

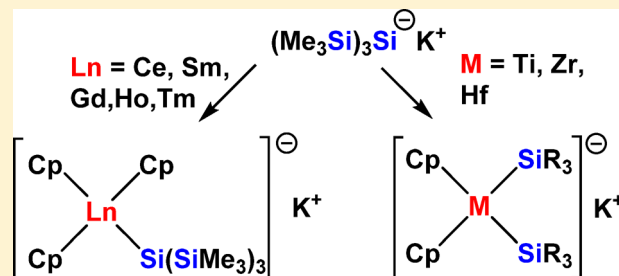
Group 4 Metal and Lanthanide Complexes in the Oxidation State +3 with Tris(trimethylsilyl)silyl Ligands

Rainer Zitz, Johann Hlina, Henning Arp, Dominik Kinschel, Christoph Marschner,*^{1b} and Judith Baumgartner*^{1b}

Institut für Anorganische Chemie, Technische Universität Graz, Stremayrgasse 9, 8010 Graz, Austria

Supporting Information

ABSTRACT: A number of paramagnetic silylated d¹ group 4 metallates were prepared by reaction of potassium tris(trimethylsilyl)silanide with group 4 metallates of the type K[Cp₂MCl₂] (M = Ti, Zr, Hf). The outcomes of the reactions differ for all three metals. While for the hafnium case the expected complex [Cp₂Hf{Si(SiMe₃)₃}₂][−] was obtained, the analogous titanium reaction led to a product with two Si(H)(SiMe₃)₂ ligands. The reaction with zirconium caused the formation of a dinuclear fulvalene bridged complex. The desired [Cp₂Zr{Si(SiMe₃)₃}₂][−] could be obtained by reduction of Cp₂Zr{Si(SiMe₃)₃}₂ with potassium. In related reactions of potassium tris(trimethylsilyl)silanide with some lanthanidocenes Cp₃Ln (Ln = Ce, Sm, Gd, Ho, Tm) complexes of the type [Cp₃Ln Si(SiMe₃)₃][−] with either [18-crown-6·K]⁺ or the complex ion [18-crown-6·K·Cp·K·18-crown-6] as counterions were obtained. Due to d¹ or fⁿ electron configuration, unambiguous characterization of all obtained complexes could only be achieved by single crystal XRD diffraction analysis.



1. INTRODUCTION

Investigations on the chemistry of group 4 silyl complexes were started in the late 1960s, with some work on silyl titanium chemistry^{1–6} and Lappert's contributions of zirconocene and hafnocene complexes.^{7–10} Systematic studies of zirconocene and hafnocene silyl complexes were carried out by Tilley and co-workers,^{11–17} who especially studied aspects of σ -bond metathesis and the catalytic dehydrocoupling polymerization of hydrosilanes catalyzed by these compounds.^{16–19} While in the initial papers by Harrod and co-workers^{20–23} on the dehydrocoupling polymerization of hydrosilanes titanium was acting as the catalytically active element, Tilley's mechanistic studies were carried out using hafnium or zirconium. Starting out from CpCp*M(Cl)Si(SiMe₃)₃ (M = Zr, Hf) it was shown that σ -bond metathesis reaction with a hydrosilane leads to (Me₃Si)₃SiH and a new metal silyl complex, which in reaction with another hydrosilane forms a disilane and a metal hydride.¹⁸

We were curious whether the same chemistry would also work for titanium but quickly realized that CpCp*Ti(Cl)Si(SiMe₃)₃ or even Cp₂Ti(Cl)Si(SiMe₃)₃ is not easily available. NMR spectroscopic analysis of the reactions of CpCp*TiCl₂ or Cp₂TiCl₂ with (Me₃Si)₃SiK (Scheme 1) did not show the expected signals but only a number of oligosilanes. However, upon crystallization of the reaction mixture an NMR-silent silylated titanium(III) species was detected using single crystal XRD analysis.²⁴

Subsequent studies revealed that silylated titanocenes with Ti(IV) tend to undergo reductive elimination to "Cp₂Ti(II)", which in a subsequent comproportionation with Cp₂TiCl₂

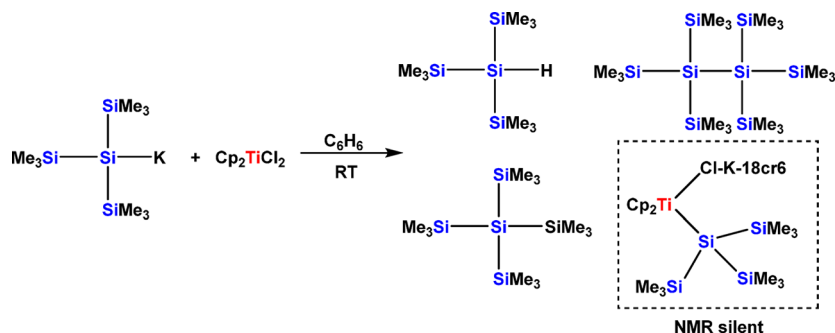
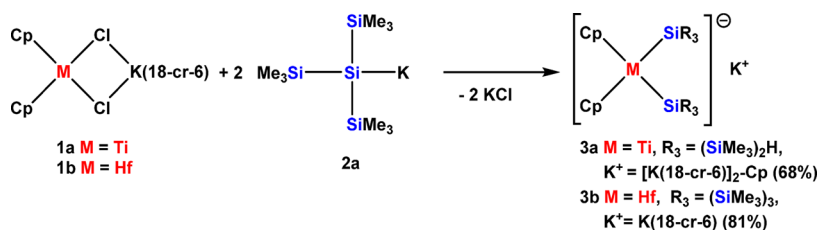
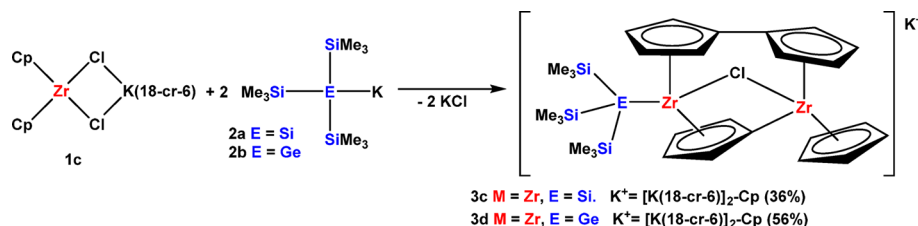
gives Cp₂TiCl or its respective KCl adduct K[Cp₂TiCl₂] which in a final step can react with (Me₃Si)₃SiK to K[Cp₂Ti(Cl)Si(SiMe₃)₃].²⁵ In order to study the chemistry of silylated Cp₂Ti(III) complexes, we reacted α,ω -oligosilylidydes with (18-crown-6)·K[Cp₂TiCl₂] or (tmeda)·Li[Cp₂TiCl₂] to titanacyclosilanes with titanium in the oxidation state +3.²⁵ Further investigations revealed that analogous metallacyclosilanes could be obtained also with Zr(III) and Hf(III).²⁵ In the current paper we wish to report on reactions of (Me₃Si)₃SiK with (18-crown-6)·K[Cp₂MCl₂] (M = Ti, Zr, Hf) to obtain d¹-complexes of the type K[Cp₂M{Si(SiMe₃)₃}₂].

Examples of compounds with lanthanide–silicon (Ln–Si) bonds are still scarce. Among all 4f-elements, samarium and the late lanthanide metals ytterbium and lutetium are best investigated for this class of compounds. In their landmark contributions, Schumann and co-workers were the first to employ a common method for the preparation of early transition-metal complexes, treating rare-earth halide complexes with the lithium silanide Me₃SiLi. Reactions with complexes of the type Cp₂Ln(μ -Cl)₂Na provided ate-complexes of the type [Li(DME)₃][Cp₂Ln(SiMe₃)₂] for Ln = Sm, Lu, Dy, Ho, Er, and Tm.^{26–28}

Similar chemistry with oligosilanides was mostly restricted to the hypersilyl [tris(trimethylsilyl)silyl] and related groups.^{29–35} Lawless and co-workers prepared [Cp*₂Yb(Si(SiMe₃)₃)(THF)₂],³² while Niemeyer synthesized the tricoordinate

