

## VIP Very Important Paper

## Siloxane Coordination Revisited: Si–O Bond Character, Reactivity and Magnificent Molecular Shapes

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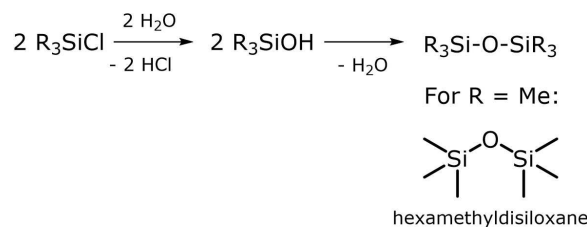
Dedicated to Prof. Robert "Bob" West for his ground-breaking research in silicon chemistry.

Siloxanes have evolved into a multi-million dollar business due to their manifold of commercial and industrial applications. As siloxanes have high hydrophobicity, low basicity, high flexibility and also high chemical inertness in common, their chemistry differs significantly from that of organic ethers. The discovery of organic crown ethers, for instance, is commonly accepted as the birth of synthetic host-guest chemistry. Regarding the chemical properties of siloxanes, cyclic siloxanes which formally resemble silicon analogues of crown ethers, have received considerably less interest in terms of their host-guest chemistry. Hence, only little is known about siloxane coordination

chemistry in the chemical community and the number of published works in this field has been very low till lately. In the last few years, the field has significantly advanced and elegant methods were established to enable the Si–O–Si unit for coordination. This review therefore summarizes the recent developments in the field, recapitulates the historical aspects of siloxane coordination chemistry and describes the specific Si–O bond character with regard to different siloxane linkages. Implications on Si–O bond activation are included and the limits of siloxane coordination are redefined.

## 1. Siloxanes: A Short Introduction

According to the IUPAC compendium of chemical terminology, siloxanes can be understood as hydrides with unbranched or branched chains of alternating silicon and oxygen atoms. This means each silicon atom is separated from its nearest silicon neighbours by single oxygen atoms. The general structure of unbranched siloxanes is  $\text{H}_3\text{Si}(\text{OSiH}_2)_n\text{OSiH}_3$ .<sup>[1]</sup> In the literature, the term siloxane is often used for organosilicon compounds in general. In this respective context, siloxane is an abbreviation for a compound containing silicon, oxygen and alkane. Thus, the general formula  $\text{R}_3\text{Si}(\text{OSiR}_2)_n\text{OSiR}_3$  is more commonly used with  $\text{R}=\text{H}$ , alkyl, aryl. The synthesis of siloxanes is generally based on the hydrolysis of chlorosilanes.<sup>[2a]</sup> Silanols form as intermediate products which eventually condensate to the respective siloxane (Scheme 1). From industrial importance is also the methanolysis of chlorosilane avoiding HCl waste and makes recycling of chloroalkanes possible which is important for preceded *Rochow*-synthesis.<sup>[3]</sup>



**Scheme 1.** General synthesis of siloxanes with hexamethyldisiloxane as a simple example.

Depending on which of the respective chlorosilanes is hydrolysed, (e.g.  $\text{Me}_3\text{SiCl}$ ,  $\text{Me}_2\text{SiCl}_2$ ,  $\text{MeSiCl}_3$  or  $\text{SiCl}_4$ ) different degrees of functionalities are reached (Figure 1: left).<sup>[3]</sup> The obtained structures range from linear (polymeric) over cyclic to cage-like and multidimensional siloxanes (Figure 1: right).

Linear polyorganosiloxanes are the academically and industrially most important siloxanes followed by cyclic diorganosiloxanes. Due to ubiquitous fields of applications, polyorganosiloxanes are nowadays the basis of a multi-million dollar industry.<sup>[4]</sup> Polydimethylsiloxanes (PDMS), for instance, are characterized by greater stability to high temperature and UV radiation in comparison to organic polymers. Furthermore, they have good dielectric properties, are strongly hydrophobic, have nearly no surface tension as well as only little temperature dependence of their physical properties. Hence, polydimethylsiloxanes are used in oils, lubricants, rubbers, sealants, resins, insulators and many more applications.<sup>[2a,3,5,6]</sup> The applications of cyclic dimethylsiloxanes overlap with those of PDMS but to mention some more specific ones, they are used in personal care products, cosmetics, cleaning agents as well as coatings for packaging and paints.<sup>[7]</sup> Silsesquioxanes, with the general formula  $(\text{RSiO}_{3/2})_n$  are frequently used on coatings in electronic

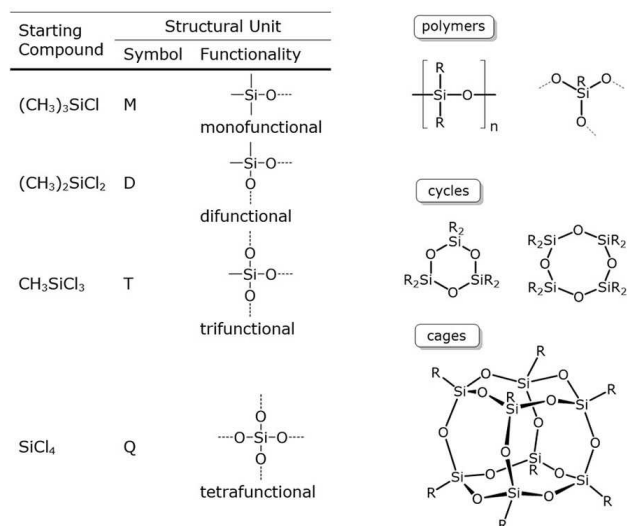
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**Figure 1.** Origin and functionality of siloxane and silicone building-blocks adapted from ref.<sup>[3]</sup> (left) and different siloxane architectures (right): Diorganopolysiloxane (top left), organopolysiloxane (top right), cyclic siloxanes (middle) and silsesquioxane (bottom).

and optical devices but also in cosmetics, ceramics, resins and in general many fields of material sciences.<sup>[8]</sup> As can be seen in Figure 1 on the right, the simplest siloxanes have the same repeating unit and are monofunctional. Chlorosilanes, however, can also be mixed within the siloxane synthesis. This yields silicones which can be understood as compounds in which the siloxane polymer often has different Si–O functionalities. Dependent on the respective functionality, the  $(\text{SiR}_2\text{O})_n$  chain lengths can be adjusted, side groups can be introduced and cross-linking can be established. The material properties of a respective silicone-polymer can thus be substantially fine-tuned.<sup>[3]</sup> The importance of silicones have impacted our modern lives immensely, which is why silicon chemistry is at the highest level of interest. Current research in polysiloxanes is directed,

among other things, towards simple and green synthetic strategies and proceedings in this area were recently highlighted.<sup>[9]</sup>

In this review, the cyclic siloxanes are of special interest. Similar to linear polyorganosiloxanes, cyclic siloxanes are also constituted of the general formula  $(\text{SiR}_2\text{O})_n$ . Systems having rings of alternating silicon and oxygen atoms are generally called cyclosiloxanes.<sup>[11]</sup> The most widespread used cyclosiloxanes are methyl substituted ( $\text{R}=\text{CH}_3$ ) and are also involved in the PDMS synthesis. Due to di-functional building blocks, they are abbreviated as D (with  $\text{D}=\text{Me}_2\text{SiO}$ ). In comparison to the polymeric species, cyclic siloxanes of the  $\text{D}_n$ -type are volatile, which makes a distillation from polymeric species possible. In PDMS synthesis, distilled material is then further processed to a polymer. Strong bases such as KOH or strong acids such as perfluoroalkanesulfonic acids and sulfuric acid are usually used to initiate ring-opening polymerization. This eventually yields clean polymer material.<sup>[3,6]</sup> However, cyclodimethylsiloxanes are obtained upon hydrolysis or methanolysis of  $(\text{CH}_3)_2\text{SiCl}_2$ . In the process of a modern silicon chemistry also novel synthetic protocols have been published. In this context *Cui* for example reported on an NHC-catalysed hydrolytic oxidation of dihydrosilanes.<sup>[10]</sup> Various cyclosiloxanes have been obtained in this way. Traditional and novel synthetic pathways are depicted in Scheme 2.

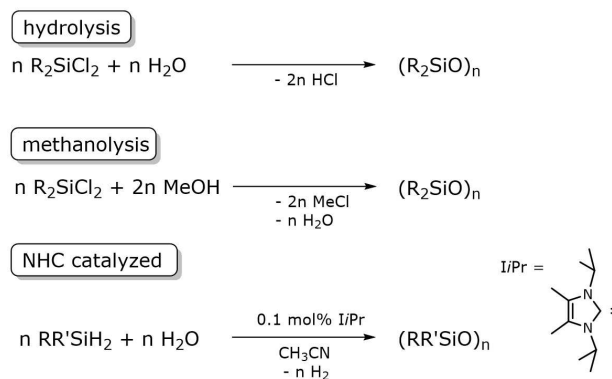
The cyclodimethylsiloxanes can structurally be compared to crown ethers and are formally isoelectronic to ring-silicates.  $\text{D}_n$  ring sizes up to at least  $n=25$  have been reported.<sup>[11,12]</sup>  $\text{D}_6$  for example is a crown-like molecule bearing six oxygen donors and is formally isoelectronic with the ring silicate  $[\text{Si}_6\text{O}_{18}]^{12-}$  (e.g. part of the beryl  $\text{Al}_2\text{Be}_3[\text{Si}_6\text{O}_{18}]^{2a}$  and, especially relevant for this review, also the minerals of the tourmaline group<sup>[2b]</sup>).  $\text{D}_6$  also structurally compares well with [18]crown-6 (Figure 2), since  $\text{C}_2\text{H}_4$  spacers are replaced by  $\text{SiMe}_2$ . Even though these *pseudo-crown ethers*<sup>[13]</sup> termed ligands have been characterized more than twenty years before conventional crown ethers, their host-guest chemistry has hardly been studied.<sup>[14,15]</sup>



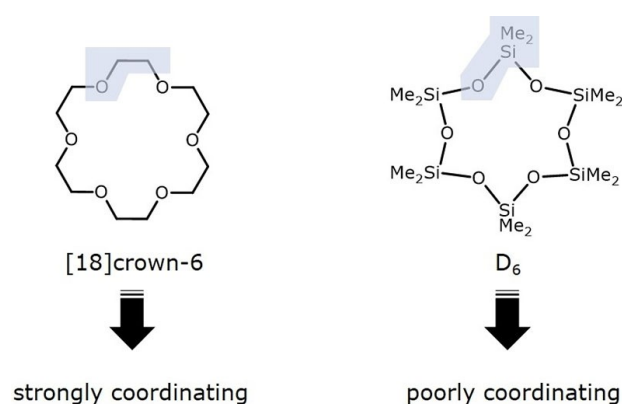
Carsten von Hänisch studied chemistry at the University of Karlsruhe where he graduated in 1994. He joined the group of Prof. Dr. Dieter Fenske for his doctoral research and received his PhD at the end of 1996. After joining the group of Prof. Dr. Matthias Drieß at the Ruhr-Universität Bochum from 1997 to 1998 for a postdoc position, he returned to Karlsruhe and worked as a junior scientist at the Institute of Nanotechnology. He finished his habilitation in 2004 and after working as an independent group leader he has been announced as a full professor at the Philipps-Universität Marburg in 2010 where he is still active. His research focusses on main-group chemistry in the light of semi-conductor materials as well as elusive coordination compounds with a predilection for the elements silicon, phosphorus and arsenic.



Fabian Dankert studied chemistry, movement, and sport science as well as education at the Philipps-Universität Marburg, where he graduated in 2016. In 2015 he joined the von Hänisch group for his thesis regarding the "Staatsexamen" and since 2017 he was working on his doctoral research with focus on siloxane coordination chemistry, Si–O bond activation and templated synthesis. At the end of 2020 he received his PhD. He recently moved to Rostock and joined Christian Hering-Junghans' group as a postdoc.



**Scheme 2.** Traditional synthesis of cyclic and/or polymeric siloxanes vs. NHC-catalysed hydrolytic oxidation of hydrosilanes.



**Figure 2.** Comparison of organic and silicon-based crown ether moieties with six donor atoms. Marked in light blue is the repeating unit which is  $\text{C}_2\text{H}_4\text{O}$  in conventional crown ethers and  $\text{SiMe}_2\text{O}$  in silicon based “pseudo” crown ethers.

Instead, they have, not least due to their water repellent properties, evolved into a completely different research area than host-guest chemistry. Conclusively, many studies were published since the 1960s which have examined the binding properties of Si–O donors in comparison to C–O donors.<sup>[16–30]</sup> Basicity of cyclic and acyclic siloxanes were intensely investigated in terms of hydrogen bonding and proton affinity. Especially IR spectroscopic investigations on hydrogen bonding towards the Si–O–Si linkage had been established as the method of choice.<sup>[16–30]</sup>

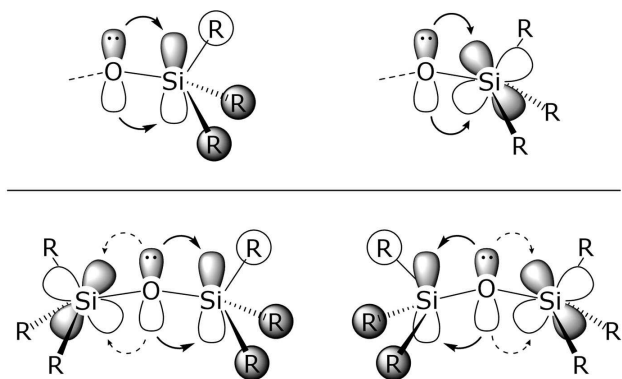
Matching with the material properties of (polymeric) siloxanes, it was found in a number of studies that the electron-donating capacity of the oxygen atom decreases in the sequence  $\text{C–O–C} > \text{C–O–Si} > \text{Si–O–Si}$ .<sup>[16–30]</sup> Even though silicon is a neighbour of carbon in the periodic table, the nature and reactivity of Si–O bonds are obviously different to C–O bonds, especially in terms of coordination and host-guest chemistry. To explain a decreased electron-donating capacity, the Si–O bond has been scrutinized over the years and various explanations have been established. A close look at the Si–O bond is part of the next chapter.

## 2. The Si–O bond: A Look at the Building Block of Siloxanes and Silicates

### 2.1. Hyperconjugation Interactions in Siloxanes

For many years, various effects altering the structural properties and reactivity principles of siloxanes are controversially discussed. Historically, the  $3d$  orbitals at silicon have played a major role. Compared to carbon based systems,  $d$ -orbitals are available to be occupied with electron density forming  $\pi$ -bonding between  $d_\pi$  and  $p_\pi$ -orbitals.<sup>[31–33]</sup> Relevant to siloxane coordination, the occupied  $2p$  orbitals at oxygen have been discussed to donate electron density into the  $3d$  orbital at silicon.<sup>[34,35]</sup> Backbonding then eventually strengthens the Si–O bond and lowers the HOMO energy. Hence, shifting electrons towards metal ions or formation of hydrogen bonds is less favoured and requires weakening of the Si–O bond. This results in limited donor capacities and a lowered basicity. This type of backbonding has been the explanation for a lower basicity of siloxanes for decades, especially in the above-mentioned hydrogen bonding studies.<sup>[16,18–25,27]</sup> Over time, the  $3d$ -orbitals were identified to be too high in energy. Instead, negative hyperconjugation interactions of the type  $p(\text{O}) \rightarrow \sigma^*(\text{Si–R})$  ( $\text{R} = \text{H}$ , alkyl, aryl, ...) were established to justify the lower basicity of siloxanes compared to ethers.<sup>[36–39]</sup> To date these interactions are seen as dominant. Even though they are also present in organic ethers, these interactions are more pronounced in siloxanes. This is especially represented by the structural properties of siloxanes compared to ethers. For instance, the calculated R–O–R angles of DME (DME = dimethylether) and HMDME (HMDME = hexamethyldimethylether) have values of  $112.7^\circ$  and  $127.9^\circ$ , respectively. The C–O single bonds have a value of  $141$  and  $145$  pm respectively which compares well with the sum of the single bond radii of  $142$  pm.<sup>[40a]</sup> In the respective silicon analogues DSE (DSE = disiloxane) and HMDSE (HMDSE = hexamethyldisiloxane), much larger values of  $150.3^\circ$  and  $156.6^\circ$  are found.<sup>[39]</sup> Further, the Si–O bond length is calculated to be  $165$  pm.<sup>[39]</sup> This value is considerably smaller than the sum of covalent radii which predicts a Si–O single bond of  $177$  pm.<sup>[40a]</sup> A correction of the bond length concerning ionic contributions, however, results in a value of  $165$  pm.<sup>[40b]</sup> Hence,  $p(\text{O}) \rightarrow \sigma^*(\text{E–R})$  ( $\text{E} = \text{C}, \text{Si}$ ) backbonding and ionic contributions (see next chapter) dictate the structural behaviour of siloxanes to a larger extent than that of organic ethers. Similar to the backbonding into the  $d$ -orbitals, backbonding into  $\sigma^*(\text{Si–R})$  orbitals causes competition between electron donation towards electrophiles and Si–O bond stabilization. Consequently, the basicity is lowered and the Si–C bonds are simultaneously weakened. Most recent investigations on the Si–O bond have even concluded that both  $p(\text{O}) \rightarrow d(\text{Si})$  and  $p(\text{O}) \rightarrow \sigma^*(\text{Si–R})$  are simultaneously present, therefore altering the structural properties of siloxanes.<sup>[41]</sup> Albeit  $p(\text{O}) \rightarrow d(\text{Si})$  to a much lesser extent. The respective Si–O bond stabilization effects are depicted in Figure 3.

