

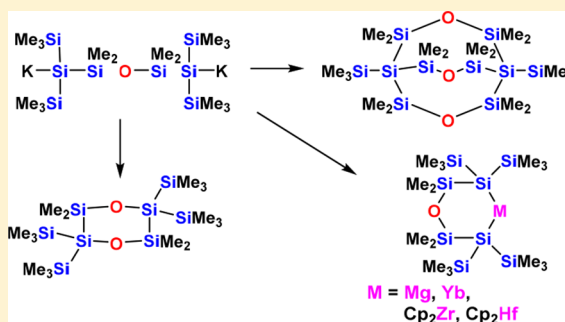
Chemistry of a 1,5-Oligosilanylene Dianion Containing a Disiloxane Unit

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S Supporting Information

ABSTRACT: Synthesis of a number of disiloxane containing cyclo- and bicyclic oligosilanes is described starting from the dipotassium 1,5-oligosiloxanylene diide derived from 1,3-bis[tris(trimethylsilyl)silyl]tetramethyldisiloxane. In addition, the use of this particular fragment as ligand for zinc and group 4 metallocene complexes was studied. Both types of compounds exhibit marked structural differences compared to related compounds containing Si-Si-Si units instead of the Si-O-Si fragment.

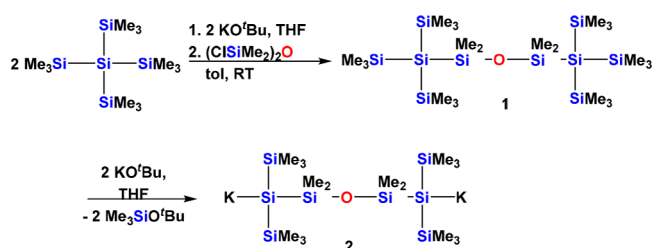


INTRODUCTION

Over the past years, we have utilized oligosilanylene diides^{1–4} for the synthesis of longer oligosilane chains,^{5–10} cyclo-silanes,^{2,7,11–14} heterocyclosilanes,^{11,12,15,16} and as ligands for silyl transition metal complexes^{1,4,17–22} and silylated low valent main group compounds.^{23–30}

Usually methylated oligosilanylene units were used as the connecting units between the two silyl anionic atoms of these compounds. Such spacer parts generally do not interact with a newly incorporated heteroatom and are mainly responsible for conformational properties. However, our recent studies concerning the use of silanides as ligands for lanthanide complexes^{31–34} have brought about the necessity of incorporating additional donor sites into the ligand backbone. These additional donor sites for the metal atom should avoid or diminish the coordination of solvent molecules like THF or DME to the metal atoms. Solvent free lanthanide complexes allow the use of vacuum during workup procedures and do not restrict the solvent use in order to ensure a homogeneous product distribution. For this reason, we have prepared several different silylated siloxanes, and in doing so, disiloxane **1** (Scheme 1) turned out to be an easily available ligand with great opportunities for further transformations, leading to a variety of interesting new compounds. Furthermore, theoretical^{35,36} and synthetic aspects^{37–41} of siloxanes have gained considerable attraction in recent times. Despite the large structural variety of oligosilanes that have been prepared over the past years, compounds with Si–Si bonds and Si–O–Si units are not very abundant. While such compounds are available by controlled hydrolysis of α,ω -dichlorooligosilanes,⁴² examples with even slightly more complex molecular architecture are rather rare. Nevertheless, Krempner et al. have shown that dendritic oligosilanes with discrete disiloxane units are interesting compounds for the modeling of oxygen defects in

Scheme 1. Synthesis of 1,3-Bis[tris(trimethylsilyl)silyl]tetramethyldisiloxane (**1**) and Its Conversion to the 1,5-Oligosilanylene Diide **2**



silicon nanomaterials⁴³ and von Hänisch and co-workers have recently incorporated oligosiloxane units into crown ethers.⁴⁴

Upon treatment with 2 equiv ^tBuOK, disiloxane **1** can be converted to the respective oligosilanylene diide **2** (Scheme 1).³³

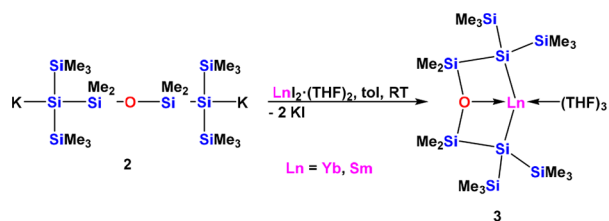
In the reactions of dianion **2** with $\text{YbI}_2 \cdot (\text{THF})_2$ and $\text{SmI}_2 \cdot (\text{THF})_2$, it acted as a tridentate ligand to Ln(II), leading to complexes **3** (Scheme 2).³³ The fact that the lanthanide ion coordinates to the very weakly basic siloxane oxygen⁴⁵ is likely caused by the ion's very strong Lewis acidity.

With a convenient access to disiloxane **1** and the respective dianionic derivative **2**, we thought it would be interesting to use these as precursors for the design of oligosilanes with even more siloxane units and also for the formation of additional silyl-metal complexes.

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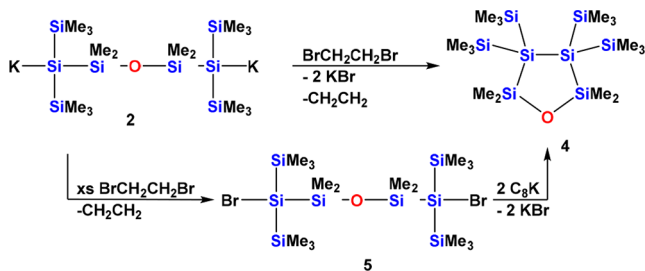
Scheme 2. Formation of Ytterbium and Samarium Disilyl Complexes **3** by Reaction of Dianion **2** with the Respective Metal Diiodides



RESULTS AND DISCUSSION

Disiloxane Containing Oligosilanes. With compound **2** readily available, we decided to study its chemistry in more detail. By addition of 1,2-dibromoethane, oxidative coupling of the two silanide moieties⁴⁶ was achieved, yielding oxacyclopentasilane **4** (Scheme 3). In the case of using a slight excess of

Scheme 3. Formation of Oxacyclopentasilane **4** by Oxidative Cyclization of **2**. Side Product **5** Can Be Converted to **4** by Reductive Coupling with Potassium Graphite



1,2-dibromoethane, in addition to **4** also the 1,5-dibromide **5** was formed as a side product, which was converted to **4** by reaction with added potassium graphite (Scheme 3).

The ²⁹Si NMR spectrum of compound **4** (Table 1) features expected values for SiMe₃ (−9.6 ppm), and Si(SiMe₃)₂ (−132.2 ppm). For the disiloxane unit, a resonance at 20.9 ppm was observed, which is somewhat downfield shifted compared to acyclic products **1** and **5** (Table 1), as can be expected for the diminished Si–O–Si angle in a cyclic compound.

