Synthesis of Oligosilanyl Compounds of Group 4 Metallocenes with the Oxidation State +3

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Supporting Information

ABSTRACT: Recently, we showed that titanocene silyls are much more stable with Ti in the oxidation state +3. The current study demonstrates that analogous Zr and Hf compounds can also be obtained by reaction of a suitable metalate precursor with an oligosilanyl dianion. As the obtained complexes formally possess a d1 electron configuration, they were investigated using EPR spectroscopy. The corresponding spectra indicate that the compounds can be considered to also exhibit some cyclosilanyl radical anion character. In order to understand the strong preference of disilylated titan(IV)ocenes for reductive elimination, a theoretical study of the thermodynamics of these reactions was conducted, revealing that this behavior is essentially caused by the weak Si−Ti(IV) bond.

INTRODUCTION

Over the last few decades alkyl-substituted group 4 metallocenes have become a very well established class of compounds, for which numerous applications have been found.¹ Analogous compounds with higher group 14 substituents have received much less attention. However, silylated metallocenes are another interesting class of compounds which can serve as catalysts or catalyst precursors for a number of important chemical transformations. Prominent among these reactions is the dehydrogenative coupling polymerization of hydrosilanes²−⁵ an important synthetic alternative to the Wurtz type coupling of chlorosilanes, which still is the most widely used method for the formation of Si−Si bonds in general and the synthesis of polysilanes⁶ in particular. The reaction was discovered by Harrod and co-workers as a source of the silylene PhSiH, which upon release could oligomerize to longer chains.⁷,⁸ Subsequently, Tilley and co-workers showed that the polymerization of phenylsilanes can also be catalyzed by zirconocenes and hafnocenes of the type Cp²ZrMe₂.⁹ Harrod’s initial mechanistic explanation involved the formation of the dinuclear Ti(III) complex [Cp₂Ti(H)SiH₂R]²,¹¹ it is interesting to note that still no examples of stoichiometric σ-bond metathesis reactions between silicon hydrides and bis(silyl)titanocenes or silylhydridotitanocenes are known. Even the syntheses of the disilylated titanocenes or Cp₂TiSi(SiMe₃)₂ have never been reported.

A survey of known silylated titanocenes reveals that while there are a fair number of Ti(III) complexes⁸,¹²−¹⁶ and even some Ti(II)−SiH σ-complexes,¹⁷−¹⁹ less than a handful of examples of silylated titanocenes with Ti(IV) have been reported. Among these compounds Cp₂TiCl(SiMe₃)(I),²⁰ prepared by Rösch et al. utilizing the reaction of Cp₂TiCl₂ with Al(SiMe₃)₃·Et₂O, is well characterized with ¹H and ¹³C NMR and IR spectra and a low-quality crystal structure (R = 16%). The titanacyclosilanes Cp₂Ti(SiPh₂)₅(n = 4 (II), 5 (III))²¹−²³ were reported as products of the reaction of Cp₂TiCl₂ with Li(Ph₂Si)Li. While for Cp₂Ti(SiPh₂)₄ ¹H and ¹³C NMR spectra in acetone were reported, the formation of Cp₂Ti-Si(SiPh₂)₅ was substantiated by multinuclear (including ²⁹Si) NMR²⁴ and a crystal structure analysis.²⁵ The reported synthesis of the silylene-bridged complex [Cp₂Ti(SiH₂)₅] obtained by Weiss from the reaction of Cp₂TiCl₂ with catalytic cycle consists of two σ-bond metathesis steps.²,¹⁰ While Harrod later expressed his belief that also in the titanium-catalyzed reaction “the key catalyst species is Cp₂Ti-(H)SiH₂R”,¹¹ it is interesting to note that still no examples of stoichiometric σ-bond metathesis reactions between silicon hydrides and bis(silyl)titanocenes or silylhydridotitanocenes are known. Even the syntheses of the disilylated titanocenes or Cp₂TiSi(SiMe₃)₂ have never been reported.

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H₃SiK²⁵ was later questioned by Harrod and co-workers, who repeated the published procedure and obtained only [Cp₂Ti-(SiH₃)₂]²⁶. One further example of a well-characterized disilylated titanocene was reported by our group. The reaction of Cp₂TiCl₂ with (Me₃Si)₂KSiSiK(SiMe₃)₂ was found to give a titanacyclotrisilane (IV).²⁷ This compound, however, can be interpreted either as containing Ti(IV) with silyl groups or as Ti(II) with a disilene ligand.

