Open-Shell Lanthanide(II+) or - (III+) Complexes Bearing σ-Silyl and Silylene Ligands: Synthesis, Structure, and Bonding Analysis

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Supporting Information

ABSTRACT: Complexes featuring lanthanide (Ln)−Si bonds represent a highly neglected research area. Herein, we report a series of open-shell LnII and LnIII complexes bearing σ-bonded silyl and base-stabilized N-heterocyclic silylene (NHSi) ligands. The reactions of the LnIII complexes Cp3Ln(Ln = Tm, Ho, Tb, Gd; Cp = cyclopentadienyl) with 18-crown-6 (18-cr-6)-stabilized 1,4-oligosilanyl dianion ([18-cr-6]K(SiMe3)2SiMe2SiMe2Si(SiMe3)2-K(18-cr-6)) (1) selectively afforded the corresponding metallacyclopentasilane salts [Cp3Ln(Si(SiMe3)2SiMe2)]2[18-cr-6] and [Cp3Ln(Si(SiMe3)2SiMe2)]2[18-cr-6]-2K[18-cr-6] (2). The first example of a complex featuring a Ce−Si bond was isolated in an alternative synthetic approach. The aryloxy-functionalized benzamidinato NHSi ligand Si(OC6H4-2-Ph)2(NHBu)2CPh (4a) and the alkoxy analogue Si(OBu)2(NHBu)2CPh (4b) were reacted with Cp₅Sn(OEt)₂, affording the corresponding silylene complexes, each featuring SmII centers: Cp₅Sn ← Si(O(C6H4-2-Ph)2(NHBu)2CPh) (6) and Cp₅Sn ← Si(O(OBu)2(NHBu)2CPh) (5). Complexes 5 and 6 are the first four-coordinate silylene complexes of any f-block element to date. All complexes were fully characterized by spectroscopic means and by single-crystal X-ray diffraction analysis. In the series 2a−2d, a linear correlation was observed between the Ln−Si bond lengths and the covalent radii of the corresponding Ln metals. Moreover, in complexes 5 and 6, notably long Sm−Si bonds are observed, in accordance with a donor−acceptor interaction between Si and Sm [5, 3.4067(18) Å; 6, 3.413(18) Å]. Density functional theory calculations were carried out for complexes 2a−2d, 5, and 6 to elucidate the bonding situation between the LnII or LnIII centers and Si. In particular, a decrease in the Mayer bond order (MBO) of the Ln−Si bond is observed in the series 2a−2d in moving from the lighter to the heavier lanthanides (Tm = 0.53, Ho = 0.62, Tb = 0.65, and Gd = 0.75), which might indicate decreasing covalency in the Ln−Si bond. In accordance with the long bond lengths observed experimentally in complexes 5 and 6, comparatively low MBOs were determined for both silylene complexes (5, 0.24; 6, 0.25).

INTRODUCTION

Compounds featuring lanthanide (Ln)−Si bonds are somewhat rare in contemporary literature,¹−³ further highlighted by the fact that, for the elements Ce, Tb, and also Pm, no examples exist. Sm and the late lanthanide metals Yb and Lu are the best-studied elements for this class of compounds, with several reported examples. Arguably, the most straightforward synthesis of lanthanide silyl compounds was described in the seminal work of Bochkarev and co-workers,⁴ who obtained neutral (Ph₃Si)₂YbIII(THF)₄ directly from elemental Yb and Ph₃SiCl in tetrahydrofuran (THF; eq 1).

2Ph₃SiCl + 2Yb → (Ph₃Si)₂Yb(THF)₄ + YbCl₃(THF)₂

Utilizing a common method for the preparation of early-transition-metal complexes, Schumann and co-workers carried out salt elimination reactions of rare-earth halide complexes with Me₃SiLi. Reactions with Cp₃Ln(μ-Cl)₂Na in 1,2-dimethoxyethane (DME) led to the respective ate complexes of the type [Li(DME)₃][Cp₃Ln(SiMe₃)₂] for Ln = Sm,⁵,⁶