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Scheme 1. Reaction of Cp_2TiCl_2 with $(\text{Me}_3\text{Si})_3\text{SiK}$ Gives a Variety of ProductsScheme 2. Reactions of $(\text{Me}_3\text{Si})_3\text{SiK}$ (**2a**) with $(18\text{-crown-6})\cdot\text{K}[\text{Cp}_2\text{MCl}_2]$ ($\text{M} = \text{Ti}, \text{Hf}$)Scheme 3. Reactions of $(\text{Me}_3\text{Si})_3\text{SiK}$ (**2a**) and $(\text{Me}_3\text{Si})_3\text{GeK}$ (**2b**) with $(18\text{-crown-6})\cdot\text{K}[\text{Cp}_2\text{ZrCl}_2]$ 

ate-complex: $\text{K}[\{(\text{Me}_3\text{Si})_2\text{N}\}_2\text{YbSi}(\text{SiMe}_3)_3]$.³⁰ More recently, Sgro and Piers reported the synthesis of yttrium and gadolinium silyl complexes by reacting potassium tris(trimethylsilyl)silanides with the respective triiodides.³¹ Earlier, Radu and Tilley prepared similar compounds by σ -bond metathesis reactions of $\text{Cp}^*_2\text{LnCH}(\text{SiMe}_3)_2$ with $\text{SiH}_2(\text{SiMe}_3)_2$ to obtain $\text{Cp}^*_2\text{LnSiH}(\text{SiMe}_3)_2$ ($\text{Ln} = \text{Sm}, \text{Nd}$).^{36–38} Our own attempts in this field were mostly concentrating on reactions of oligosilanides with iodides of $\text{Sm}(\text{II})$, $\text{Yb}(\text{II})$, and $\text{Eu}(\text{II})$.^{33–35} However, we also reported a study on the synthesis of metallacyclosilanes with lanthanidocenes, which were formed as ate-complexes reactions of α,ω -oligosilanyl dianions with lanthanidocenes Cp_3Ln .²⁹ In the course of these reactions, one cyclopentadienyl group was eliminated and a lanthanide ate-complex with two Cp and two silyl ligands was obtained.

2. RESULTS

Hypersilylated Group 4 Metallates. After the successful synthesis of $\text{Cp}_2\text{M}(\text{III})$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$) metallacyclo- or bicyclosilane ate-complexes²⁵ we decided to probe whether the chelating effect of α,ω -oligosilanyldiides is indeed required for clean formation of this type of complexes. We thus reacted the $\text{Cp}_2\text{M}(\text{III})\text{Cl}$ adducts $(18\text{-crown-6})\cdot\text{K}[\text{Cp}_2\text{MCl}_2]$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$) **1** with $(\text{Me}_3\text{Si})_3\text{SiK}$ (**2a**)^{39,40} (Scheme 2 and Scheme 3). Somewhat unexpectedly, the reactions of **2a** with **1** followed a different course for each group 4 metal.

Starting with titanium, we initially attempted reaction of **2a** with $(\text{tmeda})\cdot\text{Li}[\text{Cp}_2\text{TiCl}_2]$ without much success. Eventually, we found that optimum conditions require reaction of **1a** at low temperature with donor-free **2a**. Nevertheless, the reaction did not give the expected product $\text{K}[\text{Cp}_2\text{Ti}\{\text{Si}(\text{SiMe}_3)_3\}_2]$, but instead complex **3a** with two $\text{H}(\text{Me}_3\text{Si})_2\text{Si}$ groups was obtained (Scheme 2). Due to the fact that **3a** is a paramagnetic NMR-silent complex, its identity could only be determined using single crystal XRD analysis (Figure 1). The experiment was repeated several times to exclude possible hydrolysis as a cause for the Me_3Si to H exchange. It is not quite clear how the trimethylsilyl groups are lost; however, there is some precedence for similar reactivity that was observed as a side reaction in the synthesis of zirconium disilene complexes.⁴¹

Complex **3a** crystallizes in the monoclinic space group $P2_1/c$, where the counterion to the ate-complex $[\text{Cp}_2\text{Ti}\{\text{Si}(\text{SiMe}_2\text{H})_3\}_2]^-$ is the inverse sandwich $[\{\text{K}\cdot(18\text{-crown-6})\}_2\text{Cp}]^+$ in which a Cp[−] is coordinated on both sides by a potassium ion which on the outer side is coordinated by a crown ether unit. We and others have observed this counterion already before for group 4,^{24,25} cobalt,⁴² iron,⁴³ and f-block^{29,44–46} ate-complexes and Zintl anions.^{47,48}

Most of the known Si–Ti bond distances containing titanocenes involve Ti(III). However, Si–Ti bond lengths seem to be much more sensitive to the substitution pattern on silicon and sterics than to the oxidation state of titanium. This can be derived nicely from the series $\text{Cp}_2\text{Ti}(\text{PMe}_3)\text{SiH}_3$ (2.594(2) Å),⁴⁹ $\text{Cp}_2\text{Ti}(\text{PMe}_3)\text{SiH}_2\text{Ph}$ (2.635(7) Å), $\text{Cp}_2\text{Ti}(\text{PMe}_3)\text{SiHPh}_2$ (2.652(2) Å)⁵⁰ and $\text{Cp}_2\text{Ti}(\text{PMe}_3)\text{SiCl}_3$

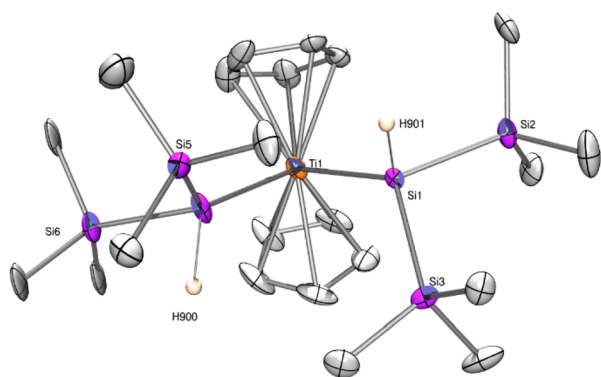


Figure 1. Molecular structure of the anionic part of **3a** (thermal ellipsoid plot drawn at the 30% probability level, counterion: $[\{K\cdot(18\text{-crown-6})\}_2\text{Cp}]^+$ not shown). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in deg). Si(1)–Si(3) 2.349(3), Si(1)–Ti(1) 2.664(2), Si(4)–Ti(1) 2.674(3), Si(2)–C(12) 1.870(8), Si(1)–H(901) 1.4791(2), Si(4)–H(900) 1.4288(3), Si(1)–Ti(1)–Si(4) 85.60(7).

(2.491(1) Å), $\text{Cp}_2\text{Ti}(\text{PMe}_3)\text{SiCl}_2\text{Me}$ (2.5167(8) Å), $\text{Cp}_2\text{Ti}(\text{PMe}_3)\text{SiClMePh}$ (2.545(2) Å).⁵¹ The distances of 2.664(2) and 2.674(3) Å, found for **3a**, are close to that found for $\text{Cp}_2\text{Ti}(\text{Cl})\text{SiMe}_3$ (2.671) Å.⁶

The number of oligosilylated titanocenes is limited to a formal disilene titanocene complex (Ti–Si: 2.596 and 2.601 Å)⁴¹ and the mentioned titanacyclo- and bicyclosilanes with Ti(III) (Ti–Si: 2.705–2.835 Å).^{24,25} A number of tris(trimethylsilyl)silylated Ti(IV) complexes is known with Ti–Si distances of 2.593–2.629 Å $\{(\text{Me}_3\text{Si})_3\text{SiTi}(\text{Np})_3\}$ (Np = neopentyl),⁵² 2.634 Å $\{(\text{Me}_3\text{Si})_3\text{SiTi}(\text{NMe}_2)_3\}$,⁵³ and 2.671 Å $\{(\text{Me}_3\text{Si})_3\text{SiTi}(\text{NET}_2)_3\}$.⁵⁴

For the case of the analogous reaction of (18-crown-6)· $\text{K}[\text{Cp}_2\text{HfCl}_2]$ (**1c**) with donor-free $(\text{Me}_3\text{Si})_3\text{SiK}$ (**2a**) no unpredicted side reaction was observed and the expected product $\text{K}[\text{Cp}_2\text{Hf}\{\text{Si}(\text{SiMe}_3)_2\}_2]$ **3b** with two $(\text{Me}_3\text{Si})_3\text{Si}$ groups was obtained (Scheme 2). Again, the structure of **3b** was unambiguously determined using single crystal XRD analysis (Figure 2). For **3b**, which crystallizes in the monoclinic space group $\text{P}2_1$, $\text{K}\cdot(18\text{-crown-6})$ acts as the cationic counterion. This structure provides the opportunity of direct comparison of the anionic d^1 -complex **3b** with its neutral d^0 -counterpart $\text{Cp}_2\text{Hf}\{\text{Si}(\text{SiMe}_3)_2\}_2$.⁵⁵ Surprisingly, we found that the Hf–Si bond lengths of **3b** (2.821(6) and 2.829(6) Å) are shorter than those of the neutral compound, for which a distance of 2.850(4) Å was observed. This is really unexpected as the general trend within the cyclic disilylmetallates is that bonds to the d^1 -metal atoms are longer than those to the d^0 -metal atoms in neutral complexes.²⁵ For the cyclic cases of hafnacyclopentasilanes the neutral compounds featured Si–Hf bond lengths of 2.791(14) and 2.823(15) Å⁵⁶ compared to 2.849(2) Å for the analogous Hf(III) compound.²⁵ The Si–Hf–Si angle of **3b** is 127.56(16)° which is larger than 117.79(14)° as was observed for the bis[tris(trimethylsilyl)silyl]hafnocene.⁵⁵ Again this is against the trend that we observed for the cyclic compounds where the neutral compound exhibits a Si–Hf–Si angle of 96.41(5)°⁵⁶ whereas the respective hafnate displayed 89.10(6)°.²⁵ It is likely that the two unusual observations are connected. A closer inspection of Hf–Cp distances seems to provide an explanation. For the cyclic Hf(III)²⁵ and Hf(IV)⁵⁶ cases the $\text{Cp}_{\text{centroid}}\text{-Hf}$ distances are 2.187/2.189 Å²⁵ and 2.181 Å,⁵⁶