For analogous germylated titanocenes with Ti(IV) the situation is quite similar. Cp₂Ti(Cl)GeMe₃ (V) was prepared by Rösch in a manner analogous to that described for Cp₂Ti(Cl)SiMe₃ utilizing Al(GeMe₃)₃·Et₂O.²⁰ The triphenylgermylated compound Cp₂Ti(Me)GePh₃ (VI)²⁸ was obtained by Harrod and co-workers from the reaction of Cp₂TiMe₂ with Ph₃GeH. Related studies from Razuvaev’s group showed that Cp₂Ti(GePh₃)₂ (VII) and Cp₂Ti(Cl)GePh₃ are relatively stable at room temperature, while Cp₂Ti(GeEt₃)₂ decomposes rapidly at room temperature to Et₆Ge₂.²⁹,³⁰ They also reported reactions of digermacylcadmium or digermylmercury with Cp₂TiCl₂ and Cp₂TiCl to give small amounts of germylated titanocenes.³¹

Our own attempts to react Cp₂TiCl₂ with (Me₃Si)₃SiM (M = K, Li, MgBr, MgSi(SiMe₃)₃) met with no success until recently.³² While observation of the reaction of Cp₂TiCl₂ with (Me₃Si)₃SiK-(18-crown-6) by means of NMR spectroscopy did not indicate formation of any type of metalated tris(trimethylsilyl)silyl compound, it was possible to isolate another product: Cp₂TiCl₂·K(18-crown-6). The presence of this paramagnetic compound indicated the formation of paramagnetic, NMR-silent Ti(III) species in the reaction.³³ Continued attempts finally allowed the isolation of Cp₂Ti(Cl)Si(SiMe₃)₂·K(18-crown-6), which was formed in a reaction that was not very clean. Changing from (Me₃Si)₃SiK to the dimetalated compound K(Me₃Si)₂Si(Me₂Si)₂Si(SiMe₃)₂K (I)³⁴ led to a much cleaner course of reaction (Scheme 1). It was found that half of 1 was converted cleanly to 1,2-bis(trimethylsilyl)tetramethylcyclotetrasilane, which was presumably formed by reductive elimination of an initially formed titanacyclosilane. The concurrently formed titanocene “Cp₂Ti” likely underwent a comproportionation with Cp₂TiCl₂ to Cp₂TiCl, which in the presence of KCl-(18-crown-6) reacted further to Cp₂TiCl₂·K(18-crown-6) (3).³² The latter could then react with the remaining 1 to give the final product, a titanacyclosilane (2) with titanium in the oxidation state +3.³²

The current study deals with further investigations concerning this reaction and, in particular, with the question whether this chemistry is also possible for the heavier metals of group 4.

## RESULTS AND DISCUSSION

### Synthesis. Dichlorinated Metalates.
Knowing that Ti(III) was involved in the reaction of Cp₂TiCl₂ with silyl anions, we set out to use another titanocene precursor to avoid wasting the metalated oligosilanes as reducing agents. While several methods for the synthesis of Cp₂TiCl and related complexes with reducing metals (such as Zn, Al, and Mn) are known,³⁵,³⁶ we thought to use comproportionation chemistry to obtain the Cp₂Ti³⁻ species in a way similar to that outlined above. Thus, the well-known “Cp₂Ti”³⁷ source Cp₂Ti(btmsa)³⁸ was reacted with Cp₂TiCl₂ (Scheme 2). This reaction turned out to be a valuable source of “salt free” (Cp₂TiCl₂). The dinuclear
(Cp₂TiCl)₂ can further be converted to a mononuclear compound by reaction either with KCl-(18-crown-6) or with LiCl in the presence of tmeda to obtain the respective base adducts of Cp₂TiCl with KCl (3) or LiCl (3a) (Scheme 2). This way the required precursors could be obtained without wasting oligosilane precursors, in a satisfying quantitative yield over two steps.

Reaction of 1 with Cp₂ZrCl₂ and Cp₂HfCl₂ was reported to lead to the formation of the respective metallacyclosilanes with the metals in the oxidation state +4, without any sign of reductive elimination. Therefore, attempts directed to the preparation of zirconium and hafnium analogues of 2 required metal salts of zirconocene and hafnocene in the oxidation state +3. The synthesis of the respective K[Cp₂ZrCl₂]-(18-crown-6) (4) and K[Cp₂HfCl₂]-(18-crown-6) (5) was thus accomplished in an even more straightforward fashion by reduction of the respective metallocene dichlorides with potassium in the presence of 18-crown-6 (eq 1).

\[
\text{Cp}_2\text{MCl}_2 + \text{K} + \text{18-crown-6} \quad \text{M} = \text{Zr, Hf}
\]

Disilylated Metalates. As anticipated, reactions of titanates 3 and 3a with the dianion 1 led to the formation of the titanacyclopentasilane 2 in a cleaner way. Using 3a, reactions with the respective 1,5-dipotassiopentasilane 6 and 1,3-dipotassiotrisilane 8 were also carried out. From the reaction of 3a with 6 the expected anionic titanacyclohexasilane 7 could be obtained. The same anion could already be isolated from the reaction of 6 with Cp₂TiCl₂. However, reaction of 6 with Cp₂TiCl₂ gave the anionic part of 7 along with the complex counterion [(K-(18-crown-6))₂Cp]⁺, indicating a reaction course more complex than was anticipated, involving abstraction of a cyclopentadienide. The use of 3a instead of Cp₂TiCl₂ provides a way to 7 with the simpler counterion [(K-(18-crown-6))-2THF]⁺ (Figure S1, Supporting Information).

Disilanide 6 can be regarded as an elongated version of 1, and in the same way 8 might be seen as the analogously shortened congener of 1. As expected, the reaction of 8 with 3a gave a complex anion comprised of a titanacyclotetrasilane ring (9) (Scheme 3). In this case, however, single-crystal structure analysis showed that the counterion consists again of the complex [(K-(18-crown-6))₂Cp].

