spectra with para-
magnetically shifted signals.

So far two examples of tris(trimethylsilyl)silylated ytter-

bium-(II) complexes are known. The neutral complex Cp*YbSi-

(SiMe₃)₂(THF)₂,⁴² reported by Lawless and co-workers, displays ²⁹Si NMR signals at −158.3 ppm (Yb–Si) and −2.9 ppm (Si(SiMe₃)₂) with a Si–Yb coupling constant of 171.9 Hz. The corresponding signals of Niemeyer’s ate-complex K[(Me₃Si)₂SiYb(N(SiMe₃)₂)]2⁸ are similar to resonances at −148.6 ppm (Yb–Si) and −4.7 ppm (Si(SiMe₃)₂) and a somewhat smaller Yb–Si coupling constant (164.8 ppm (Yb–Si) = 716 Hz). The ²⁹Si NMR spectrum of 4a is quite similar to Niemeyer’s complex with signals at −144.8 ppm (Yb–Si) and −5.3 ppm and visible ²⁹Si satellites for the central silicon signal in the ²⁹Si INEPT spectrum with a coupling constant of 171.9 Hz. The ²⁹Si NMR spectrum of the ytterbacyclopentasilane 2a in C₆D₆ shows an upfield shift for the metalated silicon atoms to a value of −154.0 ppm with the Yb–Si coupling constant not determinable. The signals for the SiMe₂ (−30.5 ppm) and SiMe₃ (−3.5 ppm) groups are within the range of expectation. Very similar spectroscopic data were found for the analogous DME complex 2a-DME with signals at −158.4 ppm (171.9 Hz) = 665 Hz, (Si(SiMe₃)₂), −29.8 ppm (SiMe₂), and −2.9 ppm (Si(SiMe₃)₂ = 204 Hz, SiMe₃). When the formation of 2a was carried out directly in C₆D₆ instead of toluene with an approximate THF concentration of 9 equiv per Yb atom, the ²⁹Si NMR spectrum of the reaction solution indicated a higher degree of shielding of the metalated silicon atom with the resonance shifted to −163.9 ppm and a ¹H NMR coupling constant of 633 Hz. The substantial shift from −154.0 to −163.0 ppm suggests a higher degree of solvatization of the Yb atom in the presence of THF.

A comparison of the ²⁹Si NMR spectroscopic data with structurally related compounds such as analogous magnesium, zirconocene, and hafnocene complexes helps to obtain some insight into the nature of the Si–Yb interaction. The oligosilanyl magnesium compounds [(Me₃Si)₂Si]₂Mg(THF)₂,⁴² ²⁹Si = −171.9 ppm (SiMe₂), −6.4 ppm (SiMe₃), [(Me₃Si)₂Si]₂Mg(TMEDA)⁴⁶ ²⁹Si = −170.2 ppm (SiMe₂), −7.5 ppm (SiMe₃), and [Me₃Si-(Me₃Si)₂Si]₂Mg(THF)₂ ³⁴ ²⁹Si = −176.6 ppm (SiMe₂), −27.1 ppm (SiMe₃), −5.4 ppm (SiMe₃)] which are quite ion compounds feature the chemical shift of the metalated silicon atoms at higher field than 2a and 4a. This is in sharp contrast to the zirconium compounds [(Me₃Si)₂Si]₂ZrCp₂,³³ ²⁹Si = −83.9 ppm (SiZr), −6.7 ppm (SiMe₂), and [Me₃Si-(Me₃Si)₂Si]₂ZrCp₂,⁴⁰,⁴¹ ²⁹Si = −65.2 ppm (SiZr), −29.2 ppm (SiMe₂), −2.4 ppm (SiMe₃)] and the hafnium compounds [(Me₃Si)₂Si]₂HfCp₂,⁴³ ²⁹Si = −82.4 ppm (SiHf), −8.2 ppm (SiMe₂), [Me₃Si(Me₃Si)₂Si]₂HfCp₂,⁴¹ ²⁹Si = −52.2 ppm (SiHf), −27.8 ppm (SiMe₂), −2.0 ppm (SiMe₃)] and [Me₃Si(Me₃Si)₂Si]₂HfCl₂(TMEDA)⁴⁴ ²⁹Si = −56.3 ppm (SiHf), −2.6 ppm (SiMe₂)] which display chemical shifts of the metalated silicon atoms considerably downfield, which is consistent with a much higher degree of covalent bonding. The closest analogues with respect to the chemical shifts of the metalated silicon atoms are the silyl zinc compounds [(Me₃Si)₂Si]₂Zn,⁴⁵ ²⁹Si = −123.9 ppm (SiZn), −8.2 ppm (SiMe₂), [(Me₃Si)₂Si]₂(Zn-bipy) ³⁵ ²⁹Si = −150.8 ppm (SiZn), −6.6 ppm (SiMe₂)] and [Me₃Si(Me₃Si)₂Si]₂ZnCl₂(TMEDA)⁴⁶ ²⁹Si = −156.8 ppm (SiZn), −8.0 ppm (SiMe₂)] and [K[(Me₃Si)₂Si]₂ZnCl]⁴⁶ ²⁹Si = −152.1 ppm (SiZn), −26.6 ppm (SiMe₂), −6.3 ppm (SiMe₃)]. Another aspect that makes a comparison with oligosilyl zinc compounds tempting is the observed upfield shift for a distorted geometry at Zn from δ = −123.9 ppm for the linear Si–Zn–Si arrangement in [(Me₃Si)₂Si]₂Zn⁴⁵ to δ = −150.8 ppm for the bent Si–Zn–Si arrangement in [(Me₃Si)₂Si]₂Zn–bipy,⁴⁵ For the Si–Yb–Si complexes 4a and 2a a similar behavior can be observed, where the shift of the distorted complex 4a of δ = −144.8 ppm is raised to δ = −154.0, −158.5 ppm for the constrained geometry of complexes 2a and 2a-DME with much smaller Si–Yb–Si angles than found for 4a. From these NMR data it seems likely that the polarization of the Si–Yb bond should be somewhat more pronounced than that of a Si–Zn bond but less than a Si–Mg bond. This conclusion seems to be consistent with the reaction of 2a with Cp₂ZrCl₂ to 5 which also hints at a high degree of polarization.

