

Evolution of Organometallasiloxanes

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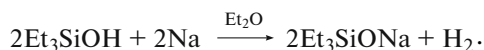
Abstract—The development of organometallasiloxane chemistry from first polymeric systems to individual organometallasiloxanes and functional oligomeric compounds is considered. The structural diversity of organosilicon precursors and the variability of metal-containing components are presented. Synthetic approaches are considered in detail, including those that allow targeted production of organometallasiloxanes of a certain structure. Using the example of organometallasiloxanes synthesized from trifunctional organoalkoxysilanes, methods for the synthesis of unique stereoregular functional cyclosiloxanes and their derivatives are highlighted. Considerable attention is given to the applied aspects of various structure organometallasiloxanes and their derivatives. The state of the art of the chemistry of organometallasiloxanes and their further evolution are evaluated critically.

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INTRODUCTION

Organometallasiloxanes are compounds containing R–Si–O–M groups, where M is a metal atom carrying the effective positive charge. This vast class of compounds takes an intermediate position between siloxane and silicates. Like silicates, organometallasiloxanes accommodate siloxane and metallasiloxanolate groups and with organosiloxanes share common structural units, such as an organic radical and a siloxane group. This class of compounds both in the past and in the present is an area of vigorous research activities since these compounds are valuable precursors for silicate materials [1–6] and, especially, model compounds of heterogeneous catalysts. One of the most effective indirect methods of studying metal oxide-based heterogeneous catalysts [7–9] involves the synthesis of surface mimicking complexes. The structural features and reactivity of these complexes should considerably contribute to understanding thorough picture of phenomena occurring on the catalyst surface at the molecular level [10].

Historically the first representative of organometallasiloxanes is sodium triethylsilanolate (Et₃SiONa), which was synthesized by Ladenburg in 1871 [11] by the interaction of triethylsilanol with metallic sodium in ether:



However, in this review, the synthesis and structure of organometallasilanolates and organosiloxanates of alkali metals will hardly be discussed, since these compounds belong to a separate subgroup of metal-containing organosilicon compounds due to their increased reac-

tivity and wide use in the synthesis of various organosiloxanes both monomeric and polymeric and their successful application in the synthesis of organometallasiloxanes of transition and rare earth metals. This class of organometallasiloxanes requires separate consideration.

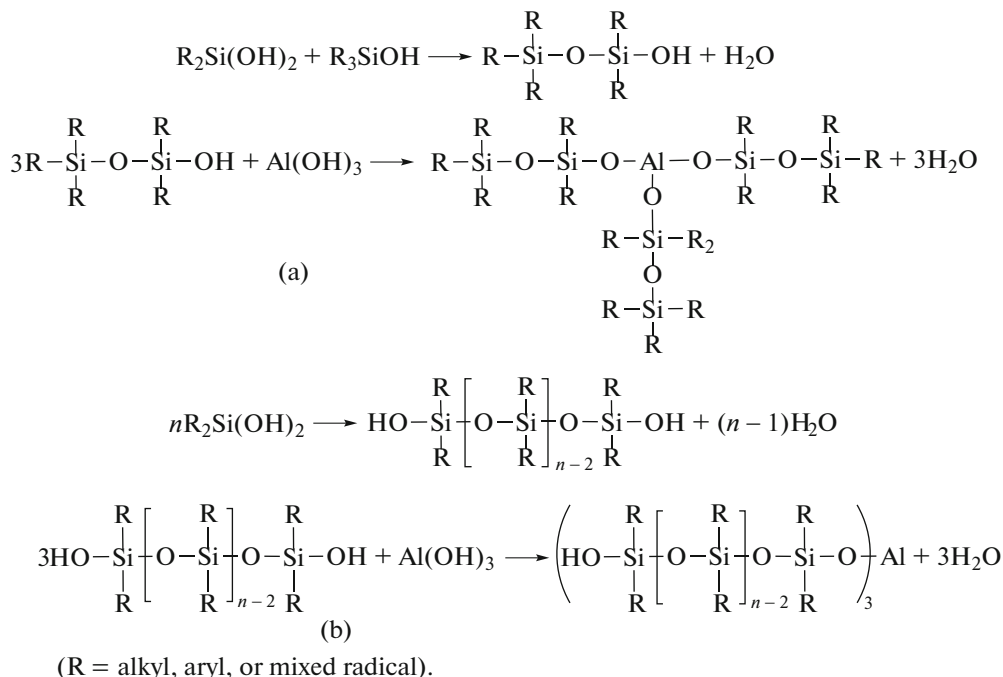
CLASSIFICATION OF ORGANOMETALLASILOXANES

Organometallasiloxanes can be divided into three unequal groups, each of which has evident distinctive features underlying the category of these objects. Surprisingly, historically, they have also progressed from simple to complex and again to simple but at the next turn of the spiral. The first group includes random organometallasiloxane polymers with the irregular arrangement of metal atoms in a polymer; the second group consists of individual organometallasiloxanes of the well-defined architecture with a wide set of metals playing the decisive role in formation of a particular structure of these compounds; and finally, the third group comprises polyfunctional organometallasiloxane oligomers with a metal atom as a branching center. All three groups have their own history, distinctive features, preparation methods, and application fields, which do not actually intersect each other, while the compounds of all three groups are sometimes composed of the same set of elements, ultimately meaning that in this area we have come from empirical approaches to the fine tuning of the structure and thus properties of target products. In what follows, we will examine successively all three groups.

POLYMERIC ORGANOMETALLASILOXANES

The first mention of the polymeric representative of organometallasiloxanes dates back to the middle of the last century, when K.A. Andrianov reported a

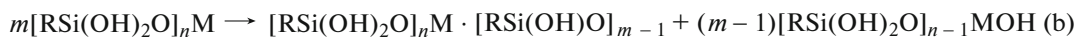
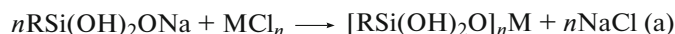
method for the synthesis of artificial resins, in which monomeric or polymeric hydroxyl-containing organosilicon products were treated with finely dispersed metals (Al, Fe, Mg, etc.) or their hydroxides [12]:



Scheme 1.