Lately, hyperconjugation interactions have also been investigated for heavier analogues of siloxanes ( $\text{R}_3\text{E}_2\text{O}$  ( $\text{E} = \text{Ge}, \text{Sn}$ ;

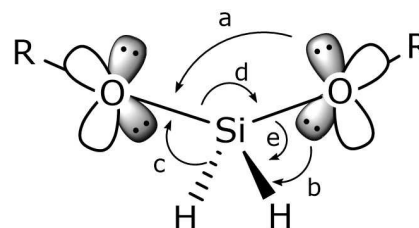


**Figure 3.** Vicinal hyperconjugation interactions in siloxanes involving *d*-Orbitals or the antibonding molecular orbital of the Si–R bonds.  $p(\text{O}) \rightarrow d(\text{Si})$  backbonding (top right),  $p(\text{O}) \rightarrow \sigma^*(\text{Si}-\text{R})$  backbonding ( $\sigma^*_{\text{SiR}}$  depicted as one of the *e*-type orbitals, top left) and both interactions (bottom).

R = alkyl, H).  $p(\text{O}) \rightarrow \sigma^*(\text{E}-\text{R})$  backbonding is also observed here.<sup>[41]</sup> These interactions were predominantly examined in linear siloxanes involving a single oxygen atom. There are, however, substantial differences, when it comes to siloxanes which contain more than one  $\text{SiMe}_2\text{O}$  repeating unit. In this context *Apeloig* and co-workers have discussed the contribution of an anomeric effect, which can alter the conformation of siloxanes. Interactions between geminal substituents at the silicon centre, especially in terms of oxygen substituents, gives further stabilization of certain conformations. The stabilization is in this case characterized by  $p(\text{O}) \rightarrow \sigma^*(\text{Si}-\text{O})$  interactions. In case of  $\text{H}_2\text{Si}(\text{OH})_2$ , these interactions even surpass  $p(\text{O}) \rightarrow \sigma^*(\text{Si}-\text{H})$  backbonding.<sup>[42]</sup> Also *Cypryk* pointed out the importance of  $p(\text{O}) \rightarrow \sigma^*(\text{Si}-\text{O})$  interactions. Contributions from this type of hyperconjugation, among other less significant stabilization effects, reduces the electron density on oxygen significantly.<sup>[43,44]</sup> Especially the polysiloxanes and thus also cyclosiloxanes, benefit from this effect. However, a reduced electron density at oxygen eventually means lower basicity. This is also the main reason why polysiloxanes are stable while polyoxodisilanes  $(-\text{SiR}_2-\text{SiR}_2-\text{O})_n$  are not.<sup>[43]</sup> By implication, disilanyl-bearing cyclosiloxanes are expected to be more basic than conventional cyclosiloxanes (see chapter 3.1 for details). The effects stabilizing a  $\text{SiH}_2\text{O}$  repeating unit in a polymeric siloxane are depicted in Figure 4.

## 2.2. Ionic contributions to Si–O bonding

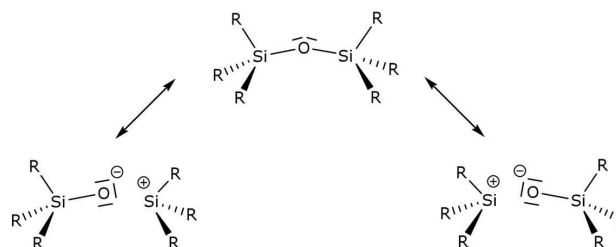
Comparing the electronegativity (=EN) differences of a C–O bond with a Si–O bond, it becomes clear that the Si–O bond is substantially more polarized than the C–O bond ( $\text{EN}_{\text{Allred-Rochow}}: \text{C } 2.50, \text{Si } 1.74 \text{ and } \text{O } 3.50$ ).<sup>[45]</sup> Hence, a lot of studies have been published, which emphasize the ionic character of the Si–O bond. In this context, it is important to mention that the high polarity of the Si–O bond and the accompanying high electron density at the oxygen atom enhance the  $\pi$ -backbonding from the oxygen to the silicon atom. Enough evidence is provided to



**Figure 4.** Strongest interactions contributing to the stability of a  $-\text{O}-\text{SiH}_2-\text{O}-$  fragment. For clarity, only a single representative of each type of interaction is depicted. a)  $p(\text{O}) \rightarrow \sigma^*(\text{Si}-\text{O})$ , b)  $p(\text{O}) \rightarrow \sigma^*(\text{Si}-\text{H})$ , c)  $\sigma(\text{Si}-\text{H}) \rightarrow \sigma^*(\text{Si}-\text{O})$ , d)  $\sigma(\text{Si}-\text{O}) \rightarrow \sigma^*(\text{Si}-\text{O})$ , e)  $\sigma(\text{Si}-\text{O}) \rightarrow \sigma^*(\text{Si}-\text{H})$ .

demonstrate ionic contributions on the structural and reactive properties of siloxanes.<sup>[46–53]</sup> An often used Lewis formula representing this aspect of siloxane bonding is depicted in Scheme 3.

*Gillespie* pointed out, that the electron pairs around oxygen are spatially diffuse and are not readily served for electron donation.<sup>[49,50]</sup> Comprehensive quantum chemical calculations indicate that, the higher the differences in electronegativity between donor atom (=oxygen) and substituents (=X) are, the more spatially diffuse and more spherical the electron pair around oxygen becomes. As the negative charge is increased at oxygen, the positive charge is increased at X. Consequently, the X–O–X bond angle approaches to larger values if  $\text{EN}(\text{X}) < \text{EN}(\text{O})$ , which is caused by electrostatic repulsion between positively polarized X atoms. *Vice versa*, the bond angle approaches smaller values if  $\text{EN}(\text{X})$  is closer to  $\text{EN}(\text{O})$  as the charges at X and O have smaller values. In other words, a sufficiently small  $\Delta(\text{EN})$  consequently supports smaller X–O–X angles and more localized electron density at oxygen.<sup>[49]</sup> The coherence between electronegativity differences and molecular structure can be seen in Table 1. The negative charge on oxygen decreases within the first period from  $\text{Li}_2\text{O}$  to  $(\text{HO})_2\text{O}$ . The same observations are made for the second period as it decreases from  $\text{Na}_2\text{O}$  to  $(\text{H}_2\text{P})_2\text{O}$  indicating an increased covalent character to the bonds. The charge on oxygen is in correlation with the respective electronegativity of the attached atom. Another key factor which determines the ionicity of a respective bond, are the substituents attached to X. An example has been provided for the siloxane linkage (see row ten and eleven in Table 1). Substitution of hydrogen by fluorine polarizes the already polar



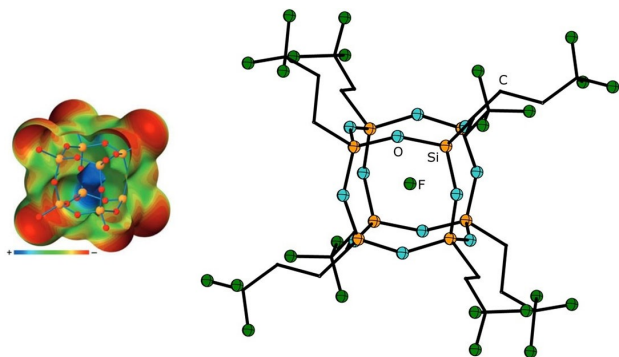
**Scheme 3.** Lewis formula representation of the ionic bond model discussed for the siloxane linkage.

**Table 1.** Atomic charges (q), X–O–X bond angles [°] and X–O atom distances [pm] obtained from quantum chemical calculations. See ref.<sup>[49]</sup> for details.

Period	Molecule	EN(X) <sup>[45]</sup>	q(O)	q(X)	∠X–O–X	X–O
1	Li <sub>2</sub> O	0.97	−1.82	+0.91	180.0	159.6
	(HBe) <sub>2</sub> O	1.47	−1.79	+1.74	180.0	139.6
	(H <sub>2</sub> B) <sub>2</sub> O	2.01	−1.68	+2.27	126.9	135.4
	(H <sub>3</sub> C) <sub>2</sub> O	2.50	−1.29	+0.78	113.9	139.0
	(H <sub>2</sub> N) <sub>2</sub> O	3.07	−0.51	−0.46	109.8	138.9
	(HO) <sub>2</sub> O	3.50	−0.04	−0.62	107.8	136.5
2	Na <sub>2</sub> O	1.01	−1.77	+0.88	180.0	197.3
	(HMg) <sub>2</sub> O	1.23	−1.77	+1.69	180.0	178.2
	(H <sub>2</sub> Al) <sub>2</sub> O	1.47	−1.76	+2.45	180.0	167.1
	(H <sub>3</sub> Si) <sub>2</sub> O	1.74	−1.72	+3.05	148.3	162.1
	(F <sub>3</sub> Si) <sub>2</sub> O	1.74	−1.68	+3.13	162.2	158.3
	(H <sub>2</sub> P) <sub>2</sub> O	2.06	−1.59	+0.75	129.8	163.6

Si–O bond even more leading to even larger Si–O–Si angles and shorter Si–O atom distances.<sup>[49]</sup> Over time, the exceptionally high ionicity of Si–O and Si–R bonds gave access to a couple of interesting compounds in the field of molecular inorganic chemistry and material sciences.<sup>[54,55]</sup>

One example where the ionic Si–O bond character is nicely illustrated, is the occupation of silsesquioxanes with F<sup>−</sup> hosts.<sup>[55–57]</sup> From the molecular electrostatic potential open surface of the hydroxy-substituted parent silsesquioxane POSS (POSS = polyoctahedralsilsesquioxane) it can be seen that the inner core of the cube has an overall positive potential due to the exceptional high polarization of the Si–O bonds (Figure 5: left).<sup>[58]</sup> In such a cube, the oxygen atoms are located above the edges and the electron density on oxygen is directed out of the cage. Thus, tetrel bonding (e.g. by F<sup>−</sup>) is favourable in the centre of the cube (Figure 5: right). The incorporation of F<sup>−</sup> hosts is supported by an EWG (EWG = electron withdrawing group; e.g. CN, CF<sub>3</sub> or in general fluoroalkane) substitution at Si.<sup>[56,57]</sup> A more ionic Si–O linkage is achieved in this way as was also demonstrated for above mentioned (F<sub>3</sub>Si)<sub>2</sub>O. In terms of investigating cation rather than anion binding *Passmore* and *Rautiainen* performed DFT calculations on 1,3-dimethylsiloxane



**Figure 5.** Molecular electrostatic potential open surface of a hydroxyl substituted polyoctahedralsilsesquioxane (left)<sup>[58,59]</sup> and crystal structure of a caged anion in [N(nBu)<sub>4</sub>][F@Si<sub>8</sub>O<sub>12</sub>(R)<sub>8</sub>] (R = 3,3,3-trifluoropropyl, right).<sup>[56]</sup> Atoms are displayed isotropically and with arbitrarily atom radii and carbon atoms are depicted as wires/sticks for clarity. Left image reproduced with permission. Copyright Wiley-VCH GmbH, see reference.<sup>[59]</sup>

(O(SiH<sub>2</sub>Me)<sub>2</sub>), diethyl ether (OEt<sub>2</sub>) and their respective metal complexes with Li<sup>+</sup> and Ag<sup>+</sup>.<sup>[52]</sup>

According to QTAIM (QTAIM = quantum theory of atoms in molecules) analysis the respective complexes have been investigated regarding gas phase stability, charge distribution and energy penalty due to conformational change. Intuitively, the electron density on oxygen of 1,3-dimethylsiloxane turned out to be higher compared to that at oxygen of diethyl ether. Gas phase reactions of the respective ligands with Li<sup>+</sup> and Ag<sup>+</sup>, however, revealed that the metal binding of diethyl ether is favoured by approximately 30 kJ mol<sup>−1</sup> over that of O(SiH<sub>2</sub>Me)<sub>2</sub>. Under consideration of various anions such as I<sup>−</sup>, [SbF<sub>6</sub>]<sup>−</sup> and [Al<sup>IV</sup>]<sup>−</sup> ([Al<sup>IV</sup>]<sup>−</sup> = [Al{OC(CF<sub>3</sub>)<sub>3</sub>]<sub>4</sub>]<sup>−</sup>) these values are even higher. QTAIM analysis indicates that the change of charge at the etheric oxygen atom becomes larger than in 1,3-dimethylsiloxane upon complexation of Li<sup>+</sup>. Hence, the ether is easier to polarize and is initiated more easily for metal binding. The already polar Si–O bond is considerably more difficult to polarize. In this context, the deformation energy of the respective ligand upon complexation plays a major role. Energy decomposition analysis (=EDA) indicates that the “energy penalty”, which results through conformational change is considerably larger in the siloxane than in the corresponding ether. The reason for this is the high polarization of the silicon atoms resulting in M<sup>+</sup>...Si<sup>δ+</sup> repulsive interactions. Overall, to achieve the same level of interaction with electrophiles, a siloxane has to pay a higher energy penalty in the form of structural changes.<sup>[52]</sup>

M<sup>+</sup>...Si<sup>δ+</sup> repulsive interactions have later also been reported for metal complexes of cyclic siloxanes by the same research group. Similar to the above mentioned model system, a weaker electrostatic attraction of D<sub>6</sub> toward M<sup>+</sup> (M = Li, Ag) is found in comparison to [18]crown-6. The reduced ability to incorporate the metal ions is attributed to the repulsion between positively charged silicon atoms and the metal ions.<sup>[53]</sup> Attractive and repulsive interactions of ethers and siloxanes with metal centres are depicted in Figure 6.

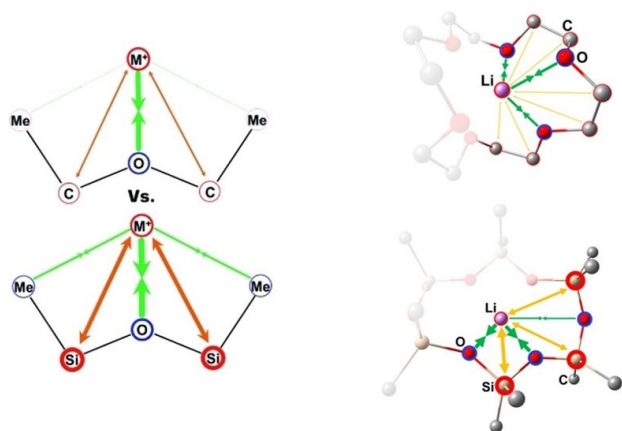
### 2.3. The Si–O–Si Angle as an Important Parameter Regarding Basicity

The previous chapters have shown that the relationship between the basicity of the oxygen atoms in siloxanes and the characteristics of the Si–O bond is complex. Both covalent and ionic aspects play an important role. Hence, it is necessary to describe the Si–O bond by means of various resonance structures (Scheme 4), which however contribute in different extent to the overall bonding situation.

