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,* and Judith Baumgartner*  
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 \( [\text{Cp}_2\text{MCl}_2] \) (M = Ti, Zr, Hf). The outcomes of the reactions differ for all three metals. While for the hafnium case the expected complex \( [\text{Cp}_2\text{H}([\text{Si(SiMe}_3]_3)_2]^- \) was obtained, the analogous titanium reaction led to a product with two \( \text{Si(H)[SiMe}_3]_2 \) ligands. The reaction with zirconium caused the formation of a dinuclear fulvalene bridged complex. The desired \( [\text{Cp}_2\text{Zr}[\text{Si(SiMe}_3]_3]_2^- \) could be obtained by reduction of \( \text{Cp}_2\text{Zr}[\text{Si(SiMe}_3]_3 \) with potassium. In related reactions of potassium tris(trimethylsilyl)silanide with some lanthanidocenes \( \text{Cp}_2\text{Ln} \) (Ln = Ce, Sm, Gd, Ho, Er, Tm) complexes of the type \( [\text{Cp}_2\text{Ln}[\text{SiMe}_3]_3]^- \) with either \( [18\text{-crown-6-K}]^- \) or the complex ion \( [18\text{-crown-6-K-Cp-K-18\text{-crown-6}]^-} \) as countermers were obtained. Due to the d1 or \( \pi^* \) 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 \( \sigma \)-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 \( \text{Cp}_2\text{M}^*\text{Cl}(\text{Cl})\text{Si}([\text{SiMe}_3])_3 \) (M = Zr, Hf) it was shown that \( \sigma \)-bond metathesis reaction with a hydrosilane leads to \( (\text{Me},\text{Si})_2\text{SiH} \) 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 \( \text{Cp}_2\text{Ti}(\text{Cl})\text{Si}([\text{SiMe}_3])_3 \) or even \( \text{Cp}_2\text{Ti}(\text{Cl})\text{Si}([\text{SiMe}_3])_3 \) is not easily available. NMR spectroscopic analysis of the reactions of \( \text{Cp}_2\text{TiCl}_2 \) or \( \text{Cp}_2\text{TiCl}_2 \) with \( (\text{Me},\text{Si})_2\text{SiK} \) (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 “\( \text{Cp}_2\text{Ti}(\text{II}) \)\)” which in a subsequent comproportionation with \( \text{Cp}_2\text{TiCl}_2 \) gives \( \text{Cp}_2\text{TiCl} \) or its respective KCl adduct \( \text{K}[\text{Cp}_2\text{TiCl}_2] \) which in a final step can react with \( (\text{Me}_3\text{Si})_3\text{SiK} \) to \( \text{K}[\text{Cp}_2\text{Ti}(\text{Cl})\text{Si}([\text{SiMe}_3])_3] \).\(^25\) In order to study the chemistry of silylated \( \text{Cp}_2\text{Ti}(\text{III}) \) complexes, we reacted \( \alpha,\omega\)-oligosila
tilidilides with \( \text{K}[\text{Cp}_2\text{TiCl}_2] \) or \( (\text{tm} 3a)\text{Li-} [\text{Cp}_2\text{TiCl}_2] \) to titanacyclosilanes with titanium in the oxidation state +3.\(^26\) Further investigations revealed that analogous metallacyclosilanes could be obtained also with \( \text{Zr(III)} \) and \( \text{Hf(III)} \).\(^27\) In the current paper we wish to report on reactions of \( (\text{Me}_3\text{Si})_3\text{SiK} \) with \( (18\text{-crown-6-K}) \) or \( (18\text{-crown-6-K-Cp-K-18\text{-crown-6})} \) as countermers were obtained. Due to the \( \pi^* \) electron configuration, unambiguous characterization of all obtained complexes could only be achieved by single crystal XRD diffraction analysis.
ate-complex: K\([\{(Me_3Si)_2N\}_2YbSi(SiMe_3)_3\] .