In the 1950–1970s, the works on the synthesis of polymeric organometallasiloxanes and the study of their properties were further elaborated both in the USSR and abroad. As one of the most suitable meth-

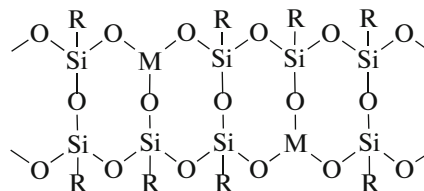
ods for the synthesis of these polymers Andrianov et al. suggested the reaction of exchange decomposition (Scheme 1a) followed by rearrangement of the resulting polymer (Scheme 1b) [13–15]:



The authors of [16] revealed that the polycondensation of organometallasiloxanes based on trifunctional organosilicon monomers is accompanied by the condensation of hydroxyl groups at the silicon atom and rearrangement processes to yield polymeric products with the variable silicon : metal ratio (Scheme 1b). Subsequently, these conclusions were verified by the example of polyphenylironsiloxane [17].

The reaction of exchange decomposition of sodium salts of organosilanetriols by metal halides is used to prepare various organometallasiloxanes containing Al, Ti, Sn, Mg, Fe, Cu, Co, Ni, Cr, and Ti ions. The properties of these metal-containing polyorganosiloxanes differ appreciably from those of already well-studied compounds. For example, they have low molecular weights and are readily soluble in organic solvents but do not pass into the viscous flow state under heating [22]. Later,

K.A. Andrianov, A.A. Zhdanov, and M.M. Levitsky assumed that the molecules of these compounds may have a branched cyclolinear structure [16]:



In modern terms this structure has little to do with reality, but the authors were certainly entitled to such a vision, since it did not contract the composition and structural analysis data accessible for them.

Despite purely probabilistic knowledge of the time about the structure of organometallasiloxanes, they were widely used in practice, indicating the major advantage of

the used methods—simplicity and good reproducibility. In accordance with Andrianov and Zhdanov developments, the industrial synthesis of polyorganometallasiloxanes, such as polyorganoaluminosiloxanes, polyorganotitanosiloxanes, and polyorganoironosiloxanes, was implemented. Polymeric organometallasiloxanes showed themselves as modifiers of acetate fibers, thermal stabilizers of siloxane rubbers, catalysts of several organic reactions, and curing agents for epoxy resins [23–31]. The most wide use was gained by polyalumosiloxanes: they were employed as additives in the manufacture of thermally stable vanishes and composite plastics as well as to improve the moisture resistance of phenol-formaldehyde resins used in the production of fiberglass laminates [32].

The studies of those years devoted to the synthesis and application of polymeric organometallasiloxanes are covered in the monographs by K.A. Andrianov [33] and M.G. Voronkov [34], the book edited by V.V. Korshak [35], and the book “Inorganic Polymers” edited by F.G.A. Stone and W.A.G. Graham [36].

This period was basically empirical. A marked practical orientation of search dictated the simplicity of the used initial compounds and techniques. It is the achievements of pioneers in this field, Zhdanov was certainly among them, predetermined its further progress.

INDIVIDUAL ORGANOMETALLASILOXANES

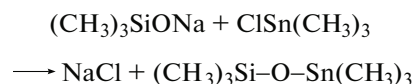
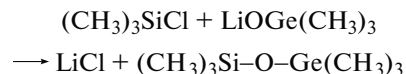
Achievements in the synthesis of polymeric organometallasiloxanes turned out to be the driving force for further studies. The discovery of new properties valuable for practice and expanding possible application fields demanded the elaboration of different approaches and, what is most important, the assessment of contributions of a particular structural element to the integral characteristics of organometallasiloxane polymers. Not surprisingly, since the 1960s, the research direction dealing with the synthesis and study of properties of individual organometallasiloxanes has begun to develop and got rapid progression at the onset of the 1990s.

Individual organometallasiloxanes are synthesized using compounds of mono-, bi- and trifunctional silicons that are basically monosilanols, disilanols, and siloxanediols as well as silanetriols and trisilanols. In

combination with assorted metal ions they provide the diverse structural forms of the resulting molecules—from simple and dimeric molecules of organometallasiloxanes to cyclic structures, complex spirocycles, and polyhedral compounds.

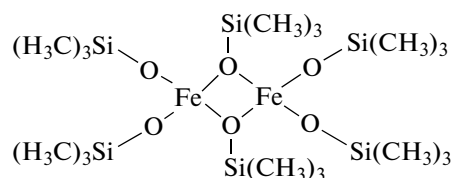
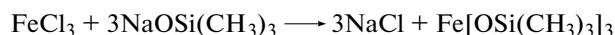
Monofunctional Organosilicon Precursors

Organometallasiloxanes derived from monofunctional silanes (R_3Si-) represent either individual metal ions connected to triorganosiloxy group $R_3Si(O)-M(CH_3)_3$ (illustrated by the example of synthesis scheme for monomeric germano- and stannosiloxanes) [37, 38]:

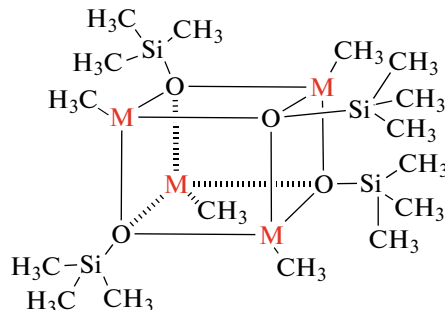
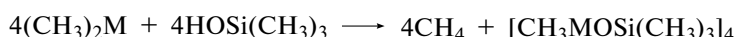


or their associates (dimers, tetramers, and sometimes heptamers), in which metal ions are separated by siloxane ligands. These compounds are commonly synthesized using silanols, alkali metal silanolates, acyloxysilanes, hexamethyldisiloxane, or alkoxy silanes. Most frequently, these are trimethylchlorosilane or trimethylsilanolates of alkali metals. The source of transition metals may be their halides (largely chlorides) or, which is less common, organometallic compounds and their alcoholates or oxides (Fig. 1 and the schematic syntheses and structures of compounds are outlined below) [39–41].