The number of silylated samarium complexes with elucidated crystal structures is scant,⁷,⁸,¹⁰,¹⁴,¹⁷ and only for one compound, Cp*SmSiH(SiMe₃)₂, are ²⁹Si NMR spectroscopic data known (δ = −23.5 ppm (SiMe₃), no signal detected for Sm–Sm),⁷,⁸ None of the known complexes for which NMR spectroscopic data are given features Sm in the oxidation state 2+. However, a comparison of the NMR spectroscopic properties of Cp*Sm⁴⁸ and Cp*Sm(THF)⁴⁹ provides some ideas as to what to expect for the NMR spectra of 2c and 4c. The ¹³C NMR resonances for the Cp* unit were found for Cp*Sm at δ = 113.2 ppm (C₅Me₅) and 28.3 ppm (C₅Me₅) while for Cp*Sm(THF) these signals were found at δ = −73.7 ppm (C₅Me₅) and 94.6 ppm (C₅Me₅). The THF resonances for Cp*Sm(THF) were found at δ = 149.5 ppm (OCH₃) and 33.4 ppm (OCH₂CH₂). It seems thus reasonable to expect ²⁹Si NMR shifts for 2c and 4c to be different from those of Sm³⁺–Si compounds. For the cyclic compound 2c the ¹¹H NMR resonances were found to be not too much off the typical values with signals at δ = 4.60 and 0.65 ppm for coordinating

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THF and at $\delta = 0.53$ and $-1.23$ ppm for the SiMe$_3$ and SiMe$_2$ groups, respectively. The $^{13}$C NMR signals at $\delta = 127.32$ and 25.35 ppm for coordinating THF are similar to that of Cp$_2$Sm·(THF)$_2$. Signals for Si(CH$_3$)$_2$ and Si(CH$_3$)$_3$ were observed at $-14.49$ and $-18.20$ ppm, respectively. The $^{29}$Si signals are again typical for spatially defined atoms. The resonance for the SiMe$_2$ downfield shifted to $\delta = 120.9$ ppm whereas the SiMe$_3$ resonance at $\delta = -98.3$ ppm is upfield shifted. The chemical shift of the metalated Si atom at $\delta = -121.1$ seems to be least shifted compared to the values found for 2a and 4a. The spectroscopic features of the bis[tris(trimethylsilyl)silylated] 4c are similar to those of 4a with similar $^1$H NMR signals for THF of $\delta = 3.17$ and $-0.90$ ppm and a conspicuously normal trimethylsilyl resonance at $\delta = 0.04$ ppm. In the $^{13}$C NMR spectrum THF signals appear at $\delta = 127.2$ and 21.8 ppm while the trimethylsilyl resonance was found at $\delta = -13.40$ ppm. In the $^{29}$Si NMR spectrum only a resonance for the SiMe$_3$ groups was detected at $\delta = -27.4$ ppm. The comparably normal chemical shifts for the trimethylsilyl groups in the $^1$H, $^{13}$C, and $^{29}$Si NMR spectra are likely caused by averaging the more extreme signals for 4c by rotation around the Si–Sm and Si–Si bonds.