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RESULTS AND DISCUSSION

Synthesis. Reactions of the readily accessible metallocenes (Cp,Ln) of the elements Gd, Tb, Ho, and Tm with the 1,4-oligosilyl dianion \(^{15,25}\) afford cleanly the corresponding metallacyclopentasilane ate complexes (2a–2d) with the Ln metals in the oxidation state 3+ together with \([\text{K}(18\text{-crown}-6)]\text{Cp}\) (where 18-cr-6 = 18-crown-6) as the counterion (Scheme 1). The ease of access to these complexes prompted us to explore the reaction with (Cp,Ce), a lighter analogue of the heavier lanthanides. Contrary to the other used metalloccenes (Cp,Ln), Cp,Ce is not commercially available but can readily be synthesized.\(^{26}\) Reaction of diion 1 with Cp,Ce did not lead to a five-membered ring but to the acyclic compound 3 (Scheme 1), which to the best of our knowledge is the first example of a compound featuring a Si—Ce bond. Each Ce\(^{\text{III}}\) atom retains all of its three Cp ligands while forming an additional Ce—Si bond. One of the Cp ligands on each Ce coordinates to the cationic moiety K(18-cr-6)-THF. All complexes 2a–2d and 3 are thermally stable but extremely sensitive to moisture and air, as expected for organometalllic Ln complexes.

In addition to these lanthanide silyl complexes, we are also interested in the synthesis of base-stabilized silylene lanthanide metal complexes because instead of featuring a σ-bonded silyl group they would rather exhibit coordinative (donor—acceptor) bonds between Si and the Ln element, which would be of interest as a comparison. As a starting point, we decided to investigate the reactivity of Cp\(^{\ast}\),Sm(OEt\(_2\)) with Sm\(^{\text{III}}\) complexes. Reaction with Cp\(^{\ast}\),Sm(OEt\(_2\)) was found to be an intermediate in the cluster formation.\(^{27,28}\) Reaction of \(\text{MeOCH}_{\text{C}}\text{H}_{\text{Si}}\text{H}_{\text{Si}}\) with \([\text{Cp}^{\ast}\text{Ln}(\mu-\text{H})]\) led to the neutral lutetium silyl complex \(\text{Cp}^{\ast}\text{LuH}_{\text{C}}\text{H}_{\text{Si}}(\mu-\text{SiOCH}_{\text{C}}\text{H}_{\text{C}})\).\(^{19}\)

Reactions of the thermally stable N-heterocyclic silylene (NHSi) Si\([\text{N(CH}_{\text{C}}\text{Bu})_{\text{C}}\text{H}_{\text{C}}]\) (Si[NN]) and Cp,Ln (Ln = Y, Yb) led to the first group 3 (Y) and lanthanide (Yb) metal silylene complexes Cp\(_3\)LnSi[NN] \(^{20}\) (eq 3). Under similar reaction conditions, Cp\(_2\)La turned out to be unreactive. Evans and co-workers reported the reaction of Cp\(^{\ast}\),Sm with West’s stable silylene, and a Sm\(^{\text{III}}\)−Si\(^{\text{II}}\) complex was obtained.\(^{21}\) That the nature of the interaction between Sm and Si is likely to be of the donor—acceptor type was shown by the fact that the silylene ligand could easily be displaced by THF, but no further studies were carried out in this direction, nor was any detailed bonding analysis carried out to date.
The dinuclear mixed-valent complex 7 (Scheme 3), featuring Sm\textsuperscript{II} and Sm\textsuperscript{III} bridged by a \(\mu\)-iodide ligand, was coincidentally isolated as a minor byproduct of the supernatant solution from the reaction mixture of complex 5. Presumably, its formation stems from trace amounts of \(\text{Cp}^*\text{Sm}^\text{II}\), present in the starting material \(\text{Cp}^*\text{Sm(OEt}_2\text{)}\), upon reaction with 5. Unfortunately, only a few crystals were obtained, which precluded further spectroscopic characterization, but nevertheless it is an interesting complex from a structural point of view.

Complexes 5 and 6 are paramagnetic, with magnetic moments \(\mu_{\text{eff}} = 2.7 \mu_B\) (5) and 2.6 \(\mu_B\) (6) (Evans' method).\textsuperscript{34} This is dramatically reduced upon comparison to the Sm\textsuperscript{II} starting material \(\text{Cp}^*\text{Sm(OEt}_2\text{)}\) (\(\mu_{\text{eff}} = 3.6 \mu_B\)) possibly because of the NHSi ligands affecting spin–orbit coupling in the Sm center. This suggests that the NHSi ligand influences the magnetic properties of the emerging Sm\textsuperscript{II} complexes considerably, which is likely attributable to the different nature of the Si: \(\rightarrow\) coordination versus the O: \(\rightarrow\) coordination of Et\textsubscript{2}O in \(\text{Cp}^*\text{Sm(OEt}_2\text{)}\).