More recently, Sgro and Piers reported the synthesis of yttrium and gadolinium silyl complexes by reacting potassium tris-(trimethylsilyl)silanides with the respective triiodides. Ear-lier, Radu and Tilley prepared similar compounds by \(\sigma\)-bond metathesis reactions of \(\text{Cp}^*\text{LnCH(SiMe}_3)\text{2}\) with \(\text{SiH}_2\text{(SiMe}_3)\text{2}\) to obtain \(\text{Cp}^*\text{LnSiH(SiMe}_3)\text{2}\) (Ln = Sm, Nd). Our own attempts in this field were mostly concentrating on reactions of oligosilanides with iodides of Sm(II), Yb(II), and Eu(II). However, we also reported a study on the synthesis of metallacyclosilanes with lanthanido-cenes, which were formed as ate-complexes reactions of \(\alpha,\omega\)-oligosilanyl dianions with lanthanidocenes \(\text{Cp}_3\text{Ln}\). In the course of these reactions, one cyclopentadienyl group was eliminated and a lanthanide ate-complex with two \(\text{Cp}\) and two silyl ligands was obtained.

2. RESULTS

Hypersilylated Group 4 Metallates. After the successful synthesis of \(\text{Cp}_2\text{M(III)}\) (M = Ti, Zr, Hf) metallacyclo- or bicyclosilane ate-complexes we decided to probe whether the chelating effect of \(\alpha,\omega\)-oligosilanyl-dianides is indeed required for clean formation of this type of complexes. We thus reacted the \(\text{Cp}_2\text{M(III)}\text{Cl}\) adducts (18-crown-6)-\(\text{K}[\text{Cp}_2\text{MCl}_2]\) (M = Ti, Zr, Hf) 1 with \((\text{Me}_3\text{Si})\text{SiK}\) (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 (tmeda)-\(\text{Li}[\text{Cp}_2\text{TiCl}_2]\) 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 \(\text{K}[\text{Cp}_2\text{TiSi(SiMe}_3)\text{3}]\), but instead complex 3a with two \(\text{H(Me}_3\text{Si})\text{2}\) 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 \text{Me}_3\text{Si} to \text{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.

Complex 3a crystallizes in the monoclinic space group \(\text{P}_{2}1/\text{c}\), where the counterion to the ate-complex \([\text{Cp}_2\text{Ti(SiMe}_3\text{H)}\text{3}]\)\(^{-}\) is the inverse sandwich \([\text{K(18-crown-6)})\text{2Cp}]^{+}\) in which a \(\text{Cp}\) 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\(^{25,44-46}\) 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 steric than to the oxidation state of titanium. This can be derived nicely from the series \(\text{Cp}_2\text{Ti(PMe}_3\text{)SiH}_3\) (2.594(2) Å), \(\text{Cp}_2\text{Ti(PMe}_3\text{)SiH}_2\text{Ph} (2.635(7) Å), \text{Cp}_2\text{Ti(PMe}_3\text{)SiHPh}_2 (2.652(2) Å)\), and \(\text{Cp}_2\text{Ti(PMe}_3\text{)SiCl}_3\)
Hf(silyl)hafnocene.55 Again this is against the trend that we predicted side reaction was observed and the expected bonds to the d1-metal atoms are longer than those to the d0-counterpart Cp2Hf{Si(SiMe3)3}2.55 Surprisingly, we found that the Hf−Si bond distances are 2.187/2.189 Å25 and 2.181 Å,56 found for 3a, are close to that found for Cp3Ti(III)−Si(alkyl)(alkyl)SiH2 (2.596 and 2.601 Å)25 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 ([(Me3Si)3SiTi(Np)3] (Np = neopentyl), 2.634 Å ([(Me3Si)3SiTi(NMe2)3]),33 and 2.671 Å ([(Me3Si)3SiTi(NEt2)3])54.