Figure 1. Some key metrical parameters from the crystal structures of the isostructural complexes 2a–c. Thermal ellipsoids at the 30% probability level and hydrogen atoms omitted for clarity. Color code: brown = lanthanide metal (Yb (2a), Eu (2b), Sm (2c)), pink = silicon, light gray = carbon.

Figure 2. Some key metrical parameters from the crystal structures of the isostructural complexes 4a–c. Thermal ellipsoids at the 30% probability level and hydrogen atoms omitted for clarity. Color code: green = lanthanide metal (Yb (4a), Eu (4b), Sm (4c)), pink = silicon, light gray = carbon.
Fluorescence Spectroscopy. Among the divalent rare-earth ions, Eu$^{2+}$ has attracted increasing attention over the past decades for its unique fluorescence properties. In Eu$^{2+}$ (4f$^7$) the emission after short wavelength excitation consists of relatively sharp f→f bands found always at the same wavelengths. In contrast the corresponding emission of Eu$^{3+}$ (4f$^6$) is much broader, and depending on the material, it can occur at wavelengths in the blue, green, or red part of the visible spectrum. This is due to the 4f$^6$5d$^1 \rightarrow 4f$ nature of the Eu$^{3+}$ emission. It is parity allowed and originates from the first excited state configuration, which involves 5d orbitals. Since the energy of the d-orbitals is strongly influenced by the surrounding crystal field, the transition can occur at different wavelengths in different Eu$^{3+}$ containing materials.

The fluorescence spectrum of solid compound 4b upon excitation at 366 nm shows a broad emission with a maximum intensity at 490 nm in the blue/green wavelength range (Supporting Information Figure S24). The fluorescence is strong enough to be seen with the naked eye. After a few minutes in the spectrometer’s sample holder, however, the yellow sample in the central region of the sample holder, where it is hit by the excitation UV light, turns black indicating its decay. As expected a comparison with the decay of solid EuI$_2$(THF)$_2$ suggests that found in Cp*=Eu$^{3+}$SiH,K(THF)$_2$ (3.239 Å). The electronic structures of all compounds 2a–c (Figure 1) and 4a–c (Figure 2) in the solid state could be determined by means of single crystal X-ray diffraction. Interestingly, neutral metallocyclopentasilanes 2a and 2c were found to crystallize in the monoclinic space group P2$_1$/n whereas 2b prefers the trigonal space group R3. The difference in the space group is caused by a different packing pattern of 2b. Within the crystal of complex 2b, channels with a diameter of 13.62 Å are formed by an alternative arrangement of CH$_2$ units from the SiMe$_3$ groups and the CH$_3$ groups of the coordinate THF molecules. Compounds 2a–c all contain four THF molecules coordinating to the lanthanide center with complex 2c crystallizing with an additional THF molecule in the asymmetric unit. The five-membered rings of 2a–c all engage in envelope conformations with one of the SiMe$_3$ units on the flap with distances of 0.73 Å for 2a, 0.56 Å for 2b, and 0.78 Å for 2c from the ring plane.

Compounds 4a and 4c (Figure 2) crystallize in the orthorhombic space group Pbcn with three THF molecules coordinating to the lanthanide atoms. The asymmetric units consist of half a molecule, with the Yb or Sm atoms and one oxygen atom of a THF molecule residing on a symmetry plane. The europium compound 4b crystallizes in the space group Pna2$_1$ but with the whole molecule in the asymmetric unit. The packing patterns of 4a and 4c are identical whereas that of the europium compound 4b is different.

The Si–Yb bond distances in 2a (3.106 and 3.171 Å) and 4a (3.0644 Å) in good agreement with published Cp-free Yb(II) complexes where the distances range from 3.039 to 3.191 Å. The bond distances of the Eu–Si bonds in 2b (3.2052, 3.2162 Å) and 4b (3.1497 Å) are comparable to that found in Cp*=Eu$^{3+}$SiH$_3$K(THF)$_2$ (3.239 Å). For 2c (3.2132 and 3.2444 Å) and 4c (3.1716 Å) the Si–Sm distances are in good agreement with the few published Sm(III)–Si bond lengths (3.133, 3.106, and 3.174 Å) and the known Sm(II)-silylene complexes (3.189$^{10}$ and 3.299$^{11}$ Å). In general compounds 4a–c with the two bulky tris(trimethylsilyl)silyl groups exhibit the shorter bond lengths compared to the metallocyclopentasilanes 2a–c.