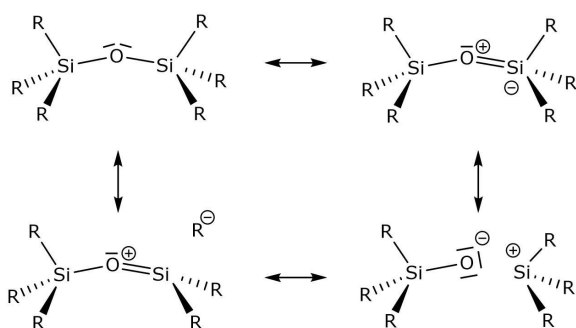
These circumstances even prompted authors to establish neologisms. *Gibbs* points out, that the Si–O bond can be understood as the *elusive bond*.<sup>[60]</sup> Its character is indicated rather to be *intermediate* than either ionic or covalent.<sup>[61]</sup>

Interestingly, there have been deliberations since the 1960s and also rare experimental evidence since the late 1970s, that the basicity of siloxanes is increased if the Si–O–Si angle is narrowed.<sup>[16,24,26,29,62]</sup> Taking this observation into account would





**Figure 6.** Schematic representation of  $M^+ \cdots X^{\delta+}$  ( $X = C, Si$ ) repulsive and  $M^+ \cdots O^{\delta-}$  attractive interactions in acyclic (left)<sup>[52]</sup> and cyclic systems (right).<sup>[53]</sup> Repulsive interactions are depicted in yellow/orange whereas attractive interactions are depicted in green. Left image reproduced with permission. Copyright Wiley-VCH GmbH. See reference.<sup>[52]</sup> The right figure was reprinted with permission from ref.<sup>[53]</sup> Copyright 2013 American Chemical Society.



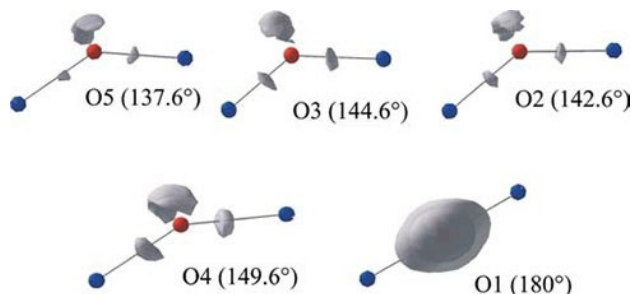
**Scheme 4.** Resonance structures to represent the intermediate bond character of the Si–O bond. Classic Lewis formula representation (top left), hypervalent Lewis formula (e.g. by  $p(O) \rightarrow d(Si)$  backbonding) (top right), no-bond Lewis structure (e.g. by strong  $p(O) \rightarrow \sigma^*(Si-R)$  backbonding) (bottom left) and ionic Lewis formula (bottom right).

mean that hyperconjugation interactions as well as ionicity of a respective siloxane (or silicate) are decreased when approaching smaller angles. To substantiate a correlation between basicity and Si–O–Si angles, experimental evidence was collected over time and backed up by means of quantum chemical calculations. Convincing studies have been carried out especially in the field of mineralogy. In this context, silica polymorphs have been analysed regarding their OH group locations. Especially coesite, a high pressure polymorph of SiO<sub>2</sub>, has been identified as a target for studies of potential electrophilic attack.<sup>[63]</sup> Coesite, unlike quartz, which has only one non-equivalent Si–O–Si angle, has five non-equivalent Si–O–Si angles, which aroused researchers attention. According to FTIR (Fourier transform infrared) studies on H-doped coesite crystals, Koch-Müller et al. reported that hydrogen atoms are bound to four of the five non-equivalent oxide ions.<sup>[64]</sup> Based on this result, Gibbs et al. performed quantum chemical calculations

(e.g. based on the ELF (ELF = electron localization function) approach) and predicted favourable proton docking sites.<sup>[65]</sup>

The results according to the ELF approach suggest that the electron density in coesite is highly localized at O2, O3 and O5 (see Figure 7), less localized in O4 and much less localized in O1. The local maximum for a nonbonding region is highest at O5 and decreases with larger Si–O–Si angles. Hence, the favourability of a non-bonding region acting as a potential docking site is expected to be larger when approaching smaller Si–O–Si angles. The determined docking sites in protonated coesite are for this reason O2–O5 but not O1.

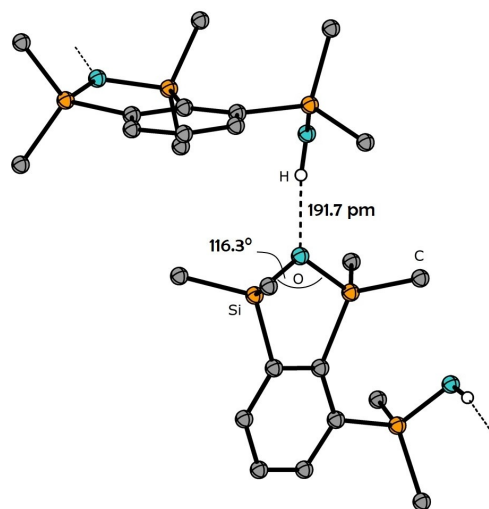
Additional studies have emerged from the field of molecular inorganic main-group chemistry. Grabowsky and co-workers provided a comprehensive study on hydrogen bonding of silanol (H<sub>3</sub>SiOH) and water towards DSE (= disiloxane) which is constrained to Si–O–Si angles ranging from 85 to 165°.<sup>[66]</sup> As expected from the aforementioned mineralogical studies, the basicity significantly increases when the Si–O–Si angle is decreased. Elucidating, PES (PES = potential energy surface) scans reveal that approaching a tetrahedral angle (110°) yields silanol...siloxane hydrogen bonding energies of –12 kJ mol<sup>–1</sup>. This value is twice as high than at 140° (–6.2 kJ mol<sup>–1</sup>). Notable is the broad range of adoptable angles in DSE. The molecule has a high bending potential associated with only a small change in energy in the region of 130 to 180°. The barrier to linearization from the ideal angle (calculated to be 151.4° in this study) is only 0.5 kJ mol<sup>–1</sup>. To decrease the ideal angle to 130° costs approximately 4.5 kJ mol<sup>–1</sup>. By further narrowing to a tetrahedral angle, however, the amount of energy, which is required to adopt this angle, rises almost exponentially. An energy loss of approximately 20 kJ mol<sup>–1</sup> is predicted here, which cannot be compensated by the values obtained from hydrogen bonding. Hence, linear siloxanes like DSE are not expected to adopt Si–O–Si angles enabling hydrogen bonding. Instead, the incorporation of a Si–O–Si linkage into a ring system proved to be a successful strategy to verify the correlation between siloxane angle and basicity. Beckmann and co-workers established the synthesis and characterization of a benzoxadisilole containing a five-membered ring with Si–O–Si moiety as well as a silanol group.<sup>[51]</sup> The respective benzoxadisilole contains a Si–O–Si moiety with an angle of 116.3°. This



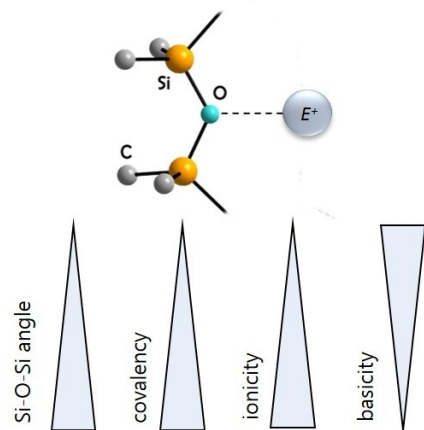
**Figure 7.** ELF isosurfaces for the five different Si–O–Si linkages in coesite with respect to the non-bonding region.<sup>[65]</sup> The ELF isosurface value is set at the 98% of the local maximum in the nonbonding region. Red spheres represent oxygen and blue spheres represent silicon. Reprinted by permission from Springer Nature.<sup>[65]</sup>

enables the formation of hydrogen bonds in the solid state with neighbouring silanol groups. Thus, hydrogen bonding determines the crystal packing and dimensionality proving Si–O groups to be a good electron donor at sufficiently small angles (see Figure 8).<sup>[51]</sup>

At this point, the correlation between siloxane basicity and Si–O–Si angle is clearly demonstrated by a variety of studies from different research areas. Experimental details as well as quantum chemical calculations were provided to substantiate a correlation. The question on how the Si–O bond character is changing with changing Si–O–Si angles remains. As recently as 2018, *Grabowsky* and co-workers scrutinized the coherence of covalency and ionicity. Meticulously performed quantum chemical calculations have been carried out to resolve an ostensible contradiction. The authors claim the analysis to be a *complementary bonding analysis* that combines methods from various



**Figure 8.** Section of the crystal structure of a benzoxadisilole comprising  $(R_3Si)_2O \cdots HO-SiR_3$  hydrogen bonding.<sup>[51]</sup> Atoms are displayed isotropically and with arbitrarily atom radii for clarity.

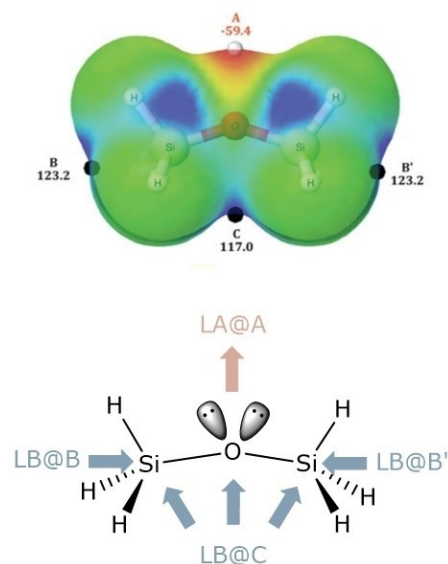


**Figure 9.** Attractive interaction between an organosiloxane linkage with an electrophile ( $= E^+$ ) as well as Si–O bond character and basicity towards  $E^+$  in correlation to the Si–O–Si angle.

different realms and demonstrates that both, covalency and ionicity increase simultaneously towards larger Si–O–Si angles.<sup>[67]</sup> These findings show the importance of considering multiple approaches to obtain a complete picture. Taking all herein presented research efforts of the past years according the Si–O–Si linkage into account, the presented picture of the Si–O–Si bond and basicity can be drawn (see Figure 9).

#### 2.4. Increasing Basicity Employing Cooperativity Effects?

The previous chapter showed the correlation between Si–O bond character, angle and basicity. Apart from straining the Si–O–Si angle, *Alkorta, Montero-Campillo* and co-workers very recently demonstrated that non-covalent interactions, in particular tetrel bonding, can alter chemical bonding and thus also Lewis basicity.<sup>[68–70]</sup> Tetrel bonds are known as non-covalent interactions involving tetrel atoms through their  $\sigma$ -hole which is a region of electropositive character.<sup>[54]</sup> In other words, a tetrel bond is a non-covalent bond between any Lewis base and a Lewis acid belonging to group 14 elements.<sup>[58]</sup> An outlook of such interactions regarding siloxanes has been given in chapter 2.1. The interaction of  $F^-$  with the electropositive centre of the silsesquioxane can be understood as such an interaction. *Alkorta, Montero-Campillo* and co-workers investigated DSE regarding tetrel bonding interactions, Lewis basicity and cooperativity effects. A MEP (MEP = molecular electrostatic potential) representation of DSE is depicted in Figure 10 (top). Based on the distributed electron density, it becomes clear that the depicted sites (A, B, B', C) can be occupied by a respective Lewis acid (A) and/or base (B, B', C) (Figure 10, bottom). Owing to this dual character of DSE, the system can form ternary

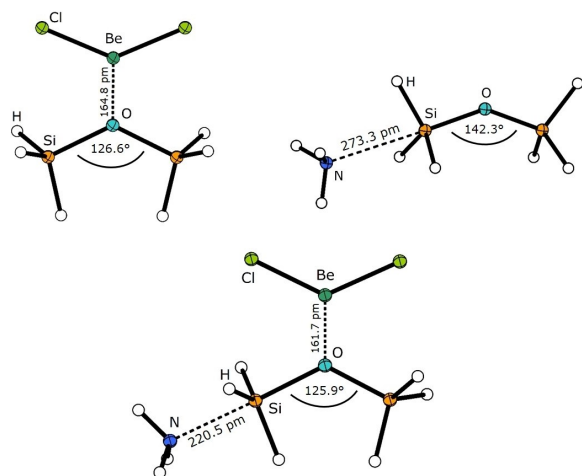


**Figure 10.** MEP of DSE (top)<sup>[69]</sup> and possible nucleophilic (blue) and electrophilic (red) docking sites (bottom). The minimum and maxima ( $\text{kJ mol}^{-1}$ ) are indicated with dots along their corresponding MEP values. The MEP is drawn at the 0.001 a.u. electron density isosurface. Top-figure reproduced with permission. Copyright Taylor & Francis Ltd. See ref. [69].

complexes and the different interactions might cooperatively influence each other.<sup>[69]</sup>

The location of the  $\sigma$ -hole is related to the  $\sigma^*(\text{Si}-\text{R})$  orbitals whereas maximum electron density is related to  $p(\text{O})$ .<sup>[68]</sup> To investigate if cooperativity exists, the authors calculated binary complexes with various Lewis acids (=LA) at position A first (=DSE:LA), followed by binary complexes with various Lewis bases at positions B and C (=LB:DSE). Cooperativity between these two types of coordination could then be verified when comparing with ternary complexes of the type LB:DSE:LA. An example is given for the coordination of DSE toward  $\text{BeCl}_2$  (Figure 11).

As can be seen by these gas-phase calculations, coordination of  $\text{BeCl}_2$  (DSE:LA, as depicted in Figure 11, top left) strains the  $\text{Si}-\text{O}-\text{Si}$  angle to a value of  $126.6^\circ$ . The  $\text{O}\cdots\text{Be}$  atom distance has a value of  $164.8\text{ pm}$ .<sup>[69]</sup> The ternary complex, involving coordination to  $\text{BeCl}_2$  and simultaneously  $\text{NH}_3$ , has an  $\text{Si}-\text{O}-\text{Si}$  angle of  $125.9^\circ$ , the  $\text{O}\cdots\text{Be}$  atom distance is  $161.7\text{ pm}$  and the tetrel bond ( $\text{N}\cdots\text{Si}$ ) has a value of  $220.5\text{ pm}$ . Thus, combining both, coordination to a Lewis acid and tetrel bonding strengthens the beryllium as well as the tetrel bond. To give some more details, it was shown that the total binding energy (=  $E_b$ ) is raised by  $\sim 50\text{ kJ mol}^{-1}$  ( $E_b(\text{DSE:LA}) = -99.2\text{ kJ mol}^{-1}$ ) vs.  $E_b(\text{LB:DSE:LA}) = -149.3\text{ kJ mol}^{-1}$ ) even though the energy penalty due to conformational change (=  $E_i$ ) is  $\sim 65\text{ kJ mol}^{-1}$  higher in the ternary than in the binary complex ( $E_i(\text{DSE:LA}) = 79.7\text{ kJ mol}^{-1}$  vs.  $E_i(\text{LB:DSE:LA}) = 145\text{ kJ mol}^{-1}$ ). This is what the authors call a *cooperative effect* and this was demonstrated for a wide range of (Lewis) acids and Lewis bases. These effects can be explained by means of a push-pull system: Coordination of the Lewis acid causes increased MEP values at positions B and C. By coordination of LB towards DSE, a decreased MEP value is obtained at position A. Hence, cooperativity established by tetrel bonding yields more stable DSE complexes.<sup>[69]</sup> This synergy was also found to be important in acid-catalysed  $\text{Si}-\text{O}$



**Figure 11.** Increased basicity of DSE employing cooperative effects with  $\text{BeCl}_2$  and  $\text{NH}_3$  as an example. Depicted are the  $\text{BeCl}_2$  adduct at position A (top left), the  $\text{NH}_3$  adduct at position B (top) and the ternary complex with both ligands (bottom). These calculated structures have been reproduced from provided xyz data.<sup>[69]</sup>

bond cleavage reactions of DSE involving  $\text{H}^+$  and  $\text{H}_2\text{O}$ .<sup>[71]</sup> Further, tetrel bonding raises the proton affinity of siloxanes. The system  $\text{NH}_3:\text{DSE}:\text{NH}_3$  increases the basicity of DSE to such an extent, that the proton affinities of the related carbon systems can be reached.<sup>[68]</sup> The conclusion drawn from this chapter is, that weak interactions can have a significant influence on the siloxane linkage. Cooperative effects might become an interesting possibility for stabilizing coordination compounds of weakly coordinating ligands in the near future. For the moment, however, these advances are solely based on quantum chemical calculations and thus gas-phase species.

