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Chemistry of metallasiloxanes. Current trends and new concepts

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Abstract. The current status of the chemistry of metallasiloxanes is surveyed. Synthetic methods affording the metallasiloxane fragments and specific transformations of metallasiloxanes governed by the coordination properties of the metal site are analysed. The emphasis is placed onto the formation of compounds with the metallasiloxane fragments and rearrangements of these fragments. Principles of the design of catalytic systems based on metallasiloxanes, in particular, containing low-coordinated metal sites, are generalised. The bibliography includes 174 references.

I. Introduction

Chemistry of metallasiloxanes (hereinafter, MS), *viz*., compounds containing a $>$Si(R)OM fragment, where M is a metal atom, initially emerged as a subfield within chemistry of organosilicon compounds, but then gradually grew into an independent scientific direction. The vast majority of transformations of MS directly involves the SiOM fragment, and the structure of MS is largely governed by the coordination properties of the constituent metal.

Intensive investigations into individual metallasiloxanes started in the 1950s. The major results of these studies are summarised in a number of reviews and monographs.[1–8] In parallel, oligomeric[9–11] and polymeric MS containing metallasiloxane fragments in the main organosiloxane chain became a subject of numerous studies. Some of these compounds came into industrial-scale production within literally years of their first synthesis.[12]

The following directions in the chemistry of metallasiloxanes have proven most fruitful over the last 15 years:

— the development of novel methods for the creation of the metallasiloxane fragment, which has led to the discovery of new structural types of MS and extended the range of metal atoms that can be incorporated in the metallasiloxane fragment;

— investigations into highly specific chemical transformations of MS;

— the development of general concepts that describe the formation of the MS structure;

— the elaboration of concepts that rationalise the regularities of rearrangements of metallasiloxane fragments in the structure of MS;

— the application of MS as catalysts in various processes of organic synthesis.

II. Synthetic methods in the chemistry of metallasiloxanes

Methods used to create the metallasiloxane fragment are rather diverse. Some early methods have been modified and are used nowadays.

The reaction of organosilanols with reactive metals, such as alkali metals,[13] zinc[14] or aluminium,[15] represents one of the historically first methods.

$$R_3SiOH \xrightarrow[-H_2]{M} (R_3SiO)_nM,$$

M = K, Na, Zn, Al; *n* is the metal oxidation state.

Presently, this method retains its preparative importance mainly for the synthesis of alkali metal organosilanolates.

The reaction of organosilanols with organometallic compounds is a less common method.[16–18]

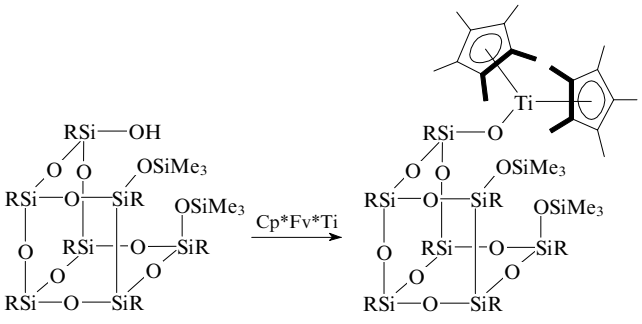
$$R_3SiOH + R'_2M \xrightarrow[-R'H]{} R_3SiOMR',$$

R = Me, Et, Ph; R′ = Me, Et; M = Zn, Cd.

Typically, this reaction is accompanied by the liberation of the corresponding hydrocarbon. However, according to recent studies,[19] in some cases hydrocarbon ligands at the metal atom undergo rearrangements (*e.g*., fulvene converts into cyclopentadienyl giving rise to compound **1**).

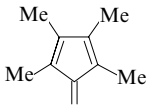
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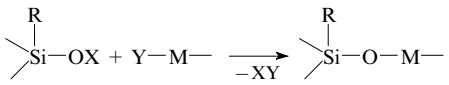
1

R = cyclo-C_6H_{11}; Cp* = η-C_5Me_5,

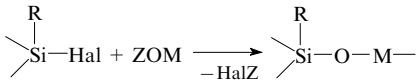
Fv* = .

The heterofunctional condensation is the most common method for the synthesis of MS; this reaction can be accomplished in different ways to afford both individual and oligomeric MS (R, R′ and R″ are organic substituents) (Scheme 1).

Scheme 1

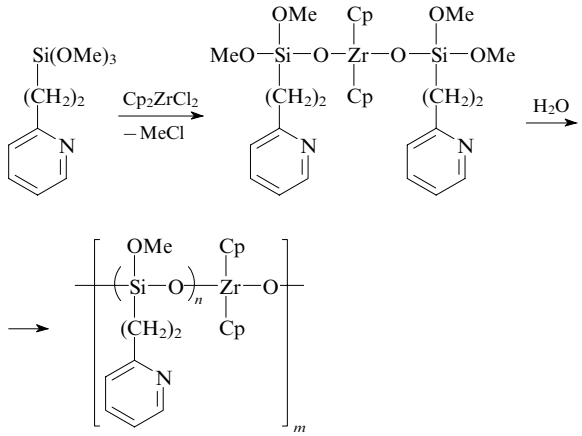


X = H: Y = Hal, R′O; X = R″: Y = Hal, AcO; X = Ac, Y = Hal.

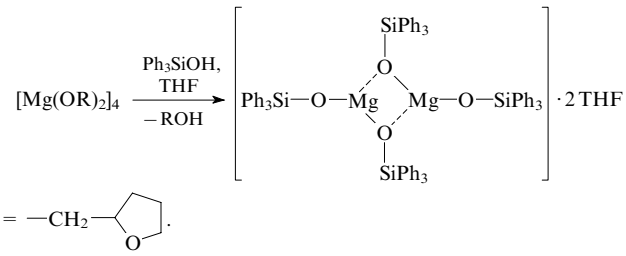


Z = H, R.

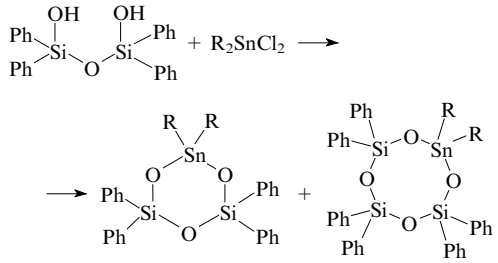
Below we consider only those versions of the heterofunctional condensation that are widely applied in modern studies. A combination X = R″ and Y = Hal (see Scheme 1) is especially suitable for the synthesis of polymeric MS, since the low-molecular-mass condensation product (R″Hal) does not destroy the main chain of the product.[20]



Organometallic derivatives with Y = OR′ should be utilised provided the self-condensation of a silanol R_3SiOH is hindered, for instance:[21]

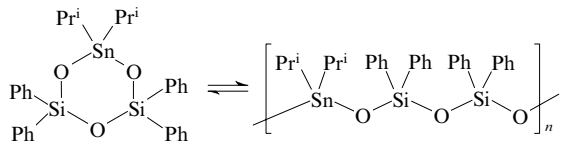


The heterofunctional condensation of silanols with metal halides (X = H and Y = Hal in Scheme 1) is useful in those cases where a silicon (or metal) atom bears a bulky branched substituent (*e.g.*, isopropyl or *tert*-butyl group).[22]

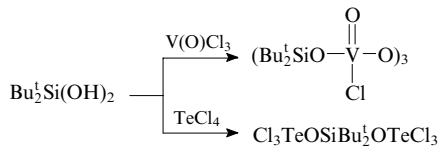


R = Pr^i, Bu^t.

If the Sn atom bears isopropyl (but not *tert*-butyl) groups, cyclic organostannasiloxanes can undergo polymerisation.



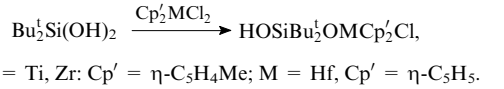
Often, the reaction of organosilanediols with metal halides results in only partial substitution of organosiloxy groups for the Cl^- ions.[23]



Derivatives with one or two Cp groups at the metal atom can be obtained provided the Si atom in the starting organosilicon compound bears the Bu^t group; this reaction is impossible with Et or Ph substituents at the silicon atom.[24]

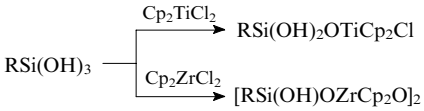


Cp′ = η-C_5Me_5, η-C_5Me_4Et;



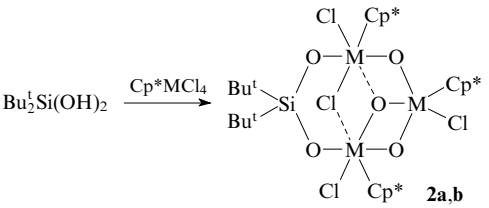
M = Ti, Zr: Cp′ = η-C_5H_4Me; M = Hf, Cp′ = η-C_5H_5.

The presence of a bulky branched group at the silicon atom allows the use of organosilanetriols in addition to diorganosilanediols in these reactions, since their self-condensation is hindered.[25]



R = 2,6-$Pr^i_2C_6H_3NSiMe_3$.

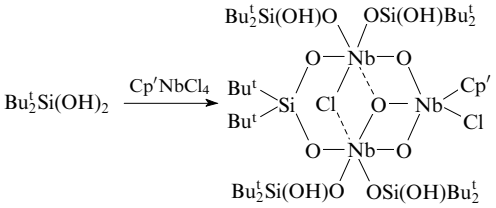
It must be noted that the synthesis of Nb- and Ta-containing MS (for instance, compounds **2a**,**b**) is accompanied by the formation of metal oxide fragments M–O–M,[26] which cannot be explained by the heterofunctional condensation mechanism. This fact suggests a rearrangement to occur during the synthesis (this is described in more detail in Section IV).



2a,**b**

M = Nb (**a**), Ta (**b**).

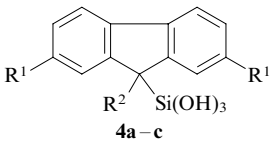
In some cases, the reaction is additionally complicated by a competing process, *viz*., organosiloxy group substitution for the π-coordinated ligand.[26] Sunthesis of compound **3** may serve as an example.



3

Cp′ = η-C_5Me_4Et.

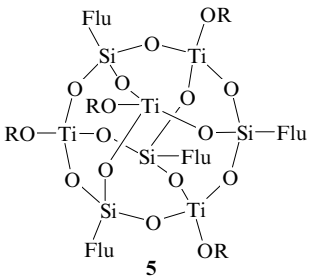
The strongest shielding effect among organic substituents studied is exerted by the fluorenyl group, which allows complete suppression of the self-condensation of the organosilanetriol upon its reaction with metal alkoxides. The heterofunctional condensation of fluorenyl-substituted organosilanetriols **4a**–**c**



4a–**c**

R^1 = H: R^2 = $SiMe_3$ (**a**), Me (**b**); R^1 = Bu^t, R^2 = $SiMe_3$ (**c**).

with titanium alkoxides $Ti(OR)_4$ yields cage titanasiloxanes **5**.[27,28]



5

Flu is a substituted fluorenyl; R = Et, Pr^i.