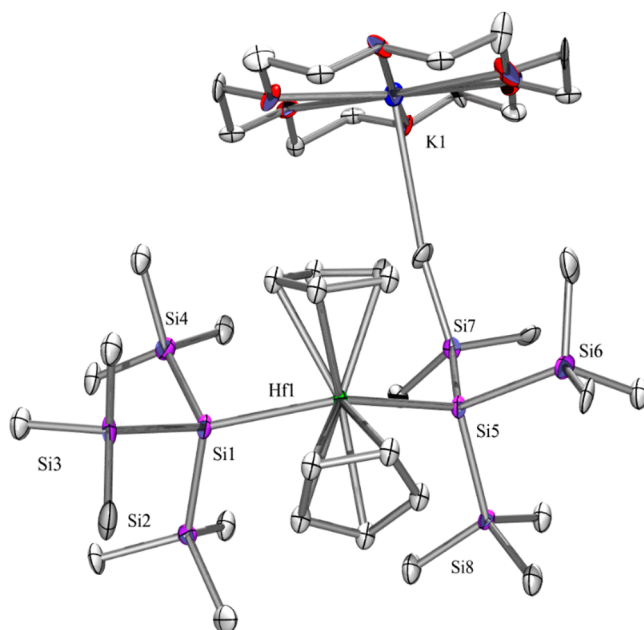


Figure 2. Molecular structure of **3b** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in deg). Hf(1)–Si(5) 2.821(6), Hf(1)–Si(1) 2.829(6), K(1)–C(26) 3.207(12), Si(1)–Si(2) 2.346(8), Si(2)–C(12) 1.88(2), Si(5)–Hf(1)–Si(1) 127.56(16).

respectively. As expected, the values for Hf(III) are slightly longer but in essence the numbers are similar. For $\text{Cp}_2\text{Hf}\{\text{Si}(\text{SiMe}_3)_2\}_2$ the $\text{Cp}_{\text{centroid}}\text{-Hf}$ distance is 2.177 Å,⁵⁵ while for **3b** this distance is elongated to 2.204/2.212 Å. We assume that the large Si–Hf–Si angle of **3b** causes some population of antibonding Cp–Hf orbitals. This increases the Cp–Hf distance and thus allows the $\text{Si}(\text{SiMe}_3)_3$ substituents to approach closer.

The potassium ion of the cationic counterion part of **3b** displays a weak interaction to one of the methyl groups (Figure 2). This is quite common, and we⁵⁷ and also others^{58,59} have observed similar potassium C–H interaction in the solid state on occasion.

The attempt to prepare the zirconium analog of **3b** by reaction of 18-crown-6· $\text{K}[\text{Cp}_2\text{ZrCl}_2]$ (**1c**) with $(\text{Me}_3\text{Si})_3\text{SiK}$ took an entirely different course. Despite the fact that we previously observed that reaction of α,ω -oligosilyl dianions with **1c** gave the expected metallacyclosilane with Zr(III), compound **3c** as isolated from the reaction of **1c** with two equivalents of $(\text{Me}_3\text{Si})_3\text{SiK}$ is a dinuclear complex with a fulvalene ligand bridging the two Zr atoms, each of which is carrying an additional Cp ligand. The two Zr atoms are further bridged by a chloride ligand and one Zr atom bears a tris(trimethylsilyl)silyl ligand, whereas the other Zr has a bond to the Cp ligand of its neighbor (Scheme 3, Figure 3).

While we do not know exactly how this complex is formed, it seems reasonable to assume that the expected intermediate $\text{K}[\text{Cp}_2\text{Zr}(\text{Cl})\text{Si}(\text{SiMe}_3)_3]$ is involved in its formation. It is likely that this compound is not as easily silylated as the intermediate in the reactions with the α,ω -oligosilyl dianions since the two silanide units are not connected and thus for the current case an entropic disadvantage can be expected. If access to the Zr atom of $\text{K}[\text{Cp}_2\text{Zr}(\text{Cl})\text{Si}(\text{SiMe}_3)_3]$ is sterically hindered, $(\text{Me}_3\text{Si})_3\text{SiK}$ might act as a base, deprotonating a Cp ligand, and this way the reaction takes a different course than

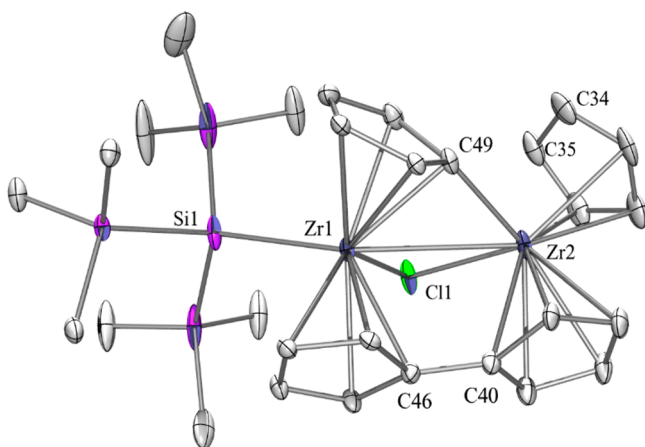


Figure 3. Molecular structure of **3c** (thermal ellipsoid plot drawn at the 30% probability level, counterion: $[\{K(18\text{-crown-6})\}_2\text{Cp}]^+$ not shown). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in deg). Zr(1)–Zr(2) 3.295(11), Zr(1)–Si(1) 2.8597(18), Zr(2)–Cl(1) 2.5733(17), Zr(2)–C(49) 2.270(6), Zr(2)–C(37) 2.523(7), Zr(2)–C(36) 2.531(7), Zr(2)–C(38) 2.537(7), Zr(2)–C(35) 2.568(8), Zr(2)–C(34) 2.581(8), Si(1)–Si(2) 2.348(2), Si(2)–C(57) 1.871(6), C(40)–C(46) 1.454(8), Cl(1)–Zr(1)–Si(1) 86.25(6), Zr(2)–Cl(1)–Zr(1) 78.62(6).

expected. This assumption is supported by the NMR spectroscopic detection of a substantial amount of $(\text{Me}_3\text{Si})_3\text{SiH}$ formed during the reaction.

Repeating the reaction of **1c** with $(\text{Me}_3\text{Si})_3\text{GeK}$ led to **3d** (Figure 4), which is analogous to **3c** but contains a $\text{Ge}(\text{SiMe}_3)_3$ instead of a $\text{Si}(\text{SiMe}_3)_3$ group (Scheme 3).