Reaction of oligosilanylene diide **2** with 1,3-dichlorotetra-methyl-disiloxane gave the expected 1,5-dioxacyclooctasilane **6** (Scheme 4). Further reaction of **6** with 2 equiv of ^tBuOK provided the respective 1,5-dioxacyclooctasilanyl-3,7-diide **7**. Subjecting **7** to 1,2-dibromoethane causes coupling of the two silanide units to form 3,7-dioxabicyclo[3.3.0]octasilane **8** (Scheme 4). Alternatively, disilanide **7** can react with another equiv of 1,3-dichlorotetra-methyl-disiloxane, yielding dodeca-methyl-1,5-bis(trimethylsilyl)-3,7,10-trioxa-octasilabicyclo-[3.3.3]undecane (**9**) (Scheme 4). NMR spectroscopic analysis of reactions leading to **8** and **9** revealed that both reactions are not entirely selective. Presumably oligomers or polymers connecting 1,5-dioxacyclooctasilane rings are formed as side products. This can be concluded from the ¹³C NMR spectra, which feature a fair number of small signals in close proximity to the SiMe₂ and SiMe₃ signals (see f.i. Figure S15).

Compound **9** still has two trimethylsilyl groups originating from precursor **1**, located at the bridgehead positions. Additions of further 2 equiv of ^tBuOK cleaved off these

Table 1. Selected NMR Spectroscopic Data of Oligosilanyl Disiloxane Containing Compounds in ppm

	²⁹ Si (SiMe ₃)	²⁹ Si (SiMe ₂ O)	²⁹ Si (Si _q)	²⁹ Si (Si–E)
1 ^a	−10.5	13.4	−132.8	n.a.
2 ^a	−7.0	27.6	n.a.	−185.7 (SiK)
3	−5.0	32.4	n.a.	−153.8 (SiYb)
4	−9.6	20.9	−132.2	n.a.
5	−13.0	6.9	−28.9	n.a.
6	−11.2	11.6	−132.2	n.a.
7	−9.9	24.7	n.a.	−188.0 (SiK)
8	−10.0	22.2	−132.9	n.a.
9	−15.3	10.9	−136.2	n.a.
10	n.a.	15.5	n.a.	−186.7 (SiK)
11	−12.6	11.9	n.a.	−116.5 (SiH)
12	−14.9	5.9	n.a.	−19.7 (SiCl)
13	−12.3	8.4	n.a.	−18.5 (SiN)
14	−16.9	1.6	n.a.	−7.0 (SiO)
15	−8.8	20.6	n.a.	−155.7 (SiYb)
16	−7.3	15.2	n.a.	−166.9 (SiMg)
17	−5.8	16.3	n.a.	−142.0 (SiZn)
18	−5.6	18.2	n.a.	−71.5 (SiZr)
19	−4.9	13.3	n.a.	−45.7 (SiHf)

^aData taken from ref 33.

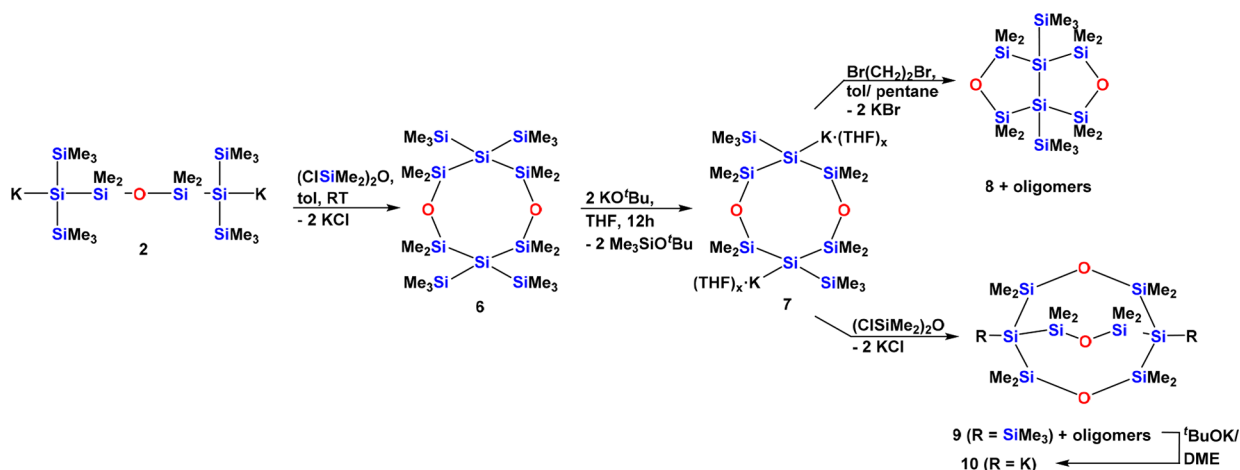
groups and converted **9** to [3.3.3]bicyclo-1,5-potassium disilanide **10** (Scheme 4).

The eight-membered ring of **6** allows for a widened Si–O–Si angle, and accordingly, the ²⁹Si NMR chemical shift of the siloxane silicon atoms (11.6 ppm) is close to that of the acyclic compound **1** (13.4 ppm) (Table 1). Correspondingly, the ²⁹Si NMR spectrum of the respective 1,4-dianionic compound **7** resembles that of compound **2** (Table 1).

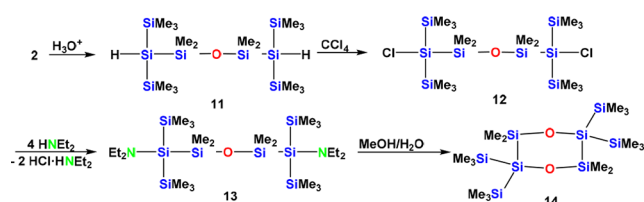
The 3,7-dioxabicyclo[3.3.0]octasilane **8** is structurally very similar to **4**. This is clearly reflected by its ²⁹Si NMR spectrum which resembles that of **4**. In a similar sense, compound **9** is structurally related to **6**. The ²⁹Si NMR resonances of the trimethylsilyl groups of **1**,³³ **6**, and **9** experience upfield shift in this order. Compound **9** is a rare example of a tricyclic oligosiloxane. A somewhat related bicyclo[3.3.3]pentasiloxane was recently obtained by Iwamoto and co-workers using *m*CPBA oxidation of a 1,3-bis(trimethylsilyl)bicyclo[1.1.1]pentasilane.³⁷ Compound **10** features a very simple ²⁹Si NMR spectrum with only two lines; the typical upfield resonances for the anionic silicon atoms (−186.7 ppm) are accompanied by a peak at 15.5 ppm for the SiO units. The compound might be regarded as a building block for the synthesis of low dimensional materials such as one-dimensional nanorods consisting of bridgehead connected bicyclo[3.3.3]trisiloxane units.³⁷

Facile protonation of oligosilanylene diide **2** yielded the respective 1,5-dihydrosilane **11**. Reaction with tetrachloromethane converted **11** to the 1,5-dichlorooligosilane **12** (Scheme 5).⁴⁷ Further reaction of **12** with excess diethylamine gave 1,5-bis(diethylamino)oligosilanyldisiloxane **13**,⁴⁷ which upon reaction with aqueous methanol led to the rather unexpected formation of 1,4-dioxacyclohexasilane **14**. We assume that **14** forms via an intermediate oligosilane diol, which in the presence of Et₂NH is partly deprotonated. Attack of the respective siloxide at a SiMe₂ unit leads to a rearranged oligosilane diol, which upon water elimination can cyclize to **14** (Scheme S1).