Another relatively rare method for the synthesis of MS, *viz*., the reaction of organosilanols with metal amides or imides can also be classified as the heterofunctional condensation.[29–31]

$$[\mu\text{-}N(SiMe_3)_2CoN(SiMe_3)_2]_2 \xrightarrow[-(Me_3Si)_2NH]{Ph_3SiOH} [Co(\mu\text{-}OSiPh_3)(OSiPh_3)THF]_2,$$

$$[(Bu^tNH)_2W(=NBu^t)_2] \xrightarrow[-Bu^tNH_2]{Bu^t_3SiOH} [(Bu^t_3SiO)_2W(=NBu^t)_2]_2,$$

6

$$[(Me_3Si)_2N]_3V \xrightarrow[-(Me_3Si)_2NH]{Bu^t_3SiOH} (Bu^t_3SiO)_3V.$$

Owing to the presence of bulky substituents at the silicon atom in compound **6**, a novel tricoordinate tungsten compound **7** was synthesised.[30]

$$\mathbf{6} \xrightarrow[-Bu^tNH_3Cl]{HCl,\ PhH} [(Bu^t_3SiO)_2Cl_2W{=}NBu^t]_2 \xrightarrow[-MgCl_2]{Mg,\ Et_2O} [(Bu^t_3SiO)_2W{=}NBu^t]_2$$

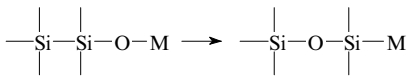
7

An analogous reaction of metal silylamides with organosilanols yields MS with the disilane bridges Si–Si; the tris(trimethylsilyl)silyl fragment $(Me_3Si)_3Si$ acts as a bulky substituent in this case.[32,33]

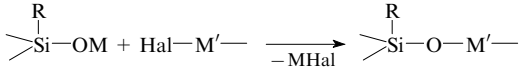
$$[(Me_3Si)_2N]_nM \xrightarrow[-(Me_3Si)_2NH]{(Me_3Si)_3SiOH,\ L} [(Me_3Si)_3SiO]_nML_m$$

M	*n*	L
Co	2	THF, DME, MeCN, PhCN, 2,2′-bipy, 4,4′-bipy, Ph_3P
Fe	2	2,2′-bipy, 4,4′-bipy
La	3	THF
Gd	3	THF, MeCN, 4,4′-bipy

The Si–Si bonds in these compounds are highly reactive. They are very sensitive to oxidation and are easily converted into the siloxane fragments Si–O–Si under the action of O_2 (Ref. 32); pyrolysis in the absence of O_2 results in the migration of an O atom, which is accompanied by a rearrangement and formation of the bond Si–M.[34,35]



The reaction of alkali metal organosilanolates with polyvalent metal halides (M′) is yet another popular version of the heterofunctional condensation; it is commonly referred to as the exchange reaction in the literature.



This reaction is most versatile. It was successfully used to synthesise MS containing Mg, Zn, Al, Ga, Ti, Zr, Fe, Co, Ni, Cu and some other metals,[8,11] which substantially extended the range of metal atoms incorporated in the metallasiloxane fragment.[36–40] The use of bulky organic groups at the silicon atom played the key role in the development of the synthetic potential of this method.

$$ScCl_3(THF)_3 \xrightarrow[-NaCl]{Bu^t_3SiONa} (Bu^t_3SiO)_3Sc(THF),$$

$$TaCl_5 \xrightarrow{Bu^t_2RSiONa} (Bu^t_2RSiO)_3TaCl_2,$$

R = H, Me, Ph;

$$Na[W_2Cl_7(THF)_5] \xrightarrow{Bu^t_3SiONa} (Bu^t_3SiO)_3W{\equiv}W(OSiBu^t_3)_2Cl,$$

$$CrCl_2(THF)_2 \xrightarrow{Bu^t_3SiONa} (Bu^t_3SiOCrCl)_4,$$

$$Cl_4WO \xrightarrow{Bu^t_3SiONa} (Bu^t_3SiO)_2Cl_2WO.$$

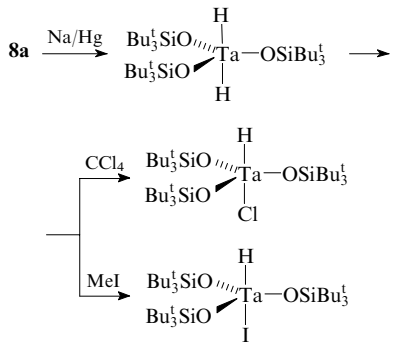
The presence of bulky substituents at the silicon atoms not only makes it possible to synthesise low-coordinate metal complexes but also deliberately change the metal oxidation state by varying the size of this group. In particular, the reduction of $(Pr^i_3SiO)_3TaCl_2$ yields a stable bridging complex of Ta(IV); an analogous complex with Bu^t in place of Pr^i is unstable and undergoes the disproportionation into Ta(V) (**8a**) and Ta(III) (**8b**) compounds.[37]

$$(R_3SiO)_3TaCl_2 \xrightarrow{Na/Hg} (R_3SiO)_3Ta\begin{smallmatrix}Cl\\Cl\end{smallmatrix}Ta(OSiR_3)_3 \xrightarrow{R = Bu^t}$$

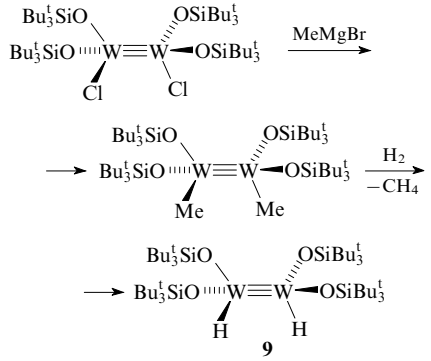
$$\longrightarrow \underset{\mathbf{8a}}{(Bu^t_3SiO)_3TaCl_2} + \underset{\mathbf{8b}}{(Bu^t_3SiO)_3Ta}$$

R = Pr^i, Bu^t.

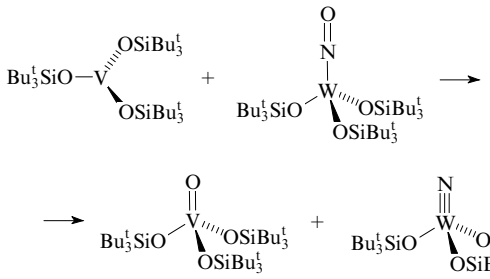
The Bu^t groups are preserved upon subsequent transformations of the MS.[37]



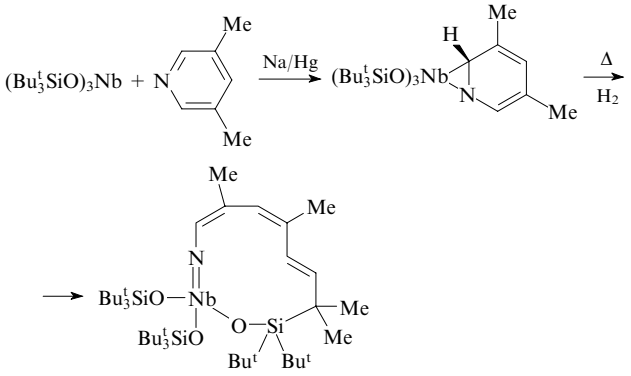
Under reductive conditions (*i.e.*, H_2, 1 atm), siloxy tungsten derivatives are converted into unusual siloxyhidrides **9**, which represent a new class of compounds.[38] They could be isolated as individual compounds due to the stabilising effect of the R_3SiO groups.



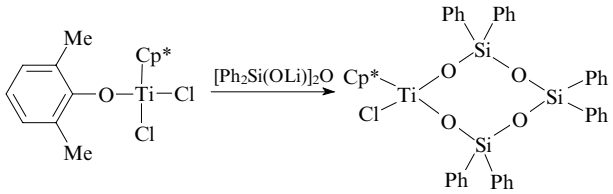
Compounds $(Bu^t_3SiO)_3M$ (M = V or W) undergo redox reactions.[31]



In the above considered examples, the triorganosiloxy groups at the metal atoms played the role of bulky substituents that enabled various redox transformations, synthesis of low-coordinate metal complexes and isolation of unstable compounds, these groups being not directly involved in the reactions. However, there are some examples of the direct involvement of the siloxy group in reactions, for instance, in the rearrangement of a heterocyclic fragment formed upon the addition of 3,5-lutidine to a metal site.[41]



In some cases, exchange reactions occur in an unusual way. In particular, the OAr group at the Ti atom can compete with the Cl ions for the reaction with the group Si—OLi. The highly strained three-membered ring is expected to form in the first step according to the general reaction route undergoes a rearrangement into a more stable four-membered ring (the diatomic fragment Si—O or M—O is taken as a ring member).[42]



A Co(I)-containing MS has been synthesised for the first time using the exchange reaction.[43]

$$CoCl\cdot 3\,PPh_3 + Me_3SiONa \longrightarrow Me_3SiOCo\cdot 3\,PPh_3 + NaCl.$$

In addition, polyhedral MS based on trifunctional organosilicon fragments $RSiO_{1.5}$ were synthesised using the exchange reactions. This gave rise to a new class of MS with unusual cage architectures.

The general reaction pathway includes hydrolysis of organotrichlorosilanes, alkali-assisted cleavage of the polysiloxane followed by the exchange reaction of the resultant organosilanolate with polyvalent metal halides. The polysiloxane produced in the first step of the process contains the silanol groups Si—OH, which are prone to self-condensation accompanied by liberation of water. This results in a partial removal

of the metal from the reaction medium in the form of hydroxide. Therefore, for alkali-assisted cleavage of the polysiloxane, definite amount of sodium (not shown in the reaction scheme below), which reacts with the silanol groups, has been added to the reaction medium in addition to alkali to maximally suppress the potential self-condensation of the silanol groups.

Two versions of this reaction have been studied,[44–49] *viz*., partial (*a*) and complete (*b*) substitution of the polyvalent metal atoms M′ for the silanolate groups SiOM.

$$RSiCl_3 \xrightarrow[-HCl]{H_2O} [RSiO_{1.5-0.5m}(OH)_m]_x \xrightarrow[-MCl]{MOH} [RSi(O)OM]_y \xrightarrow{M'Cl_n}$$

a → $[(RSiO_{1.5})_k(MO_{0.5})_l(M'O_{0.5n})_c]_y \cdot L_z$

R	M	M′
Ph	Na	Cu, Ni, Co, Nd, Gd, Dy
Vin, Et	K	Cu
Et	Na	Cu
Et	K	La

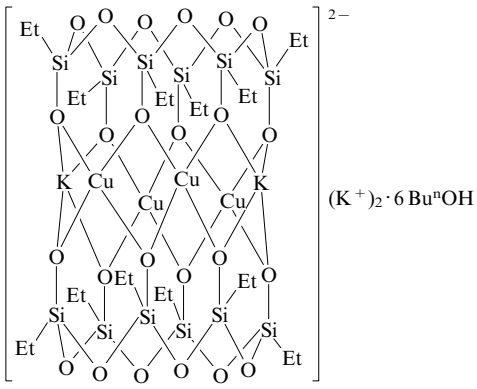
L = EtOH, Bu^nOH, H_2O.

b → $[(RSiO_{1.5})_k(M'O_{0.5n})_l]_y \cdot L_z$

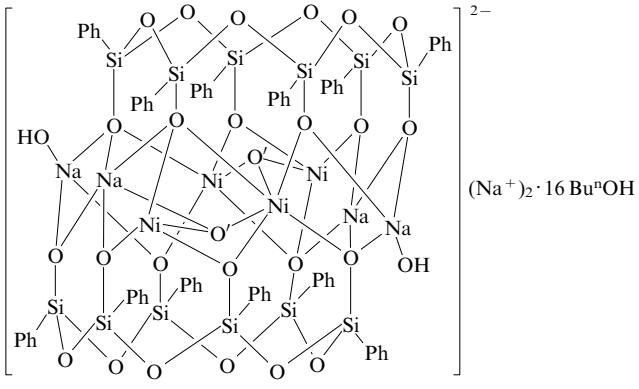
R = Ph, M′ = Co, Ni, Cu, Mn;
L = EtOH, Bu^nOH.

For *a*, *b* see text; *n* is the oxidation state of M′; Vin is vinyl.

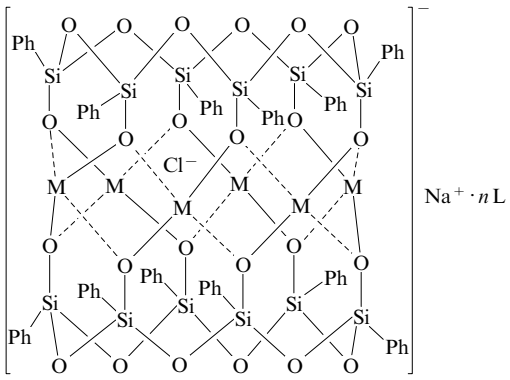
The majority of compounds synthesised according to the above scheme irrespective of partial or complete substitution of the silanolate groups have prism-shaped structures (sometimes, skewed prisms) with the cyclosiloxane fragments at the base (compounds **10**–**14**) (in the structure of compound **11**, the O′ atoms belong to coordinated water molecules).