For the case of the analogous reaction of 18-crown-6·K[Cp2HfCl2] (1c) with donor-free (Me3Si)3SiK (2a) no unpredicted side reaction was observed and the expected product K[Cp2Hf(Si(SMe3)3)2] 3b with two (Me3Si)3Si 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 P21/n, K-(18-crown-6) acts as the cationic counterion. This structure provides the opportunity of direct comparison of the anionic d0-complex 3b with its neutral d1-counterpart Cp3Ti[(Me3Si)3SiH2] (Scheme 2). Again this is against the trend that we observed for the cyclic complexes where the neutral compound exhibits a Si−H−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)26 cases the Cpcenter−Hf distances are 2.187/2.189 Å25 and 2.181 Å,56 respectively. As expected, the values for Hf(III) are slightly longer but in essence the numbers are similar. For Cp3Hf(Si(SMe3)3)2, the Cpcenter−Hf distance is 2.177 Å,54 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 Si(SMe3)3 substituents to approach closer.

The potassium ion of the cationic counterion of 3b displays a weak interaction to one of the methyl groups (Figure 2). This is quite common, and we57 and also others58,59 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·K[Cp2ZrCl2] (1c) with (Me3Si)3SiK took an entirely different course. Despite the fact that we previously observed that α,ω-oligosilanyldianions with 1c gave the expected metallacyclosilane with Zr(III), compound 3c as isolated from the reaction of 1c with two equivalents of (Me3Si)3SiK 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 K[Cp2Zr(Cl)Si(SMe3)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-oligosilanyldianions since the two silyl units are not connected and thus for the current case an entropic disadvantage can be expected. If access to the Zr atom of K[Cp2ZrCl]Si(SMe3)3 is sterically hindered, (Me3Si)3SiK 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-crown-6)]_2Cp]^+ 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) 2.5735(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).

Figure 4. Molecular structure of 3d (thermal ellipsoid plot drawn at the 30% probability level, counterion: [(K(18-crown-6))]_2Cp]^+ 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) 2.651(4), Zr(1)–Ge(1) 2.873(7), Zr(2)–C(10) 2.268(7), Zr(2)–C(1) 2.396(17), Ge(1)–Si(1) 2.373(3), Ge(1)–Si(2) 2.384(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).

Hypersilylated Lanthanidocenates. In this paper we also want to report on related chemistry of lanthanides. Reactions of a number of lanthanidocenes Cp_Ln (Ln = Ce, Sm, Gd, Ho, Tm) occur with (Me_3Si)_3SiK–18-crown-6 (2a) (Scheme 5). The reactions proceeded in all cases in a way that hypersilylated lanthanidocenates 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 was not possible, we based our...
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In our previous account on the reactions of Cp₃Ln with 1,4-dipotassium-tetramethyl-1,1,4,4-tetrais(trimethylsilyl)-tetrasilane 2c we have not included Cp₃Sm as starting material. 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 Cp₃Sm with oligosilyl dianion 2c.

Compound 9 crystallizes in the monoclinic space group P2(1)/n and is isostructural to the previously described Tb, Ho, and Gd complexes. 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.

Since complexes 4, 5, and 6 are all of the type [18-crown-6⋅K⋅Cp⋅K₃⋅Cp⋅K₃⋅18-crown-6]⋅[Cp₃LnSi(SiMe₃)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 Cp₃Ho gave [18-crown-6⋅K⋅Cp⋅K₃⋅Cp⋅K₃⋅18-crown-6]⋅[Cp₃HoSi(SiMe₃)₃] (7) (Scheme 6, Figure 10). In this case the cationic counterion consists simply of [18-crown-6⋅K]⁺ and two crystallographically independent [18-crown-6⋅K]⁺ and [Cp₃HoSi(SiMe₃)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 Cp₃Ln with (Me₃Si)₃SiK⋅18-crown-6 (2a)

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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). 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 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).

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

| entry | metal | \(d_{\text{M-Si}}\) acyclic (Å) | \(d_{\text{M-Cp}}\) | \(d_{\text{M-Ln}}\) | \(d_{\text{M-Si}}\) | \(d_{\text{M-Cp}}\) | \(\Delta d_{\text{M-Cp}}\) | \(d_{\text{M-Si}}\) cyclic (Å) |
|-------|-------|-----------------|--------|----------------|--------|--------|----------------|----------------|
| 1     | Ce (4) | 3.155(2)        | 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) |
| 4     | Ho (7) | 3.022(6),      | 2.445  | 2.425          | 0.030/ 2.999(2), 2.999(2) |
| 5     | Tm (8a) | 3.018(3)       | 2.392  | 2.392          | 0.037  | 2.980(1), 2.966(2) |
| 6     | Tm (8b) | 3.014(2)       | 2.392  | 2.392          | 0.039/ 2.999(2), 2.966(2) |

\(a\) Data taken from ref 29. \(b\) Lists an average value between three Cp-centroids and Ln ions. \(c\) Values for Cp,Gd,THF65 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) 3.155(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).