### 3. Siloxane Coordination Compounds

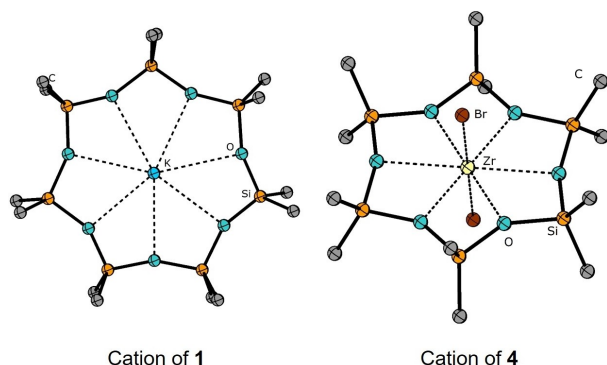
Reflecting the aforementioned discussions of the  $\text{Si}-\text{O}$  bond, it becomes clear that because of the unique character of this bond special conditions are required to obtain stable coordination compounds. Thus, various strategies have been established to bind silicon-based ligands toward electrophiles (especially metal centres). The most common strategy is to deprotonate silanols forming a respective silanolate ( $\text{R}_3\text{SiO}^-$ ). This is fairly easy through conversion of silanol and base and yields the respective silanolate salt. In comparison to neutral (crown) ethers, these ligands have a negative charge and it is inevitable for the oxygen atom to interact with the metal centre. In this way, many silanolate salts have been characterized and also gained some fields of application, mainly catalysis.<sup>[72-81]</sup> Similar to the above mentioned silanolate compounds which bear ligands constituted of  $\text{An-Si}(\text{R}_2)_2-\text{O}-\text{Si}(\text{R}_2)_2-\text{An}$  ( $\text{An}$  = any terminal anionic group),  $^-\text{Si}(\text{R}_2)_2-\text{O}-\text{Si}(\text{R}_2)_2^-$  (silicide-like) or related anionic moieties have been obtained. These compounds might show  $(\text{R}_2\text{Si})_2\text{O}\cdots\text{M}^{n+}$  interactions but these are mostly forced due to an anionic nature of the ligand. This is similar to the aforementioned silanolates. Complexes obtained in this way involve the cations  $\text{Li}^+$ ,<sup>[82-86]</sup>  $\text{Na}^+$ ,<sup>[87-89]</sup>  $\text{K}^+$ ,<sup>[85,87,89-91]</sup>  $\text{Rb}^+$ ,<sup>[89]</sup>  $\text{Cs}^+$ ,<sup>[87,89,92]</sup>  $\text{Mg}^{2+}$ ,<sup>[93]</sup>  $\text{Sr}^{2+}$ ,<sup>[94]</sup>  $\text{Ba}^{2+}$ ,<sup>[95,96]</sup>  $\text{Sn}^{4+}$ ,<sup>[97,98]</sup>  $\text{Cr}^{2+/3+}$ ,<sup>[99,100]</sup>  $\text{Fe}^{3+}$ ,<sup>[101]</sup>  $\text{Y}^{3+}$ ,<sup>[100,102]</sup>  $\text{Zr}^{4+}$ ,<sup>[103]</sup>  $\text{Sm}^{2+}$ ,<sup>[104]</sup>  $\text{Tm}^{3+}$ ,<sup>[105]</sup>  $\text{Yb}^{2+}$ ,<sup>[104,106-108]</sup>  $\text{Th}^{4+}$ ,<sup>[109-112]</sup>  $\text{U}^{4+}$ ,<sup>[109-113]</sup> and  $\text{UO}_2^{2+}$ .<sup>[114]</sup> Hence, many siloxane $\cdots\text{M}^{n+}$  contacts might have been established over the years but are rather occasionally than purposefully realized. Furthermore, these compounds have barely been published in the context of siloxane coordination chemistry.

In the context of siloxane coordination chemistry, neutral silicon-based ligands are of special interest. Due to their great resemblance to common (crown)ethers, the isolation and characterization of complexes with neutral siloxanes as ligands is the only way to learn more about the structural aspects, coordination ability and reactivity compared to ethers by all available means.

The isolation and characterization of such compounds, however, has been a challenging task over the past years. Attempts isolating stable adducts have been made since the late 1950s. Given that the basicity of siloxane oxygen atoms is low, these early attempts to coordinate simple silyl ethers like 1,3-dimethyldisiloxane, 1,1,3,3-tetramethyldisiloxane or HMDSE were attempted to bind to highly electrophilic Lewis acids such



as  $\text{BF}_3$  and  $\text{BCl}_3$ . These attempts, however, failed due to Si–O bond cleavage, even at low-temperature.<sup>[115]</sup> Over the years, extraction experiments as well as Mössbauer studies then gave, though still controversial,<sup>[116]</sup> first insights into metal binding. Alkali metal ions have successfully been extracted from organic phases with various cyclic siloxanes and could also be transferred through lipid bilayers with  $\text{D}_n$  ligands.<sup>[117–120]</sup> Observed isomer shifts in Mössbauer spectroscopy might indicate the coordination of HMDSE towards  $\text{Sn}^{4+}$ .<sup>[121]</sup> Unfortunately, no solid state structures were obtained and thus no structural proof for the silyl-ether coordination could be provided. The first structural proof of a neutral siloxane binding toward a metal centre was finally provided in the 1990s by Churchill et al.<sup>[122]</sup> The authors attempted crystallizing the highly reactive potassium species  $\text{K}[\text{In}(\text{CH}_2\text{CMe}_3)_3]$  from *n*-pentane. Due to high sensitivity of the compound, the grown single-crystals were, however, too unstable and readily shattered, probably due to solvent loss. To avoid shattering, the authors then tried to recrystallize the compound from *n*-heptane instead. To protect the material before the solvent was added, it has been covered in small amounts of silicon grease. To the surprise of the authors,  $\text{D}_7$  had formed from the silicon polymer upon crystallization. The coordination compound  $\text{K}_3[\text{K}(\text{D}_7)][\text{In}(\text{CH}_2\text{CMe}_3)_3]_4$  (1) was obtained where one of the potassium ions is coordinated by  $\text{D}_7$ .<sup>[122]</sup>  $[\text{K}(\text{D}_7)][\text{K}[\text{C}(\text{SiMe}_3)_2\text{SiMe}_2(\text{HC}=\text{CH}_2)]_2]$  (2) has been reported shortly after. The compound was obtained by recrystallizing  $\text{K}[\text{C}(\text{SiMe}_3)_2\text{SiMe}_2(\text{HC}=\text{CH}_2)]$  from methylcyclohexane/ $\text{Et}_2\text{O}$  solution in the presence of silicon grease.<sup>[123]</sup> Two more examples have been published in the meantime in which silicon grease has (unintentionally) been used as a precursor for the formation of  $\text{D}_n$  complexes. An additional potassium compound in the form of the silyl-sodate  $[\text{K}(\text{D}_7)][\text{Na}\{\text{SiMe}(\text{Si}t\text{Bu}_3)_2\}_2]$ <sup>[124]</sup> (3) was published by the group of Lerner and the zirconium(IV) complex  $[\text{Zr}(\text{D}_6)\text{Br}_2][\text{Zr}_2\text{Br}_9]_2$ <sup>[125]</sup> (4) was published by Ernst. Parts of these structures are depicted in Figure 12. Silicon grease, however, is not inevitably cleaved (e.g. by strong organometallic bases) into cyclic siloxanes. Haiduc and Saito reviewed silicon grease as precursor for

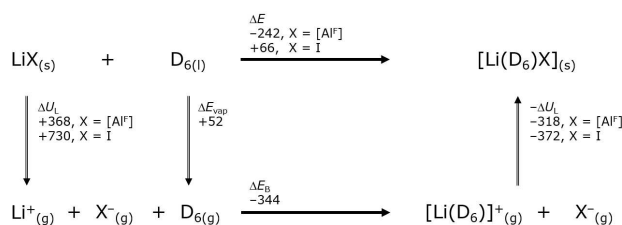


**Figure 12.** The cationic structures of  $\text{D}_n$  complexes obtained from serendipitous reactions with a silicon grease in crystal form. Depicted on the left is the cation  $[\text{K}(\text{D}_7)]^+$  of  $\text{K}_3[\text{K}(\text{D}_7)][\text{In}(\text{CH}_2\text{CMe}_3)_3]_4$ <sup>[122]</sup> and depicted on the right is the cation  $[\text{Zr}(\text{D}_6)\text{Br}_2]^{2+}$  of  $[\text{Zr}(\text{D}_6)\text{Br}_2][\text{Zr}_2\text{Br}_9]_2$ <sup>[125]</sup>. Atoms are displayed isotropically and with arbitrarily atom radii for clarity.

coordination compounds and demonstrated that various structural motifs (monomers, chains and also cages) can be obtained.<sup>[126,127]</sup> Thus, a logical consequence was the aspiration to develop synthetic protocols which selectively yield cyclo-siloxane complexes.

Passmore and co-workers studied cyclosiloxane complexes by means of quantum chemical calculations and could, according to suitable Born-Haber cycles (=BHC), demonstrate that cation encapsulation becomes favourable when weakly coordinating anions (=WCAs) are employed, such as the perfluorinated alkoxy-aluminates  $[\text{Al}^{\text{F}}]^-$  or  $[\text{Al}^{\text{PhF}}]^-$  ( $[\text{Al}^{\text{PhF}}]^- = [\text{Al}\{\text{OC}(\text{CF}_3)_2\text{Ph}\}_4]^-$ ).<sup>[128]</sup> WCAs are generally known as anions, in which the charge is delocalized over a large area of a non-nucleophilic and chemically robust moiety.<sup>[129,130]</sup> As depicted in Figure 13, the reaction enthalpy calculated from the Born-Haber cycle shows that the complexation of  $\text{Li}^+$  yields  $242 \text{ kJ mol}^{-1}$  when  $[\text{Al}^{\text{F}}]^-$  is employed as an anion. When  $\text{I}^-$  is employed, the reaction enthalpy becomes positive ( $\Delta E = 66 \text{ kJ mol}^{-1}$ ). As the main reason the differences in lattice energy were identified.

The aluminate salt has a significant lower lattice energy, which is why the vaporization costs only approximately half as much energy as vaporizing the iodide salt. This fact is indeed reflected by the experiment. Direct reaction of  $\text{D}_6$  and  $\text{Li}[\text{Al}^{\text{F}}]$  or  $\text{Li}[\text{Al}^{\text{PhF}}]$  in DCM (DCM = dichloromethane) yields the respective coordination compounds  $[\text{Li}(\text{D}_6)\text{Al}^{\text{F}}]$  (5) and  $[\text{Li}(\text{D}_6)\text{Al}^{\text{PhF}}]$  (6), whereas  $\text{D}_6$  is reluctant towards coordination of  $\text{LiI}$ . Additionally, the direct reaction of the smaller ring  $\text{D}_5$  with  $\text{Li}[\text{Al}^{\text{F}}]$  turned out to be successful forming  $[\text{Li}(\text{D}_5)\text{Al}^{\text{F}}]$  (7).<sup>[128]</sup> Encouraged by the success of these initial results, the Passmore group investigated the coordination chemistry of  $\text{D}_n$  towards  $\text{Ag}[\text{SbF}_6]$ .<sup>[131]</sup> Conversion of  $\text{D}_5$  with  $\text{Ag}[\text{SbF}_6]$  in liquid  $\text{SO}_2$  yielded indeed a stable coordination compound, but elucidated from SC-XRD experiments,  $\text{D}_7$  had formed from the  $\text{D}_5$  ligand. Bulk analysis (GC-MS and in-situ  $^{29}\text{Si}\{\text{t}^1\text{H}\}$  NMR spectroscopy) revealed that besides  $\text{D}_7$ , significant amounts of  $\text{D}_6$  and traces of  $\text{D}_8$  have also been part of the reaction mixture. Hence, complexes of these ligands also formed even though these complexes had not been elucidated by SC-XRD. The formation of these ligands is attributed to the non-innocent character of the  $[\text{SbF}_6]^-$  anion. The authors postulated formation of  $\text{SbF}_5$  and formation of fluorosilanes as the reactive species. Template directed ring-closure of  $\text{Ag}^+$  then yields the respective coordination compounds  $[\text{Ag}(\text{D}_n)\text{SbF}_6]$  ( $n = 6-8$ ,  $n = 6$ : 8,  $n = 7$ : 9 and  $n = 8$ : 10) with  $[\text{Ag}(\text{D}_7)\text{SbF}_6]$  (9) as the main component.<sup>[131]</sup> An indirect proof for this assumption was

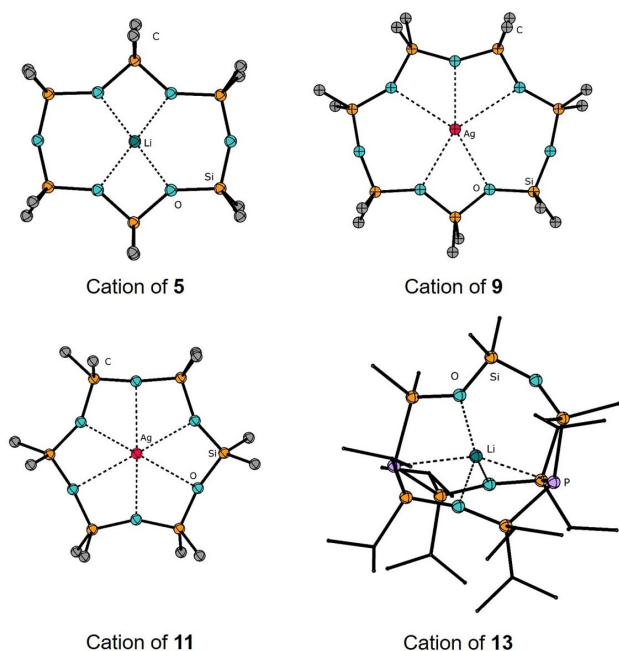


**Figure 13.** Born-Haber cycle for the complex formation of  $\text{LiX}$  ( $\text{X} = \text{I}^-$ ,  $[\text{Al}^{\text{F}}]^-$ ) with  $\text{D}_6$ .<sup>[128]</sup> The Lattice energies ( $\Delta U_L$ ), energy of vaporization ( $\Delta E_{\text{vap}}$ ), binding energies ( $\Delta E_b$ ) and the energies of formation ( $\Delta E$ ) are given in  $\text{kJ mol}^{-1}$ .

published later on. The chemically robust, non-nucleophilic anions  $[Al^F]^-$  and  $[FAl(OR^F)_3]$  ( $R^F = C(CF_3)_3$ ) do not promote  $Ag^+$  templated ring-opening polymerization. After conversion of these salts with  $D_6$  in  $SO_{2(l)}$ , the respective coordination compounds  $[Ag(D_6)Al^F]$  (**11**) and  $[Ag(D_6)FAl(OR^F)_3]$  (**12**) were isolated and characterized.<sup>[53]</sup> Besides the two-dimensional  $D_n$  ligands, our group expanded the field to three-dimensional ligand systems introducing group 15 elements.<sup>[132–135]</sup> The application of Si–O donors for coordination was unfortunately unsuccessful in the most cases. A striking result in the field, however, was published in 2007. A formal inorganic [2.1.1] cryptand was synthesized, structurally characterized and its coordination toward  $Li^+$  was realized.<sup>[132]</sup> A stepwise lithiation/silylation process gave access to  $[P_2\{O(SiPr_2)_2\}_2\{SiMe_2(OSiMe_2)_2\}]$  ( $=^{inorg}[2.1.1]crypt$ ) which can be used for coordination by conversion with  $Li[Al^F]$  forming  $[Li(^{inorg}[2.1.1]crypt)][Al^F]$  (**13**).<sup>[132]</sup> The molecular structure of the cation is depicted in Figure 14 (bottom right). Despite using a three- rather than two-dimensional ligand moiety, the coordination ability of this ligand is comparable with those of  $D_5$  and  $D_6$ . Hence, there is a lack of a “cryptate-effect” similar to the lack of a “crown-effect” in  $D_n$  ligands as well.