**NMR Spectroscopy.** NMR spectroscopic characterization of open-shell Ln complexes is somewhat challenging, particularly because of spin–orbit coupling phenomena. These properties have been exploited in Ln shift reagents.\textsuperscript{35,36} Diamagnetic complexes, however, also exist and possess either \(f^0\) (La\textsuperscript{III} and Ce\textsuperscript{IV}) or \(f^1\) (Lu\textsuperscript{III} and Yb\textsuperscript{II}) electron configurations.

Nevertheless, even for the respective lanthanide metalloocene complexes, investigations started early on,\textsuperscript{37} and currently chemical shifts for a substantial number of lanthanide metalloocene complexes are known. It is important to note that while there are certainly trends governing the chemical shift behavior, their interpretation is not straightforward. The chemical shifts of protons attached directly to cyclopentadienyl ligands are frequently dramatically different from the shifts observed for methyl groups on cyclopentadienyl ligands (see below).

A short survey on the existing NMR characterization data for \(\text{Cp}_2\text{Ln}, \text{Cp}_2\text{LnL}, \text{Cp}_2\text{LnX}, \text{Cp}_2\text{Ln},\) and related complexes [such as \(\text{CpMe}_{\text{ Kron}}\text{Cp(SiMe}_3\text{)}_{\text{ Kron}},\) etc.] of Ce, Sm, Tm, Tb, Ho, and Gd reveals numerous examples for Sm and Ce, while there are only scant examples for Tm\textsuperscript{7,38–42} Tb\textsuperscript{7,37,43,44} Ho\textsuperscript{7,37,45} and Gd\textsuperscript{7,44,46–50} Furthermore, it should be noted that usually only \(^1H\) NMR data are given, but \(^{29}\text{Si}\) or even \(^{13}\text{C}\) NMR data are neglected.

Comprehensive studies dealing with the magnetic effects of certain electronic configurations on the chemical shift behavior of ligands are extremely rare. For silylated complexes, the seminal work of Schumann and co-workers compared \(^1H\) NMR resonances of a number of complexes of the type \(\text{Cp}_2\text{Ln}(\mu-\)
Inspection of the chemical shifts in this series reveals that, in particular, the Cp–H resonances of TbIII and HoIII are strongly downfield-shifted to values close to 160 ppm, whereas the respective signals of ZrIII and TmIII are considerably upfield-shifted to values of around −60 ppm. Extremely shifted resonances of the SiMe3 groups were found for HoIII and ErIII. The sign of the magnetically induced shift of the SiMe3 resonance is, however, reversed compared to that of the Cp resonance.7

For compounds 2a–2d, we recorded 1H NMR spectra (Table 1). It is important to consider the fact that not only are NMR spectra of Ln compounds paramagnetically shifted and generally exhibit line-broadening, but chemical shifts are frequently also concentration- and temperature-dependent.51 Nuclei with reduced natural abundance are therefore frequently difficult to detect. Nevertheless, for compounds 2b–2d, it was possible to measure two-dimensional 1H–13C and 1H–29Si correlation NMR spectra at room temperature, which was indispensable for the assignments of the signals.

It is instructive to compare the 1H chemical shifts recorded for 2a–2d to those observed for the complexes of Schumann. The behavior of complex 2a was indeed very similar to what had been observed for Schumann’s compound [Cp2Tm(SiMe3)2]−. The Cp resonance of 2a at −48.3 ppm is close to [Cp2Tm(SiMe3)2]− at −56.7 ppm. A comparison similar to Schumann’s Ho compound, however, shows a completely different picture. While the CpH resonance for [Cp2Ho(SiMe3)2]− was described at very low field (164.2 ppm), we observed the analogous resonance of 2b at −22.4 ppm. It should, however, be noted that the number of NMR spectroscopically characterized CpHoIII compounds is rather limited,7,37,45 and therefore it is difficult to assess the observed chemical shift values. Compared to the Cp resonances, the SiMe signals are found to exhibit comparably normal chemical shifts. Considering the fact that the shift caused by the paramagnetic atoms decreases with 1/\(r^3\), it can be expected that more remote atoms experience a much smaller shifting effect. Only for complex 2a, which also exhibits a very strong effect on the CpH resonances (−48.3 ppm), also the SiMe3 resonances are severely shifted to 16.7 ppm. With respect to the 29Si NMR data, we were able to obtain values for compounds 2b–2d (Table 2). The values of 2b and 2c are quite similar, which is consistent with Schumann’s proton NMR study where Ho and Tb showed similar shift behavior. The values for the SiMe3 resonance of the Gd compound 2d are also in line with those observed for 2b and 2c. The resonance detected for the SiMe3 units is, however, clearly different.