Scheme 4. Preparation of 1,5-Dioxacyclooctasilane **6**, Its Conversion to the Respective 3,7-Disilanide **7**, Which Can Further Be Used for the Synthesis of 3,7-Dioxabicyclo[3.3.0]octasilane **8** and 1,5-Bis(trimethylsilyl)-3,7,10-trioxa-octasilabicyclo[3.3.3]undecane **9**



Scheme 5. Formation of 1,5-Dihydroxilane **11**, Followed by Chlorination (**12**), and Amination (**13**). Hydrolysis of **13** Yields 1,4-Dioxacyclohexasilane **14**



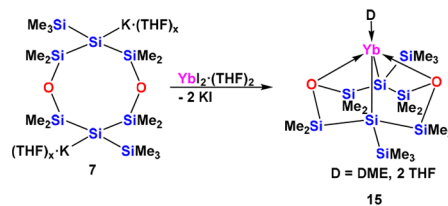
Quite typically, dihydrooligosilane **11** was obtained as an oil. Its ^{29}Si NMR spectroscopic properties are very much as expected. The Si-H resonance at -116.5 ppm is close to the respective signal of $(\text{Me}_3\text{Si})_3\text{SiH}$ (-115.4), and also the trimethylsilyl signal at -12.6 ppm is in line with the -10.9 ppm observed for $(\text{Me}_3\text{Si})_3\text{SiH}$.⁴⁶

In a similar way, the ^{29}Si NMR signature of oligosilylaldichloride **12** (5.9 (SiO), -14.9 (SiMe₃), -19.7 (SiCl) ppm) reflects the similarity of **12** to $(\text{Me}_3\text{Si})_3\text{SiCl}$ (-11.6 (SiMe₃), -13.3 (SiCl) ppm).⁴⁸ Compound **13** features the trimethylsilyl and NSi resonances at -12.3 ppm and -18.5 ppm, respectively. Compared to the previously prepared $\text{Et}_2\text{NSi}(\text{SiMe}_3)_2(\text{SiMe}_2)_2\text{Si}(\text{SiMe}_3)_2\text{NET}_2$ ($\delta = -16.0$ (SiMe₃), -23.3 (SiN), and -38.0 (SiMe₂) ppm),⁴⁷ these values are somewhat deshielded, which can be attributed to the presence of the polar Si-O-Si unit.

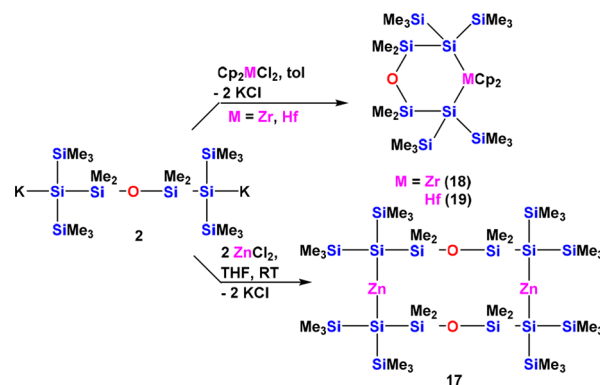
Metal Complexes with Disiloxane Containing Oligosilyl Ligands. Silylated lanthanides are an interesting field of research pioneered by Schumann and co-workers.^{49,50} Oligosilylated examples are still investigated by us^{31–34} and others.^{51–54} As mentioned, we initially devised the synthesis of oligosilylene diide **2** to employ it as a ligand for Ln(II)-silyl complexes.³³ As compound **7** can be regarded as a derivative of **2**, containing an additional disiloxane unit, we reacted it with YbI_2 (Scheme 6). ^1H NMR studies showed that the obtained product **15** was indeed coordinating to both oxygen atoms as only two THF or one DME molecules were shown to occupy the remaining two of the six coordination sites of Yb.

The clean reaction of **2** with YbI_2 encouraged us to study its coordination chemistry also with other divalent metal halides (Scheme 7). Not unexpectedly, **2** can be cleanly transmetalated

Scheme 6. Reaction of Dianion **7** with YbI_2



Scheme 7. Reaction of Dianion **2** with Other Divalent Metal Complexes



to the respective magnesium compound **16** by reaction with $\text{MgBr}_2 \cdot \text{Et}_2\text{O}$.^{4,55} **16** exhibits the typical ^{29}Si NMR spectroscopic signature known for oligosilyl magnesium compounds. The signal at -166.9 ppm (Table 1) reflects the diminished anionic character compared to **2**. While the influence of the negative charge on the directly metalated silicon atom is most pronounced, a downfield shift for attached trimethylsilyl groups compared to the neutral precursor molecules is usually observed.

Conversion of oligosilanides with zinc halides to silyl zinc compounds is a well established process.^{19,34,56–60} Reaction of **2** with ZnCl_2 was thus attempted (Scheme 7). We expected a six-membered ring to be formed in the reaction;¹⁹ however, the obtained product **17** is a 12-membered ring with close to linear Si-Zn-Si coordination geometry. Earlier studies have already shown a pronounced tendency of the Si-Zn-Si unit to

acquire linear arrangements.^{19,56} Cases with significant bending of the Si-Zn-Si unit are almost always accompanied by coordination of one or more Lewis bases to the involved Zn atom. The main reason compound **17** forms is likely that not only the Si-Zn-Si unit preference for linear arrangement but also the Si-O-Si part's tendency for engaging in larger angles. ²⁹Si NMR resonances at -5.8 (SiMe₃) and -142.0 (SiZn) ppm are close to the respective -7.2 and -123.9 ppm observed for (Me₃Si)₃SiZnSi(SiMe₃)₃.⁵⁶

In contrast to the reaction of **2** with ZnCl₂, analogous reactions with zirconocene and hafnocene dichlorides gave compounds **18** and **19** with six-membered rings (Scheme 7). At first glance, this is not unexpected. However, our previous attempts to react Cp₂MCl₂ (M = Zr, Hf) with an oligosilanyl 1,5-diide caused eventual formation of M(III) complexes.¹⁷ If we would envision a similar course as for the previous reaction, we would have expected that compound **4** would form in the reaction by reductive elimination from **18** and **19**. Although it is not quite clear why compounds **18** and **19** are stable toward the elimination process, it seems likely that the ring strain of compound **4** is higher than that of 1,1,2,2-tetrakis(trimethylsilyl)hexamethylcyclopentasilane. The reason for this increased strain seems to be the enhanced tendency of the Si-O-Si unit to acquire angles larger than tetrahedral.