There are 490 compounds in the Cambridge Crystalographic Database$^{34}$ bearing a THF molecule coordinating to an Yb atom with an average bond length Yb–O of 2.386 Å. For the Sm–O bond, this value is 2.510 Å out of 350 examples, and for the Eu–O bond the average distance is 2.565 Å out of 90 examples. In these ranges, all of our compounds fit well. The Si–Si distances also are in all four compounds within the expected range. The bond angles Si–Ln–Si vary only slightly within both the metallocyclopentasilanes 2a–c (2.76$^\circ$) and the bis[tris(trimethylsilyl)silyl] derivatives 4a–c (1.98$^\circ$). Due to the bulkiness of the two tris(trimethylsilyl)silyl groups the space for coordinating THF molecules is diminished from four for 2a–c to three in 4a–c.

Theoretical Studies. The electronic structures of 2a–c and 4a–c were calculated at the B3PW91/Basis1 level of theory. This methodology yields an adequate description of the electronic structure of f-block-silyl complexes as was shown in a previous study.$^{35}$ Table 1 lists the calculated average Ln–Si bond lengths (Å), Mayer bond orders (MBOs) of Ln–Si bonds, Natural Population Analysis Charges, and HOMO energies (eV) for 2a–c and 4a–c at B3PW91/Basis1 Level of Theory.

| compd | Ln–Si bond distance (Å) | MBO of Ln–Si bonds | NPA charges (Ln) | HOMO energy (eV) |
|-------|-------------------------|---------------------|-----------------|-----------------|
| 2a    | 3.145                   | 0.38                | +1.76/-0.83     | ~3.40           |
| 2b    | 3.217                   | 0.32                | +1.41/-0.76     | ~3.36           |
| 2c    | 3.230                   | 0.31                | +1.39/-0.76     | ~3.23           |
| 4a    | 3.076                   | 0.41                | +1.71/-0.87     | ~3.74           |
| 4b    | 3.158                   | 0.37                | +1.47/-0.82     | ~3.65           |
| 4c    | 3.176                   | 0.36                | +1.46/-0.80     | ~3.48           |

Bond lengths (Å), Mayer-bond order (MBO) of Ln–Si bonds, Natural Population Analysis charges, and HOMO energies (eV) for 2a–c and 4a–c at B3PW91/Basis1 Level of Theory.

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#### Conclusion and Summary

The chemistry of silyl lanthanides is still a poorly investigated field of research. In the current study we reported a number of lanthanide (+II) complexes with oligosilanyl ligands. The formation of these compounds occurs in a surprisingly facile way by reactions of LnI$_2$ (Ln = Yb, Eu, Sm) either with a 1,4-oligosilanyl diamin [K-Si(SiMe$_3$)$_3$SiMe$_3$SiMe$_3$Si(SiMe$_3$)$_3$K]...
(1) or with (Me₂Si)₂SiK (3) to give either the corresponding neutral metallacyclopentasilanes ((Me₂Si)(Me₂Si)₂Si)Ln·(THF)₄ (Ln = Yb (2a), Eu (2b), Sm (2c)) or the neutral disilylated complexes ((Me₂Si)₂Si)Ln·(THF)₃ (Ln = Yb (4a), Eu (4b), Sm (4c)). While the NMR spectra of the samarium complexes 2c and 4c display the extreme chemical shifts typical for paramagnetic compounds, the spectra of the diamagnetic Yb complexes 2a and 4a provide useful insight into the electronic situation, revealing strongly shielded resonances consistent with rather anionic silyl units. This picture is also supported by DFT calculations, which were carried for complexes 2a–c and 4a–c to elucidate the bonding situation between the Ln(II) centers and Si. The calculated HOMOs of the complexes resemble very much electron lone pairs at the silicon atoms attached to the metal. The ionic character of the compounds is also exemplified by a reaction of the ytterbacyclopentasilane 2a with zirconocene dichloride, which smoothly proceeded to the respective zirconacyclopentasilane.