Thus, these ligands were generally accepted as very weakly coordinating and it has been quite a long time that these four more or less random cations,  $Li^+$ ,  $K^+$ ,  $Zr^{4+}$  and  $Ag^+$  were the only cations bound within these exclusively silicon-based macrocycles.

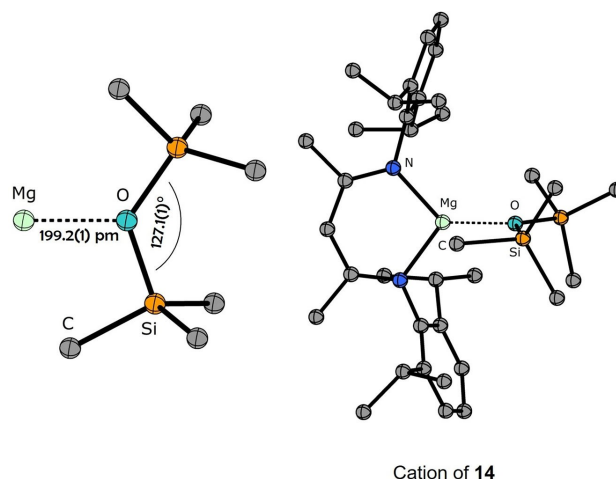
In 2018, however, it was the group of *Harder* which reached a milestone in this chemistry. The group reported on a simple



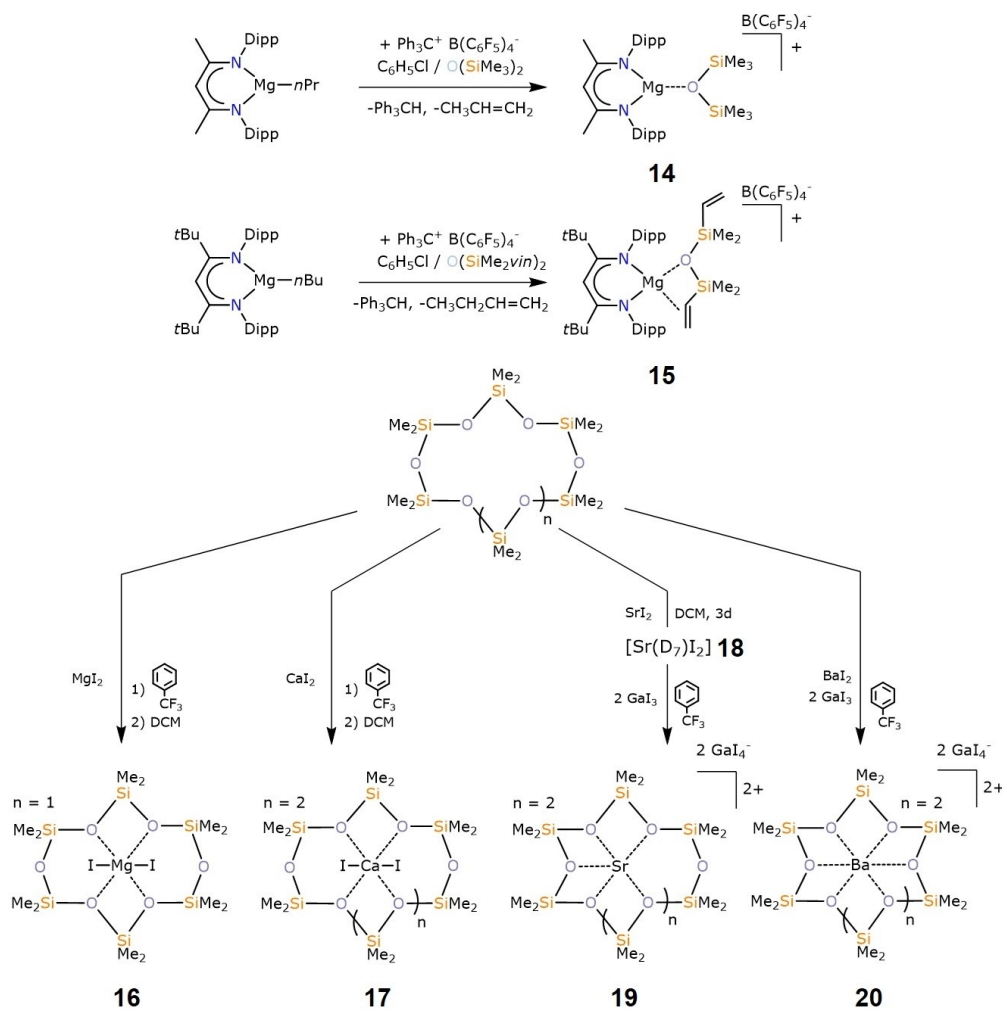
**Figure 14.** The cationic structures of siloxane complexes obtained directly from a respective ligand, weakly coordinating solvent, and a WCA salt. Depicted are the cationic parts of  $[Li(D_6)Al^F]$  (top left),<sup>[128]</sup>  $[Ag(D_7)_2][SbF_6]$  (top right),<sup>[131]</sup>  $[Ag(D_6)Al^F]$  (bottom left)<sup>[53]</sup> and  $[Li(^{inorg}[2.1.1]crypt)][Al^F]$ .<sup>[132]</sup> Atoms are displayed isotropically with arbitrarily atom radii and are partially depicted as wires/sticks for clarity.

and stable silyl-ether adduct (**14**) as coordination of HMDSE towards  $Mg^{2+}$  was realized. Measured at the first attempts coordinating DSE toward  $BX_3$  ( $X = F^-, Cl^-$ ),<sup>[115]</sup> it took roughly 60 years to obtain such a simple (and stable) silyl-ether adduct. The success is based on the synthesis of  $[Mg(BDI)][B(C_6F_5)_4]$  ( $BDI = CH[C(CH_3)N-Dipp]_2$ ,  $Dipp = 2,6$ -diisopropylphenyl) combining both, high Lewis acidity in the form of a “naked”  $Mg^{2+}$  ion and a weakly coordinating anion (Scheme 5).<sup>[136]</sup> It was this dualism which finally initiated a simple silyl-ether for coordination (Figure 15).<sup>[137]</sup> The Si–O–Si angle in this compound has a value of  $127.1(1)^\circ$ . Hence, highly increased basicity of the ligand toward the  $Mg^{2+}$  cation is indicated. Not surprisingly, a similar compound with a divinylsiloxane ( $=DVSE$ ) ligand (**15**) was published by the same group shortly after.<sup>[139]</sup> These findings motivated us reinvestigate the coordination chemistry of  $D_n$  ligands. Following the observations made by the *Harder* group, alkaline earth metals were investigated at first and revealed, that cyclodimethylsiloxanes share indeed strong interactions with early *s*-block metal ions. Counter-intuitively, the conversion of iodide salts was shown to be successful for  $Mg^{2+}$  and  $Ca^{2+}$  employed as cation. This ultimately proves that no bulky, perfluorinated anion such as  $[Al^F]^-$  is necessary to obtain stable adducts of cyclic dimethylsiloxanes with metal cations.

The X-ray structures of  $[Mg(D_6)_2]$  (**16**),  $[Mg_2(D_6)_2(Mg_2)_2]$  (**16-MgI\_2**) and  $[Ca(D_7)_2]$  (**17**) were successfully determined (see selected examples in Figure 16, top) and even show metal–anion bonds which are described to perturb silyl-ether bonding.<sup>[138]</sup> The successful incorporation of salts with relatively strongly coordinating  $I^-$  ion demonstrates that not only the nature of the anion but also the nature of the cation has to be taken into account when siloxane coordination chemistry is discussed. This was confirmed with suitable BHCs obtained from quantum chemical approaches. Despite the relatively strongly coordinating iodide ion, the overall energy gains for complexation of  $MgI_2$  has a value of  $-328 \text{ kJ mol}^{-1}$  for  $D_6$  employed and  $-313 \text{ kJ mol}^{-1}$  when  $D_7$  was employed. Slightly



**Figure 15.** The geometric features of HMDSE coordinating  $Mg^{2+}$  and molecular structure of  $[Mg(BDI)HMDSE][B(C_6F_5)_4]^-$  in the crystal.<sup>[137]</sup> The  $[B(C_6F_5)_4]^-$  anion is omitted and atoms are displayed isotropically with arbitrarily atom radii for clarity.

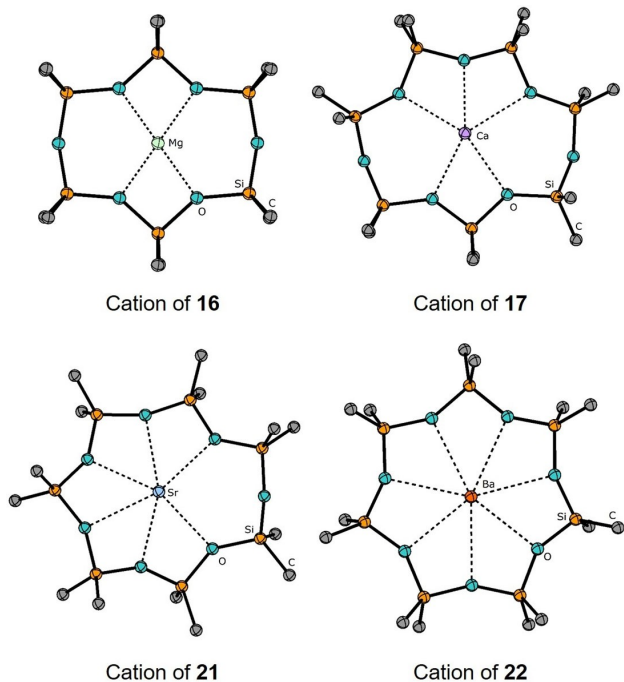


Scheme 5. Synthesis of alkaline earth metal complexes with siloxane ligands.<sup>[137–139]</sup>

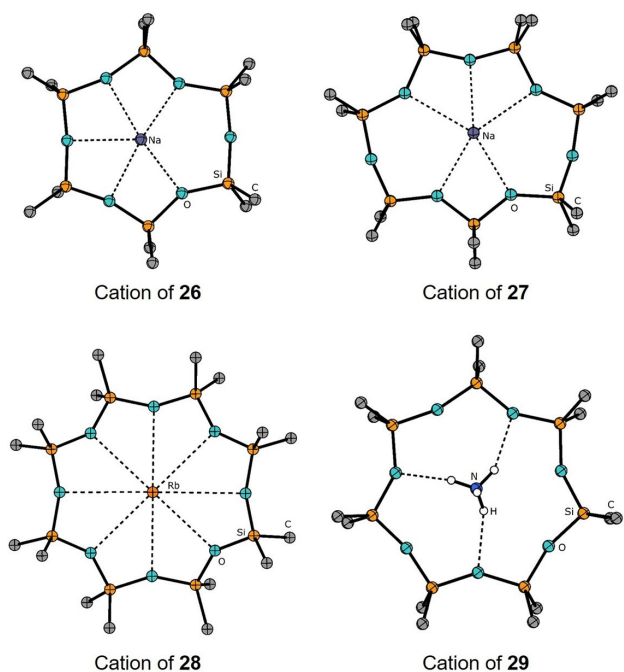
lower values are obtained for  $\text{CaI}_2$ . These are  $-125 \text{ kJ mol}^{-1}$  for  $\text{D}_6$  and  $-109 \text{ kJ mol}^{-1}$  for  $\text{D}_7$ . Things are different when the slightly softer ions  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  are employed for chemical reaction.  $-10 \text{ kJ mol}^{-1}$  ( $\text{D}_6$ ) and  $-3 \text{ kJ mol}^{-1}$  ( $\text{D}_7$ ) were obtained for  $\text{SrI}_2$  whereas  $+87 \text{ kJ mol}^{-1}$  ( $\text{D}_6$ ) and  $+79 \text{ kJ mol}^{-1}$  ( $\text{D}_7$ ) were obtained for  $\text{BaI}_2$ . These values were finely represented by experimental observations. As demonstrated, stable complexes of  $\text{MgI}_2$  and  $\text{CaI}_2$  are obtained. In case of  $\text{SrI}_2$ , the respective coordination compound was only observed by means of  $^{29}\text{Si}$  NMR spectroscopy in solution ( $\delta(\text{SrI}_2@D_7; \mathbf{18}) = -9.2 \text{ ppm}$ ) and no evidence for coordination is found in case of  $\text{BaI}_2$ .<sup>[138]</sup>

A crossover point was thus detected which demonstrates how far the silyl-ether coordination can be extended with iodide as a counter anion on an experimental level. To obtain stable coordination compounds, the iodide ion was changed into a small WCA upon  $\text{GaI}_3$  addition. The quantum chemical calculations around the BHC showed an energy gain of around  $240 \text{ kJ mol}^{-1}$  switching from  $\text{I}^-$  to  $[\text{GaI}_4]^-$ . Hence, initially unsupported silyl-ether coordination of  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  could be shown to be clearly exothermal with this small WCA. The coordination compounds  $[\text{M}(\text{D}_7)(\text{GaI}_4)_2]$  ( $\text{M} = \text{Sr}^{2+}$  (**19**),  $\text{Ba}^{2+}$  (**20**))

were consecutively obtained and the molecular structure of  $[\text{Sr}(\text{D}_7)(\text{GaI}_4)_2(\text{H}_2\text{O})][\text{GaI}_4]$  (**21**) and  $[\text{Ba}(\text{D}_7)(\text{GaI}_4)_2(\text{H}_2\text{O})_{0.94}][\text{GaI}_4]_{0.06}[\text{GaI}_4]_{0.94}$  (**22**) could successfully elucidated by means of SC-XRD (Figure 16, bottom). Even though this small WCA  $[\text{GaI}_4]^-$  is much less bulky and clearly more nucleophilic than  $[\text{AlF}_6]^-$  or  $[\text{Al}^{\text{PhF}}]^-$ , this anion serves as a promising candidate for future siloxane coordination chemistry which is evident from the aforementioned energy gain.<sup>[138]</sup> This discovery induced further experiments to explore the limits of siloxane coordination. The alkali metal salts  $\text{MGA}_4$  are readily available upon reacting the respective alkali metal iodide with  $\text{GaI}_3$  in a respective solvent. Siloxane addition then yields the target coordination compounds.<sup>[140]</sup> As already shown for  $\text{Li}^+$  and  $\text{K}^+$ , the incorporation of these salts was successful with  $\text{D}_5$  and  $\text{D}_6$  for  $\text{M} = \text{Li}^+$  and with  $\text{D}_7$  for  $\text{M} = \text{K}^+$ . The compounds  $[\text{Li}_2(\text{D}_5)(\text{D}_6)(\text{GaI}_4)_2]$  (**23**),  $[\text{Li}(\text{D}_6)\text{GaI}_4]$  (**24**) and  $[\text{K}(\text{D}_7)(\text{DCM})\text{GaI}_4]$  (**25**) were elucidated by SC-XRD. Additionally, this approach was feasible also for  $\text{Na}^+$  and  $\text{Rb}^+$ .  $\text{Na}^+$  could be trapped in  $\text{D}_6$  and  $\text{D}_7$ , the large  $\text{Rb}^+$  ion in the large ligand  $\text{D}_8$  (Scheme 6). Crystal structures of  $[\text{Na}(\text{D}_6)\text{GaI}_4]$  (**26**),  $[\text{Na}(\text{D}_7)(\text{DCM})\text{GaI}_4]$  (**27**) and  $[\text{Rb}(\text{D}_8)(\text{DCM})\text{GaI}_4]$  (**28**) have been determined (Figure 17). As the



**Figure 16.** The cationic structures of alkaline earth metal complexes with  $D_n$  ligands.<sup>[138]</sup>  $[Mg(D_6)_2]$  (top left),  $[Ca(D_7)_2]$  (top right),  $[Sr(D_7)(Gal_4)(H_2O)]Gal_4$  (bottom left) and  $[Ba(D_7)(Gal_4)(H_2O)_{0.94}(Gal_4)_{0.06}]]Gal_4]_{0.94}$  (bottom right). Atoms are displayed isotropically with arbitrarily atom radii for clarity.