10

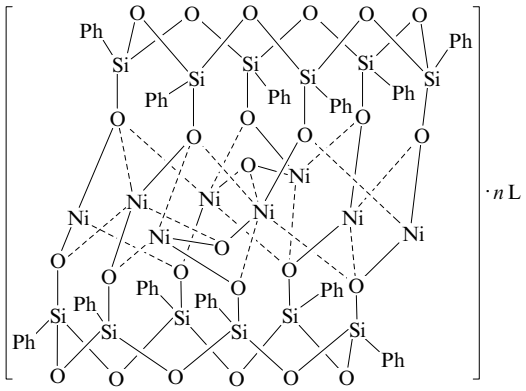


11



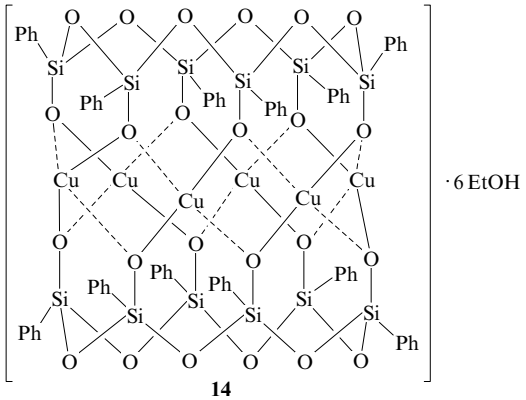
12a–c

M = Co (**a**), Mn (**b**), Ni (**c**);
L = Bu^nOH, EtOH, H_2O, Me_2CO, $CHCl_3$.



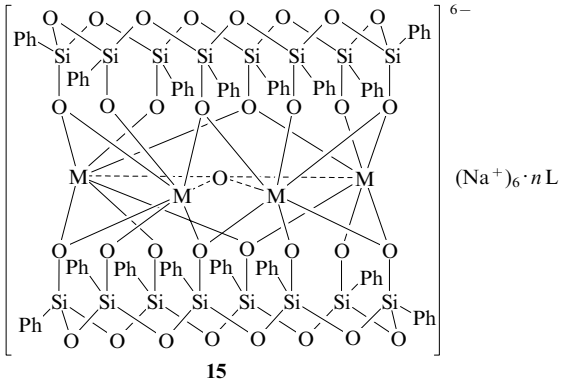
13

L = Bu^nOH, H_2O, Me_2CO.



14

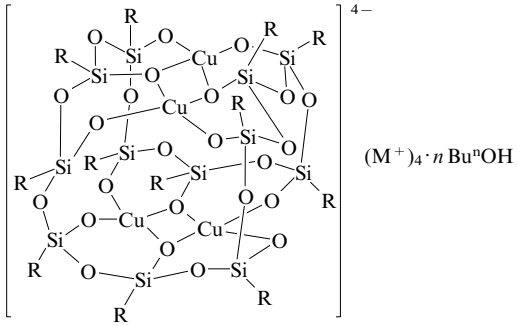
The cyclic fragments at the base of the prism are expanded from six- to eight-membered rings when lanthanides are introduced into MS [50–53] (compounds **15**).



15

M = Nd, Gd, Dy; L = EtOH, H_2O.

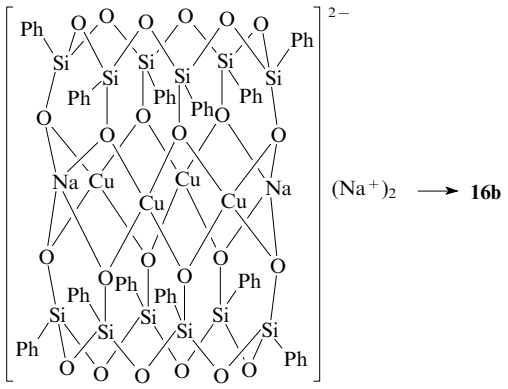
In some rather rare cases of Cu-containing MS **16a–c** also incorporating alkali metal cations, the cage is characterised by a globular shape.[54, 55]



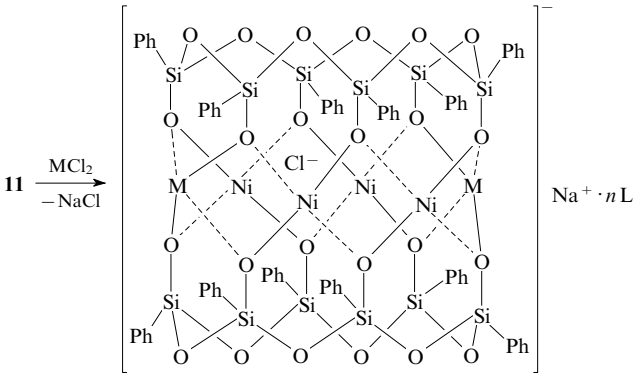
16a–c

Compound **16**	M	R	*n*
a	Na	Et	4
b	Na	Ph	8
c	K	Vin	4

It waas possible to convert the prismatic structure into the globular type cage upon prolonged heating of the compound in an organic solvent (butanol or dioxane).[56]



In those case where MS simultaneously contain transition (polyvalent) and alkali metals (in unsubstituted silanolate groups), other transition metals can substitute the alkali metal ions. Here, partial structural transformation of the metal–oxygen part of the cage occurs to yield bimetallic MS **17**, which are also characterised by prismatic structures.[57–59]

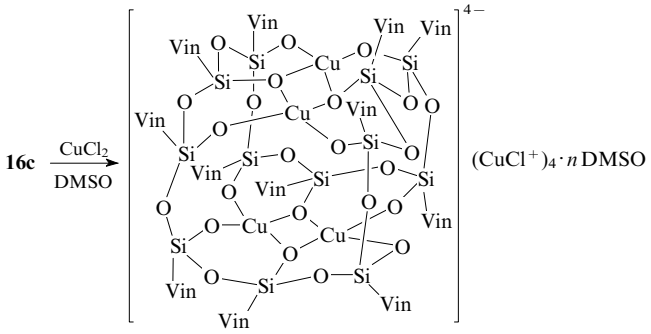


17

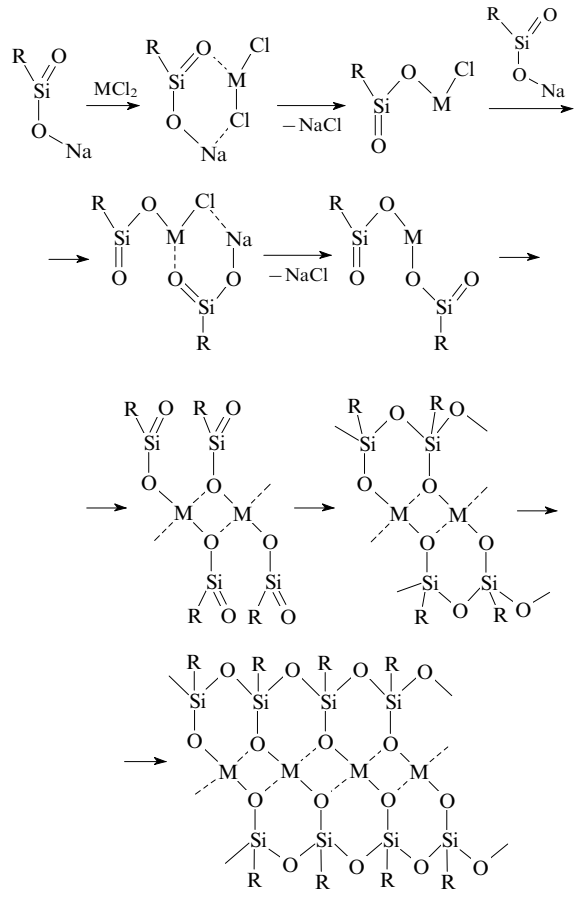
M = Co, Cu, FeOH, FeOMe; L = H_2O, DMSO.

The reaction of Cu-, Co-, Ni- and Mn-containing prismatic MS with acetylacetone gives rise to a partial removal of the metal ions from the cage in the form of the respective acetylacetonates.[60]

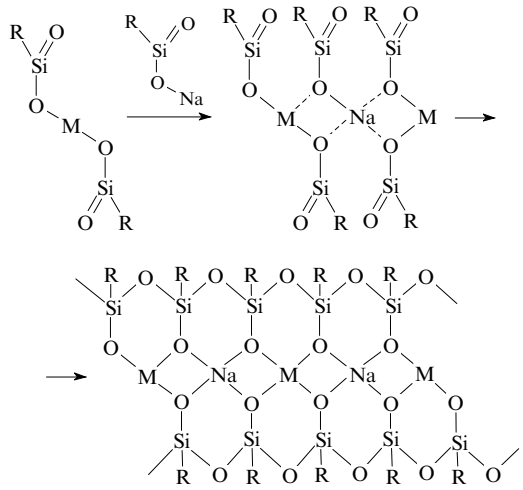
Substitution of the copper ion for an alkali metal ion in the outer sphere of the globular MS **16c** results in the incorporation of an unusual cation MCl^+ (Ref. 61).



Spirocyclic fragments assembled from the units M–O–M linked to siloxane rings are common to both types of structures (*i.e.*, prismatic and globular). The synthesis of this novel class of the cage MS stimulated chemists to try to rationalise the mechanism of their formation. A suggested general scheme of the formation of such structures postulated the presence of alkali metal silanolates in the form of associated silanone derivatives in the reaction medium. These associates rearrange to yield building blocks of the prismatic cages considered above.[62]

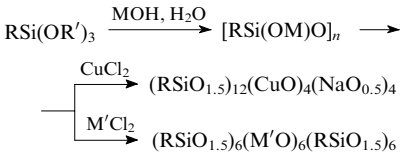


The formation of MS containing unsubstituted organosilanolate groups can be described in a similar way.



The above method for the synthesis of cage MS has several disadvantages. Thus the yields of target products are low due to the presence of free OH groups in the starting organosiloxane (despite the use of metallic sodium as described above). In addition, no cage MS with small organic substituents at the silicon atoms (*e.g.*, methyl) can be synthesised by this method, since the respective starting siloxanes are insoluble.

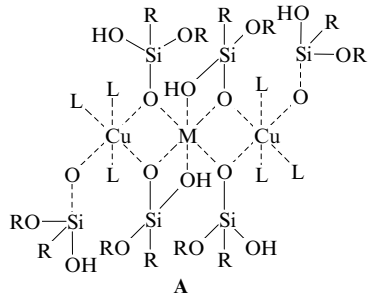
The idea of modification of the method for the synthesis of polyhedral MS has been inspired by the above scheme of the cage 'assembly'. It was the first step of the process, *viz.*, the generation of silanolates that has been modified. It was suggested to assemble a cage structure from monomeric units rather than cleave the organosiloxane into separate fragments under the action of a base. The polyvalent metal atoms were thought to act as nuclei that would arrange components of the future polyhedron. Trialkoxyorganosilanes were selected as a source of the monomeric units.[63–67]



R = Me, Et, Vin, Ph, $(CH_2)_3NH_2$; R′ = Me, Et, Bu^n;
M = K, Na; M′ = Mn, Ni.

The new version provided higher yields in the syntheses of all the above cage structures, this also enabled the synthesis of cage Na,Cu-vinyl-, K,Cu-phenyl- and Na,Cu-methylsiloxanes inaccessible earlier.[68,69]

The mechanism of the cage formation considered above was somewhat changed, as applied to trialkoxyorganosilanes. The modified mechanism assumed the generation of metallasiloxane associates **A** followed by the condensation of functional groups at the silicon atom giving rise to spirocyclic fragments around the metal atoms.[67]

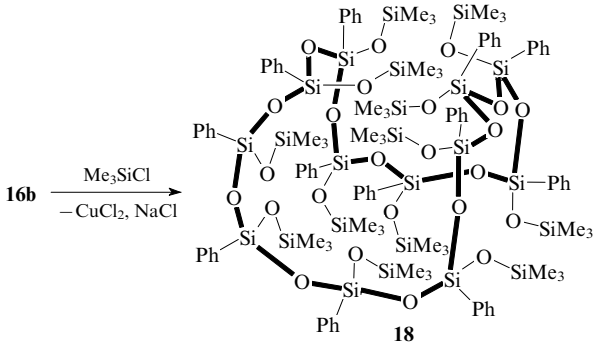


A

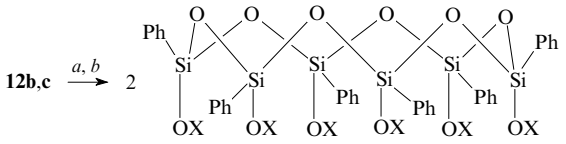
R = Me, Vin, Ph; M = K, Na; L = ROH, H_2O.