Strikingly, for the silylene complexes 5 and 6 both featuring SmII+ centers, in the respective 1H NMR spectra, most of the signals are observed in the diamagnetic spectral window, at odds with the complexes discussed above. Noteworthy, however, are dramatic shifts of the aryl protons in both complexes, to both high- and low-field regions, because of the paramagnetic influence of the SmII center (Figure 1). Some of the signals are also somewhat line-broadened. The 13C NMR spectra for both complexes also reveal most of the signals in the expected diamagnetic spectral range, some again somewhat line-broadened, although the resonance signals corresponding to the ring atoms of the coordinated Cp9 ligand could not be observed in both complexes, akin to the Cp complexes described above.

Two-dimensional HSQC and HMBC correlation experiments were also carried out for complexes 5 and 6 for an unambiguous assignment of the 13C NMR signals. Because of the paramagnetic nature of the complexes, although cross peaks were observed in alignment with the signals in the 1H NMR spectrum, these did not correspond to any observable signals in the 13C NMR spectra, in both cases. This suggests that the routine pulse sequence for these traditional two-dimensional correlation experiments is not appropriate for the SmII complexes, although with the LnIII complexes described above, it was possible. Moreover, despite extremely long (ca. 72 h) acquisition periods, at high concentrations, no signals could be observed in the 29Si NMR spectra because of the paramagnetic influence of the SmII center.

X-ray Crystallography. Single-crystal structure analyses could be carried out for all new compounds (2a–2d, 3, and 5–7). The isostructural compounds 2a, 2b, and 2d (Figure 2) crystallized in the monoclinic space group P2(1)/n, except the Tb compound 2c (P1̅) because of the four THF molecules in the asymmetric unit. In all four structures, the ion pairs are separated. The counterion (18-cr-6)K-Cp-K(18-cr-6) shows disorder in one crown ether for 2b and in both crown ethers for 2a and 2d, a fact that is reflected by the number of restraints used. The Ce complex 3 (Figure 3) crystallized in the triclinic space group P1 with an additional toluene molecule in the asymmetric unit.

### Table 1. 1H NMR Data of Compounds 2a–2d (Solvent: THF-d6)

| compound | 1H: CpLn | 1H: SiMe3 | 1H: SiMe2 |
|----------|----------|----------|----------|
| 2a (Tm)  | −48.3    | 16.71    | −11.93   |
| 2b (Ho)  | −22.41   | 1.58     | 1.66     |
| 2c (Tb)  | −24.32   | 0.63     | 0.72     |
| 2d (Gd)  | 9.23     | 2.35     | 2.20     |

### Table 2. 29Si NMR Data of Compounds 2b–2d (Solvent: THF-d6)

| compound | 29Si: SiMe3 | 29Si: SiMe2 | 29Si: Siq |
|----------|------------|------------|----------|
| 2b (Ho)  | −9.0       | −35.2      | −114.9   |
| 2c (Tb)  | −10.6      | −36.1      | −116.3   |
| 2d (Gd)  | −7.7       | −1.4       | n.d.     |

*a.n.d. = not detected.*
One of the Cp ligands coordinates to the cationic moiety K/18-cr-6/THF.

Because 2a–2d and 3 are the first structurally characterized complexes bearing a Ce–Si, Tm–Si, Ho–Si, Tb–Si, or Gd–Si bond, no data for comparison are available. The most striking features of these molecular structures are the values for the lanthanide–silyl bond lengths, which are in good agreement with the sum of the covalent radii (Figure 4). The distances between Ln and Si decrease incrementally with decreasing metal size, as expected. This indicates that the Ln–Si bond is rather polar but might possess at least some covalent character. The bond angle Si–Ln–Si varies only slightly from 94.15° in 2a (Tm) to 94.68° in 2b (Ho) to 95.47° in 2c (Tb) to 94.84° in 2d (Gd).

The cyclopentadienyl rings in all five compounds are bonded in \( \eta^5 \) fashion with increasing bond lengths between the centroids of the Cp rings and the lanthanoid atoms: in 2a (Tm) 2.335 and 2.328 Å, in 2b (Ho) 2.363 and 2.349 Å, in 2c (Tb) 2.401 and 2.388 Å, in 2d (Gd) 2.401 and 2.394, and finally in 3 (Ce) 2.565 and 2.562 Å. These distances (Cp ring centroid–metal) are in good agreement with comparable \( \text{Cp}_2\text{Ln}^{III} \) compounds (Tm, Ho, Tb, Gd, and Ce(II)). The Cp–Ce distance in 3, where the K atoms are coordinated to the Cp rings, is 2.581 Å slightly elongated.