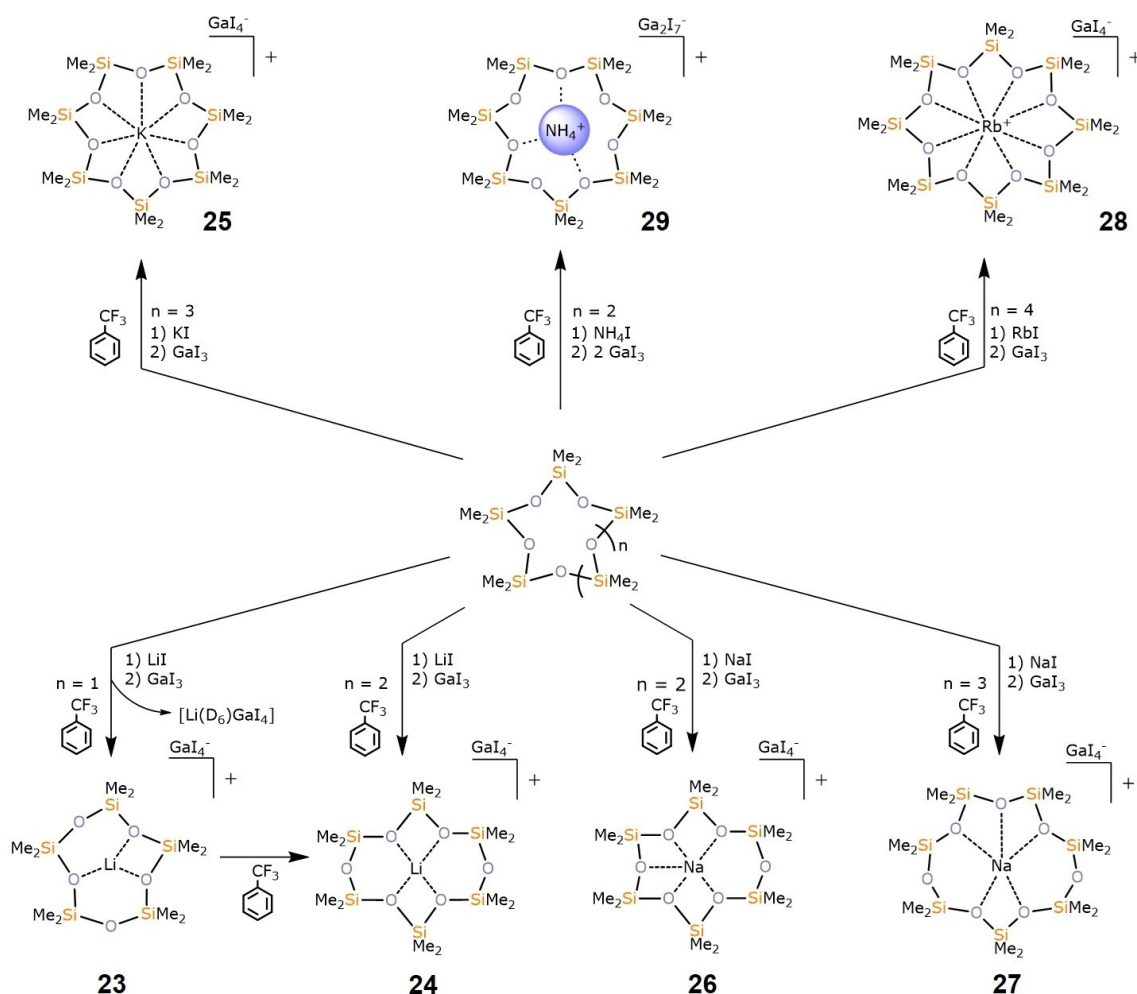
**Figure 17.** The cationic structures of alkali metal (and  $NH_4^+$ ) complexes with  $D_n$  ligands.<sup>[140]</sup>  $[Na(D_6)Gal_4]$  (top left),  $[Na(D_7)(DCM)Gal_4]$  (top right),  $[Rb(D_8)(DCM)Gal_4]$  (bottom left) and  $[NH_4(D_7)][Ga_2]_7$  (bottom right). Atoms are displayed isotropically with arbitrarily atom radii for clarity.

$Rb^+$  compound showed major instability in solution, no meaningful spectroscopic data could be obtained and was only

isolated in low yields. Supported by the failure to incorporate  $CsGal_4$  into  $D_8$ , another cross-over point was determined on how far metal-silyl ether bonding is possible. This time for a small WCA in the form of  $[Gal_4]^-$ . Another impressive example on how far silyl-ether bonding is possible, however, was obtained in form of the first non-metal complex  $[NH_4(D_7)][Ga_2]_7$  (**29**). Reaction of  $D_6$  with  $NH_4I$  and two equivalents of  $Gal_3$  turned out to be successful and hydrogen bonding of  $NH_4^+$  towards a cyclic siloxane could be realized. Ring-opening polymerization from  $D_6$  to  $D_7$  enables  $NH_4^+$  to form three hydrogen bonds in a suitable geometry. Similar to the  $Rb^+$  compound though, the complex decomposes readily in solution at ambient temperature. Hydrogen bonding is clearly weak in solution, which is in line with the aforementioned studies around hydrogen bonding with siloxane donors. Contrary to the  $Rb^+$  compound, this compound could be stabilized at low-temperatures though. IR, NMR and X-ray data confirm the interaction of  $NH_4^+$  with the siloxane.  $^{29}Si$  NMR chemical shift is found to be present at  $-15.6$  ppm at 253 K, and a single, broad N–H-stretching vibration is observed at  $3165\text{ cm}^{-1}$  in the IR spectrum. The chemical shift is in the range of potassium silyl-ether compounds and thus shows weak to moderate interactions with the Si–O–Si moieties as elucidated by means of  $^{29}Si$  NMR spectroscopy.

Much stronger interactions in solution are observed especially for the early alkali metal compounds as well as alkaline earth metal compounds. The opposite case is observed for the heavy alkali metal compounds. A selection of NMR chemical shifts is summarized in Table 2. Based on these findings, heavy alkali metal compounds have to be stabilized by other means than a small WCA. As previously shown by the group of *Passmore*,<sup>[53,128]</sup> it seems obvious that bulky, perfluorinated WCAs are the key to reach sufficient stability. Conversion of  $D_8$  with  $M[Al^F]$  ( $M = Rb^+$ ,  $Cs^+$ ) yields the compounds  $[M(D_8)Al^F]$  ( $M = Rb^+$ : **30**,  $Cs^+$ : **31**) both of which could be obtained in suitable yields and showed sufficient stability in DCM solution even though  $^{29}Si$  NMR chemical shifts indicate only very weak interactions of the metal ion with the siloxane ligand. Hence, the silyl-ether coordination was also substantiated for heavy alkali metal compounds. Not only could 1:1 complex be obtained in this way, but also 2:1 complexes were recently described (Figure 18). At low temperatures,  $K[Al^F]$  reacts with an excess of  $D_5$  and  $Cs[Al^F]$  with an excess  $D_6$  to the remarkable sandwich complexes  $[K(D_5)_2][Al^F]$  (**32**) and  $[Cs(D_6)_2][Al^F]$  (**33**). A concluding remark at this point is clearly that even though the Lewis basicity of siloxanes is impaired compared to organic ethers, they can be used for coordination towards a wide range of (metal) ions. Coordination is preferred to those cations that are chemically hard and, in most cases, a WCA is in fact necessary. Nevertheless, coordination is possible in many more cases than assumed. To the best of our knowledge, no further complexes with  $D_n$  or simple silyl ethers than the above-mentioned ones were reported so far. Based on the advances of the last few years, we see that the field significantly opened up and, in our eyes, many more compounds and coordination architectures will be discovered soon.





Scheme 6. Synthesis of alkali metal and  $\text{NH}_4^+$  complexes with  $\text{D}_n$  ligands employing the small WCAs  $[\text{GaI}_4]^-$  and  $[\text{Ga}_2\text{I}_7]^-$ .

## 4. Employing Disilanes: Access to a New Class of Ligands with Increased Basicity?

### 4.1. Difference in Hyperconjugation Interactions

Hyperconjugation interactions have extensively been discussed for (cyclic) siloxanes in chapter 2.1. A significant difference compared to common (cyclo-)siloxanes is, that disilanes do not allow for geminal  $p(\text{O}) \rightarrow \sigma^*(\text{Si}-\text{O})$  backbonding. Cypriak demonstrated this lack of backbonding on the basis of the  $-\text{O}-\text{SiH}_2-\text{SiH}_2-\text{O}-$  linkage. As outlined, a different orbital interaction pattern involving the electron pairs of oxygen is present here.<sup>[43]</sup> The  $p(\text{O}) \rightarrow \sigma^*(\text{Si}-\text{O})$  backbonding is replaced by  $p(\text{O}) \rightarrow \sigma^*(\text{Si}-\text{Si})$  backbonding which is substantially weaker. The total energy of the  $p(\text{O}) \rightarrow \sigma^*(\text{Si}-\text{Si})$  delocalization has a value of approximately  $42 \text{ kJ mol}^{-1}$  per unit. The total energy of the  $p(\text{O}) \rightarrow \sigma^*(\text{Si}-\text{O})$  delocalization, on the contrary, has a value of approximately  $88 \text{ kJ mol}^{-1}$  per unit. Thus, the energy penalty upon transformation to a disilane is  $46 \text{ kJ mol}^{-1}$  per unit.<sup>[43]</sup> Hence, electron density at oxygen is significantly more localized at oxygen when employing disilanes as a bridging unit.

This difference in hyperconjugation interaction makes  ${}^2\text{D}_2$  ( ${}^2\text{D} = \text{Si}_2\text{Me}_4\text{O}$ ), for example, a stronger base than all other dimethylcyclosiloxanes including the most reactive cyclosiloxanes  $\text{D}_3$  and  $\text{D}_4$ .<sup>[43,44]</sup> The orbital interaction pattern relevant for  ${}^2\text{D}_n$  systems is illustrated in Figure 19. Noteworthy is, as depicted here, that  $p(\text{O}) \rightarrow \sigma^*(\text{Si}-\text{H})$  backbonding interactions are equally present in this linkage as in  $\text{D}_n$  compounds. Consequently, one can conclude that the  $p(\text{O}) \rightarrow \sigma^*(\text{Si}-\text{O})$  interactions are the predominant interactions which decrease the availability of the oxygen lone-pair for donation towards electrophiles. At least in (cyclic) systems bearing several repeating units.

### 4.2. Difference in Ring Strain

Another crucial difference employing disilanes is the ligand conformation of the silicon-based macrocycle upon complexation. As demonstrated in Figure 20, the central coordination pattern of a (disila-)crown ether and an ion host is a five-membered ring.  $\text{D}_n$  ligands, however, form four-membered

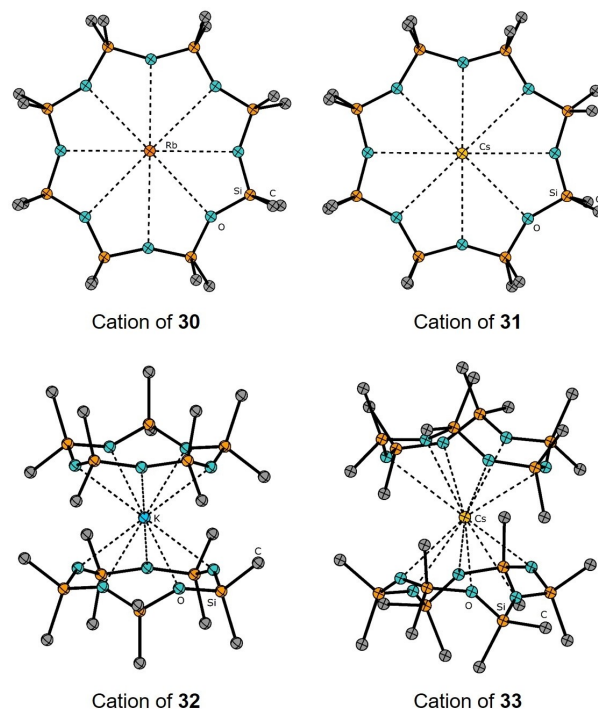
**Table 2.**  $^{29}\text{Si}$  NMR chemical shifts of different siloxane coordination compounds which were observed in solution.

Compound	$^{29}\text{Si}$ NMR shift [ppm]	Reference solvent	Reference
HMDSE	7.8	$\text{C}_6\text{D}_5\text{Br}$	[137]
$[\text{Mg}(\text{HMDSE})(\text{BDI})][\text{B}(\text{C}_6\text{F}_5)_4]$ (14)	33.5	$\text{C}_6\text{D}_5\text{Br}$	[137]
$\text{D}_5$			
	-21.6	$\text{CD}_2\text{Cl}_2$	[140]
	-21.9	$\text{SO}_2$	[131]
$[\text{Li}(\text{D}_5)\text{Al}^{\text{I}}]$ (7)	-21.3 <sup>[a]</sup>	$\text{SO}_2$	[128]
$[\text{Li}(\text{D}_5)\text{GaI}_4]$ (23)	-9.0	$\text{CD}_2\text{Cl}_2$	[140]
$[\text{K}(\text{D}_5)_2][\text{Al}^{\text{I}}]$ (32)	-21.1	$\text{CD}_2\text{Cl}_2$	[140]
	-16.6 <sup>[b]</sup>	$\text{CD}_2\text{Cl}_2$	[140]
$\text{D}_6$			
	-22.2	$\text{CD}_2\text{Cl}_2$	[138]
	-22.4	$\text{SO}_2$	[131]
$[\text{Li}(\text{D}_6)\text{Al}^{\text{I}}]$ (5)	-9.2	$\text{SO}_2$	[128]
$[\text{Li}(\text{D}_6)\text{Al}^{\text{PhF}}]$ (6)	-10.1	$\text{SO}_2$	[128]
$[\text{Li}(\text{D}_6)\text{GaI}_4]$ (24)	-7.4	$\text{CD}_2\text{Cl}_2$	[140]
$[\text{Na}(\text{D}_6)\text{GaI}_4]$ (26)	-14.9	$\text{CD}_2\text{Cl}_2$	[140]
$[\text{Mg}(\text{D}_6)\text{I}_2]$ (16)	-4.8	$\text{CD}_2\text{Cl}_2$	[138]
$[\text{Cs}(\text{D}_6)_2][\text{Al}^{\text{I}}]$ (33)	-20.8	$\text{CD}_2\text{Cl}_2$	[140]
	-18.8 <sup>[b]</sup>	$\text{CD}_2\text{Cl}_2$	[140]
$[\text{Ag}(\text{D}_6)\text{SbF}_6]$ (11)	-14.2	$\text{SO}_2$	[131]
$[\text{Ag}(\text{D}_6)(\text{FAl}(\text{OR})_3)]$ (12)	-14.2	$\text{SO}_2$	[53]
$[\text{Ag}(\text{D}_6)\text{Al}^{\text{I}}]$ (8)	-11.1	$\text{SO}_2$	[53]
$\text{D}_7$			
	-22.2	$\text{CD}_2\text{Cl}_2$	[138]
	-23.1	$\text{SO}_2$	[131]
$[\text{Na}(\text{D}_7)\text{GaI}_4]$ (27)	-12.7	$\text{CD}_2\text{Cl}_2$	[140]
$[\text{K}(\text{D}_7)\text{GaI}_4]$ (25)	-16.4	$\text{CD}_2\text{Cl}_2$	[140]
$[\text{Ca}(\text{D}_7)_2]$ (17)	-7.8	$\text{CD}_2\text{Cl}_2$	[138]
$[\text{Sr}(\text{D}_7)_2]$ (18)	-9.2	$\text{CD}_2\text{Cl}_2$	[138]
$[\text{Sr}(\text{D}_7)(\text{GaI}_4)_2]$ (19)	-5.3	$\text{CD}_2\text{Cl}_2$	[138]
$[\text{Ba}(\text{D}_7)(\text{GaI}_4)_2]$ (20)	-5.8	$\text{CD}_2\text{Cl}_2$	[138]
$[\text{NH}_4(\text{D}_7)][\text{Ga}_2\text{I}_7]$ (29)	-15.6	$\text{CD}_2\text{Cl}_2$	[140]
$[\text{Ag}(\text{D}_7)\text{SbF}_6]$ (9)	-13.6	$\text{SO}_2$	[131]
$\text{D}_8$			
	-23.0	$\text{C}_6\text{D}_6$	[141]
$[\text{Rb}(\text{D}_8)\text{Al}^{\text{I}}]$ (30)	-16.1	$\text{CD}_2\text{Cl}_2$	[140]
$[\text{Cs}(\text{D}_8)\text{Al}^{\text{I}}]$ (31)	-17.4	$\text{CD}_2\text{Cl}_2$	[140]
$[\text{Ag}(\text{D}_8)\text{SbF}_6]$ (10)	-12.8	$\text{SO}_2$	[131]