The schematic synthesis and structure of tris(trimethylsiloxy)iron are as follows [40]:



The schematic synthesis and structure of zinc and cadmium trimethylsilanolates are as follows [41]:



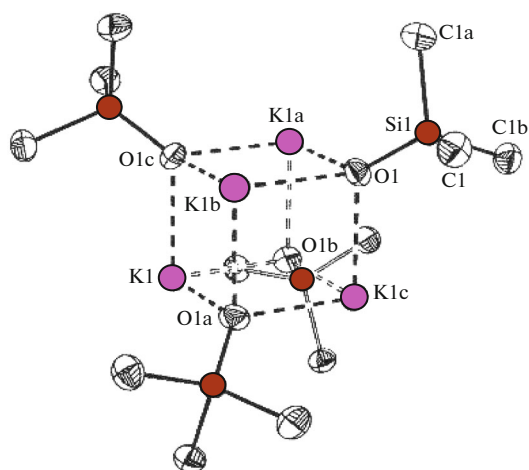
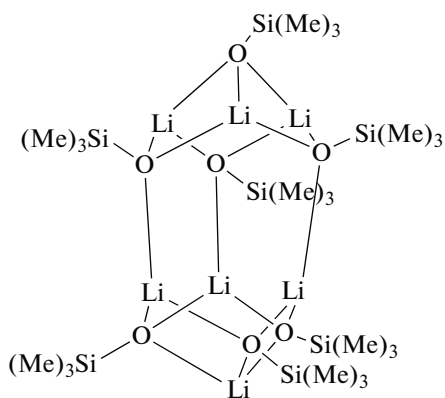


Fig. 1. Molecular structure of potassium silanolate $[\text{Me}_3\text{Si}(\text{O})\text{K}]_4$: Si is denoted as \bullet , K is denoted as \circ , O is denoted as \ominus , and Me is denoted as \oplus [39].

The syntheses of many individual organometallasiloxanes from compounds of monofunctional silicon and their structures were described in Voronkov's book [34], two reviews by H. Schmidbaur [42, 43], and papers [44, 45].

Recently, the crystalline structure of lithium trimethylsilanolate was found to be an associate composed of seven lithium trimethylsilanolate molecules $[\text{Li}_7(\text{OSiMe}_3)_7(\text{THF})]$ and one molecule of tetrahydrofuran. It was accessible by the reaction of $\text{Me}_3\text{SiOSiMe}_3$ with LiMe in THF and crystallized from toluene [46].

The structure of $[\text{Li}_7(\text{OSiMe}_3)_7(\text{THF})]$ features a capped trigonal antiprismatic arrangement of seven lithium atoms bridged by seven oxygen atoms of the $\mu_3\text{-O}$ silanolate ligand:

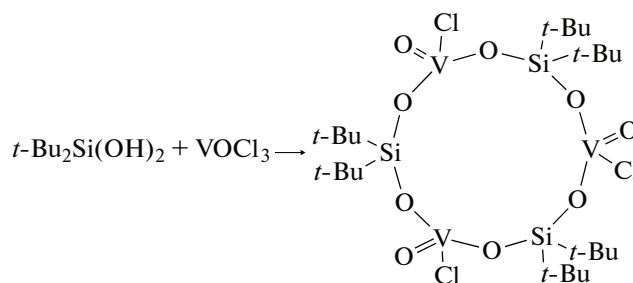


Bifunctional Organosilicon Precursors

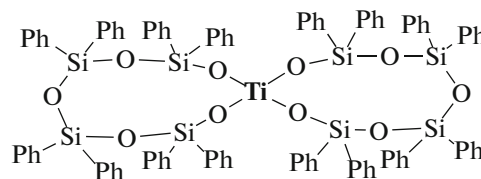
Individual organometallasiloxanes synthesized from bifunctional silanes ($\text{R}_2\text{Si}(\text{OH})_2$) and siloxanes possess a more complex structure. Initial organosilicon precursors herein are usually compounds containing

two silanol groups $-\text{Si}(\text{OH})_2$ and one or several siloxane bonds which are most often transformed into alkali metal siloxanates. The sources of metal ions are various metal-containing compounds, such as metal chlorides, oxides, oxychlorides, etc.

The molecules of the resulting compounds may represent heterocycles containing silicon and other elements (illustrated by the example of synthesis of heterocyclic vanadiumsiloxane) [47]:

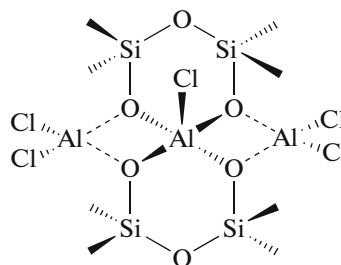


They may also contain individual metal ions but here in the form of a hetero atom in a siloxane spirocycle, while the formation of some structures may be accompanied by the condensation of silanol groups [48] with enlargement of the tetraphenyldisiloxanolate fragment of the initial organosilicon precursor to octaphenyltetrasiloxanolate fragment in the target organometallasiloxane:

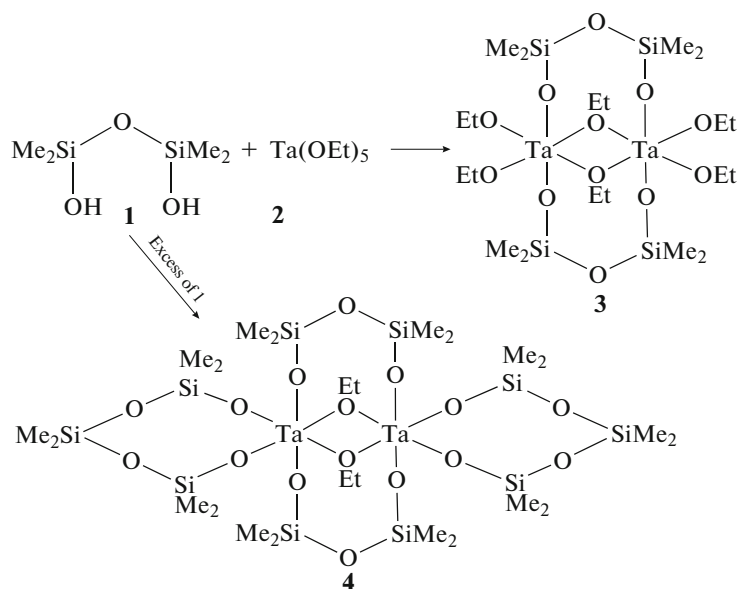


More interesting structures (presented below) contain several metal ions (one or different types) enclosed by siloxane ligands.