It must be noted that such a mechanism is equally applicable to the formation of cage MS according to the previous method (*i.e.*, without alkoxysilanes) and seems more preferable, since it does not presume the formation of extremely unstable silanones as intermediates.

The idea of exploiting different reactivities of the fragments Si—O—Si and Si—O—M in polyhedral MS proved to be the most fruitful: the fragment Si—O—Si is sensitive to the action of nucleophilic agents, whereas the fragment Si—O—M is rather susceptible to electrophiles. The reaction of cage MS with Me_3SiCl results in the cleavage of the fragments Si—O—M to yield macrocyclic organosiloxanes, in which the configuration of the starting MS is preserved.[64,70,71] Globular structures are transformed into 12-membered rings with the *cis–trans* configuration (*e.g.*, compound **18**; bonds forming a closed macrocycle are shown as thick lines), whereas prismatic structures are transformed into six-membered siloxane rings in the *cis* configuration. The reaction with a mineral acid (H_2S or dilute HCl with cooling) instead of Me_3SiCl yields Si-functionalised stereoregular hydroxycyclosiloxanes **19**.[66,72]



18



19

(*a*) is Me_3SiCl (−MCl); (*b*) is HCl or H_2S (−MCl or M_2S);
X = $SiMe_3$, H; M = Ni, Mn.

Metal sulfides, which are by-products of the reaction, form nanocomposite aggregates dispersed in the siloxane matrix, which is promising for the design of new materials. Furthermore, the highly reactive hydroxycyclosiloxanes can be regarded as active precursors of structurally organised systems.

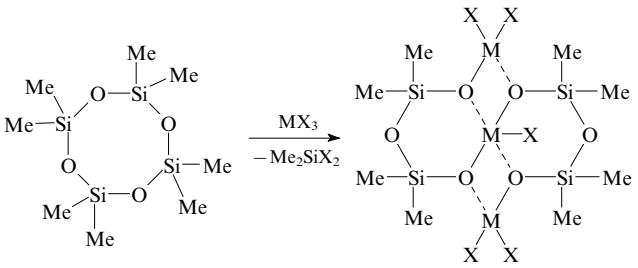
Stereoregular organosiloxane rings with smaller sizes, *e.g.* $[PhSi(OSiMe_3)O]_4$, have been synthesised [65] in a similar way by the reaction of cyclic organosilanolate $[PhSi(ONa)O]_4$ with Me_3SiCl.

Presently, it is the only method that makes it possible to synthesise stereoregular cyclosiloxanes with variable sizes. Moreover, it provides wide capabilities for further syntheses. In particular, if the organotrichlorosilane bears functional groups in the organic substituents at the silicon atom, the reaction yields stereoregular cyclosiloxanes, such as $(PhSiO)_{12}[OSiMe_2CH_2OCH_2O_2CMe]_{12}$, which can be incorporated in polymeric siloxane chains.[73,74]

In addition to the methods for the creation of fragments Si—O—M considered above, yet another method is of particular interest. It is based on the cleavage of siloxane chains under the action of metal compounds. For the first time, this reaction has been carried out [75] with metal halides.

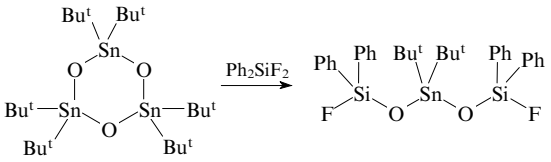
$R_3SiOSiR_3 + AlCl_3 \longrightarrow R_3SiOAlCl_2 + R_3SiCl.$

Later, it has been shown [76–80] that some metal halides as well as alkyl derivatives are capable of cleaving the siloxane bonds in organosiloxane rings.

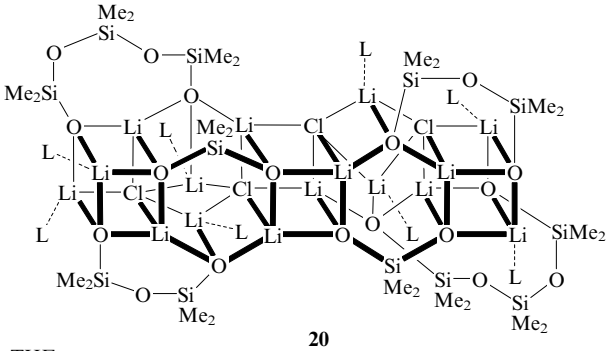


M = Al, Ga; X = Hal, Alk.

The introduction of tin atoms into MS inverts the roles played by the silicon and tin atoms, *viz*., the metallasiloxane ring is opened under the action of silicon halides.[22]



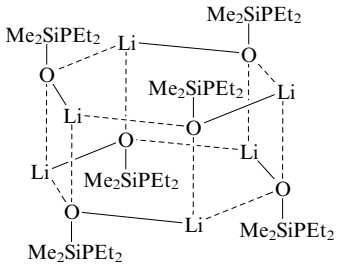
In the modifications considered above, this reaction is of limited use. However, it became widespread after the discovery of the fact that organometallic compounds can cleave polymeric organosiloxanes. Now that this fact has been reliably established it comes as no surprise. But for a long time, the very idea of a reaction of an organometallic compound with a polymeric organosiloxane seemed a nonsense. An occasional observation gave an impetus to the reconsideration of this issue: MS derivatives were detected upon storage of certain organometallic compounds in a contact with an organosilicon grease (which is often used for a ground joint sealing). In particular, a mixture of Me_2GaCl and Bu^tAsLi_2 in a contact with polydimethylsiloxane $(Me_2SiO)_n$ readily affords polynuclear lithium complex **20** containing neither Ga nor As in a yield of 48%.[81]



20

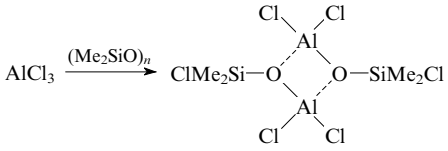
L = THF.

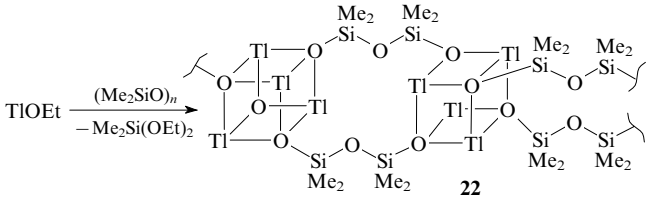
Similarly, a prolonged storage of a solution of $LiPEt_2$ in diethyl ether at 20 °C in a contact with a silicone polymer gave rise to the formation of Li-containing MS **21** with the hexagonal prismatic structure.[82]



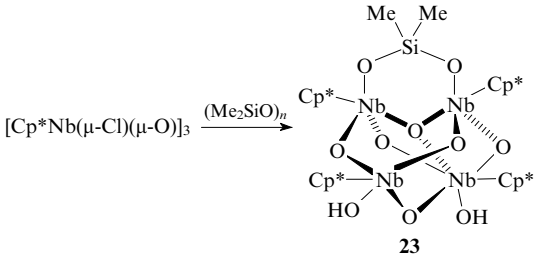
21

In the modern version of this method, a diorganosiloxane polymer rather than an individual compound [such as $Me_3SiO.SiMe_3$ or $(Me_2SiO)_4$] is used as the organosilicon component. This allows the introduction (under mild conditions) of the groups Me_2SiO, which are involved in the construction of metallasiloxane cages and can be incorporated as mono-, di- or trisiloxane units. In addition to the metal halides,[83] organic derivatives of the main group [84,85] and transition [86,87] metals as well as lanthanides [88,89] can be used as the metal-containing component in this reaction. The structural features of the resultant MS (*e.g*., **22** and **23**) are considered in detail in the next section.

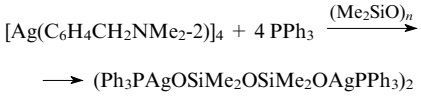


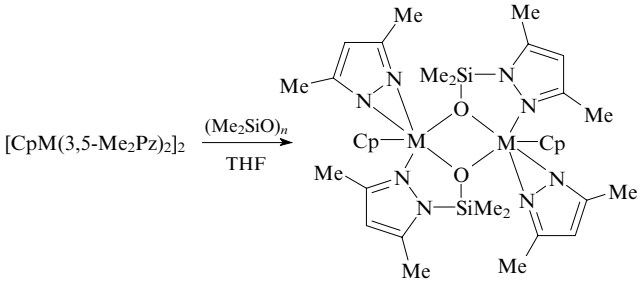


22



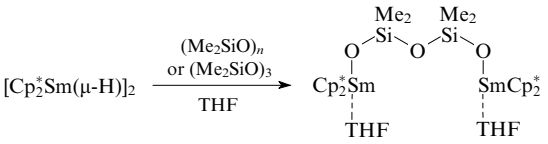
23



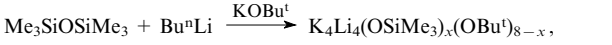


M = Yb, Tb, Dy, Ho; $HPzMe_2$ is 3,5-dimethylpyrazole.

We note that in some cases, the reactions of an organometallic compound with a polyorganosiloxane and the respective individual cyclosiloxane yield identical products.[90]

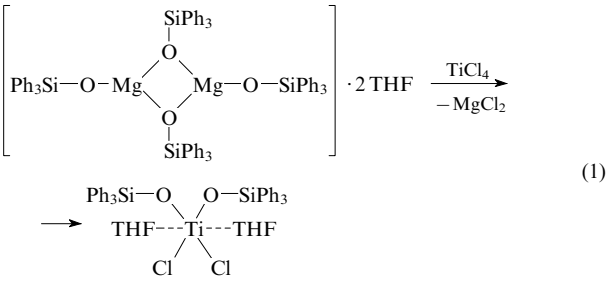


This method is versatile and can be used for the synthesis of alkali metal-contaning MS. For instance, the reactions of disiloxanes with organometallic compounds (alkali metal derivatives) (also in the presence of alkoxides) yield mixed silanolates – alkoxides with variable composition.[91]



$6.2 \leqslant x \leqslant 8$.

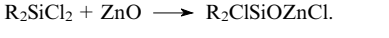
Yet another method for the synthesis of MS consists of the exchange of polyvalent metal ions. Typically, the reaction results in a change in the molecular structure.[21]



(1)

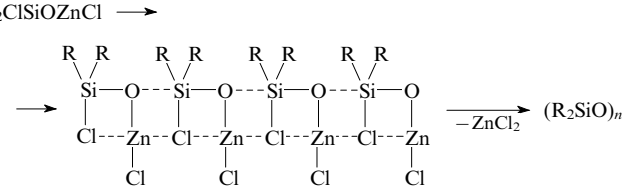
This recently discovered transformation stimulated the development of concepts underlying the structure formation in MS (this subject is addressed in more detail in subsequent sections).

Zavin and co-workers[92,93] reported a non-traditional method for the formation of metallasiloxane fragments based on the reaction of organochlorosilanes with zinc oxide.



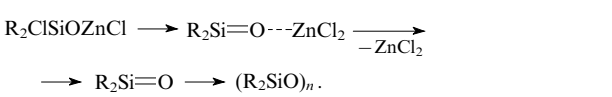
The resultant MS are intermediates in the synthesis of polysiloxanes. Two mechanisms of the transformation were considered.

1. The formation of polymeric zincasiloxane involving bridging coordination bonds:



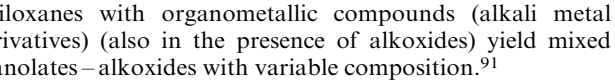
R = Me, Ph.

2. The formation of an intermediate zinc complex with the organosilanone followed by its decomposition:



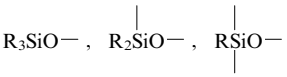
According to quantum chemical calculations, the former mechanism is more probable from the thermodynamical point of view. This reaction allows the formation of siloxane fragments in a non-hydrolytic way. In particular, completely soluble polymethylsilsesquioxane $(MeSiO_{1.5})_n$ with a molecular mass as large as ~25 000 has been successfully obtained from $MeSiCl_3$, which was nearly impossible with other methods.