²⁹Si NMR chemical shifts of silylated zirconocenes and hafnocenes typically are much deshielded compared to the respective silanides. For structurally related 1-zircona- and 1-hafna-2,2,5,5-tetrakis(trimethylsilyl)tetramethylcyclopentasilanes,¹ values of -65.2 and -52.2 ppm, respectively, were observed. The resonances for **18** (-71.5 ppm) and **19** (-45.7 ppm) are similar, but the difference between the two metals is more pronounced.

Crystal Structure Analysis. The molecular structure of **4** was determined using single crystal XRD analysis (Figure 1).

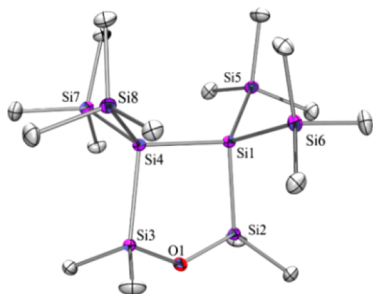


Figure 1. Molecular structure of **4** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in deg). O(1)–Si(2) 1.6472(11), O(1)–Si(3) 1.6503(11), Si(1)–Si(6) 2.3576(6), Si(1)–Si(5) 2.3616(6), Si(1)–Si(2) 2.3688(6), Si(1)–Si(4) 2.3887(6), Si(3)–Si(4) 2.3670(6), Si(2)–O(1)–Si(3) 132.37(7), Si(2)–Si(1)–Si(4) 97.10(2), O(1)–Si(2)–Si(1) 105.58(4), Si(3)–Si(4)–Si(1) 97.18(2).

The five-membered ring is almost planar (sum of angles is 537°) which is caused by a large Si–O–Si angle of 132.4° (Table 2). As a consequence of the planar arrangement, the Me₃Si–Si–Si–SiMe₃ torsional angles are small (16.2° and 17.0°), causing some steric interaction between the vicinal trimethylsilyl groups. The Si(1)–Si(4) distance is therefore slightly elongated (2.3887(6) Å).

Although compound **6** contains an eight-membered ring, in the solid state, a fairly wide Si–O–Si angle of 153.7° causes

Table 2. Selected Structural Data Derived by Single Crystal XRD Analysis of Compounds **1**, **4**, **6**, **14**, **17**, **18**, and **19**

	$d_{\text{Si-SiMe}_3}$ [Å]	$d_{\text{Si-O}}$ [Å]	$d_{\text{Si-E}}$ [Å]	$\angle_{\text{Si-O-SiO}}$ [deg]
1 ^a	2.358(2)	1.628(6)	n.a.	149.5(5)
4	2.3533(7)– 2.3616(6)	1.647(1)– 1.650(1)	n.a.	132.37(7)
6	2.3466(8)– 2.3466(9)	1.630(1)– 1.634(1)	n.a.	153.68(9)
14	2.350(1)	1.640(2)– 1.663(2)	n.a.	143.8(1)
17	2.343(4)– 2.358(3)	1.627(6)– 1.644(6)	2.358(2)– 2.380(2)	155.2(4)/ 156.9(4)
18	2.367(1)– 2.383(1)	1.652(2)– 1.653(2)	2.820(1)– 2.824(1)	139.3(2)
19	2.373(1)– 2.385(1)	1.651(2)– 1.653(2)	2.7942(8)– 2.7990(8)	138.6(1)

^aData taken from ref 33.

the molecular structure (Figure 2) to engage in a conformation that is similar to a six-membered ring chair conformer.

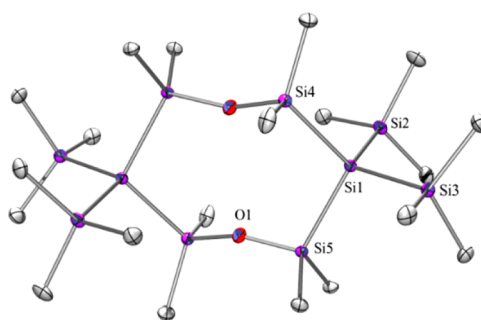


Figure 2. Molecular structure of **6** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in deg). Si(1)–Si(4) 2.3428(7), Si(1)–Si(2) 2.3465(7), Si(1)–Si(3) 2.3491(7), Si(1)–Si(5) 2.3560(7), Si(2)–C(1) 1.8739(19), O(1)–Si(4A) 1.6300(12), Si(4)–Si(1)–Si(2) 109.66(3), Si(4)–Si(1)–Si(3) 113.23(3), Si(2)–Si(1)–Si(3) 110.58(3), Si(4)–Si(1)–Si(5) 105.39(2), Si(2)–Si(1)–Si(5) 109.54(2), Si(3)–Si(1)–Si(5) 108.27(3), Si(4A)–O(1)–Si(5) 153.68(8).

Compounds similar to **14** are not abundant. The structurally related 1,4-dioxaoctamethylcyclohexasilane was prepared by hydrolysis of 1,2-dichlorotetramethyldisilane⁶¹ a long time ago, and its structure was determined by XRD methods more recently.⁶² The structure is quite similar to that of **14** (Figure 3). For both compounds, rather flat rings were observed and Si–O bond distances and Si–O–Si angles of both compounds are quite similar.

The molecular structure of **17** (Figure 4) features a 12-membered ring, which, due to almost linear Si-Zn-Si and Si-O-Si units, can be regarded as something like an eight-membered ring with very long Si-Zn-Si and long Si-O-Si edges. Its conformation resembles a twisted boat. Si–Zn distances between 2.352(2) and 2.380(2) Å are clearly longer than found for (Me₃Si)₃SiZnSi(SiMe₃)₃ which might be caused by the eclipsed arrangement of the Si(SiMe₃)₂ units attached to zinc.