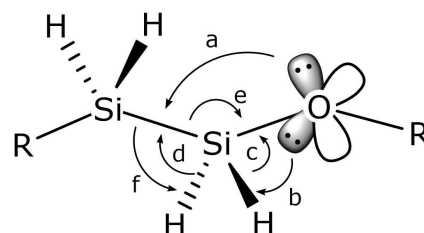
[a] This indicates dissociation in solution, [b] Measurement at 220 K.

rings upon complexation. Several studies show that a difference in ring strain can have a significant impact on the complexation ability and coordination sphere.<sup>[142–145]</sup> Olliff already pointed out in the early 80s, that the coordination ability of many  $\text{D}_n$  ligands might be lowered, solely because of their conformation: By simply using molecular construction kits, possible conformations of  $\text{D}_n$  rings were found to have either very few oxygen positions available for coordination, or exceptionally long  $\text{M}^{n+}$ ...oxygen atom distances would be required.<sup>[119]</sup>

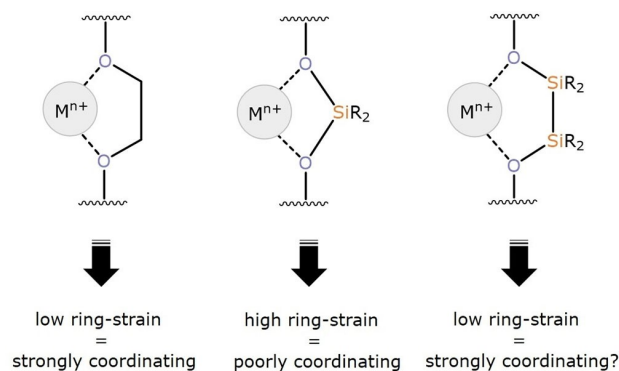
Experimental evidence for this statement was provided in the mid 80s by Inoue and Hakushi. Extraction experiments of crown ethers, ring-contracted crown ethers and mono-sila-crown ethers showed that the cation binding ability toward (alkali)metal picrates is exceptionally high for [3n]crown-n ( $n = 5, 6$ ) ethers. On the contrary, it is exceptionally low for ring contracted [3n-1]crown-n ethers as well as mono-sila-crown ethers.<sup>[142,144]</sup> Hence, an unsupported bite angle of the crown-type macrocycle reduces the cation binding ability significantly. The experimental findings are supported by the fact that a series of ring contracted and sila-crown ethers bearing several



**Figure 18.** The cationic structures of heavy alkali metal complexes with  $\text{D}_n$  ligands and the weakly coordinating  $[\text{Al}^{\text{I}}]^-$  ion.<sup>[140]</sup>  $[\text{Rb}(\text{D}_8)\text{Al}^{\text{I}}]$  (top left),  $[\text{Cs}(\text{D}_8)\text{Al}^{\text{I}}]$  (top right),  $[\text{K}(\text{D}_5)_2][\text{Al}^{\text{I}}]$  (bottom left) and  $[\text{Cs}(\text{D}_6)_2][\text{Al}^{\text{I}}]$  (bottom right). Atoms are displayed isotropically with arbitrarily atom radii for clarity.



**Figure 19.** Strongest interactions contributing to the stability of a  $-\text{SiH}_2-\text{SiH}_2-\text{O}-$  fragment. For clarity, only a single representative of each type of interaction is depicted. a)  $p(\text{O}) \rightarrow \sigma^*(\text{Si}-\text{Si})$ , b)  $p(\text{O}) \rightarrow \sigma^*(\text{Si}-\text{H})$ , c)  $\sigma(\text{Si}-\text{H}) \rightarrow \sigma^*(\text{Si}-\text{O})$ , d)  $\sigma(\text{Si}-\text{H}) \rightarrow \sigma^*(\text{Si}-\text{Si})$ , e)  $\sigma(\text{Si}-\text{Si}) \rightarrow \sigma^*(\text{Si}-\text{O})$ , f)  $\sigma(\text{Si}-\text{Si}) \rightarrow \sigma^*(\text{Si}-\text{H})$ .



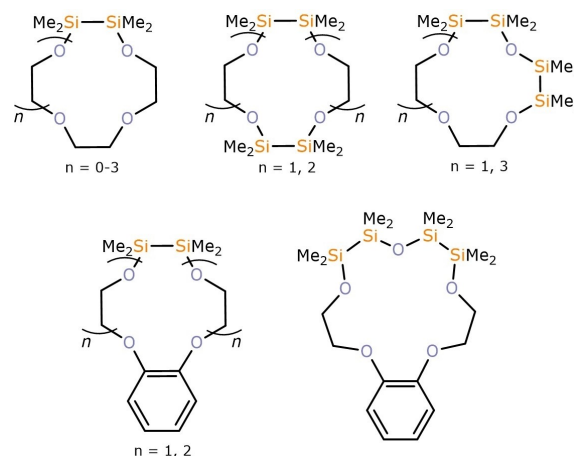
**Figure 20.** Coordination modes in macrocyclic ligands containing a  $\text{C}_2\text{H}_4$  unit (left),  $\text{SiR}_2$  unit (middle), and  $\text{Si}_2\text{R}_4$  unit (right).

—CH<sub>2</sub>—CH<sub>2</sub>—O— as well as one- or two —SiR<sub>2</sub>—O— units have been described in literature,<sup>[146–154]</sup> but, no coordination compounds have been isolated and crystallographically characterized to date.

## 5. Disila-Crown Ethers: Coordination Ability, Activation and Reactivity

The previous chapter gave insights into the bonding situation of cyclic siloxanes bearing disilanes. Evidence is found that <sup>2</sup>D<sub>n</sub> ligands are more basic than D<sub>n</sub> ligands. Further, a large enough bite angle can be provided which prevents disordered conformations. Hence, more basic ligands in combination with suitable ligand conformations might be promising systems for host-guest chemistry.

Unfortunately <sup>2</sup>D<sub>n</sub> ligands (except for n = 2, 3) are relatively unstable. It has been shown that D<sub>n</sub> ligands can be prepared by hydrolysis of diorganodichlorosilanes such as dimethyldichlorosilane (Chapter 1). The hydrolysis of the 1,1,2,2-tetramethyldichlorosilane, however, yields almost exclusively <sup>2</sup>D<sub>2</sub>.<sup>[162]</sup> Formation of <sup>2</sup>D<sub>3</sub> in low yields can also be observed at low temperatures. Higher homologues were not isolated upon hydrolysis of the aforementioned silane. Traces of <sup>2</sup>D<sub>4</sub> and polymeric species have so far only been observed in gas-liquid chromatography after ring opening polymerization of <sup>2</sup>D<sub>2</sub> initiated with triflic acid.<sup>[163,164]</sup> Hence, synthetic protocols to obtain the macrocycles <sup>2</sup>D<sub>n</sub> (n = 3–6) in suitable yields have not yet been established. Host-guest chemistry of these “inorganic” crown ether analogues can thus not be straightforwardly performed. To obtain meaningful experimental data of disila-bridged macrocycles, we started embedding Si<sub>2</sub>Me<sub>4</sub> bridges into crown ether moieties. In this way, organic ethers are partially substituted by silicon-based “inorganic” building blocks. The synthesis of such ligand systems is mostly achieved through conversion of a respective organic glycol, a chlorosilane and an auxiliary base such as NEt<sub>3</sub>.<sup>[155–158,165–168]</sup> Suitable solvents, proved to be THF (THF = tetrahydrofuran) or Et<sub>2</sub>O. Dependent on the chain length of the glycol and type of dichlorosilane, various crown ethers are accessible (Figure 21). The crown ether analogues depicted in Figure 21 proved to be suitable ligands for a large range of cations including various anions. Cations considered for complexation were Li<sup>+</sup>–K<sup>+</sup>,<sup>[155,156,159,169]</sup> NH<sub>4</sub><sup>+</sup>,<sup>[170]</sup> Mg<sup>2+</sup>–Ba<sup>2+</sup>,<sup>[157–159,171]</sup> and very recently also various cations of the p-block such as Ga<sup>3+</sup>, In<sup>+3+</sup>, Tl<sup>+</sup>, Ge<sup>2+</sup>–Pb<sup>2+</sup>, Sb<sup>3+</sup> and Bi<sup>3+</sup> (please note that these are preliminary results, though).<sup>[172]</sup> Hence, the successful incorporation of these cations, and partially also elusive electrophiles such as Ge<sup>2+</sup> showed that cooperative effects of carbon-substituted oxygen donors as well as partially silicon substituted oxygen donors allow for effective binding of cations. In case of Li<sup>+</sup>, not only could molecular structures be determined but also the complexation ability of three different disila-crown ethers were determined by means of gas-phase calculations. Relative energies of the Li<sup>+</sup> exchange from [12]crown-4 to 1,2-disila[12]crown-4 yields –10 kJ mol<sup>–1</sup>. Li<sup>+</sup> exchange from [12]crown-4 to



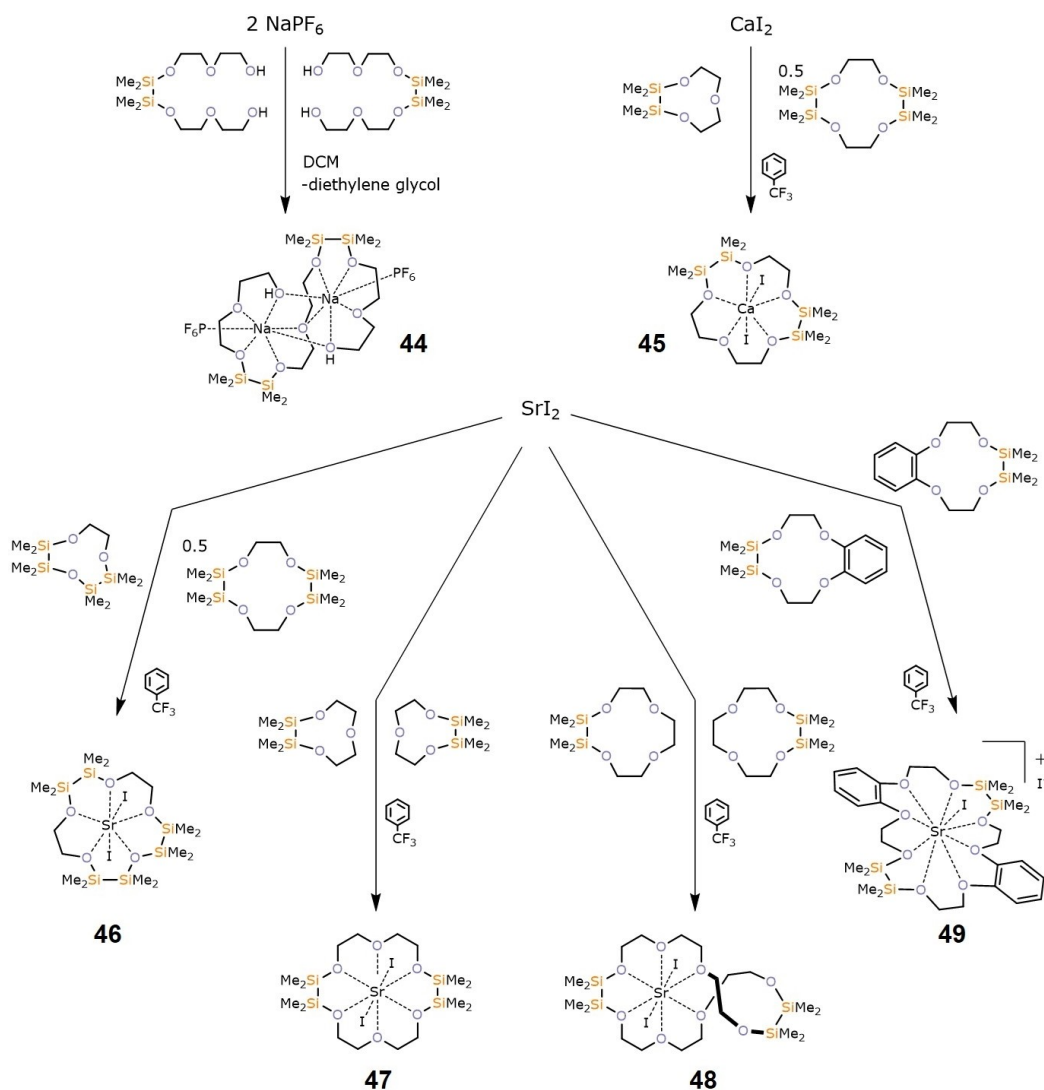
**Figure 21.** Partially silicon-based crown ether analogues synthesized directly from chlorosilanes and a respective glycol. For details see refs. [155–161].

1,2,7,8-tetrasilal[12]crown-4 or 1,2,4,5-tetrasilal[12]crown-4 yields 3 kJ mol<sup>–1</sup> and –29.5 kJ mol<sup>–1</sup>, respectively. Furthermore, dynamic <sup>1</sup>H NMR spectroscopic studies revealed that 1,2,7,8-tetrasilal[12]crown-4 coordinates reasonably well when compared with [12]crown-4. Enough evidence is thus provided, that these new classes of ligands have a significant coordination potential. This, however, is true only as long as the cavity matches well with the respective cation. A drastic decrease in cation binding ability was observed in “mismatched” complexes of hybrid disila-crown ethers. Cations which are too small for the cavity of a respective crown ether are not coordinated in a coplanar manner by the ligands O atoms. Some oxygen atoms are even reluctant toward coordination in certain cation-ligand combinations.<sup>[158]</sup> Such drastically reduced coordination ability is for example observed for [Ca(1,2-disila[18]crown-6)OTf<sub>2</sub>]. Whereas [18]crown-6 uses all six oxygen donors for coordination, the disila-crown ether allows only five oxygen atoms for coordination due to its larger cavity size. Hence, the cation binding ability of [18]crown-6 was determined to be considerably higher by means of NMR spectroscopy.<sup>[157]</sup> Interestingly, the non-coordinating oxygen atoms are not inevitably silicon substituted. Clearly though, a suitable match between ion radius of the cation and crown ether cavity significantly improves the complex stability and supports coordination of the three types of oxygen donors O<sub>Si</sub>, O<sub>Si/C</sub> and O<sub>C</sub>.