Figure 2. Some key metrical parameters from the crystal structures of the isostructural complexes 2a–2d. Thermal ellipsoids are at the 30% probability level and hydrogen atoms omitted for clarity. Color code: purple ellipsoid, Ln metal [Tm (2a), Ho (2b), Tb (2c), Gd (2d)]; pink ellipsoid, silicon; light gray, carbon.

Figure 3. Molecular structure of 3 (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. Bond lengths (Å) and angles (deg): Ce1–C1 2.817(3), Ce1–C6 2.844(3), Ce1–Si1 3.2283(2), Si1–Si4 2.3601(15), Si1–Si3 2.3784(13), Si1–Si2 2.3981(13); Si4–Si1–Si3 99.54(5), Si4–Si1–Si2 102.43(6), Si3–Si1–Si2 98.81(5), Si4–Si1–Ce1 115.26(5), Si3–Si1–Ce1 111.43(4), Si2–Si1–Ce1 125.37(5).

Figure 4. Plot of Si–M (M = Tm, Ho, Tb, Gd) versus covalent radii. Si–M is the average bond length in 2a–2d.

Figure 5. Molecular structure of 5 (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. Bond lengths (Å) and angles (deg): Sm1–C19 2.772(6), Sm1–C12 2.853(6), Sm1–Si1 3.4396(15), Si1–O1 1.645(4), Si1–N1 1.875(5), Si1–N2 1.876(5); O1–Si1–N1 107.6(2), O1–Si1–N2 107.2(2), N1–Si1–N2 114.23(16), N1–Si1–Sm1 128.16(16), N2–Si1–Sm1 122.14(18).

Figure 7. Molecular structure of 7 (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. Bond lengths (Å) and angles (deg): Sm1–C19 2.772(6), Sm1–C12 2.853(6), Sm1–Si1 3.4396(15), Si1–O1 1.645(4), Si1–N1 1.875(5), Si1–N2 1.876(5); O1–Si1–N1 107.6(2), O1–Si1–N2 107.2(2), N1–Si1–N2 114.23(16), N1–Si1–Sm1 128.16(16), N2–Si1–Sm1 122.14(18).
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Figure 6. Molecular structure of 6 (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. Bond lengths (Å) and angles (deg): Sm1−Si1 3.3142(18), Si1−O1 1.683(7), Si1−N1 1.865(7), Si1−N2 1.872(7), O1−Si1−N1 96.8(3), O1−Si1−N2 100.0(3), N1−Si1−N2 69.7(3), O1−Si1−Sm1 125.2(2), N1−Si1−Sm1 107.9(2), N2−Si1−Sm1 134.2(2).

Figure 7. Molecular structure of 7 (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. Bond lengths (Å) and angles (deg): Sm1−I1 3.1069(6), Sm1−Si1 3.2992(18), Sm2−I1 3.2962(7), N1−Si1 1.888(5), N2−Si1 1.884(6), O1−Si1 1.626(5), I1−Sm1−Si1 89.80(3), Sm1−I1−Sm2 160.89(2), O1−Si1−N2 108.4(3), O1−Si1−N1 108.3(3), N2−Si1−N1 70.0(2), O1−Si1−Sm1 106.61(17), N2−Si1−Sm1 130.7(2), N1−Si1−Sm1 128.09(19).

Figure 8. HOMO (left) and HOMO−1 (right) of 2a calculated at the B3PW91/Basis1 level of theory (isovalue: 0.02). White, gray, blue, and teal refer to H, C, Tm, and Si atoms, respectively.

DFT Calculations. The electronic structures of synthesized complexes (2a−2d, 5, and 6) at the B3PW91/Basis1 level of theory were calculated. According to these calculations, the Tm−Si bond distances (2.958 and 2.971 Å) in the optimized geometry of 2a show perfect agreement with the experimentally characterized distances (2.966 and 2.980 Å, respectively). Natural bond orbital (NBO) analysis suggests that the negative charge of 2a is mainly localized on the Si atoms (−0.25) connected to the Tm center (Table 3), whereas other Si atoms show large positive natural population between 0.3+ and 0.55+.

In addition, NBO analysis shows lone pairs on the Si atoms. Interestingly, the shape of the highest occupied molecular orbital (HOMO) and HOMO−1 exhibits some covalent and ionic character bonding as well. The HOMO (−0.54 eV) depicted in Figure 8 shows a lone pair on the Si center, which can be interpreted in light of the negative charge of 2a as a bond with strongly polarized or even ionic character where the Si bears the two electrons. In contrast to that, HOMO−1 (−0.86 eV) denotes more covalent character because the orbital is extended toward the Tm center as well. This also agrees with the Mayer bond order (MBOs) that supports the picture of weak, very polarized bonds (0.53).