Without much mechanistic speculation about the formation of **3c** and **3d**, it should be mentioned that the formation of fulvalene bridged Zr(III) complexes is not without prece-

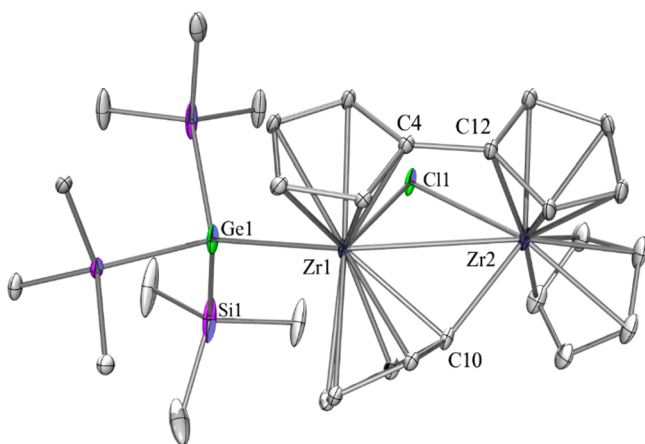


Figure 4. Molecular structure of **3d** (thermal ellipsoid plot drawn at the 30% probability level, counterion: $[\{K(18\text{-crown-6})\}_2\text{Cp}]^+$ not shown). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in deg). Zr(1)–Zr(2) 3.299(11), Zr(1)–C(10) 2.327(6), Zr(1)–C(4) 2.410(6), Zr(1)–Cl(1) 2.6514(19), Zr(1)–Ge(1) 2.8737(11), Zr(2)–C(10) 2.268(7), Zr(2)–Cl(1) 2.5961(17), Ge(1)–Si(1) 2.373(3), Ge(1)–Si(2) 2.3845(19), Ge(1)–Si(3) 2.397(3), Si(2)–C(24) 1.870(7), C(4)–C(12) 1.460(8), C(10)–Zr(1)–C(4) 96.9(2), Cl(1)–Zr(1)–Ge(1) 86.23(5), C(10)–Zr(1)–Cl(1) 84.07(18), C(10)–Zr(2)–C(12) 90.5(2), C(12)–Zr(2)–Cl(1) 86.73(15), Zr(2)–Cl(1)–Zr(1) 77.90(6), Si(1)–Ge(1)–Zr(1) 117.65(7), Zr(2)–C(10)–Zr(1) 91.8(2).

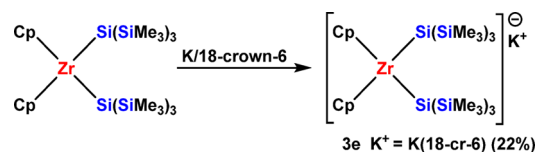
dence.^{60–62} Both reduction of Cp_2ZrCl_2 with sodium amalgam^{60,61} and the comproportionation of $\text{Cp}_2\text{Zr}(\text{PMe}_3)_2$ with Cp_2ZrCl_2 ⁶² provide access to $\text{Fv}[\text{Cp}_2\text{Zr}(\mu\text{-Cl}_2)]$ ($\text{Fv} = \eta^5\eta^5\text{-fulvalene}$).

A look at the solid state structure of compound **3c** reveals that Zr1 and Zr2 are bridged by a chloride. Depending on the assignment of a covalent interaction of the Cl atom with one Zr atom and a dative interaction with the other Zr atom, we can categorize the Zr atom with the covalent interaction as Zr(IV) and the other one as Zr(III). The Cl–Zr distances of 2.573(1) Å (Zr2–Cl) and 2.627(2) Å (Zr1–Cl) suggest that Zr1 should be assigned Zr(III). Nevertheless, the Si–Zr distance of 2.858(2) Å is not really significant as we observed very similar distances for Si–Zr(IV) bond lengths of 2.853(2) Å in $\text{Cp}_2\text{Zr}(\text{Cl})\text{Si}(\text{SiMe}_3)_2(\text{SiMe}_2\text{Thex})$ ⁵⁵ and 2.878(1) Å and 2.876(1) Å for $\text{Cp}_2\text{Zr}\{\text{Si}(\text{SiMe}_3)_3\}_2$.⁵⁵ The only comparable Si–Zr(III) bond lengths of 2.850(1) Å and 2.895(1) Å for the 2,2,5,5-tetrakis(trimethylsilyl)tetramethylzirconacyclopentasilane²⁵ are also quite close to those values.

It is somewhat difficult to assess the Ge–Zr bond length of 2.874(1) Å found in the molecular structure of **3d**. The number of structurally characterized Zr–Ge distances is rather small^{41,63,64} and consists of rather special examples of a digermene (2.870(1) and 2.913(1) Å),⁴¹ a germylene (2.632(1) Å),⁶³ and a germole (2.907(3) Å)⁶⁴ coordinating to Zr(IV). Nevertheless, the value for the Ge–Zr distance of **3d** is only slightly larger than that of Si–Zr for **3c**. Zr–Zr distances in **3c** and **3d** are almost identical (3.295(11) Å and 3.299(11) Å, respectively) and are thus only slightly elongated compared to $\text{Fv}[\text{Cp}_2\text{Zr}(\mu\text{-Cl}_2)]$ (3.233(2) Å).⁶² The Zr–Cl distances in the latter complex are between 2.571(2) and 2.591(2) Å, which are close to what we observe for the Zr2–Cl bond lengths of **3c** and **3d**.

Our previous study had shown that apart from reactions of silanides with group 4 metallocenes, it is also possible to access silylated group 4 Zr(III) complexes by reduction of the respective Zr(IV) silyl complex. We therefore subjected $\text{Cp}_2\text{Zr}\{\text{Si}(\text{SiMe}_3)_3\}_2$ to reaction with elemental potassium in the presence of crown ether and indeed obtained dark red crystals of $(18\text{-crown-6})\cdot\text{K}[\text{Cp}_2\text{Zr}\{\text{Si}(\text{SiMe}_3)_3\}_2]$ (**3e**) (Scheme 4, Figure 5).

Scheme 4. Reduction of Bis{tris(trimethylsilyl)silyl}zirconocene with Potassium/18-crown-6



Hypersilylated Lanthanidocenes. In this paper we also want to report on related chemistry of lanthanides. Reactions of a number of lanthanidocenes Cp_3Ln ($\text{Ln} = \text{Ce}, \text{Sm}, \text{Gd}, \text{Ho}, \text{Tm}$) occur with $(\text{Me}_3\text{Si})_3\text{SiK}\cdot 18\text{-crown-6}$ (**2a**) (Scheme 5). The reactions proceeded in all cases in a way that hypersilylated lanthanidocenes were formed. However, the nature of the positively charged counterion was different for the particular examples (Scheme 5).

All of the investigated lanthanides contain unpaired f-electrons and thus are paramagnetic. As straightforward NMR spectroscopic evaluation thus was not possible, we based our

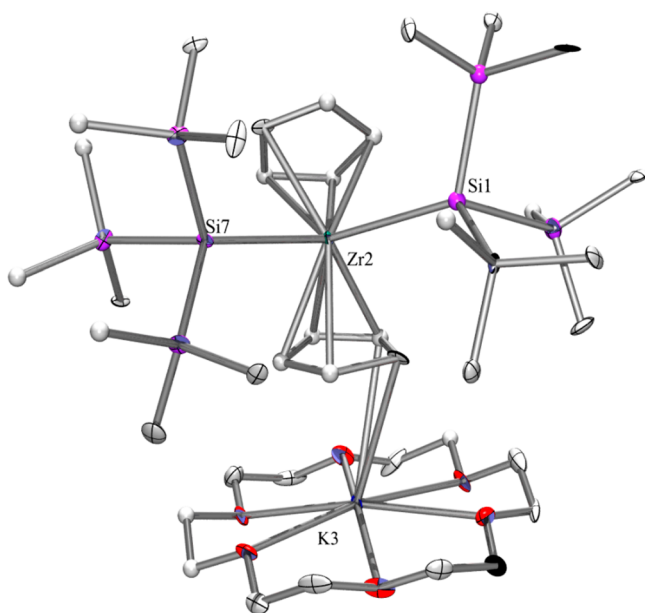


Figure 5. Molecular structure of **3e** (thermal ellipsoid plot drawn at the 30% probability level. All hydrogen atoms are omitted for clarity. Due to a bad data set only atom-connectivity was deduced from the structure.

analysis on single crystal XRD diffraction of the obtained metallates (see Table 1 for a compilation of acyclic and cyclic cases of Si–Ln metallates including oligosilyl ligands).

Reaction of **2a** with Cp_3Ce gave the complex $[\text{18-crown-6}\cdot\text{K}\cdot\text{Cp}\cdot\text{K}\cdot\text{18-crown-6}][\text{Cp}_3\text{CeSi}(\text{SiMe}_3)_3]$ (**4**) (Scheme 5, Figure 6). This is somewhat surprising because the presence of the extra CpK in the complex cationic counterion clearly indicates a more complex reaction than indicated in Scheme 5. The fact that two K-18-crown-6 ether units are present in the product suggests that two equivalents of **2a** is required for product formation and that one Cp_3Ce molecule is losing at least one of its Cp units. While we have observed frequently that silanides can replace cyclopentadienides from early metal complexes,^{24,25} the current case is special as the formed product contains four Cp units from a starting material containing only three of those. However, this behavior is not totally unprecedented as similar examples for terbium and erbium have been reported by the Evans (Tb)⁴⁴ and Zheng (Er)⁴⁵ groups.

The structure of the anionic metallate part of **4** (Figure 6) is not unexpected, since also the reaction of Cp_3Ce with an 1,4-oligosilylyldiide did not give the anticipated ceracyclopentasilane but led to the formation of two silanylene bridged silyl cerate units.²⁹ However, two K-18-crown-6 units were the cationic counterions in this case. The Si–Ce distance of 3.155(2) Å is somewhat shorter than the one found for this bridged compound (3.228(2)Å), reflecting the fact that the

bridging ligand is sterically somewhat more demanding than the $\text{Si}(\text{SiMe}_3)_3$ group.²⁹ No other examples of silylated cerium compounds are known.