Single crystal structure analysis was performed also on complexes **18** (Figure 5) and **19** (Figure 6). As expected, molecular structures are similar to those of the related zircona- and hafnacyclopentasilanes.¹ Due to the larger ring size, the Si–M–Si angles of 103.17(3)° and 101.89(2)° for **18** and **19**,

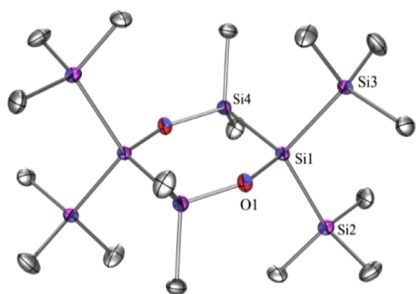


Figure 3. Molecular structure of **14** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in deg). Si(1)–O(1) 1.664(2), Si(1)–Si(3) 2.3500(11), Si(1)–Si(2) 2.3504(11), Si(1)–Si(4) 2.3948(13), Si(2)–C(1) 1.869(3), Si(4)–O(1A) 1.640(2), Si(3)–Si(1)–Si(2) 112.12(4), Si(3)–Si(1)–Si(4) 111.67(4), Si(2)–Si(1)–Si(4) 111.76(4), Si(4A)–O(1)–Si(1) 143.77(14).

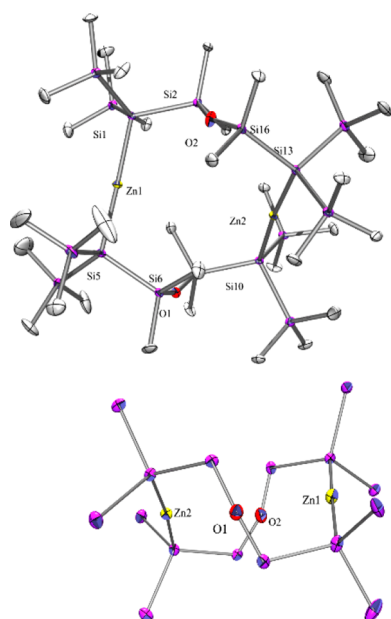


Figure 4. Top: molecular structure of **17** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. Bottom: ring conformation without methyl groups (bond lengths in Å, angles in deg). Zn(1)–Si(1) 2.358(2), Zn(1)–Si(5) 2.373(2), Zn(2)–Si(13) 2.376(2), Zn(2)–Si(10) 2.380(2), Si(1)–Si(2) 2.345(3), Si(1)–Si(3) 2.346(3), Si(2)–O(2) 1.630(6), Si(2)–C(2) 1.861(8), Si(6)–O(1) 1.644(5), Si(9)–O(1) 1.641(5), Si(16)–O(2) 1.626(6), Si(1)–Zn(1)–Si(5) 175.90(8), Si(13)–Zn(2)–Si(10) 174.33(8), Si(2)–Si(1)–Si(3) 106.87(10), Si(2)–Si(1)–Si(4) 113.65(10), Si(3)–Si(1)–Si(4) 110.70(11), Si(9)–O(1)–Si(6) 155.2(4), Si(16)–O(2)–Si(2) 156.9(4).

respectively, are widened compared to the 97.70(6)° and 96.42(4)° of the related metallacyclopentasilanes. Si–Zr bond distances of 2.8197(9) and 2.8237(10) Å are slightly shorter than those of the zirconacyclopentasilane (2.826(2)/2.850(2) Å),¹ and the same is true for the Si–Hf bond distances of 2.7943(8) and 2.7990(8) Å (hafnacyclopentasilane: 2.791(1)/2.826(2) Å). Comparison of the ring conformations of **18** and **19** to those of the related zircona- and hafnacyclopentasilanes¹ reveals that, despite of the fact that Si2 and Si3 are naturally further apart, the conformation is nearly identical.

The Si–O–Si angle of hexamethyldisiloxane has a calculated value of 156.7° with a very small bending potential.^{35,36} The

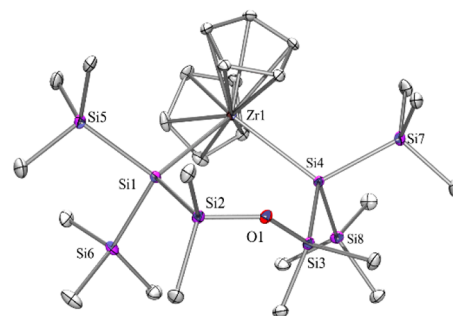


Figure 5. Molecular structure of **18** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in deg). Zr(1)–Si(1) 2.8197(9), Zr(1)–Si(4) 2.8237(10), Si(1)–Si(2) 2.3736(12), Si(1)–Si(5) 2.3817(13), Si(2)–O(1) 1.651(2), Si(2)–C(11) 1.869(3), Si(3)–O(1) 1.653(2), Si(3)–Si(4) 2.3723(12), Si(1)–Zr(1)–Si(4) 103.17(3), Si(2)–Si(1)–Zr(1) 105.49(4), Si(3)–Si(4)–Zr(1) 104.14(4), Si(2)–O(1)–Si(3) 139.26(14).

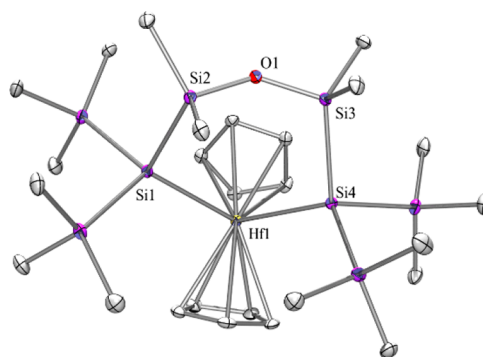


Figure 6. Molecular structure of **19** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in deg). Hf(1)–Si(4) 2.7943(8), Hf(1)–Si(1) 2.7990(8), O(1)–Si(2) 1.6510(18), O(1)–Si(3) 1.6534(18), Si(1)–Si(2) 2.3713(10), Si(1)–Si(5) 2.3726(11), Si(2)–C(12) 1.869(3), Si(4)–Hf(1)–Si(1) 101.89(2), Si(2)–O(1)–Si(3) 138.59(12), Si(2)–Si(1)–Hf(1) 105.49(3), Si(3)–Si(4)–Hf(1) 106.57(3).

angles in the starting material **1** (149.5°), in the big rings of **6** (153.7°), and of **17** (155.2°) are close to this number. For the six-membered rings of **14**, **18**, and **19**, the angles are diminished to 138.6–143.8° and once further to a value of 132.4° for the five-membered ring in **4**. As the hyperconjugative effect depends on angular bending, a diminished hyperconjugation in the six- and five-membered rings can be assumed.^{35,36}

CONCLUSION

The current work continues our studies of the transformation of siloxane **1** to higher oligosiloxanes and illustrates the use of these compounds as ligands for metal complexes. Utilizing **1**, we could demonstrate that cyclic and bicyclic oligosilanes with one or more siloxane units can be prepared. Most of these compounds still contain peripheral trimethylsilyl units and thus can be converted to synthetic building blocks by simple reaction with potassium *tert*-butoxide.