Concluding the section devoted to synthetic methods of MS chemistry we note that the possibility of MS synthesis under conditions of the mechanochemical activation has been demonstrated quite recently; this makes it possible to accomplish a solvent-free process. The reaction of copper acetylacetonate with diphenylsilanediol can serve as an example.[94]



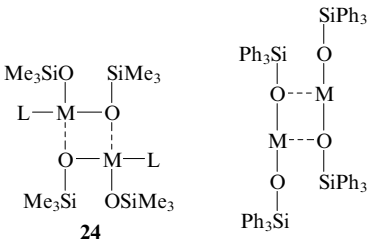
III. The structure of metallasiloxanes

The methods for the synthesis and transformations of MS considered in the previous section are difficult to systematise. On the contrary, the classification of structures of individual MS is rather straightforward. Most conveniently, all the MS synthesised can be divided into three large groups according to the type of the constituent organosilicon fragment:



Similar structures within this classification would fall into the same group. Meanwhile, the general principles of the formation of the coordination sphere of the metal atom remain common for all these groups.

In the vast majority of cases, the coordination sphere of the metal atom is filled by bridging oxygen atoms from the neighbouring fragments Si–O–M. The formation of coordination dimers is typical of MS containing monofunctionalised fragments R_3SiO (compounds **24**–**26**). Similar structures occur for a variety of main group and transition metals,[21,29,95–98] including Ru, Rh and Pd.[99–104]

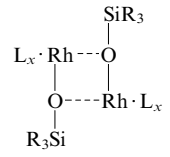


24

L = Me_3SiO, Me;
M = Al, Fe, Au, Ga.

25

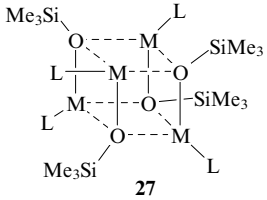
M = Mg, Co.



26

R = Me, Ph;
L = CO (x = 2), cycloocta-1,5-diene (x = 1), norborna-2,5-diene (x = 1), PPh_3 (x = 2).

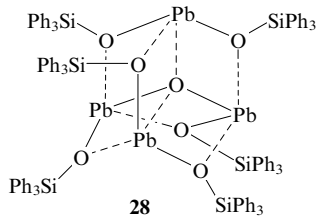
In a few cases, coordination tetramers (*e.g.*, compound **27**)[16,105] or hexamers (compound **21**) are formed.



27

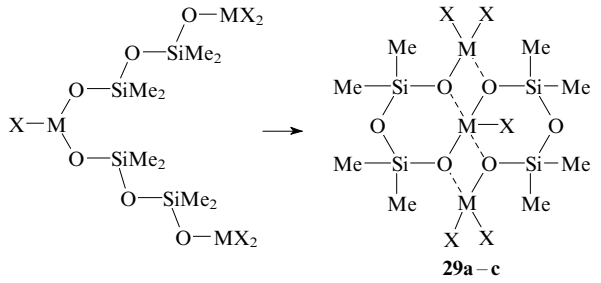
L = Me: M = Cd, Zn; L = PPh_3, M = Cu.

In addition to the oxygen atoms from the Si–O–M groups, highly basic O atoms from the M–O–M groups can be involved in the coordination sphere of the metal atoms [as, for instance, in Nb (**23**) and Pb organosiloxanes (**28**)][106] as well as anions, usually halides (as in compounds **2** and **3**).



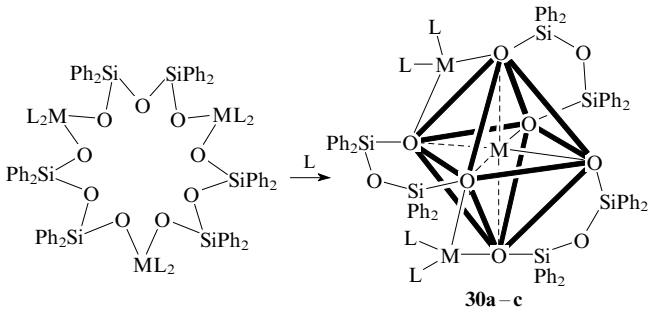
28

In MS bearing flexible difunctionalised organosilicon fragments $SiR_2-O-SiR_2$, the filling of the metal coordination sphere requires the respective change in the molecular conformation. The major driving force of the change, *viz*., the coordination unsaturation of the metal atom, sometimes makes molecules fold in intricate way. The coordination sphere of the metal atoms involves O atoms of the Si–O–M groups. This can be seen in metallasiloxanes containing aluminium or gallium (compounds **29a–c**),[76–80] alkali-earth metals (compounds **30a–c**) [107, 108] or silver (compound **31**).[87]



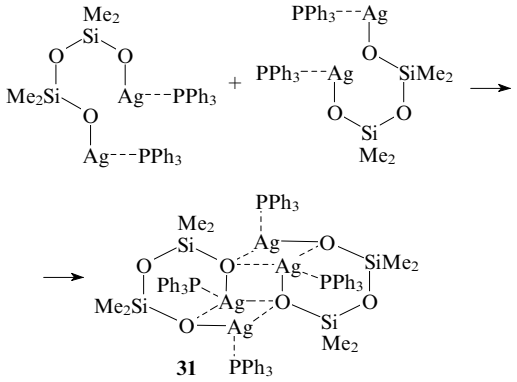
29a–c

M = Al: X = Cl (**a**), Br (**b**); M = Ga, X = Cl (**c**).



30a–c

M = Ca (**a**), Sr (**b**), Ba (**c**); L = Py, tetraglyme.

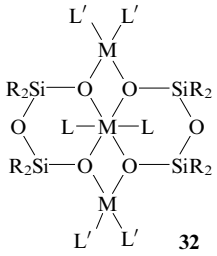


31

Trifunctionalised fragments $RSiO_{1.5}$ give rise to MS with totally different structures, although the basic principle of the metal coordination sphere formation, *viz*., the involvement of the O atoms from the fragments Si–O–M and M–O–M and sometimes stabilising Hal^- anions, is preserved. This can be seen in cage structures **12–14**.

It is noteworthy that there are only a few types of the coordination polyhedra of the metal atom; in the majority of cases, the polyhedron is close to either tetrahedron [the coordination number (CN) is 4] or tetragonal bipyramid (CN = 6).

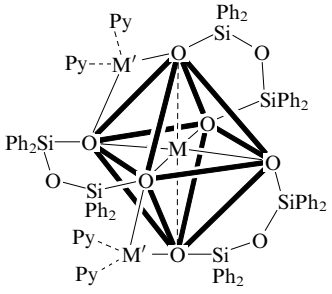
Among ligands that fill the coordination sphere of the metal atom in MS, one ligand takes a special place. This is the silanolate anion, SiO^-. This appears in the structures of MS containing a polyvalent metal and the silanolate groups Si–O–M, where M is an alkali metal. As a result, mixed-metal MS involving metal atoms of different nature (*i.e*., polyvalent and alkali metals) are formed, the alkali metal atoms being not incorporated in the cage. The existence of anions in these systems was confirmed by electrochemical techniques.[109] The majority of individual crystalline MS obtained so far fall into this type of compounds. They are obtained in high yields (> 90% in some cases) [63] and are rather stable and do not change composition upon subsequent recrystallisations. Different structures involving the silanolate anion have been synthesised with a variety of metal atoms. For instance, a series of compounds **32** with Mg,[110] Cr,[111] Co,[112] Cu,[113] Gd,[114] V [115] and Sn,[116] which are characterised by a structure similar to the tetracyclic Al- and Ga-containing MS (*e.g*., structures **29a–c**), have been synthesised.



32

M = Mg, Cr, Co, Cu, Gd, V, Sn; R = Me, Ph; L, L′ = Py, THF.

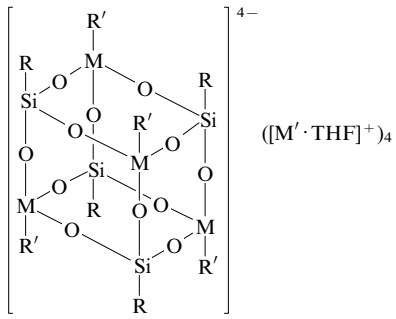
Similarly, transition metals, such as Ti,[117] Zr,[118] Hf [119] and Ta [116] (compounds **33**), have been successfully incorporated into octahedral MS structures closely related to the Ca, Sr and Ba organosiloxanes (compounds **30a–c**) owing to the silanolate anions.



33

M = Ti, Zr, Hf, Ta; M′ = Na, Li.

MS based on trifunctional fragments $RSiO_{1.5}$ and containing the silanolate anions are equally numerous. Prismatic Cu,K (**8**), Mn, Co and Cu organosiloxanes (**12a–c**) as well as cubane-like Al [120] and Ga(In) organosiloxanes [121] (compounds **34**) can be given as examples.

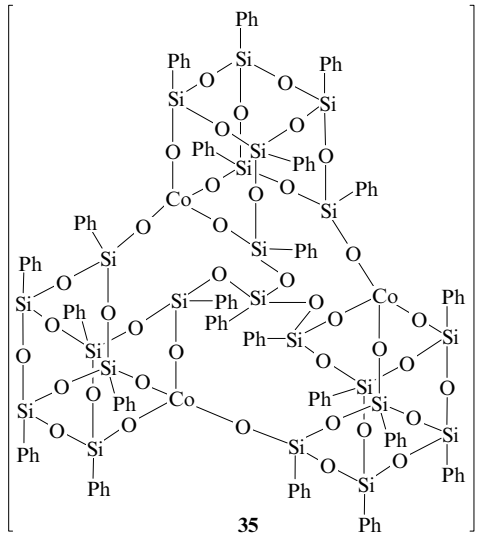


$([M' \cdot THF]^+)_4$

34

M = Al, Ga, In; M′ = Li, Na; R = 2,6-$Pr^i_2C_6H_3NSiMe_3$; R′ = Me, Et.

Some cage molecules with the silanolate anions specific to this group of compounds have been synthesised, for instance, basket-like Co organosiloxane **35**[48] and globular structures **16a**–**c**.

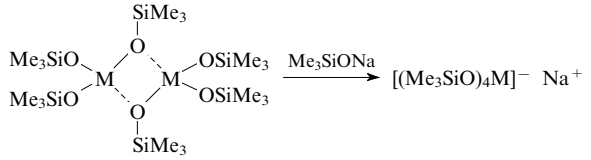


$([Na \cdot H_2O]^+)_6$

35

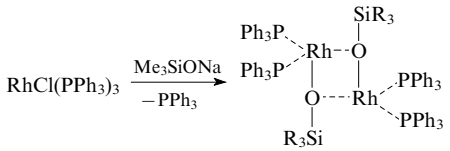
The coordination ability of the silanolate anion is so high that it can replace other ligands in the coordination sphere of the metal atom, in particular, n-donor ligands [105] and the O atoms of the fragments Si—O—M, which are typical ligands for MS.[97, 122]

$$[(Me_3SiOCu)\cdot 2PMe_3]_4 \xrightarrow{Me_3SiOLi} [(Me_3SiO)_2Cu]^-\ Li^+$$



M = Al, Fe, Au.

It is worth noting that the O atoms of the fragments Si—O—M can replace n-donor ligands in the coordination sphere of the metal atom both in individual [102] and oligomeric MS.[123]



$$[RSi(ONa)O]_n \xrightarrow[-PPh_3,\ -NaCl]{MCl_2\cdot 2Ph_3P} [(PhSiO_{1.5})_2(MO)]_k,$$

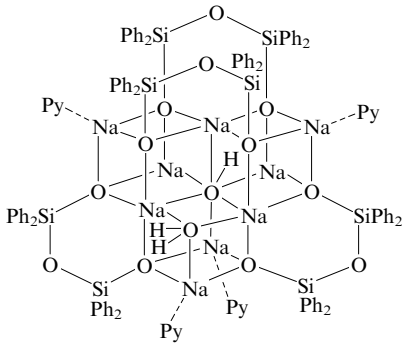
R = Ph, Bu^t; M = Co, Ni; n = 3, 4; $k \neq n$;

$$[RSi(ONa)O]_n \xrightarrow[-Ph_3PO,\ -NaCl]{FeCl_3\cdot 2Ph_3PO} [(PhSiO_{1.5})(FeO_{1.5})]_k,$$

R = Ph, Bu^t; n = 3, 4; $k \neq n$.

Therefore, the coordination environment of the metal atom becomes most stable with the introduction of the silanolate anions. For some transition metals (Cr, Co, Cu, V, Ti, Zr and Hf), only MS containing the silanolate anions have been synthesised so far.