Reaction of **2a** with Cp_3Sm proceeded similarly to what was observed for Cp_3Ce and gave $[\text{18-crown-6}\cdot\text{K}\cdot\text{Cp}\cdot\text{K}\cdot\text{18-crown-6}][\text{Cp}_3\text{SmSi}(\text{SiMe}_3)_3]$ (**5**) (Scheme 5, Figure 7). The same complex cationic counterion as for **4** was observed. The Si–Sm distance of **5** is 3.103(2) Å, which is substantially longer than the 2.880 Å reported by Schumann and co-workers for $[\text{Li}(\text{dme})_3][\text{Cp}_2\text{Sm}(\text{SiMe}_3)_2]$.²⁶ The latter compound was, however, later reassigned as $[\text{Li}(\text{dme})_3][\text{Cp}_2\text{Lu}(\text{SiMe}_3)_2]$ ²⁷ but its structure still remains in the Cambridge Crystallographic Database. Our own examples of silylated samarium complexes include the tris(trimethylsilyl)silylated Sm(II) complex $[\{(\text{Me}_3\text{Si})_3\text{Si}\}_2\text{Sm}(\text{THF})_3]$ with Si–Sm distances of 3.172 Å.³³

In our previous account on the reactions of Cp_3Ln with 1,4-dipotassium-tetramethyl-1,1,4,4-tetrakis(trimethylsilyl)-tetrasilane **2c** we have not included Cp_3Sm as starting material.²⁹ In order to have a suitable comparison compound we caught up on the synthesis of samaracyclopentasilane **9** (Scheme 6, Figure 8), which was obtained by reaction of Cp_3Sm with oligosilyl dianion **2c**.

Compound **9** crystallizes in the monoclinic space group $P2(1)/n$ and is isostructural to the previously described Tm, Ho, and Gd complexes.²⁹ The Si–Sm distances of 3.063(3) and 3.049(3) Å found for **9** are significantly shorter than the 3.103(2) Å found for **5**.

Reaction of **2a** with Cp_3Gd gave $[\text{18-crown-6}\cdot\text{K}\cdot\text{Cp}\cdot\text{K}\cdot\text{18-crown-6}][\text{Cp}_3\text{GdSi}(\text{SiMe}_3)_3]$ (**6**) (Scheme 5, Figure 9), and the same complex cationic counterion $[\text{18-crown-6}\cdot\text{K}\cdot\text{Cp}\cdot\text{K}\cdot\text{18-crown-6}]$ as for **4** and **5** was observed. The Si–Gd distance of **6** is 3.067(3) Å, which again is longer than the 3.037(1) and 3.018(1) Å found in our gadolinacyclopentasilane ate-complex.²⁹ The only other structurally characterized silyl gadolinium complex we are aware of is $(\text{Me}_3\text{Si})_2\text{EtSi}\cdot\text{GdI}_2(\text{THF})_3$, reported by Sgro and Piers,³¹ which compared to **6** features a significantly shortened Si–Gd distance of 2.989(2) Å.

Since complexes **4**, **5**, and **6** are all of the type $[\text{18-crown-6}\cdot\text{K}\cdot\text{Cp}\cdot\text{K}\cdot\text{18-crown-6}][\text{Cp}_3\text{LnSi}(\text{SiMe}_3)_3]$ it is probably not unexpected that their cell constants are similar to cell axes of $a = 9.3$, $b = 17.2$, and $c = 20$ Å, all crystallizing in monoclinic space groups Pn and Pc.

Reaction of **2a** with Cp_3Ho gave $[\text{18-crown-6}\cdot\text{K}][\text{Cp}_3\text{HoSi}(\text{SiMe}_3)_3]$ (**7**) (Scheme 5, Figure 10). In this case the cationic counterion consists simply of $[\text{18-crown-6}\cdot\text{K}]^+$ and two crystallographically independent $[\text{18-crown-6}\cdot\text{K}]^+$ and $[\text{Cp}_3\text{HoSi}(\text{SiMe}_3)_3]^-$ units are present in the asymmetric unit. Compared to complexes **4**, **5**, and **6** the structural parameters of **7**, which crystallizes in the monoclinic space group $P2(1)/c$ are therefore quite different (Tables S2 and S3).

Scheme 5. Formation of Lanthanide Metallocene Silyl Ate-Complexes by Reaction of Cp_3Ln with $(\text{Me}_3\text{Si})_3\text{SiK}\cdot\text{18-crown-6}$ (**2a**)

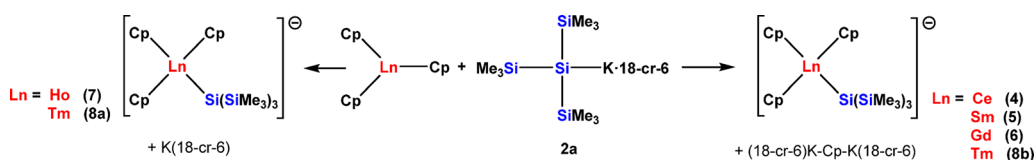


Table 1. Comparison of Acyclic and Cyclic Oligosilylanyl Lanthanides and Lanthanidocenes

entry	metal	$d_{\text{M-Si}}$ acyclic (Å)	$d_{\text{M-Cp}}^b$ average values $\text{Cp}_3\text{LnSi}(\text{SiMe}_3)_3$ (Å)	$d_{\text{M-Cp}}^b$ average values Cp_3Ln (Å)	$\Delta d_{\text{M-Cp}}$	$d_{\text{M-Si}}$ cyclic (Å)
1	Ce (4)	3.155(2) 3.228(2) ^a	2.587	2.545	0.042	n.a.
2	Sm (5,9)	3.103(2)	2.515	2.487	0.028	3.063(3), 3.049(3)
3	Gd (6)	3.066(3)	2.495	2.485	0.010	3.037(1), 3.018(1) ^a
4	Ho (7)	3.022(6), 3.024(5)	2.455 2.464	2.425	0.030/ 0.039	2.999(2), 2.999(2) ^a
5	Tm (8a)	3.018(3)	2.429	2.392	0.037	2.980(1), 2.966(2) ^a
6	Tm (8b)	3.014(2)	2.431 2.437	2.392	0.039/ 0.045	

^aData taken from ref 29. ^b $d_{\text{M-Cp}}$ lists an average value between three Cp-centroids and Ln ions. ^cValues for $\text{Cp}_3\text{Gd}\cdot\text{THF}^{65}$ were used as no structural info on the base-free compound is available.

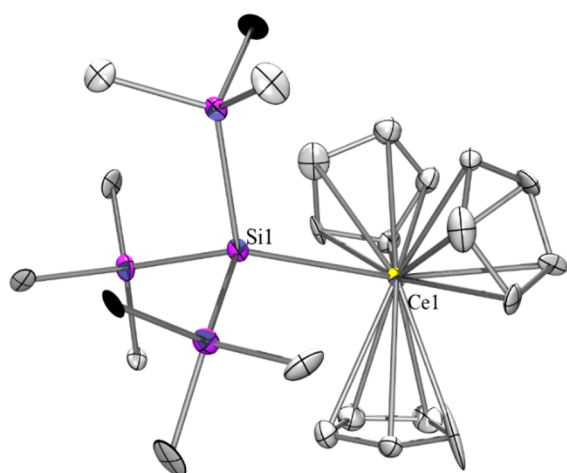


Figure 6. Molecular structure of 4 (thermal ellipsoid plot drawn at the 30% probability level). Only the anionic part is shown, and all hydrogen atoms are omitted for clarity (bond lengths in Å, angles in deg). Si(1)–Ce(1) 3.1551(19), Ce(1)–C(7) 2.807(16), Ce(1)–C(13) 2.825(16), Si(1)–Si(4) 2.353(7), Si(2)–C(21) 1.863(17), Si(4)–Si(1)–Si(2) 100.7(2), Si(4)–Si(1)–Si(3) 101.2(2), Si(2)–Si(1)–Si(3) 101.6(2), Si(4)–Si(1)–Ce(1) 117.5(2), Si(2)–Si(1)–Ce(1) 115.9(2), Si(3)–Si(1)–Ce(1) 117.2(2).

As for the previous cases, the Si–Ho distance of 3.022(5) Å is longer than observed in the cyclic case (2.999(2) Å).²⁹ Unfortunately, no other examples of structurally characterized complexes with Si–Ho interaction are known so far.