The analogous Gd complex, 2d, features a half-filled f shell (S = 7/2), and the Gd−Si bond distances (3.025 and 3.030 Å) in

Table 3. Calculated Average Ln−Si Bond Lengths (Å), MBOs of Ln−Si Bonds, Natural Population Analysis Charges, and HOMO Energies (eV) for 2a−2d, 5, and 6 at the B3PW91/Basis1 Level of Theory

| compound | Ln−Si bond distance (Å) | MBO of Ln−Si bonds | NPA charge (Ln/Si) | HOMO energy (eV) |
|----------|------------------------|---------------------|-------------------|------------------|
| 2a (Tm)  | 2.965                  | 0.53                | +2.28/−0.25       | −0.54            |
| 2b (Ho)  | 2.996                  | 0.62                | +2.41/−0.21       | −0.66            |
| 2c (Tb)  | 3.017                  | 0.65                | +2.35/−0.23       | −0.86            |
| 2d (Gd)  | 3.028                  | 0.75                | +2.27/−0.22       | −0.77            |
| 5 (Sm)   | 3.411                  | 0.24                | +1.99/±1.50       | −1.67            |
| 6 (Sm)   | 3.278                  | 0.25                | +2.01/±1.66       | −1.72            |

...
the optimized geometry also show agreement with the experimentally characterized distances (3.018 and 3.038 Å, respectively). HOMO (−0.77 eV) and HOMO−1 (−0.97 eV) (Figure 10) depict more covalent character than that in the case of 2a because HOMO−1 exhibits uniform extension between the Gd and Si atoms. MBOs of Gd−Si bonds (0.73 and 0.75) are larger than that of Tm−Si bonds (0.53), although NBO analysis still suggests lone pairs on the Si atoms. For 2b and 2c, the calculated bond distances, bond orders, and charges (Table 3) are between the discussed theoretical results of 2a and 2d; therefore, the calculated parameters follow the experimentally characterized series of bond lengths, providing further evidence of the partial covalent character of the Ln−Si bonds as HOMO and HOMO−1 also suggest (Figures 9–11). The calculated

Data in the series of 2a−2d might also indicate, in agreement with the previously suggested relationship of bond lengths, some covalency in the bonding character (Figure 4).39

Samarium silylene complexes (5 and 6) have triplet ground states in accordance with the Evans magnetometric measurements. The calculated structures are in moderate agreement with the experimentally characterized geometries; the calculated Sm−Si distances are somewhat shorter (3.411 and 3.278 Å, respectively; Table 3) than the experimental values (3.440 and 3.315 Å, respectively). In spite of the shorter Sm−Si distance, none of the applied methods suggests considerable covalent character of the Sm−Si bond, which is in good agreement with the relatively large bond distances. NBO analysis displays a lone pair on the Si centers because the HOMOs of 5 and 6 exhibit the same (Figure 12) features. MBOs indicate very low bond order of 0.24 and 0.25 for 5 and 6, respectively.

### CONCLUSION AND SUMMARY

In summary, a range of novel open-shell Ln complexes in the II + or III+ oxidation state bearing σ-bonded silyl groups or coordinated NHSi ligands have been reported, characterized spectroscopically and by structural means, and further elucidated by DFT methods. The σ-bonded silyl complexes feature Ln−Si bonds with much higher MBO indices compared to the LnSi complexes bearing coordinated NHSi ligands. A general trend is a decrease in the covalent nature of the Ln−Si bond for complexes \([\text{CP}_2\text{Ln}((\text{SiMe}_3)_2\text{SiMe}_2)])\] ([K18-cr-6]CP) \(\text{Ln} = \text{Gd (2a), Ho (2b), Gd (2c), Tb (2d)}\) on moving from left to right across the lanthanides, as evidenced by an incremental decrease in the MBOs. The ease of synthetic access to these open-shell complexes featuring Ln−Si bonds highlighted herein is of fundamental importance and potentially opens the door to further fundamental investigations of these hitherto poorly investigated complexes.

### 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.67 Chemicals were obtained from different suppliers and used without further purification. Silyl dianion \(1\),\(^{24,25}\) \(\text{CP}_2\text{Ce},26\) \(\text{CP}_3\text{Sm(OEt)}_2,27\) and ligands \(4a\)\(^{32}\) and \(4b\)\(^{33}\) were prepared following reported procedures.