While the formation of 2, 9, and 7 utilizing 3a proceeded in an expected way, it was also interesting to test whether the same reaction could also be accomplished for the analogous zirconium and hafnium cases. Therefore, the reactions of 1 with 4 and 5, respectively, were carried out and found to proceed much in the same way as was observed for the titanium case (Scheme 4). This was striking, as the obtained products 10 and 11 contained the same metallacyclopentasilane units with a d¹ electron configuration that were previously obtained as d⁰ fragments. As it was possible to analyze the solid-state structures of all four compounds, a structural comparison allows some interesting conclusions about the relationship between geometry and electronic state (vide infra).

The subsequently arising question of whether the d¹ complex could be obtained also by direct reduction of the neutral metallacyclosilane was addressed by the reaction of the respective zirconacyclopentasilane 12 with 1 equiv of potassium in the presence of crown ether. It was found that this reaction yielded the d¹ complex directly (Scheme 4). However, while

Scheme 2

\[\text{Cp}_2\text{TiCl}_2 + 2\text{KCl} \rightarrow \text{KCl} + \text{Cp}_2\text{TiCl}_2\]

Scheme 3. Formation of 2, 7, and 9

\[\text{Cp}_2\text{TiCl} \rightarrow \text{Cp}_2\text{TiCl}_2\]
crystal structure analysis of the resulting compound (10a) confirmed the identity of the expected d1 zirconacyclopentasilane, it also featured the complex counterion [(K·(18-crown-6))2Cp]+, which clearly indicates additional chemistry with cyclopentadienide acting as a leaving group, thus providing the possibility for the formation of [(K·(18-crown-6))2Cp]+.

The successful preparation of the d1 complexes of zirconacyclopentasilanes 10 and 11 and the strange behavior of the titanocenes forced us to revisit some chemistry that we found rather puzzling some years ago. While we found clean conversion of 1,4-dipotasiotetrasilane 1 with Cp2ZrCl2 and Cp2HfCl2,34,39 attempts to achieve the same conversion with the respective 1,4-dipotassiocyclohexasilane 1340 with Cp2ZrCl2 and Cp2HfCl2 did not give any indication of the formation of the expected bicyclic metal-bridged compounds. Considering the course of the reaction of 1 with Cp2TiCl232 and the fact that our judgment of the reactions was based primarily on NMR spectroscopic analysis, it seemed reasonable to reinvestigate the reaction of 13 with Cp2HfCl2. Again, NMR spectroscopic observation gave no indication for the formation of the respective coupled cyclosilane but provided evidence for the decomposition of this compound by reductive elimination, which gives the respective cyclosilane that is already known.40 However, crystallographic analysis revealed that the disilylated metalocene 14 was formed with the metal being in the oxidation state +3 (Scheme 5). A similar course of reaction had already been found for the titanocene case.32

A simple explanation as to why it is possible to prepare some disilylated zirconocenes and hafnocenes with the metal in the oxidation state +4, while others that are seemingly very similar cannot be formed, is difficult to give. The question certainly seems to be related to the equally puzzling behavior of silylated titanocenes. It seems reasonable to assume that in the reaction of two silyl anions with Cp2MCl2 the expected disilylated metalocenes form initially but then undergo reductive elimination as the first step of the sequence, concluding with the formation of disilylated metalocenes in the oxidation state +3. This leads directly to the question of why certain reductive elimination processes are more facile than others.

**Computational Study.** To understand the outlined unexpected reductive elimination behavior of disilylated titanocenes, we set out to conduct a computational study of these compounds and their zirconocene and hafnocene counterparts at the density functional MPW1PW91/3DD (Ti, Zr, Hf) and 6-311G(d,p) (H, C, Si) level of theory.41,42

In order to obtain some initial insights, the thermodynamics involved in the reaction depicted in eq 2 were studied. In this reaction the facility of reductive cyclosilane elimination from cyclic disilylated metallocone(IV) compounds is investigated as a function of metal and different ring size. The results of the calculations given in Table 1 correlate qualitatively with the observed experimental situation. While the reductive elimination of a disilene from the formal metallacyclotrisilane is endothermic (only slightly for the Ti case) for all three

| Table 1. Calculated Free Enthalpy Differences at 298.15 K, ΔG°, (kJ mol⁻¹), for the Reductive Elimination Reactions of Metallasilacycles with Concurrent Formation of Cyclosilanes According to Eq 2 |
|-----------------------------------------------|---------------|---------------|---------------|---------------|
| elimination product | n = 0 disilene | n = 1 cyclotrisilane | n = 2 cyclo tetrasilane | n = 3 cyclopentasilane |
| metallocycle | three-membered | four-membered | five-membered | six-membered |
| Ti | 3 | -42 | -121 | -176 |
| Zr | 154 | 135 | 50 | 8 |
| Hf | 172 | 160 | 78 | 37 |
metals, the elimination is strongly favored for all other ring sizes of titanacyclosilanes and it is more favorable for large ring sizes. This calculated trend for the ease of the reductive elimination process from titanacyclosilanes follows the experimental observation. That is, we were able to synthesize and isolate a titanacyclotrisilane\textsuperscript{21,22} but no larger titanacycles. For the zirconia- and hafnacyclosilanes the same trend is found: the thermodynamic stability decreases with increasing ring size of the metallacilycles. However, the situation is more delicate, as in all investigated cases the reductive elimination is predicted to be endothermic. In the experiment, however, reductive elimination is not an isolated process but is followed by subsequent reactions; therefore, the trend visible through the data summarized in Table 1 provides a rationalization for the experimental facts that the respective metallacyclotetrasilanes and -pentasilanes are stable while the metallocyclohexasilanes undergo reductive elimination.