In the case of synthesis of the thulium complex 8 (Scheme 5) two different kinds of crystals were formed which could be separated under the microscope and led to structures 8a (Figure 11) and 8b (Figure 12). The difference between 8a and 8b is located in the cationic part: 8a crystallizes in infinite chains with one K-18-crown-6 unit bridging two Cp-ligands; thus, two of the three cyclopentadienyls of each Tm are coordinating to a potassium ion. For the structure of 8b also infinite chains in the crystal are observed, but while 8a only contains K-18-crown-6 units as counterions, in 8b one K-18-crown-6 unit and one of the inverse sandwich units [18-crown-6-K-Cp-K-18-crown-6] are present. One potassium ion of the [18-crown-6-K-Cp-K-18-crown-6] unit interacts weakly with a trimethylsilyl group (see bottom left side of Figure 12).

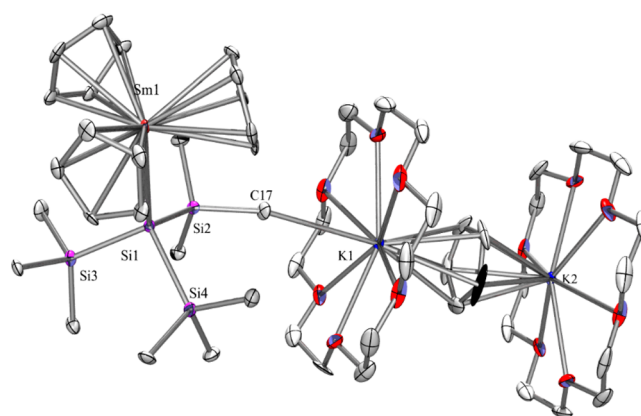
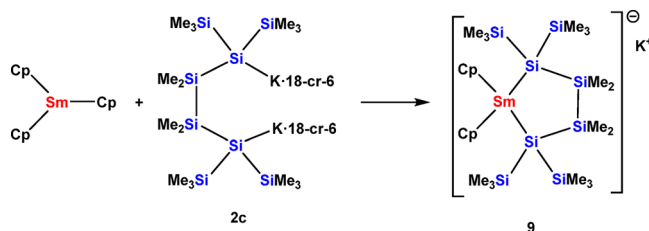


Figure 7. Molecular structure of 5 (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in deg). Sm(1)–Si(1) 3.103(2), Sm(1)–C(10) 2.776(7), Sm(1)–C(1) 2.793(6), Si(1)–Si(3) 2.355(2), Si(1)–Si(4) 2.356(2), Si(1)–Si(2) 2.359(2), Si(2)–C(18) 1.892(7), Si(3)–Si(1)–Sm(1) 117.36(7), Si(4)–Si(1)–Sm(1) 117.60(7), Si(2)–Si(1)–Sm(1) 116.04(7).

Scheme 6. Formation of Samaracyclopentasilane Ate-Complex 9 by Reaction of Cp_3Sm with $[(18\text{-crown-6-K}(\text{Me}_3\text{Si})_2\text{SiSiMe}_2)]_2$ (2c)



Consistently, the Si–Tm distances of 3.018(3) Å in 8a and 3.014(2) Å in 8b are longer than the 2.980(1) and 2.966(2) Å observed for the thullacyclopentasilane ate-complex.²⁹

In the course of the single crystal XRD analysis of complexes 4, 5, 6, 7, 8a, 8b, and 9, we were interested in the presence of the additional $\text{Si}(\text{SiMe}_3)_3$ group coordinating to the Cp_3Ln unit causing a large distortion of the Cp–Ln distances. Table 1 lists the distances between Cp centroids and the respective Ln ions for the neutral lanthanidocenes^{65–68} and the new complexes. Despite the fact that for all silyl metallates the Cp–Ln distances are longer compared to the neutral

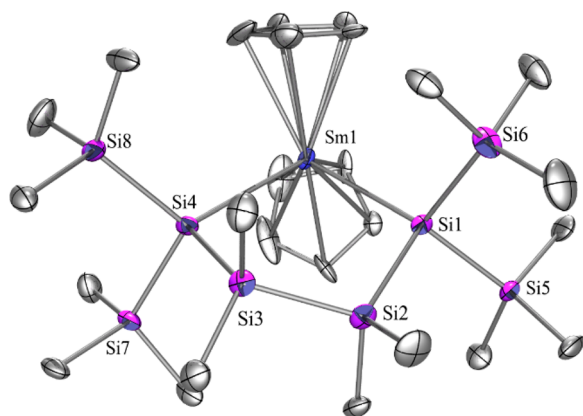


Figure 8. Molecular structure of the anionic part of **9** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in deg). Sm(1)–C(1) 2.678(14), Sm(1)–Si(1) 3.049(3), Sm(1)–Si(4) 3.063(3), Si(1)–Si(5) 2.340(5), Si(1)–Si(6) 2.348(5), Si(2)–C(11) 1.898(14), Si(1)–Sm(1)–Si(4) 94.81(9), Si(5)–Si(1)–Si(6) 101.89(19), Si(5)–Si(1)–Si(2) 103.04(18).

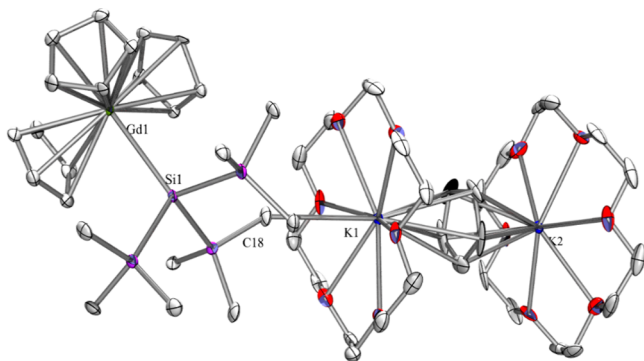


Figure 9. Molecular structure of **6** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in deg). Si(1)–Gd(1) 3.0665(27), Gd(1)–C(12) 2.729(10), Gd(1)–C(4) 2.759(11), Si(1)–Si(2) 2.360(3), Si(2)–C(19) 1.863(12), Si(4)–Si(1)–Si(2) 100.60(12), Si(4)–Si(1)–Si(3) 100.83(14), Si(2)–Si(1)–Si(3) 101.32(12), Si(4)–Si(1)–Gd(1) 117.80(11), Si(2)–Si(1)–Gd(1) 116.07(12), Si(3)–Si(1)–Gd(1) 117.33(11).

lanthanidocenes, the observed values of 0.03 to 0.05 Å elongation are rather small.

Attempted Spectroscopic Characterization. Our earlier studies on silylated d¹-group 4 metallocenes^{24,25} have shown that these compounds are NMR-silent. The same was found true for the complexes of the current study. EPR spectroscopy of cyclic compounds²⁵ indicated some delocalization of the electron between the metal and the attached silicon atoms.

Our attempts to do EPR spectroscopy of the hypersilylated lanthanidocenes were futile. As lanthanides are in the regime of strong spin–orbit interaction, due to very short relaxation times EPR spectra frequently can be observed only at temperatures below 20 K.⁶⁹

On the other hand, NMR spectroscopy of paramagnetic compounds is well established. However, not all paramagnetic compounds are simple to measure.⁷⁰ As we have reported NMR data for the related metallacyclopentasilane complexes,²⁹ it seemed reasonable to expect the same for the current

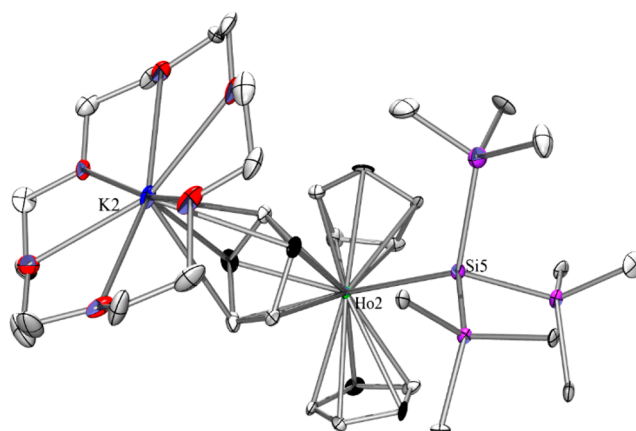


Figure 10. Molecular structure of **7** (thermal ellipsoid plot drawn at the 30% probability level, of the two crystallographically independent [18-crown-6·K][Cp₃HoSi(SiMe₃)₃] units present in the asymmetric unit only one is shown). All hydrogen atoms except Si–H are omitted for clarity (bond lengths in Å). Si(1)–Ho(1) 3.0215(53), Si(5)–Si(6) 2.360(6), Ho(1)–C(8) 2.722(19), Si(3)–Si(1)–Ho(1) 118.1(2), Si(4)–Si(1)–Ho(1) 116.8(2), Si(2)–Si(1)–Ho(1) 115.8(2).