**EXPERIMENTAL SECTION**

**General Remarks.** All reactions involving air sensitive compounds were carried out under an atmosphere of dry nitrogen or argon using either Schlenk techniques or a glovebox. All solvents were dried using a column based solvent purification system. Chemicals were obtained from different suppliers and used without further purification. [Me₂Si(Me₂Si)₂SiK]₂ (1) and (Me₂Si)₂SiK (3) were prepared following reported procedures. SmI₂(THF)₂, YbI₂(THF)₂, and EuI₂(THF)₂ were prepared by treatment of the metals in THF with 1,2-diodooctane. Elemental analysis was carried out using a Heraeus VARIO ELEMENTAR instrument.

**NMR Spectroscopy.** 1H (300 MHz), 13C (75.4 MHz), and 29Si (59.3 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer. To compensate for the low isotopic abundance of 29Si the INEPT pulse sequence was used where possible for the amplification of the signal. To obtain reliable 1H, 13C, and 29Si NMR shifts, samples with tетramethylsilane (TMS) added were used to obtain a reference point. gHMBC 1H NMR shifts, samples with tetramethylsilane (TMS) added were used to compensate for the low isotopic abundance of 29Si experiments (without TMS added) were carried out to determine all 29Si NMR shifts.

**Fluorescence Spectroscopy.** The fluorescence of solid compounds 4b and EuI₂(THF)₂ was recorded with a PerkinElmer LS55 spectrofluorometer equipped with a Xe flash lamp as the light source. The solid compound was transferred to the instrument’s solid sample holder in the glovebox and kept under nitrogen atmosphere until the sample holder was introduced to the sample chamber of the spectrometer.

**X-ray Structure Determination.** For X-ray structure analyses the crystals were mounted onto the tip of glass fibers. Data collection was performed with a BRUKER-AXS SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (0.71073 Å). The data were reduced to F² and corrected for absorption effects with SAINT59 and SADABS60,61 respectively. The structures were solved by direct methods and refined by full-matrix least-squares method (SHELX97).62 If not noted otherwise all non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles. Crystallographic data (excluding structure factors) for the structures of compounds 2a, 2b, 2c, 4a, 4b, and 4c reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-1062936 (2a), 1062935 (2b), 1026159 (2c), 1062933 (4a), 1042934 (4b), and 1026158 (4c). Copies of data can be obtained free of charge at http://www.ccdc.cam.ac.uk/products/csd/request/. Figures of solid state molecular structures were generated using Ortep-3 as implemented in WINGX3 and rendered using POV-Ray 3.6.44

DFT calculations were carried out by using the GAUSSIAN 09 program. Geometry optimization was performed with the B3PW91 functional,66–68 since it was effectively applied for analogous f-block element-carbene complexes.69 We employed the Stuttgart RSC 1997 ECP basis set from Basis Set Exchange70,71 for lanthanide atoms and 6-31G(d,p) basis for the other atoms, denoted as Basis 1 in the manuscript. Natural Population Analysis was performed with NBO program 5.075 implemented in Gaussian 09. Five-Membered Yb–Si–Complex (THF)₂ (2a). The reaction was done under strict exclusion of light. To a solution of YbI₂(THF)₂ (114 mg, 0.20 mmol) in toluene (4 mL) was added 1 (0.20 mmol, in 2 mL toluene) dropwise. The completeness of the reaction was confirmed after 15 min by 29Si and 1H NMR. To remove insoluble salts the mixture was filtered over Celite and rewashed with toluene (3 mL). After the solvent was removed a dark orange oil was obtained. Crystallization (pentane (15 mL), −37 °C, for several days) afforded 2a (91% NMR) as orange crystals. Mp 146–148 °C. NMR (CD₂Cl₂) δ in ppm: 1H: 3.57 (bs, 16H, THF), 1.38 (bs, 16H, THF), 0.76 (s, 12H, SiMe₂). 13C: 70.5 (DME), 59.7 (DME), 7.3 (SiMe₂). 29Si: −3.5 (Jfp-Si = 20 Hz, SiMe₂), −30.5 (SiMe₃), −154.0 (SiL). When the reaction was carried out in CD₃OD instead of toluene with an approximate THF concentration of 9 equiv per Yb, the 29Si NMR spectrum indicated a higher degree of shielding of the metalated silicon atom. NMR (CD₂Cl₂) δ in ppm 29Si: −3.3 (Jfp-Si = 21 Hz, SiMe₂), −29.1 (SiMe₃), −163.9 (Jfp-Si = 663 Hz, SiL). Yb–Si–Complex (DME)₅. This involved the same procedure as above only using DME instead of THF as the solvent: NMR (CD₂Cl₂) δ in ppm: 1H: 3.26 (s, 9H, DME), 2.95 (s, 6H, DME), 0.67 (s, 12H, SiMe₂), 0.49 (s, 36H, SiMe₃), 0.3 (DME), 70.5 (DME), 59.7 (DME), 7.3 (SiMe₂), 1.8 (SiMe₃). 29Si: −2.9 (Jfp-Si = 20.4 Hz, SiMe₂), −29.8 (SiMe₃), −158.4 (Jfp-Si = 656 Hz, SiL).