While the study of the reaction of eq 2 reflects the real systems qualitatively well, it does not provide an intuitive explanation. For this reason it was decided to vary the parameters of the system in order to obtain further insight.

The first variation applied was the replacement of the trimethylsilyl groups at the positions $\beta$ to the metals by methyl groups (eq 3). The calculated free enthalpies $\Delta G^\text{298}$ according to these reactions are given in Table 2. In principle the picture is the same as was found for eq 2, but all results are shifted to more endothermic values. For this system also the three- and four-membered titanacyclosilanes are predicted to be stable and reductive elimination becomes only a feasible process for five-membered and larger rings. For the heavier metals zirconium and hafnium six-membered rings should be stable. Although no calculations were carried out for phenyl substituents at the silicon atoms in $\alpha$ positions, the stability of this substitution pattern might be even higher, given the fact that a titanacyclotrisilene\textsuperscript{21,22} and even a titanacyclotetrasilene is known.\textsuperscript{23,24} The trend outlined here also provides an explanation for the fact that Cp\textsubscript{2}Ti(Cl)SiMe\textsubscript{3} was found to be a stable compound while the synthesis of the analogous tris(trimethylsilyl)silyltitanocene chloride failed.\textsuperscript{32}

In order to eliminate the potential influence of ring strain of the formed cyclosilane the reductive elimination of two silyl substituents to give a disilane was studied computationally for comparison (eq 4). The steric requirements and the silylation degree of the silyl substituents were varied from trimethylsilyl to tris(trimethylsilyl)silyl, and the results of the calculations are shown in Table 3. All disilylated metallocenes(IV) were found to be prone to facile reductive elimination. For zirconium and hafnium no energetically favorable eliminations were detected. This result clearly identifies the inherent weakness of the Ti(IV)–Si linkage as one of the major factors that determines the instability of silyltitanocenes(IV) and is further supported by the calculated mean bond dissociation energy, $D_w$ of the metal–silicon bond in Cp\textsubscript{2}MIV(SiMe\textsubscript{3})\textsubscript{2}, which increases significantly with increasing atomic number of the metal (M = Ti, $D_w = 136$ kJ mol\textsuperscript{-1}; M = Zr, $D_w = 206$ kJ mol\textsuperscript{-1}; M = Hf, $D_w = 223$ kJ mol\textsuperscript{-1}).\textsuperscript{32} Less clear is the trend revealed by the calculation upon $\alpha$-silylation. For titanium a higher silylation degree was found again to correspond with a more favored elimination. For zirconium and hafnium, however, the stability of the metal–silicon bond does not decrease monotonically with increasing silylation degree, which seems to suggest that a higher silylation degree stabilizes the bond but becomes detrimental once steric interactions between the silyl groups or between the silyl and Cp ligands arise. For the disilylated metallocenes (M = Zr, Hf) this situation occurs for (trisilyl)silyl substituents.

As the results of this reaction (eq 4, Table 3) are clearly different from those of the metallacycle reductive eliminations (eqs 2 and 3, Tables 1 and 2), a profound influence of ring strain can be assumed. However, as in the actual reaction both the starting material and the product are cyclic in nature, the thermodynamics of the isodesmic reaction\textsuperscript{25} depicted in eq 5 were studied in order to assess the influence of ring strain of the metallacycle (Table 4). The results indicate that only the three-membered zircona- and hafnacycles are somewhat strained and,

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**Table 2. Calculated Free Enthalpy Differences at 298.15 K, $\Delta G^\text{298}$ (kJ mol\textsuperscript{-1}), for the Reductive Elimination Reactions of Metallacilycles with Methyl Substituents at the $\alpha$-Silicon Atoms and with Concurrent Formation of Cyclosilanes According to Eq 3**

| elimination product | $n = 0$ disilene | $n = 1$ cyclotrisilane | $n = 2$ cycloketrasilane | $n = 3$ cyclopentasilane | $n = 4$ cyclohexasilane |
|---------------------|----------------|-----------------------|------------------------|----------------------|-----------------------|
| metallacycle        | three-membered| four-membered         | five-membered          | six-membered         | seven-membered        |
| Ti                  | 82            | 15                    | $-62$                  | $-108$               | $-151$                |
| Zr                  | 215           | 170                   | 75                     | 30                   | 0                     |
| Hf                  | 237           | 194                   | 106                    | 61                   | 31                    |