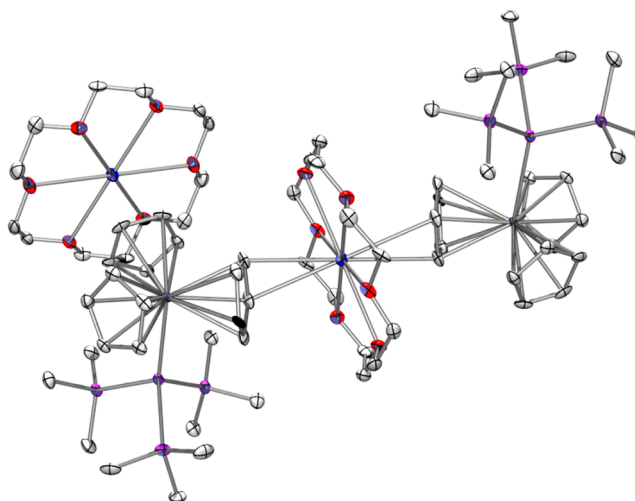


Figure 11. Molecular structure of **8a** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in deg). Si(1)–Tm(1) 3.0178(25), Tm(1)–C(1) 2.693(9), Si(1)–Si(2) 2.357(4), Si(2)–C(18) 1.890(10), Si(2)–Si(1)–Si(3) 101.15(14), Si(2)–Si(1)–Tm(1) 118.13(11), Si(3)–Si(1)–Tm(1) 117.30(11), Si(4)–Si(1)–Tm(1) 117.91(12).

complexes. We have therefore extensively tried to obtain NMR spectra for the metallates of the type [Cp₃CeSi(SiMe₃)₃][−]. For {K₂(18-c-6)₂-Cp}[Cp₃CeSi(SiMe₃)₃] (**4**) no meaningful NMR spectra could be obtained at all. For the other compounds, especially complexes **7** (Ho) and **8** (Tm), the situation was different. We were able to get fairly meaningful ¹H NMR spectra, and using 2D-NMR techniques (HSQC and HMBC) we tried to get ¹³C and ²⁹Si data. However, we also found that chemical shifts of the compounds are extremely concentration dependent with strongly shifted signals. We assume that this effect was much less pronounced with the bidentate ligand used before because the latter is connected to the metal fragments electrostatically. While we realize that concentration

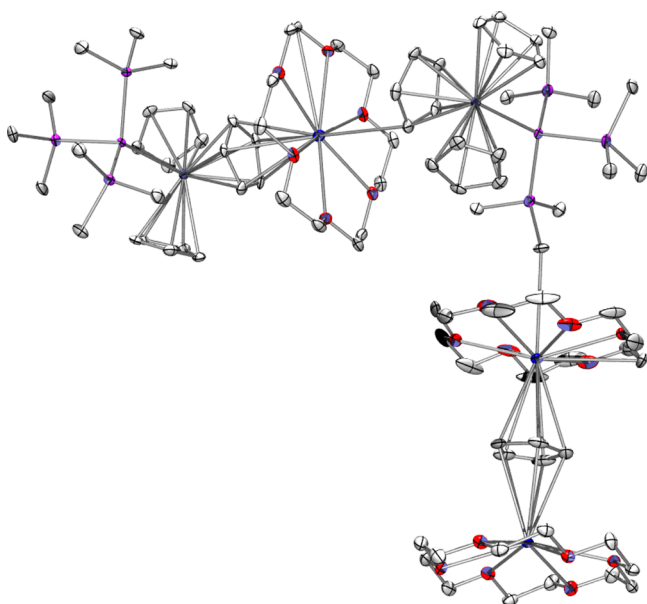


Figure 12. Molecular structure of **8b** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in deg). Si(1)–Tm(1) 3.0145(21), Tm(2)–C(27) 2.726(6), Si(1)–Si(2) 2.347(3), Si(2)–C(31) 1.849(9), Si(8)–C(47) 1.889(6), Si(2)–Si(1)–Tm(1) 118.06(10), Si(4)–Si(1)–Tm(1) 117.96(9), Si(3)–Si(1)–Tm(1) 118.11(9).

dependent magnetic behavior is interesting, we intend to study it in more detail in a future investigation.

3. CONCLUSION

Some years ago we could show that reactions of group 4 metallocene dichlorides ($M = \text{Zr}, \text{Hf}$) with oligosilylidydes give metallacyclosilanes. Later, we found that double silylation of Cp_2TiCl_2 is more difficult as the two silyl ligands tend to undergo reductive elimination to a cyclosilane and “ Cp_2Ti ”. The latter reacts with Cp_2TiCl_2 to Cp_2TiCl or more likely to an adduct thereof such as $[\text{Cp}_2\text{TiCl}_2]^-$. Further reaction with disilanide then gave titanacyclosilanes with Ti(III). Alternatively, these compounds and also analogous Zr and Hf complexes could be obtained directly by reaction of $\text{K}[\text{Cp}_2\text{MCl}_2]$ with the respective oligosilylidydes.

Somewhat unexpectedly, analogous chemistry with potassium tris(trimethylsilyl)silanide gave the expected complexes of the type $\text{K}[\text{Cp}_2\text{M}\{\text{Si}(\text{SiMe}_3)_3\}_2]$ only for the hafnium case. Reaction with $\text{K}[\text{Cp}_2\text{TiCl}_2]$ with 2 equiv of $\text{KSi}(\text{SiMe}_3)_3$ provided $\text{K}[\text{Cp}_2\text{Ti}\{\text{SiH}(\text{SiMe}_3)_2\}_2]$. The reaction with $\text{K}[\text{Cp}_2\text{ZrCl}_2]$ is most unusual as it leads to a dinuclear complex with a fulvalene ligand bridging two Zr atoms. The desired $\text{K}[\text{Cp}_2\text{Zr}\{\text{Si}(\text{SiMe}_3)_2\}_2]$ could eventually be obtained by reduction of $\text{Cp}_2\text{Zr}\{\text{Si}(\text{SiMe}_3)_3\}_2$ with potassium.

Related reactions of $\text{KSi}(\text{SiMe}_3)_3$ with some lanthanidocenes Cp_3Ln ($\text{Ln} = \text{Ce}, \text{Sm}, \text{Gd}, \text{Ho}, \text{Tm}$) gave complexes of the type $[\text{Cp}_3\text{Ln} \text{Si}(\text{SiMe}_3)_3]^-$ with either $[\text{18-crown-6-K}]^+$ or the complex ion $[\text{18-crown-6-K}\cdot\text{Cp}\cdot\text{K}\cdot\text{18-crown-6}]$ as counterion. The presence of $[\text{18-crown-6-K}\cdot\text{Cp}\cdot\text{K}\cdot\text{18-crown-6}]$ suggests a more complicated course of reaction as it implies that part of the lanthanidocenes are stripped of their Cp ligands. Depending on the metal, the ease of Cp abstraction in the formation process seems to be different as Ce, Gd, and Sm all crystallize with the complex counterion $[\text{18-crown-6-K}\cdot\text{Cp}\cdot\text{K}\cdot\text{18-crown-6}]$, whereas for Tm crystals with and without

complex counterion were observed and for Ho only $[\text{18-crown-6-K}]^+$ was detected as counterion.

Due to d^1 or f^n electron configuration, unambiguous characterization of all obtained complexes could only be achieved by single crystal XRD diffraction analysis.

4. EXPERIMENTAL PART

General Remarks. All reactions involving air-sensitive compounds were carried out under an atmosphere of dry nitrogen using either Schlenk techniques or a glovebox. All solvents were dried using a column based solvent purification system.⁷¹ Chemicals were obtained from different suppliers and used without further purification. $(\text{18-crown-6})\text{-K}[\text{Cp}_2\text{TiCl}_2]$ ($M = \text{Ti}, \text{Zr}, \text{Hf}$),²⁵ donor free tris(trimethylsilyl)silyl potassium (**2a**),^{30,40} tris(trimethylsilyl)germyl potassium (**2b**),⁷² 1,4-dipotassium-tetramethyl-1,1,4,4-tetrakis(trimethylsilyl)tetrasilane: $(\text{18-crown-6})_2$ (**2c**),⁷³ $\text{Cp}_2\text{Zr}\{\text{Si}(\text{SiMe}_3)_3\}_2$,⁵⁵ and Cp_3Ce ⁷⁴ were prepared following reported procedures. Elemental analysis was carried out using a Heraeus VARIO ELEMENTAR instrument.