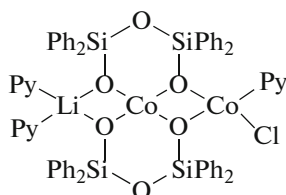
The example can be provided by the structure of $\{[(\text{O})\text{Si}(\text{Me})_2-\text{O}-\text{Si}(\text{Me})_2(\text{O}))_2[\text{AlCl}_2)_2(\text{AlCl})]\}$ [49, 50]:



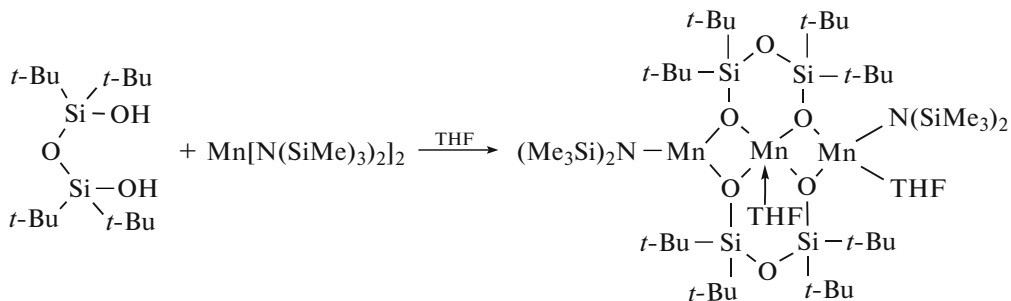
Another rare example is the structures of metallasiloxane complexes containing methyl groups at the silicon atom [51]. They are prepared by the reaction of $\text{Ta}(\text{OEt})_5$ with 1,1,3,3-tetramethyl-1,3-disiloxanediol ($\text{HOSiMe}_2\text{OSiMe}_2\text{OH}$). Depending on the reagent ratio (1 or 2), this reaction yields either dimeric complex 3 or complex of a more complex structure 4:



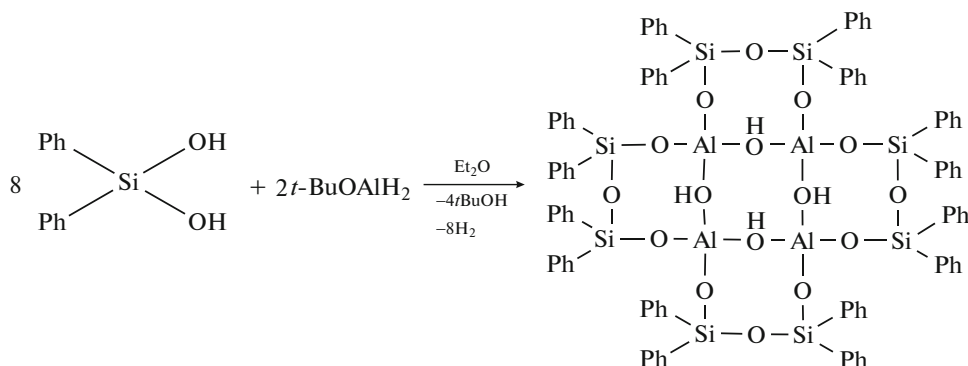
The reaction of cobalt(II) chloride with lithium tetraphenylsiloxanolate in THF followed by extraction with pyridine solution in toluene after THF removal affords a complex containing two different metals (bimetallic), $[\text{Co}\{\text{O}(\text{Ph}_2\text{SiO})_2\}_2\text{-}\mu\text{-(LiPy)}_2\text{-}\mu\text{-(CoClPy)}]$ [52]:



The reaction of disiloxanediol carrying *t*-Bu group with manganese bis(trimethylsilyl)amide in THF gives a mono-metallic spirocyclic compound containing three manganese ions, $\{[\text{O}(\text{Ph}_2\text{SiO})_2\}_2\text{Mn}_3[\text{N}(\text{SiMe}_3)_2]\cdot(\text{THF})_2(\text{THF})_{0.5}$ [53]:



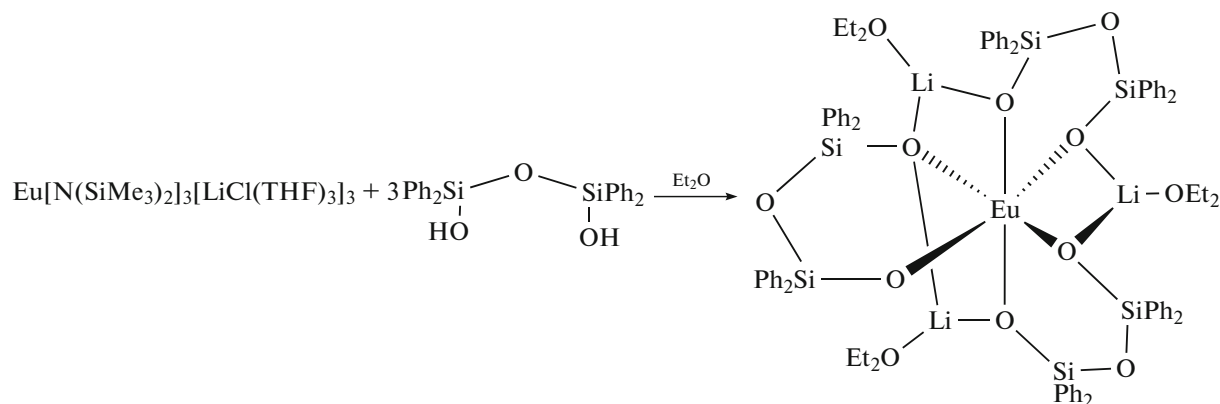
Interesting polycyclic alumosiloxane $[\text{Ph}_2\text{SiO}]_8[\text{Al}(\text{O})\text{OH}]_4\cdot\text{Et}_2\text{O}$ was synthesized by the reaction of diphenylsilanediol with *tert*-butoxyaluminum hydride [54]:



The examples of synthesis and structures of organometallasiloxanes derived from bifunctional diphenylsilanediol, tetraphenyldisiloxanediol, or tetra(*tert*-butyldisiloxanediol) are presented in reviews [55–57].