Five-Membered Eu–Si–Complex (THF)₂ (2b). The same procedure as for 2a was used except with 1 (0.16 mmol) and EuI₂(THF)₂ (90 mg, 0.16 mmol). Yellow crystals of 2b (93 mg, 63% yield) were obtained from pentane at −37 °C after several days. Mp: 117–120 °C.

Five-Membered Sm–Si–Complex (THF)₂ (2c). The same procedure as for 2a was used except with SmI₂(THF)₂ (288 mg, 0.525 mmol) and 1 (0.500 mmol) in THF and 6 h reaction time. The toluene extract was concentrated to 10 mL and stored at −35 °C for 2 days affording green crystals of 2c (167 mg, 37%). Mp 170–173 °C. NMR (δ in ppm in CD₃OD) 1H: 4.60 (bs, 16H, THF), 0.65 (bs, 16H, THF), 0.53 (s, 36H, SiMe₂), −1.23 (s, 12H, SiMe₂). 13C: 127.32
(THF), 25.35 (THF), −14.49 (SiMe₃), −18.20 (SiMe₃). ²⁵Si: 120.9 (SiMe₃), −98.3 (SiMe₃), −121.1 (Si₃). Anal. Calcd For C₉₂H₆₅SmO₄Si₈ [904.34]: C 42.52, H 8.92. Found: C 42.33, H 8.32. Anal. Calcd For C₉₂H₆₅SmO₄Si₈ [904.34]: C 42.52, H 8.92. Found: C 42.33, H 8.32.

Bis[(trimethylsilyl)silyl]ytterbium(THF) (4a). The same procedure as that for 2a was used except with 3 (0.31 mmol) and YbI₂(THF)₂ (89 mg, 0.16 mmol). Yellow-orange crystals of 4a (98 mg, 71%) were obtained from pentane at −37 °C after 24 h. Mp: 154–157 °C. NMR (δ in ppm in C₂D₆) ¹H: 6.32 (bs, 12H, THF), 1.33 (bs, 12H, THF), 0.48 (s, 54H, SiMe₃). ¹³C: 68.2 (THF), 24.7 (THF), 6.3 (SiMe₃). ²⁵Si: −5.3 (δᵣₛₛ = 41 Hz, SiMe₃) −144.8 (δᵣₛₛ = 729 Hz, Si₃).

Bis[(trimethylsilyl)silyl]europium(THF)₃ (4b). The same procedure as that for 2a was used except with 3 (0.31 mmol) and EuI₂(THF)₂ (86 mg, 0.16 mmol). Yellow-orange crystals of 4b (92 mg, 68%) were obtained from pentane at −37 °C after several days. Mp: 156–158 °C.

Bis[(trimethylsilyl)silyl]samarium(THF)₃ (4c). SmI₂(THF)₂ (290 mg, 0.525 mmol) was dissolved in THF (10 mL), and 3 (0.500 mmol) in THF (6 mL) was added dropwise. The reaction mixture was stirred for 24 h. The solvent was removed under reduced pressure and the residue extracted with pentane (4 times 10 mL) leaving a gray precipitate. The solvent was removed and the residue dissolved in a minimum amount of THF, layered with pentane, and stored at −35 °C for 24 h. Red crystals of 4c (190 mg, 44%). Mp: 150–153 °C. NMR (δ in ppm in C₂D₆) ¹H: 3.17 (bs, 16H, THF), 0.04 (s, 72H, SiMe₃), −0.90 (bs, 16H, THF). ¹³C: 127.20 (THF), 21.81 (THF), −13.40 (SiMe₃). ²⁵Si: −27.4 (SiMe₃), not detected (Si₃). Anal. Calcd For C�鲐₈₂H₆₅SmO₄Si₈ [862.33]: C 41.80, H 9.12. Found: C 41.34, H 8.89.