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 $K\alpha$ radiation (0.71073 Å). The data were reduced to F^2 and corrected for absorption effects with SAINT⁷⁵ and SADABS,^{76,77} respectively. Structures were solved by direct methods and refined by full-matrix least-squares method (SHELXL97).⁷⁸ 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. All diagrams were drawn with 30% probability thermal ellipsoids, and all hydrogen atoms were omitted for clarity. Crystallographic data (excluding structure factors) for the structures of compounds **3a**, **3b**, **3c**, **3d**, **3e**, **4**, **5**, **6**, **7**, **8a**, **8b** and **9** reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-1891714 (**3a**), 767188 (**3b**), 767186 (**3c**), 1891716 (**3d**), 1904333 (**3e**), 1891721 (**4**), 1891720 (**5**), 1891718 (**6**), 1891719 (**7**), 1891715 (**8a**), 1891717 (**8b**), and 1891722 (**9**). 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 WINGX⁷⁹ and rendered using POV-Ray 3.6.⁸⁰

Dicyclopentadienylbis[bis(trimethylsilyl)silyl]titanate(III) (3a). To a green suspension of **1a** (453 mg, 0.82 mmol) in toluene (10 mL) was added dropwise a solution of **2a** (1.64 mmol) in pentane (10 mL) at -90°C . After 2 h the reaction mixture was allowed to come to rt and the stirring was continued for another 16 h. The mixture was filtered and the solvent reduced to 3 mL. Crystallization was achieved by overlaying of 10 mL of pentane within 24 h. Crystalline red-brown needles of **3a** (673 mg, 68%) were obtained. Mp.: $153\text{--}155^\circ\text{C}$. Anal. Calcd for $\text{C}_{51}\text{H}_{105}\text{Si}_8\text{O}_{12}\text{K}_2\text{Ti}$ (1261.13): C 48.57, H 8.39. Found: C 48.38, H 8.42.

Dicyclopentadienylbis[tris(trimethylsilyl)silyl]hafnate(III) (3b). To a solution of **1b** (368 mg, 0.54 mmol) in toluene (5 mL) was added dropwise a solution of **2a** (1.08 mmol) in pentane (5 mL) at -60°C . After 1 h the reaction mixture was allowed to come to rt and the stirring was continued for another 3 h. The solid components were removed by filtration and the solvent reduced to 3 mL. Crystallization was achieved by overlaying by 5 mL of pentane within 24 h. Crystalline orange needles of **3b** (354 mg, 81%) were obtained. Mp.: $174\text{--}176^\circ\text{C}$. Anal. Calcd for $\text{C}_{40}\text{H}_{88}\text{Si}_8\text{O}_6\text{KHF}$ (1107.41): C 43.38, H 8.01. Found: C 43.02, H 8.12.

Bis(trimethylsilyl)silyl Zirconium Fulvalene Complex (3c). To a solution of **1c** (150 mg, 0.25 mmol) in toluene (5 mL) a solution of **2a** (0.50 mmol) in pentane (5 mL) at -60°C was added dropwise. After 1 h the reaction mixture was allowed to come to rt and the stirring was continued for another 3 h. The solid components were removed by filtration and the solvent reduced to 3 mL. Crystallization was achieved by overlaying by 5 mL pentane within 24 h. Crystalline

orange-red **3b** (45 mg, 36%) was obtained. Anal. Calcd for $C_{29}H_{45}Si_4ClZr_2$ (723.92): C 48.12, H 6.27. Found: C 47.98, H 6.32.

Bis(trimethylsilyl)germyl Zirconium Fulvalene Complex (3d). To a solution of **1c** (298 mg, 0.50 mmol) in benzene (5 mL) was added dropwise a solution of **2b** (0.50 mmol) in benzene (5 mL) at rt. After 5 h the precipitate was removed by centrifugation and the solution concentrated to 5 mL. Crystallization was achieved by overlaying by 5 mL of pentane within 24 h. Crystalline orange-red **3b** (430 mg, 56%) was obtained. Anal. Calcd for $C_{29}H_{45}Si_3GeClZr_2$ (768.46): C 45.33, H 5.90. Found: C 45.13, H 5.92.

Dicyclopentadienylobis[tris(trimethylsilyl)silyl]zirconate(III) (3e). In a scintillation vial charged with potassium (6 mg, 0.15 mmol) was stirred a mixture of 18-crown-6 (40 mg, 0.15 mmol) and $Cp_2Zr[Si(SiMe_3)_3]_2$ (108 mg, 0.150 mmol) in toluene (4 mL) as a red suspension at ambient temperature for 18 h. The resulting dark red-brown reaction mixture was filtered over glass filter paper, and the dark red-brown solution was layered with pentane and stored at $-35^\circ C$ for 18 h to yield **3e** as dark red crystals (34 mg, 22%).

Ce-Silyl Compound (4). A solution of **2a** (obtained from 18-crown-6 (132 mg, 0.50 mmol), tetrakis(trimethylsilyl)silane (160 mg, 0.50 mmol), and KO^tBu (59 mg, 0.53 mmol)) in toluene (3 mL) was added dropwise to a solution of Cp_3Ce (168 mg, 0.50 mmol) in THF (4 mL). After stirring for 1 h pentane (1 mL) was added to the yellow solution, and after 24 h yellow crystals of **4** (447 mg, 71%) were obtained. Anal. Calcd for $C_{53}H_{95}Si_4O_{12}K_2Ce$ (1254.98): C 50.72, H 7.63. Found: C 50.52, H 7.57.

Sm-Silyl Compound (5). Same procedure as described for **4** using Cp_3Sm (86 mg, 0.25 mmol) and **2a** (0.25 mmol). Crystalline, orange **5** (132 mg, 41%) was isolated. Anal. Calcd for $C_{53}H_{95}Si_4O_{12}K_2Sm$ (1265.44): C 50.31, H 7.57. Found: C 50.02, H 7.63.

Gd-Silyl Compound (6). Same procedure as described for **4** using Cp_3Gd (88 mg, 0.25 mmol) and **2a** (0.25 mmol). Crystalline, pale yellow **6** (132 mg, 41%) was isolated. Anal. Calcd for $C_{53}H_{95}Si_4O_{12}K_2Gd$ (1272.12): C 50.04, H 7.53. Found: C 49.56, H 7.49.

Ho-Silyl Compound (7). Same procedure as described for **4** using Cp_3Ho (80 mg, 0.22 mmol) and **2a** (0.22 mmol). Crystalline, pale yellow **7** (167 mg, 82%) was isolated. Mp. 163–168 $^\circ C$. Anal. Calcd for $C_{36}H_{66}Si_4O_6KH_o$ (911.29): C 47.45, H 7.30. Found: C 47.39, H 7.37.

Tm-Silyl Compound (8). Same procedure as described for **4** using **2a** [obtained from tetrakis(trimethylsilyl)silane (930 mg, 0.29 mmol), KO^tBu (35 mg, 0.31 mmol), 18-crown-6 (770 mg, 0.29 mmol)] and Cp_3Tm (100 mg, 0.29 mmol). Yellow crystalline **8** (231 mg, 87%) was obtained. Under the microscope two different shaped crystals were observed: yellow plates of **8a** and yellow blocks of **8b**. Anal. Calcd for $C_{53}H_{95}Si_4O_{12}K_2Gd$ (1283.80): C 49.59, H 7.46. Found: C 49.48, H 7.49.

Sm-Silyl Compound (9). Same procedure as described for **4** using **2c** [obtained from 2,2,5,5-tetrakis(trimethylsilyl)decamethylhexasilane (100 mg, 0.16 mmol), KO^tBu (38 mg, 0.36 mmol), 18-crown-6 (86 mg, 0.33 mmol)] and Cp_3Sm (57 mg, 0.16 mmol). Crystalline orange **9** (185 mg, 81%) was isolated. Anal. Calcd for $C_{55}H_{111}Si_8O_{12}K_2Sm$ (1417.72): C 46.60, H 7.89. Found: C 46.28, H 7.95.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b00866.

Tabulated crystallographic data for compounds **3a**, **3b**, **3c**, **3d**, **3e**, **4**, **5**, **6**, **7**, **8a**, **8b**, and **9** (PDF)

Accession Codes

CCDC 1891714–1891722, 1904333, 767186, and 767188 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.ac.uk

or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: baumgartner@tugraz.at. Phone: (+43) 316 873 32107. Fax: (+43) 316 873 1032112.

*E-mail: christoph.marschner@tugraz.at. Phone: (+43) 316 873 32112. Fax: (+43) 316 873 1032112.

ORCID

Christoph Marschner: 0000-0001-8586-2889

Judith Baumgartner: 0000-0002-9938-1813

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Notes

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DEDICATION

Dedicated to Dietmar Seyferth, a fantastic chemist, a great editor and a good friend, on the occasion of his 90th birthday.

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