Several general regularities not mentioned above that are somewhat hidden by the multitude of structural types of silanoxanes can be revealed. First, oxygen atoms located between two silicon atoms, *i.e.*, in the siloxane units Si—O—Si, virtually never enter into the coordination sphere of the metal atom. This can clearly be seen in the structures **20**, **29** and **30**. In sodium diphenylsilanolate **36**, the O atoms of the disiloxane fragments are also located outside the coordination cluster.[124]

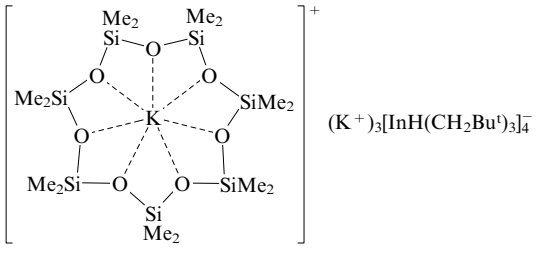


$\{[(Ph_2SiONa)_2O]_4\cdot(NaOH)\cdot(H_2O)\}\cdot n\,Py$ (**36**)

A similar situation is observed in the structure of tallasiloxane **22** where metal oxide cubic fragments are linked together into a chain with disiloxane bridges.

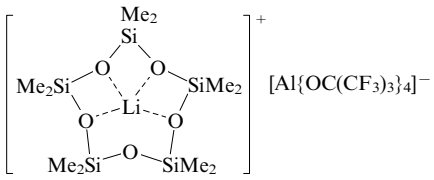
This regularity is also strictly obeyed in prismatic structures built up of trifunctionalised fragments $RSiO_{1.5}$ (*e.g.*, compounds **12**–**14**). This behaviour of the siloxane fragments in MS is due to the ultimately low basicity of the O atom in the unit Si—O—Si. This fact is nearly completely ignored in the literature devoted to MS but it is actually of no surprise. Independently of MS studies, this property of the siloxane bonds has been established for organosiloxanes.[125] Diorganocyclosiloxanes $(Me_2SiO)_n$ (n = 6–8) cannot be used as crown ethers for the same reason.[126]

Nevertheless, there are examples of structures violating this rule: in complex **37**, the K^+ cation is coordinated to a seven-membered organosiloxane ring,[127] in complexes **38** and **39**, the cations Li^+ are coordinated to five- and six-membered organosiloxane rings, respectively.[128]

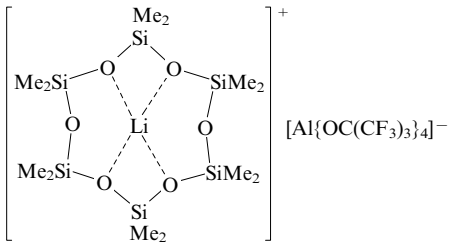


$(K^+)_3[InH(CH_2Bu^t)_3]_4^-$

37



38



39

These results however should not be interpreted as a manifestation of increased basicity of the O atoms of the fragments Si—O—Si, especially taking into account that the cations are located not exactly in the plane of the ring but rather above it.

Another structural feature of MS nearly completely missed by researchers consists of the formation of metal oxide fragments M—O—M in some cases (*e.g.*, compounds **2**, **3**, **4**, **13**, **23** and **28**). This concerns units linked by σ-bonds rather than coordination interactions. The appearance of such fragments cannot be explained by the schemes of synthesis of these MS and is due to the secondary process, *viz*., the rearrangement of metallasiloxane chains. It has to be emphasised that no formation of the fragments M—O—M occurs in structures containing the silanolate anions.

IV. Rearrangements of metallasiloxanes

The structural diversity of synthesised MS raised questions on basic principles of their structure formation. The influence exerted by the nature of organic and alkoxy groups at the silicon atom in trialkoxysilanes $RSi(OR')_3$ as well as by conditions of synthesis on the selective formation of a certain type of cage (prismatic *vs*. globular) in the synthesis of individual Na,Cu and K,Cu organosiloxanes has been thoroughly studied.[57]

Wide potential of the synthesis of some inaccessible MS provided by the use of bulky R_3SiO groups is now adopted as a specific concept, which considers these groups as an alternative to the cyclopentadienyl ligand due to their rather similar sizes and electron donor properties.[129]

In the majority of studies, the emphasis is placed onto regularities of the synthesis and structural features of the target MS, whereas possible side reactions and post-synthetic transformations of MS have eluded the appropriate consideration for a long time. Nevertheless, from experimental evidence gathered, it gradually became apparent that the as-synthesised compounds partly or sometimes completely rearrange into other compounds with increased or decreased metal content (with respect to the parent compound). Some syntheses ultimately afforded metal-free or silicon-free compounds. Such rearrangements are often accomanied by the formation of metal oxide M—O—M chains (in the reaction equations below, reaction products enriched with silicon are indicated first and those enriched with metal are indicated second).

$(Me_3SiO)_2SnR_2 \longrightarrow$

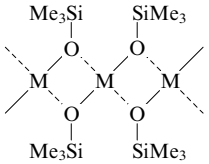
$\longrightarrow (Me_3Si)_2O + Me_3SiO(R_2SnO)_2SiMe_3$ (Ref. 130),

$(Ph_3SiO)_2Hg \longrightarrow Ph_3SiO(Ph_2SiO)_nHgPh + Ph_3SiOHgPh$ (Ref. 131),

$(Ph_3SiO)_2Pb \longrightarrow (Ph_3SiO)_2O +$

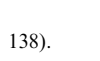
$+ [(Ph_3SiO)_2Pb]_2 \cdot (Ph_3SiOPbOPbOSiPh_3)$ (Ref. 106),

$(Me_3SiO)_3Sb \xrightarrow{\Delta} (Me_2SiO)_3 + Me_3Sb$ (Ref. 132),



$\xrightarrow{\Delta} (Me_2SiO)_n + (Me_3SiOMMe)_4$ (Ref. 4),

M = Zn, Hg;

$(Et_3SiO)_2Ti(OBu^n)_2 \longrightarrow Et_2Si(OBu^n)_2 +$  (Ref. 133),

$(Me_3SiO)_3V{=}O \xrightarrow{\Delta} Me_3SiOSiMe_3 + (Me_3SiOVO_2)_n$ (Ref. 134),

$(Me_3SiO)_2M \longrightarrow (Me_2SiO)_2 + MO$ (Refs 135–137),

M = Ni, Co;

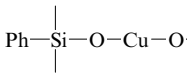
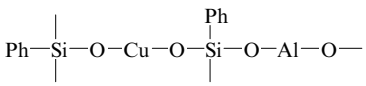
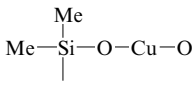
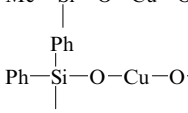
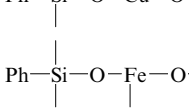
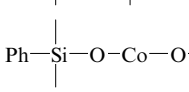
$(Me_3SiOCu)_4 \longrightarrow (Me_3Si)_2O + (Me_3SiO)_{14}Cu_{18}O_2$ (Ref. 138).

As has been established upon the extension of the range of compounds under study, similar transformations also occur with oligomeric MS.[139–144]

In the majority of cases considered in the previous section, the rearrangements are suppressed (typically, due to the presence of stabilising anions). In the absence of suppressing factors, the rearrangments of oligomeric MS can be detected using fractionation. The fractions isolated differ in the metal content, *i.e*., the M : Si atomic ratio, which gradually decreases from the first fractions to successive ones, rather than in the molecular mass, which is typical of the majority of polymers (Table 1).

In the case of individual MS, the influence of the metal nature (transition *vs*. main group metal) is somewhat masked except for the fact that the synthesis of MS with several transition metals (*viz*., Cr, Co, Cu, V, Ti, Zr and Hf) was possible only in the presence of the silanolate ions. Meanwhile,

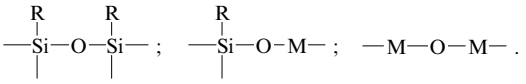
Table 1. Rearrangement products of oligomeric metallasiloxanes.

Monomeric unit	Range of the M : Si ratios in fractions	Ref.
	0.5–1	139
	0.27–0.32 [a] 0.05–0.28 [b]	139
	0.31–2.0	140, 143
	0.21–2.5	140, 143
	0.18–1.6	142, 144
	0.14–0.9	142, 144

[a] Al : Si; [b] Cu : Si.

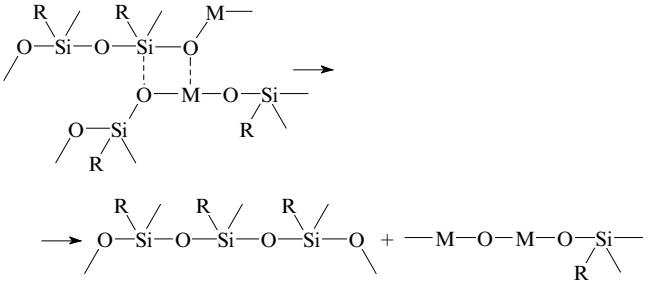
this is not required for main group metals. It can be assumed that the syntheses of MS with the transition metals listed above in the absence of the silanolate anions were accompanied by rearrangements to yield products that were of low importance for synthetic chemists. Thus, these results were not reported and the rearrangements eluded the discussion.

In contrast, in the case of oligomeric MS, the influence of the metal nature is more prominent: the rearrangements are manifested more clearly with transition metals. According to the current concepts,[142, 143] the rearrangements are driven by coordination unsaturation of the metal atoms in siloxane structures. In oligomeric MS, there are three inequivalent types of the oxygen atoms, *viz*., those present in siloxane, metallasiloxane and metal oxide units:

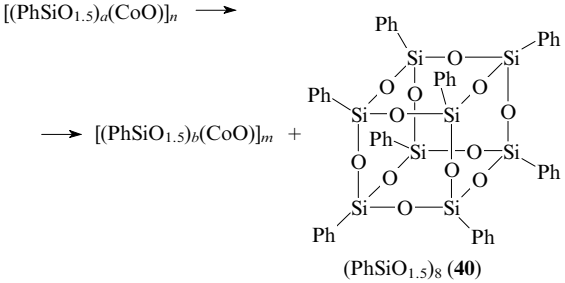


As has been noted above, the oxygen atoms of the siloxane fragments cannot be involved into the coordination sphere of the metal atom due to their ultimately low basicity. On the contrary, the O atoms of the metallasiloxane (Si—O—M) and metal oxide (M—O—M) units are sufficiently basic and thus readily occupy the coordination sphere of the metal atom.

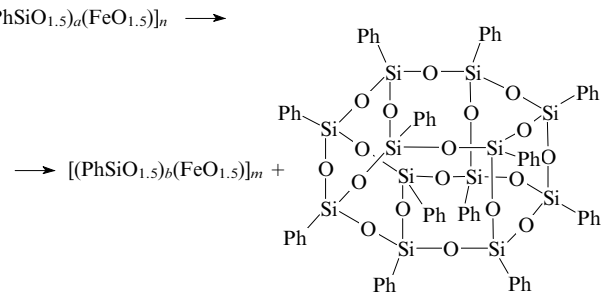
Thus the driving force of rearrangements consists of the formation of compounds with increased amount of such fragments. They proceed *via* intermediate complexes and further give rise to metal oxide fragments,[142] which cannot be explained by the mechanism of the MS synthesis.



Under certain conditions (primarily, with an appropriate solvent), one of the rearrangement products (either the one enriched with metal or that enriched with silicon) is eliminated from the reaction medium due to its lower solubility. In such cases, the rearrangement can be observed even without fractionation. Two different processes are possible, depending on the composition of the reaction medium, *viz*., precipitation of poorly soluble crystalline metal-free organosilsesquioxanes $(RSiO_{1.5})_n$ (*e.g*., compounds **40** and **41**) [141, 145]

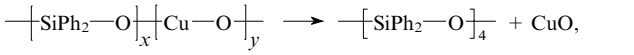


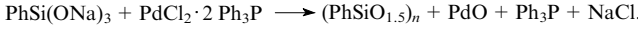
$(PhSiO_{1.5})_8$ (**40**)



$(PhSiO_{1.5})_{12}$ (**41**)

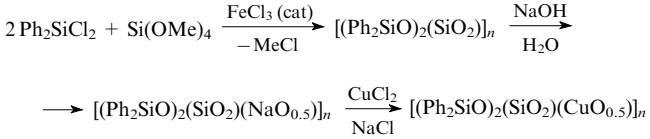
or, alternatively, of poorly soluble fractions enriched with metal. Sometimes, the process results in complete removal of metal in the form of the respective oxide from siloxane chains:[146]





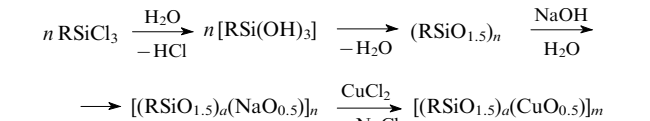
In order to gain a deeper insight into the rearrangement of MS, the kinetics of this process was studied using UV spectroscopy. Co-containing oligophenylsiloxanes were selected as the subjects of this study.[147] It was found that the rearrangement obeys the first-order law with a mean apparent reaction rate constant $k_{app} = (4.5 \pm 0.5) \times 10^{-6}$ s^{-1}. The first order of the reaction implies that the total rate of the rearrangement is limited by the decomposition of the intermediate complex to yield compounds with increased metal content with respect to the original MS.