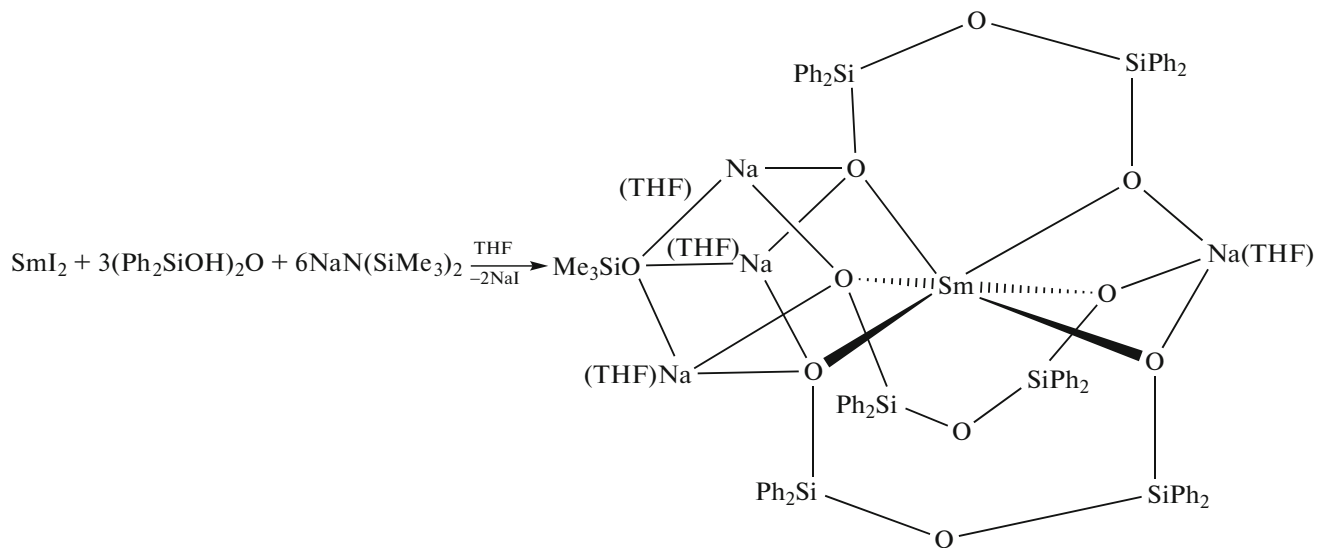
A large number of complex spirocyclic organometallasiloxanes was synthesized by the team of professor Edelmann [57] using rare earth and other metal ions. Synthesis was performed largely via the reaction of tetraphenyldisiloxanediol with lanthanide silylamide precursors in the

salt form $\text{Ln}[(\text{NSiMe}_3)_2]_3[\text{LiCl}(\text{THF})_3]_3$. The authors used tetraphenyldisiloxanates of alkali metals (lithium, sodium, and potassium) prepared by in situ interaction with *n*-butyl lithium or bis(trimethylsilyl)amides of alkali metals $\text{MN}(\text{SiMe}_3)_2$, where $\text{M} = \text{Li}, \text{Na}, \text{K}$, which were then allowed to react with anhydrous rare earth chlorides in THF or dimethoxyethane. One of the first examples of these compounds is the complex of lithiumeuropiumsiloxane [58]:



Note that for the synthesis of various organometallasiloxane the “silylamide” approach is considered currently successful for reactions with silanols of various molecular structure, since in this case hexamethyldisilazane is the only reaction byproduct.

Another molecular structure of organometallasiloxane was prepared by the reaction of sodium silylamide with tetraphenyldisiloxanediol and subsequent interaction with samarium iodide, $[\text{Me}_3\text{SiO}\{\mu\text{-Na}(\text{THF})_3\}\text{Sm}\{\mu\text{-}[(\text{Ph})_2\text{SiO}]_2\}_3\text{Na}(\text{THF})]_3$ [59]:



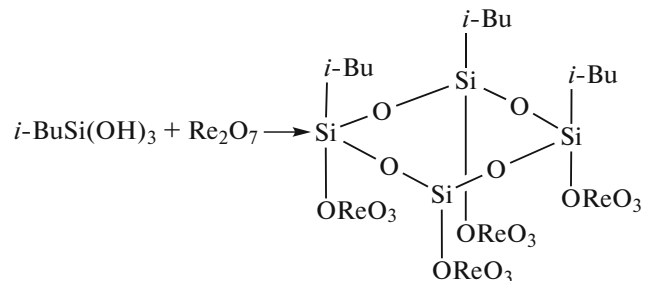
Thus, Edelmann’ team demonstrated how diverse the structural chemistry of heterobimolecular (Ln/M , M is alkali metal) complexes with rare earth metals can be. Their studies are addressed in reviews [57, 60] and papers [61–66].