\(^1\text{H}\) (300 MHz), \(^{13}\text{C}\) (75.4 MHz), and \(^{29}\text{Si}\) (59.3 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer or on Bruker spectrometers (AV400 or AV200). To compensate for the low isotopic abundance of \(^{29}\text{Si}\), the INEPT pulse sequence was used where possible for amplification of the signal.\(^{34,35}\) To obtain reliable \(^1\text{H}\), \(^{13}\text{C}\), and \(^{29}\text{Si}\) NMR shifts, samples with trimethylsilylane (TMS) added were used to obtain a reference point. \(^1\text{H}\) CP signals could be observed with more concentrated samples that were referenced using the shifts obtained from the dilute spectra. gHMBC \(^1\text{H}−\(^{29}\text{Si}\) experiments (without TMS added) were carried out to determine all \(^{29}\text{Si}\) NMR shifts. To rule out measurement of the most plausible side product \(1,1,2,2\)-tetrakis(trimethylsilyl)tetramethylecyclooctasilane, which might resonate at different chemical shifts because of paramagnetic interaction, several of the gHMBC \(^1\text{H}−\(^{29}\text{Si}\) experiments were repeated with the deliberate addition of 1,1,2,2-tetrakis(trimethylsilyl)tetramethylecyclooctasilane, exhibiting the expected additional set of signals.

High-resolution (HR) electrospray ionization mass spectrometry (ESI-MS) spectra were recorded on an Orbitrap LTQ XL of a Thermo Scientific mass spectrometer and the raw data evaluated using the Xcalibur computer program. UV spectra were measured on a PerkinElmer Lambda 35 spectrometer using spectroscopic grade pentane as the solvent.

#### 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) for 2a−2d and 3 and on an Agilent Technologies SuperNova (single source, Cu Kα radiation, \(λ = 1.5418 \text{ Å}\)) for 5 and 7. The data were reduced to \(F^2\) and corrected for absorption effects with SADABS\(^{71,72}\) respectively. The structures were solved by direct methods and refined.

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Figure 9. HOMO (left) and HOMO−1 (right) of 2b calculated at the B3PW91/Basis1 level of theory (isovalue: 0.02). White, gray, blue, and teal refer to H, C, Ho, and Si atoms, respectively.

Figure 10. HOMO (left) and HOMO−1 (right) of 2d calculated at the B3PW91/Basis1 level of theory (isovalue: 0.02). White, gray, blue, and teal refer to H, C, Gd, and Si atoms, respectively.

Figure 11. HOMO (left) and HOMO−1 (right) of 2c calculated at the B3PW91/Basis1 level of theory (isovalue: 0.02). White, gray, blue, and teal refer to H, C, Tb, and Si atoms, respectively.
by a full-matrix least-squares method (SHELXL97). If not noted otherwise, all non-H atoms were refined with anisotropic displacement parameters. All H atoms were located in calculated positions to correspond to standard bond lengths and angles. All diagrams were drawn with 30% probability thermal ellipsoids, and all H atoms were omitted for clarity. Crystallographic data (excluding structure factors) for the structures of compounds 2a–2d, 3, and 5–7 reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 1024428 (2a), 1024431 (2b), 1024432 (2c), 1024433 (2d), 1024434 (3), 1024435 (5), and 1024437 (7). Copies of these data can be obtained free of charge at http://www.ccdc.cam.ac.uk/products/csd/request/.

**DFT Calculations.** DFT calculations were carried out using the Gaussian 09 program. Geometry optimization was performed with the B3PW91 functional 75–77 because it was effectively applied for analog f-block element carbene complexes. 78 We employed the Stuttgart RSC 1997 ECP79 basis set from Basis Set Exchange 80, 81 for f–block (lanthanide) elements, 6–31+G(d) 82 for Si atoms and 6–31G(d) 83, 84 basis for the other atoms, denoted as Basis1 in the paper. Natural population analysis was performed with NBO program 5.0 85–87 implemented in Gaussian 09.

**Potassium (18-Crown-6)[1,4-1,4,4-tetrakis(trimethylsilyl)tetramethyltetrasilanylene]dicyclopentadienylholmiate (2a).** A suspension of Cp,Tm (98 mg, 0.27 mmol) and GdCp3 (106 mg, 0.30 mmol). Yellow crystals of 2a (321 mg, 0.30 mmol) and GaCp3 (106 mg, 0.30 mmol). Yellow crystals of 2c (137 mg, 32%) were obtained after 2 days at −60 °C. MP: 172–175 °C. HR ESI-MS. Calculated for C26H58TmO2Si8: m/z 1788.4157. Found: m/z 1788.4156. H NMR (THF-d8): δ 6.97 (s, 5H, Cp), 7.85 (s, 5H, Cp), 4.00 (18-cr-6), 2.35 (18-cr-6), 2.10 (12H, SiMe3). 131C [H] NMR (THF-d8): δ 68.9 (18-cr-6), 3.6 (SiMe3), not detected (Cp signals). 23Si [H] NMR (THF-d8): δ −10.6 (SiMe3), −36.1 (SiMe3), −116.3 (Si).