According to studies of the MS rearrangement as a function of the number of identical organic groups at the silicon atom,[148] branched structures containing fragments $RSiO_{1.5}$ suppress the rearrangement to a larger extent than linear structures with the fragments R_2SiO. This observation pointed to a possible means to suppress the rearrangement, *viz*., an increase in the steric hindrance of the molecule with the introduction of sildioxane fragments SiO_2 (Ref. 149).



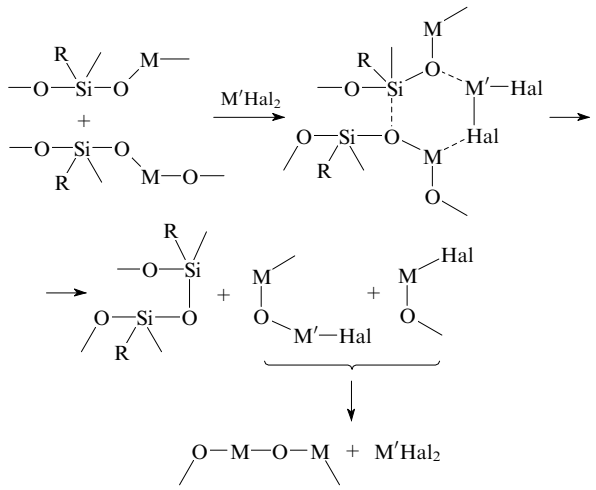
It has been established [149] that the introduction of sildioxane fragments into oligomeric MS impedes the formation of an intermediate complex, which appears in the course of the rearangement.

Alternatively, the rearrangement can be suppressed by using bulky aliphatic groups at the silicon atom, which sterically hinder the interchain coordination of MS.[150]



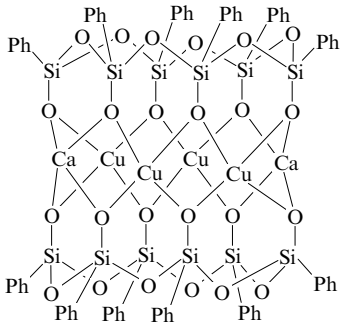
R = n-C_9H_{19}, Bu^t.

Conditions accelerating the rearrangement have also been found. It has been established that the presence of a catalytic amount of metal halides promotes rapid rearrangement towards compounds enriched with metal.[149] Presumably, the rearrangement proceeds *via* a six-membered ring intermediate, which is most typical of organosiloxane compounds.

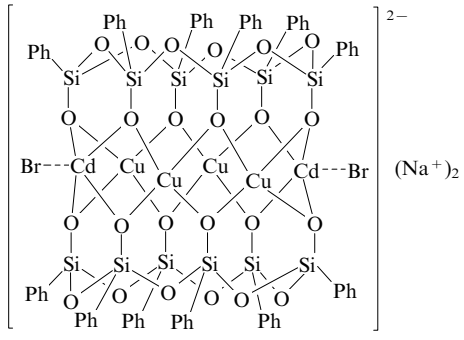


M = Cu, Co; M′ = Co, Fe.

The reaction (1) discussed in Section II, in which the Ti atom substitutes the Mg atom in the MS structure, indicates that magnesium can act as an alkali metal as regards the exchange reaction. The electronegativity of Mg (1.2) is close to the respective values for alkali metals (0.91–0.97), which naturally leads to a conclusion that the Mg ion is capable of generating the stabilising silanolate anions in the MS structure. A bimetallic Cu,Ca organosiloxane **42** has been synthesised to verify this suggestion.[151] The choice of the alkaline-earth metal was dictated by the fact that calcium, in terms of electronegativity (1.04), is rather more similar to alkali metals and thus a prominent stabilising effect could be expected. Another bimetallic Cu,Cd organosiloxane **43** has been synthesised for comparison [151] (for both structures, coordinated solvent molecules are omitted for clarity).



42



43

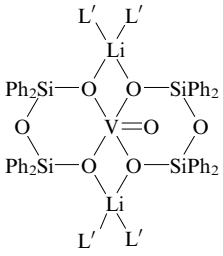
A comparison of the two structures, **42** and **43**, indicates that the silanolate anions introduced into the structure together with two calcium ions are accomodated in the coordination spheres of four Cu ions. Meanwhile, the cadmium ions, which are characterised by a substantially higher electronegativity (1.46) as compared to calcium, cannot bring the silanolate ions into the structure. As a result, a stable crystalline structure can be formed only with the assistance of additional coordinated anions (Br^- in the present case).

V. Metallasiloxanes in catalysis

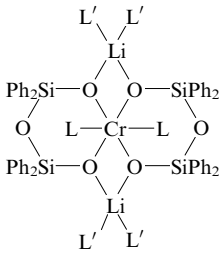
Alkali metal organosilanolates are traditional catalysts of the anionic polymerisation of organocyclosiloxanes aimed at the production of linear organosiloxane polymers.[8] More recently, it was found that the use of mixed silanolates–alkoxides $K_4Li_4(OSiMe_3)_{6-8}(OBu^t)_{1-2}$ allows the synthesis of high-molecular-mass organosiloxanes with a low polydispersity.[91]

In the majority of cases, the catalytic properties of MS are caused by the nature of the metal atom, which acts as the catalitically active site. As a rule, the siloxy groups play only a secondary role forming a specific environment of the catalytic site. Nevertheless, the involvement of the siloxane matrix becomes decisive in certain cases.

A series of studies have been devoted to the catalytic activity of MS towards the alkene conversion. Catalysts mimicking the Ziegler–Natta catalysts have been developed. In these systems, a transition metal complex is combined with AlR_3. In particular, it has been demonstrated [111, 115] that spirocyclic V(IV) and Cr(II) organosiloxanes (compounds **44** and **45**, respectively) combined with $AlMe_3$ efficiently catalyse the ethylene and propylene polymerisation.



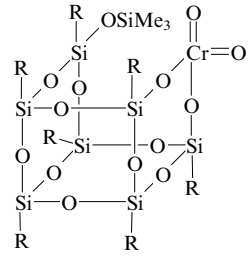
44



45

L, L′ = Py, THF.

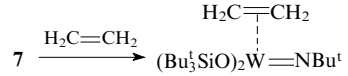
According to an original idea,[152] organosiloxane cage can be used as a support for catalytic sites instead of traditional inorganic silicate matrix. For instance, polyhedral Cr(VI) organosiloxane **46** possesses [153] as high activity as the classical Philips catalyst (Cr/SiO_2).

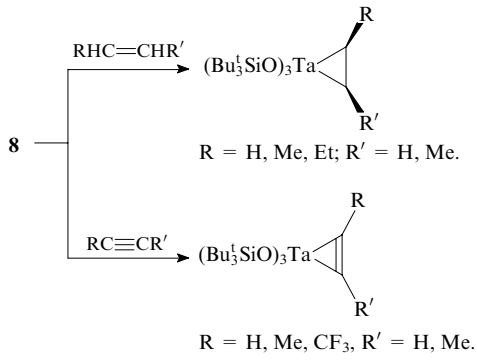


46

R = cyclo-C_6H_{11}.

Modern investigations into the MS-based catalysts of the alkene conversion are dominantly focused on the utilisation of low-coordinate complexes. Several metal triorganosiloxy derivatives (in particular, a tricoordinate tungsten complex **7**) are promising catalysts for the alkene and alkyne activation:

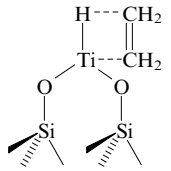




R = H, Me, Et; R′ = H, Me.

R = H, Me, CF_3, R′ = H, Me.

Diorganosiloxyhydridotitanium (promoted with trimethylphosphine) forms an intermediate with ethylene [154] and thus catalyses its conversion into but-1-ene and higher ethylene oligomers.



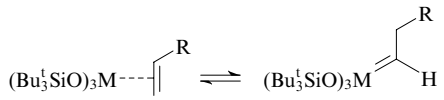
In specific cases, an alkene is generated upon the conversion of a metal (alkyl)siloxy derivative: for instance, thermolysis of tungsten compound **47** yields alkenes upon β-elimination of the alkyl groups in parallel to alkene complexes.[40]

$$(Bu^t_3SiO)_2R_2W{=}O \longrightarrow (Bu^t_3SiO)_2(\text{alkene})W{=}O + RH + \text{alkene},$$

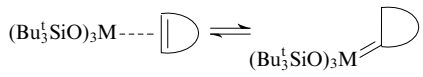
47

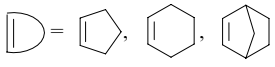
R = Et, Bu^n.

The advantage of bulky triorganosiloxy substituents at the metal atom is manifested most prominently in studies of catalytic properties of Nb and Ta organosiloxanes. It has to be emphasised that it is with these two metals that Richard Shrock (the 2005 Nobel Prize winner in chemistry) started his search for metathesis catalysts by introducing the *tert*-butoxy groups into the coordination environment of the metal sites in order to impart stability to metallacarbenes generated from them. According to more recent studies,[155] this purpose can alternatively be achieved with *tert*-butylsiloxy groups and it is even more efficient since a larger number of bulky organic groups can be attached to the catalytic site in this case. It has been established [155] that niobium and tantalum triorganosiloxy derivatives add alkenes with the generation of the respective metallacarbenes that catalyse the metathesis reaction.

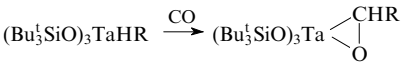


M = Nb: R = H, Me, Et, Bu^t, Ph, 4-$MeOC_6H_4$;
M = Ta: R = H, Me, Et, Ph, 4-$MeOC_6H_4$, 4-$CF_3C_6H_4$.

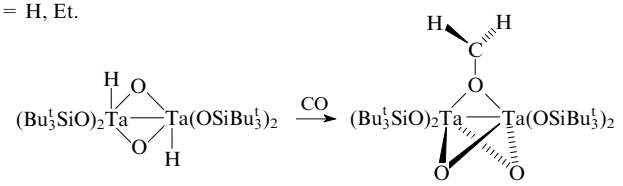


M = Nb, Ta; 

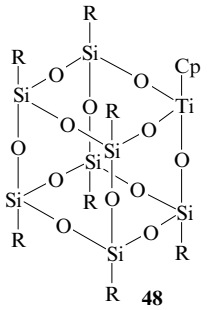
Triorganosiloxy-substituted tantalum hydrides represent another type of catalysts. They efficiently bind CO, which makes them promising catalysts of the Fischer–Tropsch reaction.[156–159]



R = H, Et.



Polyhedral Ti^{III} and Ti^{IV} silsesquioxanes, which are characterised by closed (compound **48**) or partly closed (compound **1**) structures,[160, 161] are used as either homogeneous or heterogeneous alkene epoxidation catalysts.



R = cyclo-C_6H_{11}.

Triorganosiloxy derivatives of platinum metals traditionally find wide applications determined by the nature of the metal. The organosiloxy groups increase the stability of these catalysts in the repeated use. Rhodium triorganosiloxy derivative $[Ph_3SiORh(CO)_2]_2$ performs as a highly efficient hydroformylation catalyst.[100]

$$MeCH{=}CH_2 \xrightarrow[80\ ^\circ C]{CO,\ H_2,\ Cat} MeCH_2CH_2CHO.$$

Complexes $RMSiPh_3 \cdot 2\,L$ (M = Pt or Pd; R = Me, Et or Ph; L is cycloocta-1,5-diene) provide a higher catalytic activity towards the CO hydrogenation than compounds $R_2M \cdot 2\,L$ or supported catalysts H_2PtCl_6/SiO_2 (Ref. 162).