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**Table 3. Calculated Free Enthalpy Differences at 298.15 K, $\Delta G^\text{298}$ (kJ mol\textsuperscript{-1}), for the Reductive Elimination Reactions of Disilylated Group 4 Metallocenes with Concurrent Formation of Disilanes According to Eq 4**

| R$_3$        | M          | (SiMe$_3$)$_2$H | (SiMe$_3$)$_3$SiMe$_3$H | (SiMe$_3$)$_4$ |
|--------------|------------|----------------|-------------------------|----------------|
| Ti           | $-118$     | $-150$         | $-150$                  | $-155$         |
| Zr           | $+33$      | $+46$          | $+40$                   | $+26$          |
| Hf           | $+62$      | $+73$          | $+66$                   | $+53$          |
Table 4. Calculated Energies, $\Delta E$ (kJ mol$^{-1}$), for the Isodesmic Reactions (Eq 5) Which Determine the Ring Strain of the Metallacycles

| $n$ | metallacycle       | three-membered | four-membered | five-membered | six-membered |
|-----|--------------------|----------------|---------------|---------------|--------------|
| 0   | Ti                 | 7              | 24            | 30            | 23           |
| 1   | Zr                 | -14            | 22            | 14            | 15           |
| 2   | Hf                 | -21            | 16            | 15            | 17           |

Table 5. Calculated Energies, $\Delta E$ (kJ mol$^{-1}$), for the Isodesmic Reactions (Eq 5) Which Determine the Ring Strain of the Polysilacycles ($\text{Me}_2\text{Si}_n$) ($n = 1$–$4$)

| starting material | $n$ | $\Delta E$ |
|-------------------|-----|------------|
| tetramethylsilane  | 0   | -207       |
| hexamethyldisilane| 1   | -134       |
| octamethyldisilane| 2   | -47        |
| decamethyldisilane| 3   | -8         |
| dodecamethyldisilane| 4   | 3          |

While the calculations might not reproduce the actual system accurately because of the added steric interaction involved in the formation of the 1,1,2,2-tetrakis(trimethyl)disilanylene unit, it is not accounted for, it gives a good idea that five- and six-membered rings essentially experience no or only little ring strain. This tells us that for the cases of the three-, four-, and five-membered metallacycles a ring strain component works against a facile reductive elimination to give cyclic products. The behavior of the respective zirconium and hafnium compounds is consistent with this.

**EPR Spectroscopy.** While the d$^1$ configuration of the studied complexes does not permit NMR spectroscopic investigations, it allows the use of EPR spectroscopy. Especially for the study of titanocene and to some extent zirconocene d$^1$ complexes this is a very established technique. In fact, there exists even a prior EPR study of radical anions of group 4 metallacycles, namely titan- and zirconodecaphenylcyclohexasilane, which addressed the question of electron delocalization within the cyclosilane framework.

In the course of this study we investigated compounds 2, 4, 10, and 11. The dichlorinated metalate 4 exhibited a signal at g = 1.970 with the expected hyperfine coupling to $^{91}\text{Zr}$ ($a(I = 5/2) \approx 27$ G), which is in excellent agreement with the values reported by Samuel et al. for $[\text{Cp}_2\text{ZrCl}_2]^-$ ($g = 1.970$, $a(I = 5/2) \approx 29.7$ G). In contrast to this, the EPR spectrum of 10 shows a slightly more complex signal with coupling also to the $\alpha$-silicon atoms (Figure 1). The smaller value of the hyperfine splitting (hfs) constant to $^{91}\text{Zr}$, $a(I = 5/2) = 19.4$ G, indicates a delocalization of the electron between the metal and the attached silicon atoms. A hfs of 10.2 G to $^{29}\text{Si}$ can be compared to the value of 7.1 G measured for the coupling to trimethylsilyl groups in (Me$_3$Si)$_2$Si$\cdot$.$^4$ Due to the presence of $^{47}\text{Ti}$ ($I = 5/2$) and $^{90}\text{Ti}$ ($I = 7/2$), which both display a hfs of 8.8 G, the spectrum of 2 (Figure 2) is more complicated; still, the hfs to the $\alpha$-$^{29}\text{Si}$ atoms is 12.6 G, of the same magnitude as observed for 10. In addition, the simulation of the spectrum provides a hfs owing to another spin $1/2$ nucleus with the double natural abundance of silicon with a magnitude of 4.8 G. For reasons of symmetry as well of geometry, we assign this coupling to the SiMe$_3$ groups in (Me$_3$Si)$_3$Si$\cdot$.$^4$8 Due to the presence of $^{47}\text{Ti}$ ($I = 5/2$) and $^{90}\text{Ti}$ ($I = 7/2$), which both display a hfs of 8.8 G, the spectrum of 2 (Figure 2) is more complicated; still, the hfs to

![Figure 1. EPR spectrum of 10 at rt in C$_6$H$_6$.](image1)

![Figure 2. EPR spectrum of 2 at rt in C$_6$H$_6$.](image2)
The structure analysis of compounds 10 and 11 is interesting, as in these cases a comparison of the same structural units with the metal in the oxidation state +4 is possible. Structural differences reflect therefore most likely the different oxidation states.