**Potassium (18-Crown-6)[1,4-1,4,4-tetrakis(trimethylsilyl)tetramethyltetrasilanylene]dicyclopentadienyldoladolinate (2d).** The same procedure as for that 2a was used except for 1 (321 mg, 0.30 mmol) and GdCp3 (106 mg, 0.30 mmol). Yellow crystals of 2c (137 mg, 32%) were obtained after 2 days at −60 °C. MP: 172–175 °C. HR ESI-MS. Calculated for C26H58GdO2Si8: m/z 1834.4166. Found: m/z 1834.4164. H NMR (THF-d8): δ 6.93 (s, 5H, Cp), 7.85 (s, 5H, Cp), 4.00 (18-cr-6), 2.35 (18-cr-6), 2.20 (12H, SiMe3). 131C [H] NMR (THF-d8): δ −14.8 (SiMe3), −17.7 (SiMe3), not detected (Si). UV/vis (Et2O): λ1 = 252 nm and ε1 = 3.8 × 104 L mol−1 cm−1, λ2 = 287 nm and ε2 = 1.1 × 105 L mol−1 cm−1; λ3 = 342 nm and ε3 = 3.2 × 104 L mol−1 cm−1; λ4 = 395 nm and ε4 = 9.4 × 103 L mol−1 cm−1.

**Dipotassium (18-Crown-6)[μ-1,4-1,4,4-tetrakis(trimethylsilyl)tetramethyltetrasilanylene]bis(tricyclopentadienyleracete) (3).** The same procedure as for 2a was used except with 1 (160 mg, 0.15 mmol) and CeCp3 (100 mg, 0.30 mmol). Very sensitive yellow crystals of 3 (208 mg, 79%), suitable for single-crystal XRD analysis, were obtained after 16 h at room temperature.

Cp2Si–Sm = [Si(OtBu)][(NtBu)2CPh] (5). A Schlenk tube was charged with Cp2Si (0.173 g, 0.351 mmol) and ligand 4b (0.117 g, 0.351 mmol). A total of 10 mL of degassed toluene was concentrated onto this solid mixture by sublimation thereof in a liquid-nitrogen cold trap, under a static vacuum. After the condensation was complete, the solvent was degassed once more upon thawing and allowed to slowly warm to room temperature with rapid stirring. Upon warming to room temperature, the reaction solution had a dark-green color. After stirring for 3 h at room temperature, an in situ 1 H NMR spectrum of the reaction solution revealed the selective formation of a new product. The reaction solution was concentrated in vacuo under reduced pressure to ca. 2 mL and cooled to −30 °C for 1 h to complete the precipitation of the product. The light-green supernatant was removed by cannula filtration at −50 °C, and the remaining emerald-green solid was dried in vacuo for 1 h at a pressure of 3 × 10−2 mbar. Crystals of the dinuclear complex 7 were obtained from the light-green supernatant solution as a trace byproduct and structurally characterized by single-crystal XRD analysis. The product was recovered after 5–10 mL of toluene. 1H NMR spectrum of the reaction solution revealed the selective formation of a new product. The reaction solution was concentrated in vacuo under reduced pressure to ca. 2 mL and cooled to −30 °C for 1 h to complete the precipitation of the product. The light-green supernatant was removed by cannula filtration at −50 °C.
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O2\(+\) Magnetic moment (Evans \(s\), 2N \(\mu\)) and >72 h data acquisition time.

18H, N for 1 h at a pressure of 3 mbar and cooled to \(-50^\circ\)C for 1 h to complete the precipitation of the product. A light-brown supernatant was removed by cannula filtration at \(-50^\circ\)C, and the remaining emerald-green solid was dried in vacuo for 1 h at a pressure of 3 x 10\(^{-2}\) mbar. The product was afforded as 6 (0.177 g, 55\%).

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ASSOCIATED CONTENT

**S Supporting Information**
X-ray crystallographic data in CIF format, details of the XRD studies, EPR, ESI-MS, and UV/vis spectra, tables of Cartesian coordinates, and absolute energies for all of the complexes studied. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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