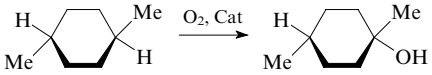
The formation of fragments Si–O–Pd in intermediates is postulated [163] for the Pd-catalysed cross-coupling processes involving organosilicon reactants.

Oligomeric MS are also applicable in catalysis. It has to be noted that their use as a binder for supported catalysts shows little promise due to the fact that they form most often polymeric systems with a relatively low molecular mass (2000–5000), which are characterised by a low mechanical strength. Nevertheless, studies of their catalytic properties gave rise to interesting and sometimes surprising results.

These compounds were primarily tested in processes of petrochemical synthesis due to their close analogy to inorganic silicates. It has been found that oligomeric MS gradually lose organic substituents being converted into inorganic silicates upon the high-temperature polycondensation, although structural features of the starting MS are preserved. These compounds successfully compete with inorganic silicates with similar compositions, but they possess higher catalytic activities and selectivities in a number of processes, including cracking, halogenation, dehydration, alkylation, *etc.*[11]

More recently, oligomeric MS found application as catalysts for other reactions where metal silicates were inactive. These include, for instance, the stereoselective oxidation of

hydrocarbons (*e.g.*, 1,4-dimethylcyclohexane) in the presence of oligophenylferrasiloxane.[164, 165]



Probably, the most important catalytic application of oligomeric MS relates to the halohydrocarbon conversion. A number of large-scale industrial processes are based on these reactions (*e.g.*, the production of polyvinyl chloride, dichloroethane, chlorobenzene, chloroalkanes, *etc.*). Halohydrocarbons are poor ligands for the majority of metal complexes, which complicates the choice of a proper catalyst. This selection was however made on the basis of the following idea: the most efficient catalysis is expected in those cases where the chain-radical mechanism involving a variable-valence metal atom becomes possible. Transition metals incorporated in the structure of the organosiloxane matrix can change their oxidation state (this is the key step for the catalysis of this type of reactions) remaining within the siloxane cage. Of other advantages of the utilisation of oligomeric MS, their solubility in organic solvents enables their application as homogeneous catalysts. In the case of heterogeneous catalysts, they can be chemically grafted to widely adopted inorganic supports (SiO_2, Al_2O_3 and so on). Furthermore, diverse systems incorporating nearly any transition metals and their combinations in specified ratios are now available. Their properties can be additionally adjusted by varying parameters of the high-temperature condensation processes, which strongly affect surface characteristics of the target catalysts.

Oligomeric Cu, Co and Fe organosiloxanes have been tested [166] as catalysts of the isomerisation of non-symmetric 3,4-dichlorobut-1-ene into symmetric 1,4-dichlorobut-2-ene (it is the key step in the industrial production of chloroprene rubber). The Cu-containing MS manifested the highest activity, which confirmed the current concept assuming the partial reduction of the metal ions in the course of the catalytic reaction: the copper ions undergo the reduction most readily among the compounds studied. Still, the Co- and Fe-containing MS are also of interest, since they provide higher selectivity: no *cis*-1,4-dichlorobut-2-ene is formed in their presence. The major difference of the oligomeric MS from traditional catalysts (*i.e.*, copper naphthenate or halides) consists of their prominent stability: even repeated use (6–10 cycles) does not lead to any significant decrease in activity, whereas traditional catalysts are nearly completely deactivated after the first cycle.

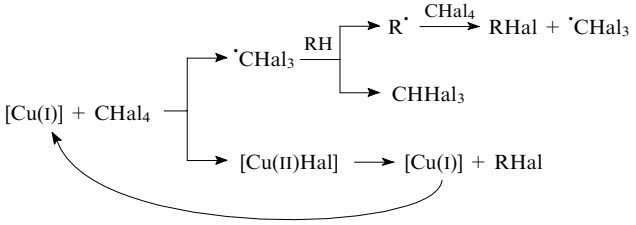
Oligomeric MS have been tested as catalysts in the exchange halogenation processes, which enable the production of halohydrocarbons avoiding the use of halogens as elementary substances.

$$RH + CHal_4 \xrightarrow{Cat} RHal_4 + CHHal_3$$

R = Alk, Ar; Hal = Cl, Br.

In the case of chlorohydrocarbons, a more environmentally friendly industrial process can be implemented using this method. This is especially important for brominated derivatives, since the direct bromination with molecular bromine usually proceeds with difficulty and non-selectively; furthermore, syntheses of bromides are usually multi-step processes.

Detailed investigations [148, 167, 168] into the exchange halogenation of hydrocarbons, including n-$C_{10}H_{22}$, n-$C_{12}H_{26}$, cyclo-C_6H_{12}, *p*-$Me_2C_6H_4$ and C_6H_5Me, with CCl_4 or CBr_4 (in the presence of a catalytic amount of oligomeric Cu phenylsiloxane) shed light on the mechanism of the procees. The reaction follows the radical mechanism: the transfer of the radical centre along the chain from the $^{\bullet}CCl_3$ radical to the hydrocarbon molecule is shown in the upper half of the scheme, whereas transformations of the catalytic site are shown in the lower half (according to classical view, the catalyst returns to the initial state after the catalytic cycle, which is indicated by the bent arrow). The activity of oligomeric Cu phenylsiloxane remains nearly constant over five catalytic cycles, whereas the standard catalyst $CuCl_2 \cdot (DMF)_n$ is deactivated within one cycle.

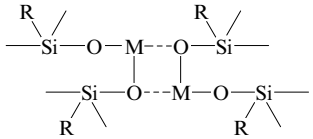


The above exchange halogenation reaction yields a mixture of monohalogenated derivatives with different locations of the halogen atom. The addition of halohydrocarbons to alkenes proceeds more selectively, since the location of the double bond determines the sites of attachement of the Cl atom and CCl_3 fragment.

$$CCl_4 + \text{n-}C_6H_{13}CH{=}CH_2 \xrightarrow{\text{Cat, 130 °C}} \text{n-}C_6H_{13}CHClCH_2CCl_3.$$

Oligomeric monophenyl and diphenyl Cu-containing organosiloxanes have been tested as catalysts in this reaction.[169] The process follows the radical mechanism detailed above. The only difference is that the formation of a radical site is facilitated due to the involvement of the alkene double bond. Structured monophenyl derivatives (*i.e.*, molecules with cage fragments) bearing trifunctional fragments $RSiO_{1.5}$ are characterised [169] by a poorer accessibility of the active site and thus lower catalytic activity with respect to diphenyl derivatives built up of linear fragments.

As has been shown by kinetic studies of the two aforementioned types of halogenation, a substantial fraction of potential catalytic sites is 'switched off' the catalytic process since they are involved into the formation of interchain coordination clusters. The metal atoms tend to complete their coordination spheres by coordinating oxygen atoms from the neighbouring fragments Si–O–M (as has been discussed in previous sections).



As a result, these metal atoms become coordinatively saturated and structurally inaccessible for the interaction with CCl_4. Therefore, the main task is to prevent the formation of the interchain metal oxide clusters. If a metal atom is screened by a ligand, this effectively suppresses the interchain coordination, but does not solve the main problem, since the additional ligand equally hinders the approach of the reactant. A rather easily realisable solution of the problem consists of [150] the use of nonyl instead of phenyl groups at the silicon atoms. According to UV spectroscopy, the Cu ion in the oligononylsiloxane remains coordinatively unsaturated.

Thus, the bulky aliphatic group efficiently suppresses the coordinative interactions between the copper atoms of neighbouring chains by screening the metal sites. In solutions, it

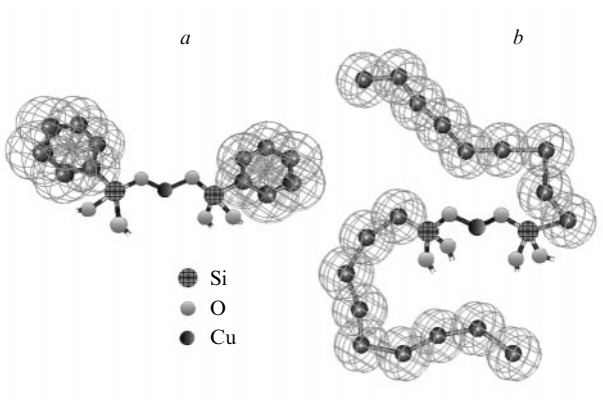


Figure 1. The structure of fragments $(-O)_2RSi-O-Cu-O-SiR(O-)_2$: R = Ph (*a*), n-$C_9H_{19}$ (*b*). Contour lines schematically indicate van der Waals surfaces around the molecules.

possesses the mobility of a polymer segment and does not prevent the approach of the organic reactant (CCl_4) to the catalytic site (Fig. 1).

The implementation of this idea gives quite impressive results:[170] the activity of nonyl-containing polymeric Cu MS with respect to the addition of CCl_4 to oct-1-ene is twice larger than that of phenylcuprasiloxanes.

VI. Conclusion

The experimental data considered above clearly demonstrate that metallasiloxanes are very interesting from both theoretical and practical points of view. This explains the multitude of studies devoted to their synthesis and consequent diversity of synthetic approaches to the formation of the fragment $Si-O-M$. The method based on the cleavage of the siloxane bonds with organometallic compounds has been developed to the large extent. The utilisation of bulky aliphatic groups as substituents at the silicon atom has proven its practical usefulness. Many niobium, tantalum, tungsten, *etc*. MS inaccessible earlier have been successfully synthesised, including low-coordinate complexes of these metals.

Metallasiloxanes themselves can be regarded as precursors in the synthesis of siloxanes that cannot be obtained by other methods. In particular, the cleavage of cage MS with electrophilic reagents yields stereoregular organocyclosiloxanes.

From the theoretical point of view, problems related to the structural features of MS are of particular importance, including the factors governing the formation of specific structural types of MS. As has been reliably established to date, the products of many reactions are actually formed due to rearrangements of the initially generated MS. These rearrangements give rise to compounds enriched with either metal or silicon (ultimately, the metal can be completely excluded from the siloxane matrix in the form of the respective oxide). A number of efficient methods for the suppression or *vice versa* facilitation of the rearrangements have been elaborated, depending on the specific goal of the synthesis. Structures stable against the rearrangements emerge in those cases where anions and, primarily, silanolate anions, are involved into the coordination sphere of the transition metal atom.

Spherical fullerene-like organosiloxane molecules can be assembled from cage MS, which can hardly be synthesised by other methods.[171, 172] According to quantum chemical calculations,[173, 174] nanotube-like assemblies are also possible for certain combinations of structural parameters.

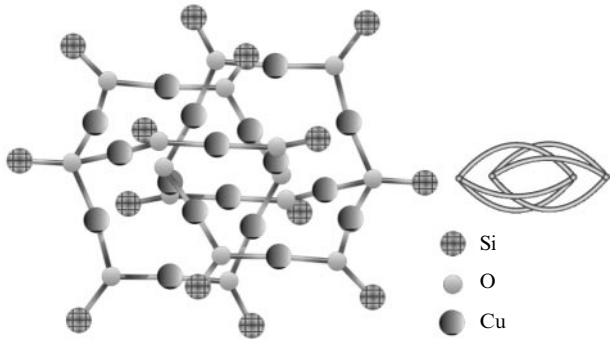


Figure 2. The structure of metallasiloxane $Cu_{18}O_2(OSiMe_3)_{14}$ (Ref. 138).

Catenane MS should be anticipated in the nearest future. The first representative of this class has already been synthesised:[38] it is characterised by an unusual topology built up of two interpenetrating bicyclic fragments (Fig. 2, methyl groups at the Si atoms are omitted for clarity).

Practical applications of metallasiloxanes primarily relates to catalysis. As a rule, the catalytic properties are determined by the nature of the constituent transition metal. Low-coordinate metal (in particular, tungsten) complexes bearing bulky organic substituents at the silicon atom have been attracting much attention from researchers over the recent years.

Oligomeric MS has a huge potential as catalytic systems. Initially, they were considered exclusively as analogues of inorganic silicates for the petrochemical synthesis. But their prominent catalytic activities in other industrially important reactions, in particular, halohydrocarbon conversion and exchange halogenation, have been discovered recently. It has to be emphasised that the type of the siloxane matrix plays equally important role as the nature of the metal in the case of oligomeric MS, since it determines the accessibility of the catalytic site.

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