Reactions of the siloxane containing dipotassium oligosilanylene diide **2** with magnesium and zinc halides proceeded smoothly, but for both metals, no interaction with the siloxane oxygen was detected. Somewhat unexpectedly, reactions of **2**

with zirconocene and hafnocene dichlorides occurred to the respective 1-metalla-4-oxacyclohexasilanes. We initially assumed that the latter compounds would undergo reductive elimination to form an oxacyclopentasilane. A likely reason for the stability of the 1-metalla-4-oxacyclohexasilanes is ring strain in the potential reaction product caused by a strong tendency of Si–O–Si units to acquire larger than tetrahedral angles. The synthesized metallaoxacyclosilanes as well as the oxacyclo- and bicyclosilanes exhibit structural features that are different from isostructural homocyclo- and bicyclosilanes, which is mostly caused by Si–O–Si angles significantly larger than the corresponding Si–SiMe₂–Si angles.

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. Solvents were dried using a column based solvent purification system.⁶³ 1,3-Bis[tris(trimethylsilyl)silyl]-1,1,3,3-tetramethyldisiloxane (**1**) and 1,3-bis[potassiobis(trimethylsilyl)silyl]-1,1,3,3-tetramethyldisiloxane (**2**) were prepared according to previously published procedures.³³ All other chemicals were obtained from different suppliers and used without further purification.

¹H (300 MHz), ¹³C (75.4 MHz), and ²⁹Si (59.3 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer and are referenced to tetramethylsilane (TMS) for ¹H, ¹³C, and ²⁹Si. If not noted otherwise, the used solvent was C₆D₆ and samples were measured at rt. In the case of reaction samples, a D₂O capillary was used to provide an external lock frequency signal. To compensate for the low isotopic abundance of ²⁹Si, the INEPT pulse sequence^{64,65} was used for the amplification of the signal for some of the spectra.

Elemental analyses were carried out using a Heraeus VARIO ELEMENTAR instrument. For a number of compounds, obtained elemental analysis showed too low carbon values, which is a typical problem for these compounds likely caused by silicon carbide formation during the combustion process. Multinuclear NMR spectra (¹H, ¹³C, ²⁹Si) of these compounds are presented in the Supporting Information (SI) as proof of purity.

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 K α radiation (0.71073 Å). The data were reduced to F² and corrected for absorption effects with SAINT⁶⁶ and SADABS,^{67,68} respectively. The structures were solved by direct methods and refined by full-matrix least-squares method (SHELXL97).⁶⁹ If not noted otherwise, all non-hydrogen atoms were refined with anisotropic displacement parameters and all hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles. Crystallographic data (excluding structure factors) for the structures of compounds **4**, **6**, **14**, **17**, **18**, and **19** reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC- 1818448 (**4**), 1853659 (**6**), 1853663 (**14**), 1853662 (**17**), 1853660 (**18**), and 1853661 (**19**). The 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 WINGX⁷⁰ and rendered using POV-Ray 3.6.⁷¹

2,2,5,5-Tetramethyl-3,3,4,4-tetrakis(trimethylsilyl)-1-oxacyclopentasilane (4**).** From a solution of oligosilanylene diide **2** (1.59 mmol) in THF (5 mL), the solvent was removed in vacuum and replaced by toluene (5 mL). To this solution, 1,2-dibromoethane (1.65 mmol) in pentane (10 mL) was added dropwise, whereupon the decolorization and precipitation of a salt occurred. The solvent was removed in vacuum and the residue extracted with pentane three times. Crystallization from a concentrated solution at –37 °C gave **4** (0.703 g, 92%) as colorless crystals. Mp.: 144–146 °C. NMR (δ in ppm): ¹H: 0.46 (s, 12H, SiMe₂), 0.35 (s, 36H, SiMe₃). ¹³C: 6.3

(SiMe₂), 3.9 (SiMe₃). ²⁹Si: 20.9 (Me₂SiO), –9.6 (SiMe₃), –132.2 (Si_q). Anal. Calcd for C₁₆H₄₈O₂Si₈ (481.24): C 39.93, H 10.05. Found C 37.09, H 10.20.

In the case of using a slight excess of 1,2-dibromoethane, the formation of 1,3-bis[bromobis(trimethylsilyl)silyl]tetramethyldisiloxane (**5**) is observed as a side product, which can be converted into **4** by addition of potassium graphite (C₈K). Selective formation of **5** can be achieved when adding **2** to a solution containing three-fold excess of 1,2-dibromoethane. **5**: NMR (δ in ppm, toluene-D₂O): ²⁹Si: 6.9 (SiO), –13.0 (SiMe₃), –28.8 (SiBr).

3,7-Dioxa-1,1,5,5-tetrakis(trimethylsilyl)octamethylcyclooctasilane (6**).** A mixture of **1** (10.0 g, 15.9 mmol) and ^tBuOK (3.66 g, 32.5 mmol) in THF (20 mL) was stirred for 12 h at rt. After complete conversion to **2** (checked by ¹H and ²⁹Si spectroscopic analysis of a reaction sample), THF was removed in vacuum and replaced by toluene (8 mL). This solution was added dropwise to a solution of 1,3-dichlorotetramethyldisiloxane in toluene (10 mL). After 3 h, the solvent was removed in vacuum from the orange solution. The residue was extracted with three portions of pentane and the extract filtered over Celite. After concentrating the volume of the solution, compound **6** was obtained as colorless crystals (4.59 g, 47%) by crystallization at –37 °C. Crystals suitable for crystallographic analysis were obtained by a further crystallization step from toluene. Mp.: 181–182 °C. NMR (δ in ppm): ¹H: 0.46 (s, 24H, SiMe₂), 0.30 (s, 36H, SiMe₃). ¹³C: 8.5 (SiMe₂), 3.2 (SiMe₃). ²⁹Si: 11.6 (SiO), –11.2 (SiMe₃), –135.2 (Si_q). Anal. Calcd for C₂₀H₆₀O₂Si₁₀ (613.55): C 39.15, H 9.86. Found C 37.59, H 9.82.

Dipotassium 3,7-Dioxa-1,5-bis(trimethylsilyl)octamethylcyclooctasilanyl-1,5-diide-(THF)_x (7**).** A mixture of dioxacyclooctasilane **6** (250 mg, 0.41 mmol) and ^tBuOK (94 mg, 0.84 mmol) in THF (2 mL) was stirred at ambient temperature for 12 h. Removal of solvent gives the product in quantitative yield as a brownish solid. NMR (THF/D₂O-capillary, δ in ppm): ²⁹Si: 23.3, –9.6, –190.7. NMR (C₆D₆-THF (a very small amount of THF was added as the product is nearly insoluble in C₆D₆)): ¹H: 3.53 (THF), 1.55 (THF), 0.47 (s, 24H, SiMe₂), 0.24 (s, 18H, SiMe₃). ¹³C: 67.9 (THF), 25.9 (THF), 11.8 (SiMe₂), 6.8 (SiMe₃). ²⁹Si: 24.7 (SiO), –9.9 (SiMe₃), –188.0 (SiK).