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) 2.77(7), Sm(1)–C(1) 2.79(6), Si(1)–Si(3) 2.355(2), Si(1)–Si(4) 2.356(2), Si(1)–Si(2) 2.359(2), Sm(2)–C(18) 1.89(2), 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 Cp3Sm with [(18-crown-6-K(Me3Si)2SiSiMe2)]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 Si(SiMe3)3 group coordinating to the Cp-Ln 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 lanthanidocenes65–68 and the new complexes. Despite the fact that for all silyl metallates the Cp-Ln distances are longer compared to the neutral
lanthanidocenes, the observed values of 0.03 to 0.05 Å elongation are rather small.

**Attempted Spectroscopic Characterization.** Our earlier studies on silylated d^1-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 compounds \(^{25}\) indicated some delocalization of the electron between the metal and the attached silicon atoms.

Our attempts to do EPR spectroscopy of the hypersilylated lanthanidocenates 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 complexes. We have therefore extensively tried to obtain NMR spectra for the metallates of the type \([\text{Cp}_3\text{Me}_3\text{Si}]+\). For \([\text{K}_2(18\text{-crown-6})\text{Cp}_3\text{HoSi}^+\text{SiMe}_3]+\) 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 \(^1\text{H}\) NMR spectra, and using 2D-NMR techniques (HSQC and HMBC) we tried to get \(^13\text{C}\) and \(^29\text{Si}\) 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

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**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).

**Figure 10.** Molecular structure of 7 (thermal ellipsoid plot drawn at the 30% probability level, of the two crystallographically independent \([\text{Cp}_3\text{HoSi}^+\text{SiMe}_3]+\) 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).
complex counterion were observed and for Ho only [18-crown-6-H\(^+\)] was detected as counterion.

Due to d\(^5\) or f\(^0\) 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. \((18\text{-crown-6})\cdot [\text{TiCl}_2\cdot \text{Cp}_2]\) \((M = \text{Ti}, \text{Zr}, \text{Hf})\),\(^{73}\) donor free tris-(trimethylsilyl)silyl potassium (2a),\(^{60,62}\) tris(trimethylsilyl)germyl potassium \((2b)\),\(^{2} \) 1,4-dipotassium-tetramethyl-1,1,4,4-tetrakis-(trimethylsilyl)tetrasilane-\((18\text{-crown-6})\) \((2c)\),\(^{7} \) \(\text{Cp}_2\text{Zr}\{\text{Si(\text{SiMe}_3)}_2\}_2\) and \(\text{Cp}_2\text{Ce}^\text{IV}\) 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 SADAB,\(^{76,77}\) 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, 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), 190433 (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 WINGX\(^{79}\) and rendered using POV-Ray 3.6\(^{80}\)

Dicyclopentadienyl[bis(trimethylsilyl)silyl]titanate(III) \((3a)\). To a green suspension of 1a \((453 \text{ mg}, 0.82 \text{ mmol})\) in toluene \((10 \text{ mL})\) was added dropwise a solution of 2a \((1.64 \text{ mmol})\) in pentane \((10 \text{ mL})\) at \(-90^\circ\text{C}\). 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. Crystalization was achieved by overlayering of 10 mL of pentane within 24 h. Crystalline red-brown needles of 3a \((673 \text{ mg}, 68\%)\) were obtained. Mp.: 153–155 \(^\circ\text{C}\). 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 48.57, H 8.39.\) Found: C 48.57, H 8.39.