To what extent a Si-substituted oxygen atom is coordinating, is well-represented by means of <sup>29</sup>Si NMR spectroscopy in solution. Such NMR experiments turned out to be a very good indicator for the strength of the interaction between a metal ion and the siloxane backbone as the <sup>29</sup>Si NMR chemical shift is very sensitive toward coordination.<sup>[159]</sup> As also shown for the D<sub>n</sub> complexes (Table 2), coordination causes a characteristic down-field shift. Figure 22 shows solid-state structures of various complexes and corresponding <sup>29</sup>Si NMR chemical shifts are compiled in Table 3. As can be seen here, Li<sup>+</sup> shares strong interactions with –SiSi–O–SiSi– when bound in 1,2,4,5-tetrasilal[12]crown-4 (**34**) (Figure 22: **35**). So do Ca<sup>2+</sup> and







Scheme 7. Templated synthesis of different hybrid disila-bridged ligand systems.<sup>[171,173]</sup>

The first ever hexasila-crown ether was obtained in this way which contains more disila than ethylene units. The compound [Sr(1,2,4,5,10,11-hexasila[15]crown-5)]<sub>2</sub> (**46**) has been successfully isolated and characterized. Due to three different Si atoms, three respective resonances are found in the <sup>29</sup>Si NMR spectrum for this compound. The resonances are observed at 19.4 ppm, 19.3 ppm and 13.3 ppm comparing well with other disila-ligands coordinating Sr<sup>2+</sup>.<sup>[157,159]</sup> Crystal structure elucidation was possible for the respective [Ga<sub>4</sub>]<sup>-</sup> complex [Sr(1,2,4,5,10,11-hexasila[15]crown-5)(Ga<sub>4</sub>)<sub>2</sub>] (**46**·2Ga<sub>3</sub>). A similar Ca<sup>2+</sup> complex (**45**) was obtained after cross-coupling 1,2,7,8-tetrasila[12]crown-4 and 1,2-disila[9]crown-3 with CaI<sub>2</sub>. The molecular structures of the cations of these two examples (**45**·2I<sub>2</sub> and **46**·2Ga<sub>3</sub>) are depicted in Figure 23.

By using various synthetic protocols and templated coupling reactions, the silicon content of such ring systems was increased stepwise over the years. As ethylene bridges remained as building blocks for such rings, it was not possible to obtain an all-silicon version of crown ethers. However, very

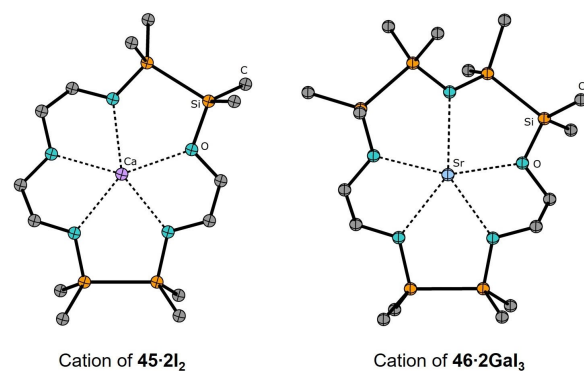
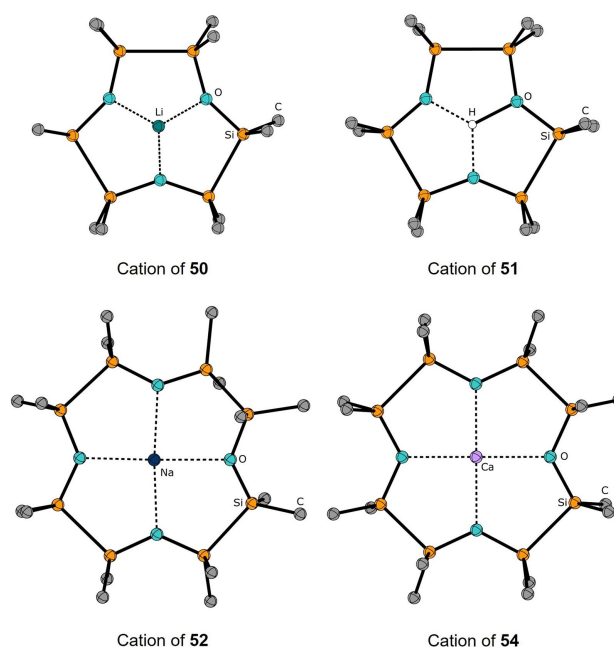


Figure 23. Two ligand architectures obtained by cross-coupling of disila-crown ethers with alkaline earth metal salts. Selected examples are the cationic parts of [Sr(1,2,4,5,10,11-hexasila[15]crown-5)(Ga<sub>4</sub>)<sub>2</sub>] (left) and [Ca(1,2,7,8-tetrasila[12]crown-4)(I<sub>3</sub>)<sub>2</sub>] (right). Atoms are displayed isotropically with arbitrarily atom radii for clarity.

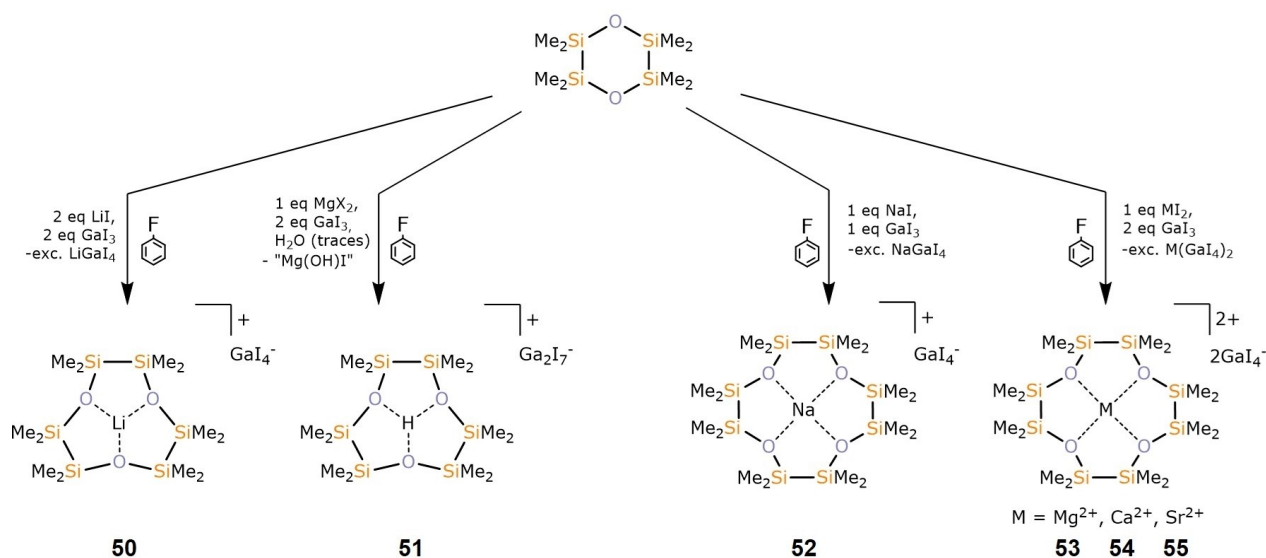
recently, it was shown, that the template approach is feasible to obtain exclusively silicon-based ligands.  ${}^2D_2/s$ -block metal iodide/gallium(III)iodide Lewis acid systems have been established which made the synthesis of such systems possible (Scheme 8).<sup>[174]</sup> Combining both, sufficient Lewis acidity of an early s-block metal ion and the *in-situ* generated, small WCA  $[\text{GaI}_4]^-$  were the key to find access to these new all-silicon versions of crown ethers. The cation recognition of these systems is substantially different to that of organic crown ethers, though.  $\text{H}^+$  and  $\text{Li}^+$  are coordinated by  $\text{Si}_6[9]\text{crown-3}$  ( ${}^2D_3$ ) instead of  $[\text{12}]\text{crown-4}$  (see **50** and **51**) and  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  are coordinated by  $\text{Si}_8[12]\text{crown-4}$  ( ${}^2D_4$ ) (see **52–55**) instead of  $[\text{3n}]\text{crown-n}$  ( $n=5, 6$ ) according to the solid state structures (Figure 24). DOSY (=diffusion ordered spectroscopy) experiments confirm these structures in solution,  ${}^{29}\text{Si}$  NMR shifts are given in Table 4.<sup>[174]</sup> Using MeCN as a donor solvent readily removes the respective metal centre from the ligand. As long as the metal is present, the respective ligand moiety is maintained. As soon as it is removed, though, oligo- and monomerization occurs which has been elucidated by means of multinuclear NMR spectroscopy and combined LIFDI MS spectrometry. The larger rings  ${}^2D_5$  and  ${}^2D_6$  have then also been observed by means of NMR and/or MS spectrometry. Hence, these  ${}^2D_n$  type crown ethers do not form substantially more stable complexes than  $D_n$  systems and are unstable as free ligands. Nevertheless, we see these results as a significant advance in synthetic silicon chemistry as finally also cyclic polyethers were successfully reconstructed based on silicon. Quantum chemical calculations further demonstrated that coordination of a cation is clearly undesirable when  ${}^2D_2$  is employed for coordination. Especially  ${}^2D_4$  is found to coordinate much stronger. Hence, these crown ethers also exhibit a macrocyclic effect, though to a less extent than observed for organic crown ethers.<sup>[174]</sup>

As there are so far only six examples of such coordination compounds of inorganic crown ether systems known to date, we



**Figure 24.** The cationic parts of selected complexes with inorganic crown ether ligands.  $[\text{Li}({}^2D_3)\text{GaI}_4]$  (top left),  $[\text{H}({}^2D_3)]\text{[GaI}_4]$  (top right),  $[\text{Na}({}^2D_4)\text{GaI}_4]$  (bottom left) and  $[\text{Ca}({}^2D_4)(\text{GaI}_4)_2]$  (bottom right). Atoms are displayed isotropically with arbitrarily atom radii for clarity.

assume this chemistry to be still at an early stage. It took several decades to establish siloxanes for effective coordination and over time, more and more strategies have been established to stabilize siloxane-coordination compounds. We hope that the field further opens up by time and that novel compounds with inorganic crown ethers are characterized very soon. Synthesizing such systems is however limited by several restrictions, though. Besides the special requirements in terms of siloxane



**Scheme 8.** Templated synthesis of inorganic crown ether analogues.<sup>[174]</sup>

**Table 4.**  $^{29}\text{Si}$  NMR chemical shifts of  $^2\text{D}_2$  and inorganic crown ether complexes.

Compound	$^{29}\text{Si}$ NMR shift [ppm]	Reference solvent	Reference
$^2\text{D}_2$	3.6	$\text{CD}_2\text{Cl}_2$	[175]
$[\text{H}(^2\text{D}_3)\text{Ga}_4] \text{ (51)}$	21.2	$\text{CD}_2\text{Cl}_2$	[174]
$[\text{Li}(^2\text{D}_3)\text{Ga}_4] \text{ (50)}$	15.5	$\text{CD}_2\text{Cl}_2$	[174]
$[\text{Na}(^2\text{D}_4)\text{Ga}_4] \text{ (52)}$	13.1	$\text{CD}_2\text{Cl}_2$	[174]
$[\text{Mg}(^2\text{D}_4)(\text{Ga}_4)_2] \text{ (53)}$	25.7	$\text{CD}_2\text{Cl}_2$	[174]
$[\text{Ca}(^2\text{D}_4)(\text{Ga}_4)_2] \text{ (54)}$	19.2	$\text{CD}_2\text{Cl}_2$	[174]
$[\text{Sr}(^2\text{D}_4)(\text{Ga}_4)_2] \text{ (55)}$	16.6	$\text{CD}_2\text{Cl}_2$	[174]

coordination, it was shown recently that the aforementioned Lewis acid systems as well as various salts of hard metal cations are quite aggressive and tend to activate  $^2\text{D}_2$  as well as CF-bonds.

It was shown that the rather chemical inert  $\text{CF}_3$  group of  $\alpha,\alpha,\alpha$ -trifluorotoluene is completely deconstructed either by  $^2\text{D}_2/\text{M}_{\text{EA}}\text{Br}_2/\text{GaBr}_3$  ( $\text{M}_{\text{EA}} = \text{Be}^{2+}, \text{Mg}^{2+}$ ) mixtures or exclusively by  $\text{BeBr}_2, \text{BeI}_2, \text{GaI}_3, \text{HfI}_4$  and  $\text{ThI}_4$  [175]  $[\text{Ph}-\text{C}(\text{O}_2\text{Si}_2\text{Me}_4)][\text{GaX}_4]$  ( $\text{X} = \text{Br}$  (55),  $\text{I/F}$  (56)),  $\alpha,\alpha,\alpha$ -tribromotoluene or  $\alpha,\alpha,\alpha$ -triiodotoluene have been characterized as the respective degradation products. Hence, we recommend non-coordinating, even more inert solvents such as  $\text{Ph}-\text{F}$  for this chemistry but we emphasize that activating various chemical bonds with these strongly Lewis acidic systems is without a doubt also an interesting possibility for further investigations.

## 6. Concluding Remarks and Outlook

Even though cyclic siloxanes have been known even before the conventional crown ethers, coordination compounds of these systems have evaded facile synthesis until recently. The field has significantly developed in the last decade and new ways to initiate the elusive Si–O–Si unit for effective coordination have been theoretically and experimentally established. With this review, it should now be clear, that these complexes are by no means curiosities, but can be prepared for many combinations of ligands and cations. Especially templated ring-opening polymerizations enabled the synthesis and characterization of several new compounds including cyclic siloxanes, hybrid disilacrown ethers and most astonishingly also inorganic crown ethers. We therefore hope that this review will also give rise to the synthesis of more ring-systems based on siloxane linkages. There is a lot more reactivity to be discovered such as with trisilanes, cage-like siloxanes or related (ring-)systems. We assume that the Si–O bond activation reactions might also be the starting point for templated (cyclo-)siloxane synthesis from polydiorganosiloxanes which would then also bridge the gap between fundamental research and material sciences. Further, as has been extensively evaluated for the conventional crown ethers, research efforts on catalysis are without a doubt also an interesting possibility employing these ligands.

A take-home message should be, that the earlier consideration of siloxanes as very weakly coordinating ligands should be dropped. Moreover, (metal-)templated synthesis gives val-

uable access to a variety of siloxane ligands, which cannot be synthesized by other means.

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## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** Siloxanes · Si–O bond activation · Coordination chemistry · Host-guest chemistry · Macrocycles · Inorganic macrocycles · Templates

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- [2] a) A. F. Hollemann, N. Wiberg, *Lehrbuch der Anorganischen Chemie*. Walter de Gruyter, Berlin 2007; b) All minerals of the tourmaline supergroup bear six-membered cyclosilicates and a trigonal crystal symmetry. The general formula is  $\text{XY}_3\text{Z}_6(\text{T}_6\text{O}_{18})(\text{BO}_3)_3\text{V}_3\text{W}$ , where  $\text{X} = \text{Na}^+, \text{Ca}^{2+}, \text{K}^+, \text{Pb}^{2+}$  and vacancy;  $\text{Y} = \text{Fe}^{2+}, \text{Mg}^{2+}, \text{Mn}^{2+}, \text{Al}^{3+}, \text{Li}^+, \text{Fe}^{3+}$ , and  $\text{Cr}^{3+}$ ;  $\text{Z} = \text{Al}^{3+}, \text{Fe}^{3+}, \text{Mg}^{2+}$ , and  $\text{Cr}^{3+}$ ;  $\text{T} = \text{Si}^{4+}, \text{Al}^{3+}$ , and  $\text{B}^{3+}$ ;  $\text{V} = \text{OH}^-$  and  $\text{O}^{2-}$ ; and  $\text{W} = \text{OH}^-, \text{F}^-$ , and  $\text{O}^{2-}$ . In these minerals, the ring-silicate coordinates six-fold towards  $\text{Na}^+, \text{K}^+, \text{Ca}^{2+}$  or also  $\text{Pb}^{2+}$  with its ring oxygen atoms, similar as demonstrated also for cyclic siloxanes in this review. A comprehensive overview is provided in the mineralogical database *mindat* (see: <https://www.mindat.org/min-4003.html>) and in: D. J. Henry, M. Novák, F. C. Hawthorne, A. Ertl, B. L. Dutrow, P. Uher, F. Pezzotta, *Am. Mineral.* 2011, 96, 895–913.
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