3,7-Dioxa-1,5-bis(trimethylsilyl)octamethylbicyclo[3.3.0]-octasilane (8**).** A mixture of dioxacyclooctasilane **6** (360 mg, 0.59 mmol) and ^tBuOK (135 mg, 1.20 mmol) in THF (5 mL) was stirred at ambient temperature for 12 h. After almost complete removal of THF, toluene (5 mL) was added and then a solution of 1,2-dibromoethane (119 mg, 0.63 mmol) in pentane (5 mL) was added dropwise, whereupon a white precipitate was observed. After 15 min, the solvents were removed in vacuum and the remaining residue was extracted with three portions of pentane (4–5 mL each). Evaporation of the solvent gave product **8** and some oligomeric byproducts (0.257 g) as a colorless oil. NMR (C₆D₆, δ in ppm): ¹H: 0.46 (s, 12H, SiMe₂), 0.42 (s, 12H, SiMe₂), 0.31 (s, 18H, SiMe₃). ¹³C: 6.5 (SiMe₂), 5.6 (SiMe₃), 2.8 (SiMe₃). ²⁹Si: 22.2 (SiO), –10.0 (SiMe₃), –132.9 (Si_q). Anal. Calcd for C₁₄H₄₂O₂Si₈ (467.17): C 35.99, H 9.06. Found C 35.06, H 8.99.

3,7,10-Trioxa-1,5-bis(trimethylsilyl)octamethylbicyclo[3.3.3]undecasilane (9**).** A solution of dipotassium 3,7-dioxacyclooctasilanyl-1,5-diide **7** (obtained from **6** (470 mg, 0.77 mmol) and ^tBuOK (176 mg, 1.57 mmol)) in THF (3 mL) and pentane (3 mL) was added dropwise to a solution of 1,3-dichlorotetramethyldisiloxane (156 mg, 0.77 mmol) in pentane (8 mL). Immediately, the formation of a white precipitate was observed. After complete conversion (detected by NMR spectroscopy), the solvent was removed in vacuum, followed by extraction of the residue with pentane, filtration over Celite, and evaporation of the compound was obtained as a colorless oil. Dissolving the oil in acetone and slow evaporation eventually gave **9** (376 mg) as colorless crystalline blocks, still contaminated with a small amount of oligomeric byproduct. Mp.: 205–208 °C. NMR (δ in ppm): ¹H: 0.48 (s, 36H, SiMe₂), 0.17 (s, 18H, SiMe₃). ¹³C: 7.6 (SiMe₂), 2.2 (SiMe₃). ²⁹Si: 10.9 (SiO), –15.3 (SiMe₃), –136.2 (Si_q).

3,7,10-Trioxaocetamethylbicyclo[3.3.3]undecasilyl-1,5-dipotassium(DME)_x (10). A solution of bicyclosilane **9** (227 mg, 0.38 mmol) and ^tBuOK (87 mg, 0.78 mmol) in DME (3 mL) was stirred for 12 h. After removal of the solvent in vacuum, product **10** was isolated in quantitative yield as a yellowish semisolid. NMR (DME/D₂O-capillary, δ in ppm): ¹H: 0.10 (s, 36H, SiMe₂), ²⁹Si: 15.5 (SiMe₂), -186.7 (SiK).

1,3-Bis[bis(trimethylsilyl)silyl]tetramethyldisiloxane (11). A solution of **2** (3.19 mmol) in THF (2 mL) was added dropwise to a H₂SO₄ (0.5 M)/ice/Et₂O mixture. The aqueous layer was extracted with Et₂O (3 × 5 mL) and the combined organic phases were dried with Na₂SO₄. After evaporation of the solvent, dihydrosilane **11** (1.36 g, 88%) was obtained as a colorless oil. NMR (C₆D₆, δ in ppm): ¹H: 2.57 (s, 2H, ¹J_{H-Si} = 154 Hz, SiH), 0.45 (s, 12H, SiMe₂), 0.28 (s, 36H, SiMe₃). ¹³C: 7.0 (SiMe₂), 2.1 (SiMe₃). ²⁹Si: 11.9 (SiO), -12.6 (SiMe₃), -116.5 (SiH). Anal. Calcd for C₁₆H₅₀O₈Si₈ (483.26): C 39.77, H 10.43. Found C 38.43, H 10.59.

1,3-Bis[chlorobis(trimethylsilyl)silyl]tetramethyldisiloxane (12). A solution of disiloxane **11** (1.36 g, 2.81 mmol) in CCl₄ (12 mL) was stirred at rt for 1 week. All volatiles were removed in vacuum, and dichlorodisiloxane **12** (1.53 g, 98%) was obtained as a colorless oily liquid. NMR (C₆D₆, δ in ppm): ¹H: 0.45 (s, 12H, SiMe₂), 0.25 (s, 36H, SiMe₃). ¹³C: 4.3 (SiMe₂), 0.6 (SiMe₃). ²⁹Si: 5.9 (SiMe₂), -14.9 (SiMe₃), -19.7 (SiCl). Anal. Calcd for C₁₆H₄₈O₈Si₈Cl₂ (552.14): C 34.81, H 8.76. Found C 33.75, H 8.73.

2,5-Dioxa-1,1,4,4-tetrakis(trimethylsilyl)tetramethylcyclohexasilane (14). After stirring a mixture of dichlorodisiloxane **12** (1.33 g, 2.41 mmol) and diethylamine (1.76 g, 24.1 mmol) in toluene (25 mL) for 1 week, complete conversion to the diaminodisiloxane was detected by NMR spectroscopy. All volatiles were removed in vacuum, the residue was extracted with pentane (3 × 6 mL), and filtered over Celite. Evaporation of the solvent gave raw diaminodisiloxane **13** (1.06 g, 70%) as a yellowish oil. (²⁹Si: 8.4 (SiMe₂), -12.3 (SiMe₃), -18.5 (SiN)). Then over a solution of **13** (86 mg, 0.16 mmol) in Et₂O (1 mL) carefully a layer of MeOH (3 mL) was placed. By slow evaporation of the solvent mixture, dioxacyclohexasilane **14** (39 mg, 49%) was obtained as colorless crystals. Mp.: 158–160 °C. NMR (C₆D₆, δ in ppm): ¹H: 0.36 (s, 12H, SiMe₂), 0.28 (s, 36H, SiMe₃). ¹³C: 5.6 (SiMe₂), -0.4 (SiMe₃). ²⁹Si: 1.6 (OSiMe₂), -7.0 (OSi), -16.9 (SiMe₃). Anal. Calcd for C₁₆H₄₈O₂Si₈ (497.24): C 38.65, H 9.73. Found C 37.99, H 9.69.