The zircona(III)cyclopentasilane 10 (Figure 5) crystallizes in the monoclinic space group $P2_1/c$, whereas the related hafna(III)cyclopentasilanes 11 and 11a crystallize in the triclinic space group $P1$. The asymmetric unit of 10 contains the halves of a potassium crown ether unit coordinated by two THF molecules.
Figure 4. Crystal structure of 4. Thermal ellipsoids are represented at the 30% probability level, and hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Zr(1)–Cl(1) = 2.5841(11), Zr(1)–Cl(2) = 2.5883(11), Cl(1)–K(2) = 3.1196(13), Cl(2)–K(2) = 3.2204(15), Cl(1)–Zr(1)–Cl(2) = 82.31(3), Zr(1)–Cl(1)–K(2) = 99.17(4), Zr(1)–Cl(2)–K(2) = 96.57(3), Cl(1)–K(2)–Cl(2) = 64.92(3), Cl(1)–K(2)–Zr(1) = 35.84(2), Cl(2)–K(2)–Zr(1) = 36.17(2).

Figure 5. Crystal structure of 10 (the cationic part is omitted for reasons of clarity). Thermal ellipsoids are represented at the 30% probability level, and hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Zr(1)–Cl(1) = 2.487(3), Zr(1)–Cl(2) = 2.488(3), Zr(1)–Cl(3) = 2.499(3), Cl(1)–Zr(1)–Cl(2) = 82.31(3), Cl(1)–Zr(1)–Cl(3) = 82.31(3), Zr(1)–Cl(2)–Cl(3) = 89.10(6), Si(1)–Zr(1)–Si(2) = 102.82(6), Si(1)–Zr(1)–Si(3) = 103.45(6), Si(2)–Zr(1)–Si(3) = 103.45(6), Si(1)–Si(2)–Si(3) = 103.45(6), Si(1)–Si(2)–Si(3) = 103.45(6), Si(2)–Si(3)–Si(4) = 103.45(6), Si(1)–Si(2)–Si(3) = 103.45(6), Si(2)–Si(3)–Si(4) = 103.45(6), Si(1)–Si(2)–Si(3) = 103.45(6), Si(2)–Si(3)–Si(4) = 103.45(6), Si(1)–Si(2)–Si(3) = 103.45(6), Si(2)–Si(3)–Si(4) = 103.45(6), Si(1)–Si(2)–Si(3) = 103.45(6), Si(2)–Si(3)–Si(4) = 103.45(6).

Similar to the discussed relationship between Cp₂TiCl₃ and 3, the Si–Zr–Si bond angle of 10 of 85.7° is diminished by some 12° in comparison to the structure with Zr(IV). Also the Zr–Si bond lengths within the zirconacyclopentasilane ring are somewhat elongated (2.85/2.89 Å) in relation to the Zr(IV) compound (2.86/2.85 Å), but not to the same extent as observed for the Cp₂MCl₃ cases. The zirconacyclopentasilane ring of 10 adopts a perfect envelope conformation with one of the SiMe₃ units on the flap, whereas the Zr(IV) ring shows a half-twisted conformation.

The crystals for the structures of 11 (Figure 6) and 11a (Figure S3, Supporting Information) were grown in the same solution and were separated under the microscope. For 11 the potassium crown ether unit is coordinating to a SiMe₃ group, whereas in 11a two potassium crown ether units are coordinating to a cyclopentadienide, thus forming the complex cation we found also frequently in oligosilylated titanocenes in the oxidation state +3. For 11a there are two additional toluene molecules in the asymmetric unit. The comparably small Si–Hf–Si bond angle of 89° for 11 is again diminished compared to a value of 96.4° for the compound with Hf(IV). The hafnate 11 features Hf–Si bond distances of 2.85/2.86 Å, which are again elongated in comparison to the neutral Hf(IV) case (2.79/2.83 Å). For 11 and 11a relatively high residual electron density was located close to the Hf atoms.

Compound 14 (Figure 7) crystallizes in the monoclinic space group P2₁/c with one toluene in the asymmetric unit. The structure of the anionic 7-metallala[b.2.1]bicycloheptasilane was already found for the analogous titanocene. However, while the titanocene featured the complex cation [(K(18-crown-6))₂Cp]⁺, we found for 14 a plain K(18-crown-6) moiety which coordinates to a Cp of the metallocene. In comparison to 11 the Hf–Si bonds of 14 are much shorter (2.785/2.790 Å), even shorter than those found for the neutral hafnacyclopentasilane. As a consequence of the bicyclic nature of 14 the Si–Hf–Si angle is only 76°.