Trifunctional Organosilicon Precursors

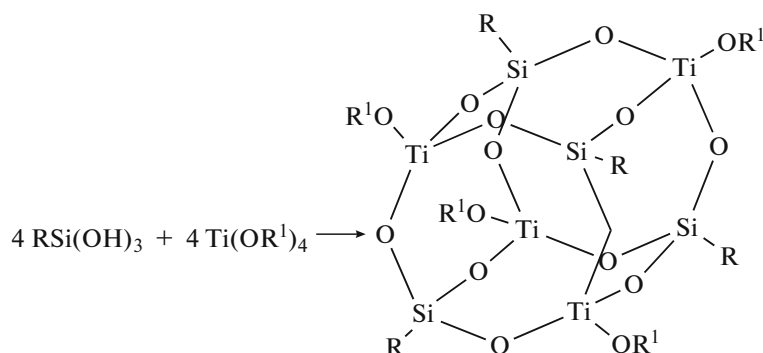
Organometallasiloxanes derived from trifunctional silicon compounds ($\text{RSi}\langle\text{---}\rangle$) also have different molecular organizations. Their structure is determined by

both the structure of the initial silicon-containing reagent and the synthesis pathway. In accordance with H.W. Roesky et al. [56, 67–74], the use of bulky substituents allows the tendency of trisilanol to condense via silanol groups to be suppressed. It was shown that, like organometallasiloxanes based on monofunctional silicon, organometallasiloxanes synthesized from monomeric organosilanetriols $\text{RSi}(\text{OH})_3$ with organic substituents, such as *t*-Bu, $(\text{SiMe}_3)_3\text{CSi}-$, $(\text{SiMe}_3)_3\text{SiSi}-$, $(\text{SiMe}_2\text{Ph})_3\text{CSi}-$, $(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{N}-(\text{SiMe}_3)\text{Si}-$, etc., can have different structural forms depending on the used trisilanol and metal ion (their examples are outlined below).

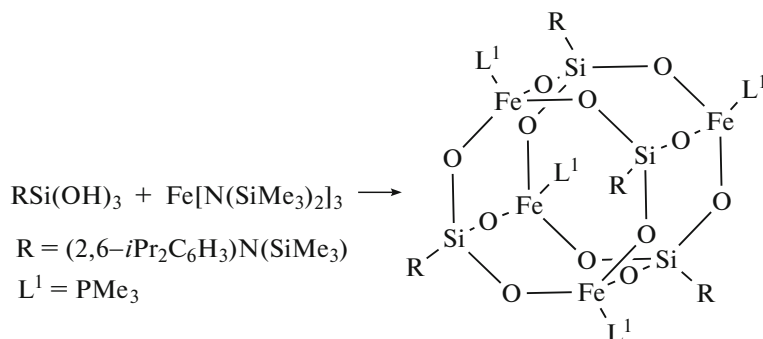
The synthesis and structure of $[\textit{t}\text{-BuSi}(\text{O})(\text{OReO}_3)]_4$ can be depicted as [68]:



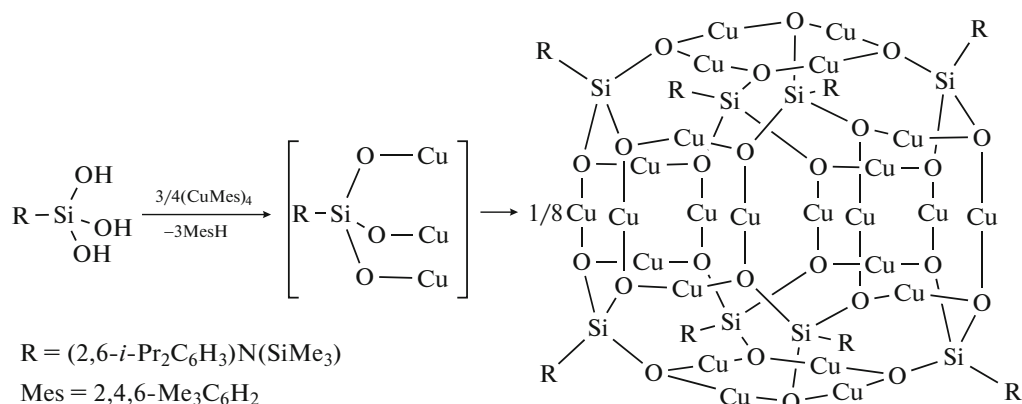
The synthesis and structure of cubic titanasiloxane can be depicted as [68]:



The synthesis and structure of cubic organoironsiloxane can be depicted as [69]:



The authors of [74] reported probably the most impressive example—the 56-membered coppersiloxane cage compound $[\text{RSi}(\text{OCu})_3]_8$, which was synthesized by the reaction of $\text{RSi}(\text{OH})_3$ ($\text{R} = \text{N}(\text{SiMe}_3)\text{-}2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$) with $(\text{CuMes})_4$ ($\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$):

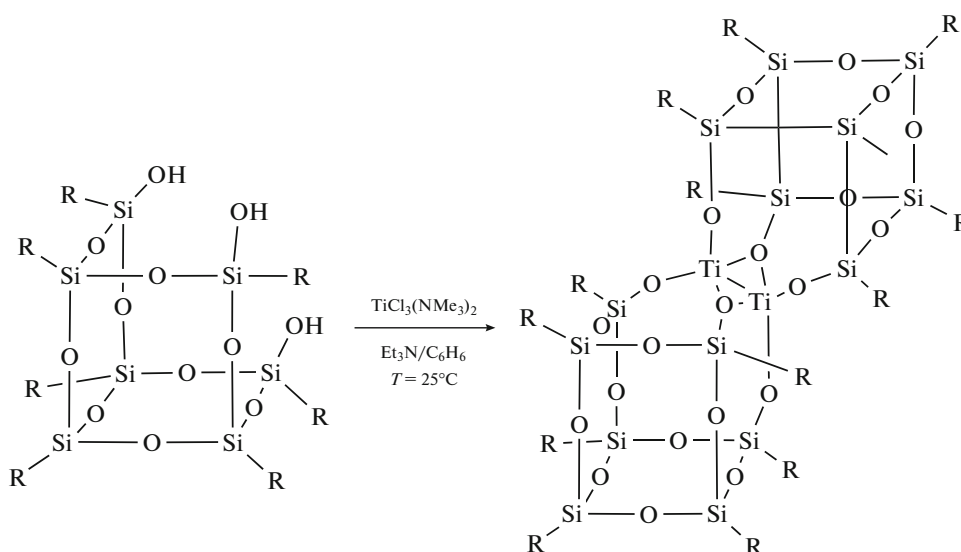


Polyhedral Organosilicon Precursors

An important and logical development of the chemistry of polyhedral organometallasiloxanes involved the use of incompletely condensed organosilsesquioxane cubane containing silanol groups. The examples of these compounds were first described in [75–77]. Compounds containing one or several silsesquioxane fragments in a molecule were termed organometallasilsesquioxanes. They were synthesized by the team of F.J. Feher [75–82] engaged in the construction of homogeneous models applied to describe molecular processes occurring on heterogeneous catalysts, SiO₂-supported metal oxides, which are in wide use in the petrochemical industry. The authors assumed that incompletely condensed polyhedral oligosilsesquioxanes (**IPOSS**) having a bulky siloxane

cage should be very similar to silica in their electronic behavior and available reactive functional groups Si–OH can be used to “bind” metal ions into various complexes. Therefore, various organometallasilsesquioxane structures were obtained by reactions with main group and transition metal compounds, metal alcoholates, amides, oxychlorides, etc.