3,7-Dioxa-1,5-bis(trimethylsilyl)-9-ytterbaocetamethylbicyclo[3.3.1]nonasilane (15). To a suspension of YbI₂·(THF)₂ (140 mg, 0.25 mmol) in DME (1 mL), a solution of dipotassium cyclooctasilandiide **7** (obtained from **6** (150 mg, 0.24 mmol) and ^tBuOK (56 mg, 0.50 mmol)) in DME (1 mL) was added dropwise, causing immediate orange-brown colorization and formation of a precipitate. After stirring for 15 min, the solvent volume was reduced by 50% and the residue was extracted with pentane (3 × 5 mL) and filtered over Celite. After 24 h, complex **15** (55 mg, 32%) was isolated as crystalline orange plates (55 mg). Mp.: 160–162 °C. NMR (DME/D₂O, δ in ppm): ¹H: 0.30 (s, 12H, SiMe₂), 0.16 (s, 12H, SiMe₂), 0.03 (s, 18H, SiMe₃). ¹³C: 10.8 (SiMe₂), 10.3 (SiMe₂), 5.6 (SiMe₃). ²⁹Si: 20.6 (SiO), -8.8 (SiMe₃), -155.7 (SiYb).

4-Oxa-2,2,6,6-tetrakis(trimethylsilyl)tetramethylmagnesiacyclohexasilane(DME) (16). A solution of **2** (freshly prepared from disiloxane **1** (157 mg, 0.250 mmol), KO^tBu (57 mg, 0.50 mmol) in DME (4 mL)) was evaporated to dryness. The orange residue was dissolved in Et₂O (4 mL) and added dropwise to a stirred solution of MgBr₂·(Et₂O) (65 mg, 0.25 mmol) in Et₂O (4 mL). The white suspension was stirred for another 30 min. Quantitative formation of **16** was detected after 90 min by NMR spectroscopy of an aliquot sample. NMR (D₂O-cap/Et₂O, δ in ppm): ¹H: 3.32 (ether), 1.05 (ether), 0.22 (s, 12H, SiMe₂), 0.13 (s, 36H, SiMe₃). ¹³C: 65.2 (ether), 14.6 (ether), 8.6 (SiMe₂), 4.7 (SiMe₃). ²⁹Si: 15.2 (SiMe₂), -7.3 (SiMe₃), -166.9 (SiMg). For the purpose of further reaction, the obtained solution of **16** can be used as such. For analytical characterization, all volatiles were evaporated under reduced pressure, the colorless residue was extracted with pentane (2 × 5 mL), and the combined extracts evaporated under vacuum, yielding **16** as a

colorless, microcrystalline solid (61 mg, 41%). The title compound can be crystallized from concentrated solutions in pentane at -35 °C. NMR (C₆D₆, δ in ppm): ¹H: 2.97 (s, 6H, DME), 2.58 (bs, 4H, DME), 0.66 (s, 6H, SiMe₂), 0.66 (s, 6H, SiMe₂), 0.43 (s, 18H, SiMe₃), 0.43 (s, 18H, SiMe₃). ¹³C: 69.6 (DME), 59.4 (DME), 9.9 (SiMe₂), 5.8 (SiMe₃). ²⁹Si: 15.2 (SiMe₂), -7.8 (SiMe₃), -166.7 (SiMg).

4,10-Dioxa-2,2,6,6,8,8,12,12-octakis(trimethylsilyl)octamethyl-1,7-dizincacyclododecasilane (17). To a solution of compound **2** (obtained from **1** (200 mg, 0.32 mmol) and ^tBuOK (74 mg, 0.66 mmol)) in THF (3 mL), a solution of ZnCl₂ in THF (2 mL) was added dropwise. The previously dark orange solution turned pale yellow, and after 12 h, the solvent was removed in vacuum and the residue extracted with pentane (3 × 4 mL). After filtration over Celite, the product was crystallized at -37 °C to give **17** (132 mg, 76%) as colorless needles. Mp.: 222–223 °C. NMR (C₆D₆, δ in ppm): ¹H: 0.62 (s, 24H, SiMe₂), 0.41 (s, 72H, SiMe₃). ¹³C: 9.7 (SiMe₂), 4.6 (SiMe₃). ²⁹Si: 14.0 (SiO), -8.7 (SiMe₃), -125.6 (SiZn). NMR (THF, D₂O-capillary, δ in ppm): ¹H: 0.32 (s, 12H, SiMe₂), 0.21 (s, 36H, SiMe₃). ²⁹Si: 16.3 (SiO), -5.8 (SiMe₃), -142.0 (SiZn). Anal. Calcd for C₃₂H₉₆O₂Si₁₆Zn₂ (1093.24): C 35.16, H 8.85. Found C 34.88, H 8.42.

1,1-Dicyclopentadienyl-4-oxa-2,2,6,6-tetrakis(trimethylsilyl)tetramethylzirconacyclohexasilane (18). To a suspension of zirconocene dichloride (47 mg, 0.16 mmol) in toluene (2 mL), a solution of **2** (0.16 mmol) in toluene (1 mL) was added dropwise, causing the solution to turn first orange and then deep red. Formation of a precipitate was observed, and after 1 h, complete conversion was detected by NMR spectroscopy. Removal of solvent, extraction of the residue with pentane (3 × 2 mL), filtration over Celite, and slow evaporation of pentane gave **18** (104 mg, 93%) as deep red crystalline blocks. Mp.: 131–132 °C. NMR (δ in ppm): ¹H: 6.28 (s, 10H, Cp), 0.45 (s, 12H, SiMe₂), 0.39 (s, 36H, SiMe₃). ¹³C: 107.9 (Cp), 9.7 (SiMe₂), 6.1 (SiMe₃). ²⁹Si: 18.2 (SiMe₂), -5.6 (SiMe₃), -71.5 (SiZr).

1,1-Dicyclopentadienyl-4-oxa-2,2,6,6-tetrakis(trimethylsilyl)tetramethylhafnacyclohexasilane (19). In an analogous way as described above for the synthesis of **18**, the hafnium compound **19** was obtained using **2** (0.16 mmol) and hafnocene dichloride (60 mg, 0.16 mmol). Crystallization of **19** (0.106 g, 84%) as deep red crystalline blocks was achieved from the pentane extract at -37 °C. Mp.: 180–182 °C. NMR (δ in ppm): ¹H: 6.22 (s, 10H, Cp), 0.49 (s, 12H, SiMe₂), 0.39 (s, 36H, SiMe₃). ¹³C: 108.1 (Cp), 10.0 (SiMe₂), 6.6 (SiMe₃). ²⁹Si: 13.3 (SiMe₂), -4.9 (SiMe₃), -45.7 (SiHf).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00013.

Tabulated crystallographic data for **4**, **6**, **14**, **17**, **18**, and **19**. Mechanistic proposal for the formation of **14** by hydrolysis of **13**. ¹H, ¹³C{¹H}, and ²⁹Si{¹H} INEPT spectra of compounds **4**–**19** (PDF)

Accession Codes

CCDC 1818448 and 1853659–1853663 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.

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