For compound 14 parts of the geometries of the anionic moieties and some solvent molecules are strongly disordered. Attempts to treat these disorders did not result in diminished residual electron density. As the concerned parts of the structures are not involved in the discussion of structural parameters, it was decided to refrain from the introduction of restraints which would only result in brightened pictures without real improvement of the model.
Figure 7. Crystal structure of 14. Thermal ellipsoids are represented at the probability 30% level, and hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Hf(1)−Si(1) = 2.785(2), Hf(1)−Si(4) = 2.7900(19), Si(4)−Si(8) = 2.342(3), Si(4)−Si(3) = 2.356(3), Si(4)−Si(5) = 2.357(3), Si(1)−Si(7) = 2.345(3), Si(1)−Si(6) = 2.356(3), Si(1)−Si(2) = 2.363(3), Si(2)−Si(3) = 2.366(3); Si(1)−Hf(1)−Si(4) = 75.98(5), Si(3)−Si(4)−Si(5) = 100.49(11), Si(6)−Si(1)−Si(2) = 100.37(11), Si(1)−Si(2)−Si(3) = 102.19(10), Si(4)−Si(3)−Si(2) = 103.89(10), Si(6)−Si(5)−Si(4) = 102.49(10), Si(5)−Si(6)−Si(1) = 104.06(11).

**CONCLUSION**

The current study attempts to generalize the chemistry of silylated titanocenes. It was shown that chloride adducts of Cp₂TiCl can simply be obtained by comproportionation of Rosenthal’s Cp₂Ti(btmsa) with Cp₂TiCl₂ in the presence of either LiCl or KCl and an additional coordinating base (tmeda or 18-crown-6). The lithium or potassium salts of [Cp₂TiCl₂]⁻ either LiCl or KCl and an additional coordinating base (tmeda or 18-crown-6). Also, these metalates could be reacted with oligosilylanes. Analogous dichlorinated metalates of zirconium and hafnium could be prepared by reduction of the respective metallocene dichlorides with potassium in the presence of 18-crown-6. Also, these metalates could be reacted with oligosilylanes to give metallacyclosilanes with Zr and Hf in a d₁ electron configuration.

In order to gain some insight into the question as to why cyclic disilylated titanocenes seem to be highly unstable and why analogous zircono- and hafnocenocenes are stable only with certain ring sizes, a theoretical study was conducted. The results show that the strong preference for the reductive elimination of disilylated titanocenes is mainly caused by the rather weak Si−Ti bond. The thermodynamic driving force of the reductive elimination of the titanacyclopentasilane in comparison to the analogous Zr and Hf compounds is substantial (171 kJ mol⁻¹ vs Zr) and 199 kJ mol⁻¹ (vs Hf). The reductive elimination to form cyclosilanes is also feasible for zirconoc- and hafnacyclosilanes. However, for these cases the energetic situation is more delicate, as the ring strain in the formed cyclosilanes constitutes a decisive contribution as to whether the reaction is thermodynamically favorable or not.

EPR spectroscopy of a set of d₁ metallacyclosilanes was particularly interesting, because these compounds can be regarded either as group 4 d₁ metal complexes or alternatively also as cyclosilyl radical anions. While for the d₁ metal the unpaired electron would be considered to be largely localized at the metal, such electrons are considered to be delocalized along the ring atoms in cyclosilyl radical anions. A comparison of the EPR spectra of the Zr(III) compounds 4 and 10 shows that, while no hfs to the attached chloride atoms in 4 was observed, coupling to the attached silicon atoms indicates delocalization.

**EXPERIMENTAL SECTION**

**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 solvent purification system. Chemicals from different suppliers were used as received without further purification. Elementary analyses were carried out using a Heraeus VARIO ELEMENTAR instrument. EPR spectra were recorded on a Bruker ELEXSYS spectrometer at X-band. Simulation of EPR spectra was done with WinSim2002.

**X-ray Structure Determination.** For X-ray structure analyses the crystals were mounted onto the tip of glass fibers, and data collection was performed with a Bruker AXS SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (0.71073 Å). The data were reduced to F² and corrected for absorption effects with SADABS respectively. The structures were solved by direct methods and refined by full-matrix least-squares methods (SHELXL97). If not noted otherwise, all non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located at 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, 7, 9, 10, 11, 11a, and 14 reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publications CCDC 825205 (3a), 767184 (4), 854110 (7), 825206 (9), 767185 (10), 767187 (11a), and 705715 (14). Copies of the data can be obtained free of charge at http://www.ccdc.cam.ac.uk/products/csd/request/.

Titanocenebis(trimethylsilyl)acetylene, 1,1-bis(cyclopentadienyl)-2,2,4,4-tetrakis(trimethylsilyl)tetratetramethyltetrasilane (12), 1,3-dipotassio-1,1,3,3-tetakis(trimethylsilyl)dimethyltrisilane (8) and 1,4-dipotassio-1,4-bis(trimethylsilyl)octamethylcyclohexasilane (13) were prepared by following published procedures.

**General Procedure for the Comproportionation of Cp₂TiCl₂ (btmsa) with Cp₂TiCl.** To a mixture of Cp₂TiCl₂ (249 mg, 1.0 mmol) and Cp₂Ti(btmsa) (349 mg, 1.0 mmol) was added THF (5 mL). Immediately a green solution developed, which was stirred for an additional 30 min. All volatiles were removed in vacuo, and the green residue was washed with pentane (2 mL) to yield 426 mg (100%) of [Cp₂TiCl₄]− as a green powder.