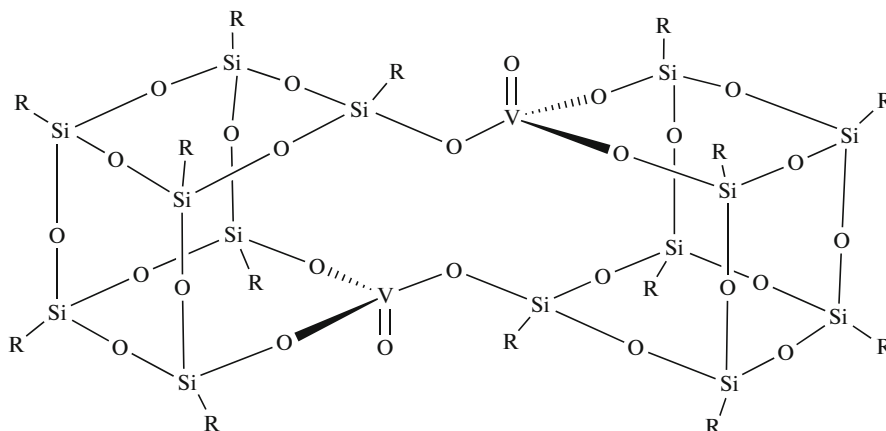
It was proposed that owing to the rigid geometry of the silsesquioxane ligand the resulting monomeric complex should contain a trivalent metal unbound to other ligands (“pure” metal). However, it turned out that a high electrophilicity of this complex facilitates the formation of various dimeric structures. For example, the reaction of incompletely condensed silsesquioxanetriol with TiCl₃(NMe₃)₂ yields the dimeric compound [78]:



Similar dimeric complexes with vanadium and aluminum (from AlMe₃ or (*i*-PrO)₃Al) were also synthesized [79, 80].

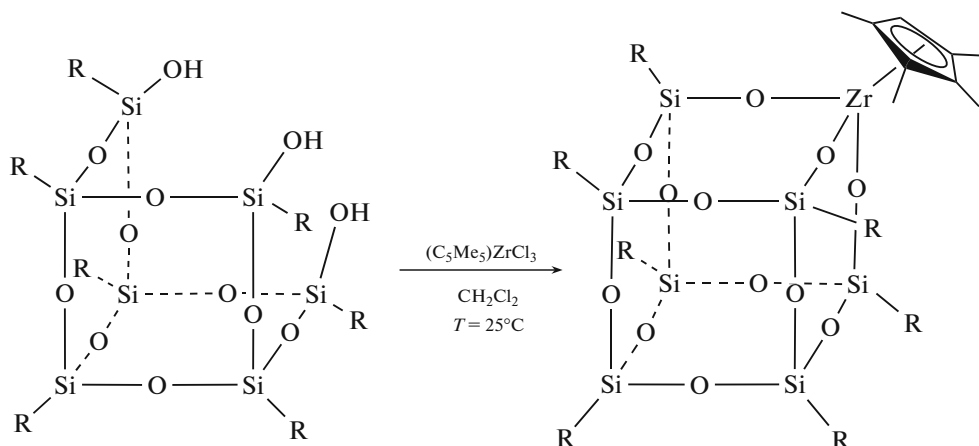
It is interesting that monomeric and dimeric vanadium silsesquioxanes are contained in the reaction mass

resulting from the interaction of silsesquioxanetriol with vanadium(V) compounds, such as (*n*-PrO)₃VO, (Me₃SiCH₂)₃VO, or VOCl₃ (in the latter case, in the presence of acceptor HCl) [81], but in the crystalline state the authors managed to isolate only the dimer:

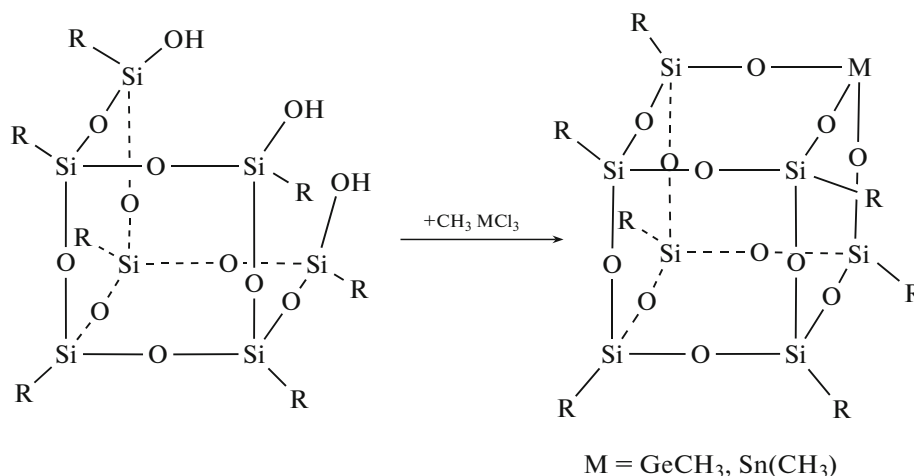


Monomeric metallasilsesquioxanes are prepared by the reaction of an incompletely condensed cube with the following compounds MeGeCl_3 , MeSnCl_3 , and $(\text{C}_5\text{Me}_5)\text{ZrCl}_3$ [75, 76].