Dicyclopentadienyl[tris(trimethylsilyl)silyl]hafnate(III) \((3b)\). To a solution of 1b \((368 \text{ mg}, 0.54 \text{ mmol})\) in toluene \((5 \text{ mL})\) was added dropwise a solution of 2a \((1.08 \text{ mmol})\) in pentane \((5 \text{ mL})\) at \(-60^\circ\text{C}\). 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. Crystalization was achieved by overlayering of 5 mL of pentane within 24 h. Crystalline orange needles of 3b \((354 \text{ mg}, 81\%)\) were obtained. Mp.: 174–176 \(^\circ\text{C}\). Anal. Calcd for \(\text{C}_{60}\text{H}_{100}\text{Si}_{9}\text{O}_{13}\text{K}_{2}\text{Hf}(1220.5): C 43.83, H 8.39.\) Found: C 43.83, H 8.39.\) Found: C 43.83, H 8.39.

Bis(trimethylsilyl)silyl Zirconium Fulvalene Complex \((3c)\). To a solution of 1c \((150 \text{ mg}, 0.25 \text{ mmol})\) in toluene \((5 \text{ mL})\) a solution of 2a \((0.35 \text{ mmol})\) in pentane \((5 \text{ mL})\) at \(-80^\circ\text{C}\) was added dropwise. After 4 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. Crystalization was achieved by overlayering of 5 mL of pentane within 24 h. Crystalline

3. CONCLUSION

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

Somewhat unexpectedly, analogous chemistry with potassium tris(trimethylsilyl)silane gave the expected complexes of the type \([\text{Cp}_2\text{M}(\text{Si(\text{Me}_3}3)\text{Si})_3]\) only for the hafnium case. Reaction with \(K[\text{Cp}_2\text{TiCl}_2]\) with 2 equiv of \(\text{KSi(\text{SiMe}_3)_3}\) provided \(K[\text{Cp}_2\text{Ti}(\text{SiH(\text{SiMe}_3)}_3)]_2\). The reaction with \(K[\text{Cp}_2\text{ZrCl}_2]\) is most unusual as it leads to a dinuclear complex with a fulvalene ligand bridging two Zr atoms. The desired \(K[\text{Cp}_2\text{Zr}(\text{Si(\text{SiMe}_3)}_3)]_2\) could eventually be obtained by reduction of \(K[\text{Cp}_2\text{Zr}(\text{Si(\text{SiMe}_3)}_3)]_2\) with potassium.

Related reactions of \(\text{KSi(\text{SiMe}_3)_3}\) with some lanthanidoenes \(\text{Cp}_2\text{Ln}(\text{Ln} = \text{Ce, Sm, Gd, Ho, Tm})\) gave complexes of the type \([\text{Cp}_2\text{Ln Si(\text{SiMe}_3)}_3]\)\(^{-}\) with either \([18\text{-crown-6-H}^+]\) or the complex ion \([18\text{-crown-6-K-Cp}_2\text{K}-18\text{-crown-6}]^+\) as counterion. The presence of \([18\text{-crown-6-K-Cp}_2\text{K}-18\text{-crown-6}]^+\) suggests a more complicated course of reaction as it implies that part of the lanthanidoenes 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 \([18\text{-crown-6-K-Cp}_2\text{K}-18\text{-crown-6}]^+\), whereas for Tm crystals with and without dependent magnetic behavior is interesting, we intend to study it in more detail in a future investigation.

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).

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orange-red 3b (45 mg, 36%) was obtained. Anal. Calcd for C53H95Si4O12K2Gd (1272.12): C 50.04, H 7.53. Found: C 49.56, H 7.95.

Bis(trimethylsilyl)germyl Zirconium Fulvalene Complex (3d). To a solution of 1e (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 3 (430 mg, 56%) was obtained. Anal. Calcd for C53H95Si4O12K2Gd (1272.12): C 50.04, H 7.53. Found: C 49.56, 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.inorg-chem.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.cam.ac.uk/data_request/cif, 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 103211.

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

**ORCID**

Christoph Marschner: 0000-0001-8586-2889
Judith Baumgartner: 0000-0002-9938-1813

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The authors declare no competing financial interest.

**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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