The respective alkali-metal chloride adducts could be obtained by adding equimolar amounts of LiCl/tmeda or KCl/K₂(MoO₄) and why analogous zircono- and hafnocenocenes are stable only with certain ring sizes, a theoretical study was conducted. The results show that the strong preference for the reductive elimination of disilylated titanocenes is mainly caused by the rather weak Si−Ti bond. The thermodynamic driving force of the reductive elimination of the titanacyclopentasilane in comparison to the analogous Zr and Hf compounds is substantial (171 kJ mol⁻¹ vs Zr) and 199 kJ mol⁻¹ (vs Hf). The reductive elimination to form cyclosilanes is also feasible for zircono- and hafnocyclusilanes. However, for these cases the energetic situation is more delicate, as the ring strain in the formed cyclosilanes constitutes a decisive contribution as to whether the reaction is thermodynamically favorable or not. The EPR spectra of the Zr(III) compounds 4 and 10 shows that, while no hfs to the attached chlorine atoms in 4 was observed, coupling to the attached silicon atoms indicates delocalization.

**General Procedure for the Reduction of Group 4 Metalocene Dichlorides with Potassium/18-crown-6.** To a mixture of the respective metalocene dichloride (0.49 mmol), 18-crown-6 (130 mg, 1 equiv), and potassium (19 mg, 1 equiv) was added toluene (5 mL). After 1 h the color started to change and after stirring for 24 h a deeply colored solution was obtained. The reaction mixture was treated with pentane (10 mL), whereupon the product was isolated by filtration.
(349 mg, 100%, mp 124–125 °C). Anal. Calc. for C_{12}H_{24}Cl_{2}HBrO_{7} (683.00): C, 38.69; H, 3.02. Found: C, 38.47; H, 3.15.

**Reactions of Dipotassiohologasilanes 1, 6, and 8 with Titanate 3a.** A solution of 1,4-dipotassio-1,1,4,4-tetrakis(trimethylsilyl)tetramethyldisiloxane-(18-crown-6) (1; 0.82 mmol) in THF (5 mL) was added to a solution of [Cp₂TiCl₂][Li(tmeda)] (3a; 305 mg, 0.82 mmol) in THF (5 mL) at room temperature. Stirring for 3 h was followed by removal of solvent under vacuum. The residue was treated with toluene (5 mL), and the salts were removed by centrifugation. A layer of pentane (8 mL) was placed on the solution, and after 12 h orange-red crystals of 2 (457 mg, 86%) were isolated by decantation.

A solution of 1,5-dipotassio-1,1,5,5-tetrakis(trimethylsilyl)hexamethylpentasilane-(18-crown-6) (6; 0.27 mmol) in THF (4 mL) was added to a solution of [Cp₂TiCl₂][Li(tmeda)] (3a; 100 mg, 0.27 mmol) in THF (ca. 2 mL) at room temperature. Stirring for 3 h was followed by addition of pentane (6 mL) to the red solution. After removal of salts and solvent by centrifugation and vacuum the residue was dissolved in toluene (5 mL). A layer of pentane (8 mL) was placed on the solution, and after 16 h red needles of 7 (218 mg) were isolated by decantation.

To a solution of 1,3-dipotassio-1,1,3,3-tetrakis(trimethylsilyl)diphenylsilyliridane-(18-crown-6) (8; 0.55 mmol) in toluene (5 mL) was added a solution of [Cp₂TiCl₂][Li(tmeda)] (3a; 213 mg, 0.55 mmol) in THF (ca. 5 mL) at −60 °C. Warming to room temperature and stirring for 15 h was followed by addition of pentane (5 mL) to the red solution. After removal of salts by centrifugation and stirring for 16 h red needles of 9 (354 mg, 0.26 mmol, 48%; mp 130 °C) were obtained.

The identities of 2, 7, and 9 were unambiguously established by single-crystal X-ray diffraction analysis.

**Reactions of 1,4-Dipotassio-1,1,4,4-tetrakis(trimethylsilyl)-2,2,3,3-tetramethyltetrasilane (1) with 4 and 5.** To a stirred solution of 1,4-dipotassio-1,1,4,4-tetrakis(trimethylsilyl)-tetramethyldisiloxane (1) in toluene (6 mL) and stirred at room temperature for 16 h the initially red suspension turned into an orange-red solution. The reaction mixture was centrifuged and layered during this period. The reaction mixture was centrifuged and layered. The deeply colored solution was again treated with the complex of (18-crown-6)° and 60 °C. The identities of 11 were unambiguously established by single-crystal X-ray diffraction analysis.

**Reduction of Zirconacyclopentasilane 12 with Potassium in the Presence of 18-crown-6.** A mixture of potassium (12 mg, 0.30 mmol), 18-crown-6 (79 mg, 0.30 mmol), and 12 (0.51 mmol) in THF (5 mL) was added to a solution of [Cp₂TiCl₂][Li(tmeda)] (3a; 100 mg, 0.27 mmol) in THF (ca. 2 mL) at room temperature. Stirring for 3 h was followed by addition of pentane (6 mL) to the red solution. After removal of salts and solvent by centrifugation crystallization was achieved by cooling to −60 °C for 72 h. Deep red needles of 9 (354 mg, 0.26 mmol, 48%; mp 130–132 °C dec) were obtained.

The identities of 2, 7, and 9 were unambiguously established by single-crystal X-ray diffraction analysis.

**Supporting Information**

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