The schematic synthesis of monomeric zirconium-containing metallasilsesquioxane is outlined below [75]:



The schematic synthesis of and structure of germanium- and tin-containing metallasilsesquioxanes can be depicted as [76]:



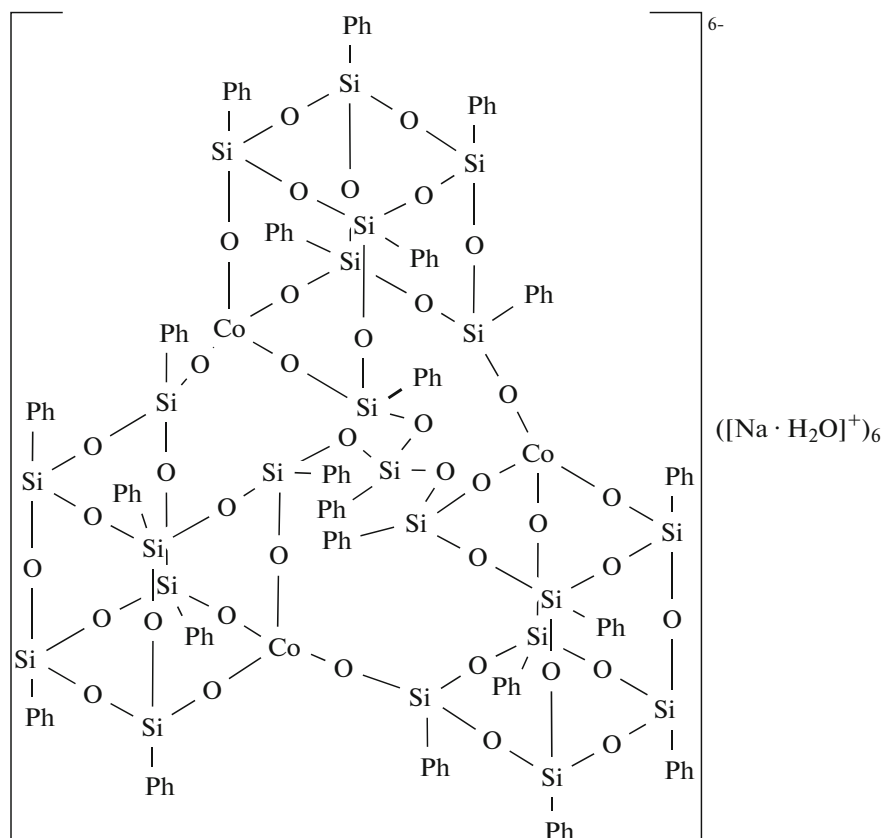
These monomeric structures are formed with compounds in which the metal atom additionally contains an organic substituent hindering the formation of dimers.

The authors surveyed their works on this theme in [82].

It should be emphasized that almost at the same time Zhdanov and Levitsky et al. [83] reported cobalt complex of the general formula $\{[\text{PhSi}]_7\text{O}_{13}\text{Co}\}_3\text{SiPh}\}^{6-} \cdot (\text{Na}^+)_6(\text{H}_2\text{O})_6$ with the most complex architecture of that time. It was prepared from a mixture of $[\text{PhSi}(\text{O})\text{ONa}]_3 \cdot 3\text{H}_2\text{O}$ and

$[\text{PhSiO}_{1.5}]_n$ with NaOH and CoCl_2 at a reagent ratio of 6.6 : 7.5 : 20 : 10.

In this complex, each silsesquioxane “cubic” subunit acts as a trifunctional one containing a cobalt atom in one apex. In the synthesized Si_7Co cube, one of $\text{Si}-\text{O}-\text{Si}$ edges is broken and one of the two resulting functions is used to form a covalent bridge through the central group $\text{PhSi}(\text{O}_{1.5})_3$ and the second function participates in coordination of the Co atom chelated by the neighboring Si_7Co “cube.” “Olate” oxygen atoms are coordinated to both the Co atom and the Na^+ ion, which in turn are coordinated by solvate water molecules:

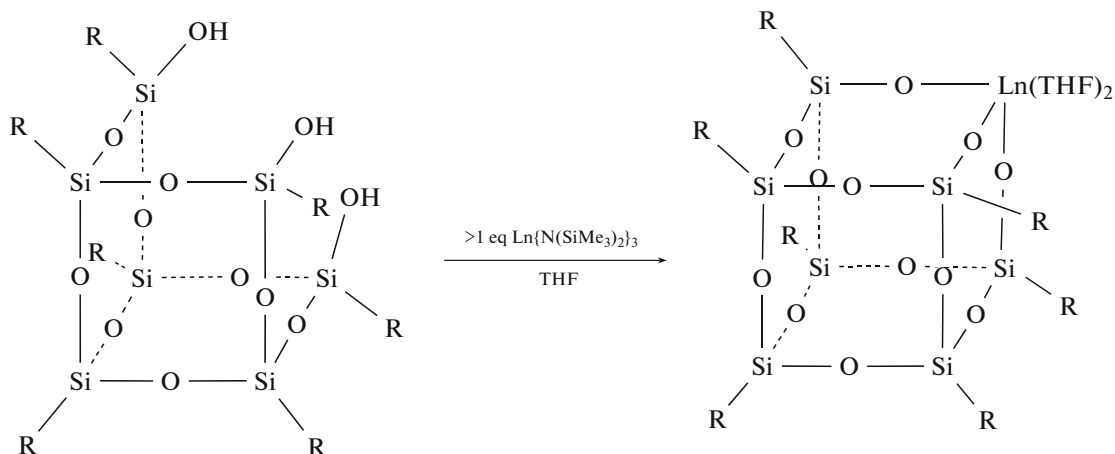


Studies concerning the use of incompletely condensed silsesquioxane cube evolved further. Metal-silsesquioxanes containing two silsesquioxane ligands and many metals, including Li, K, Be, Al, In, Sc, Sm, Yb, U, Ti, Zr, V, Ta, Cr, and Cu, were synthesized [84].

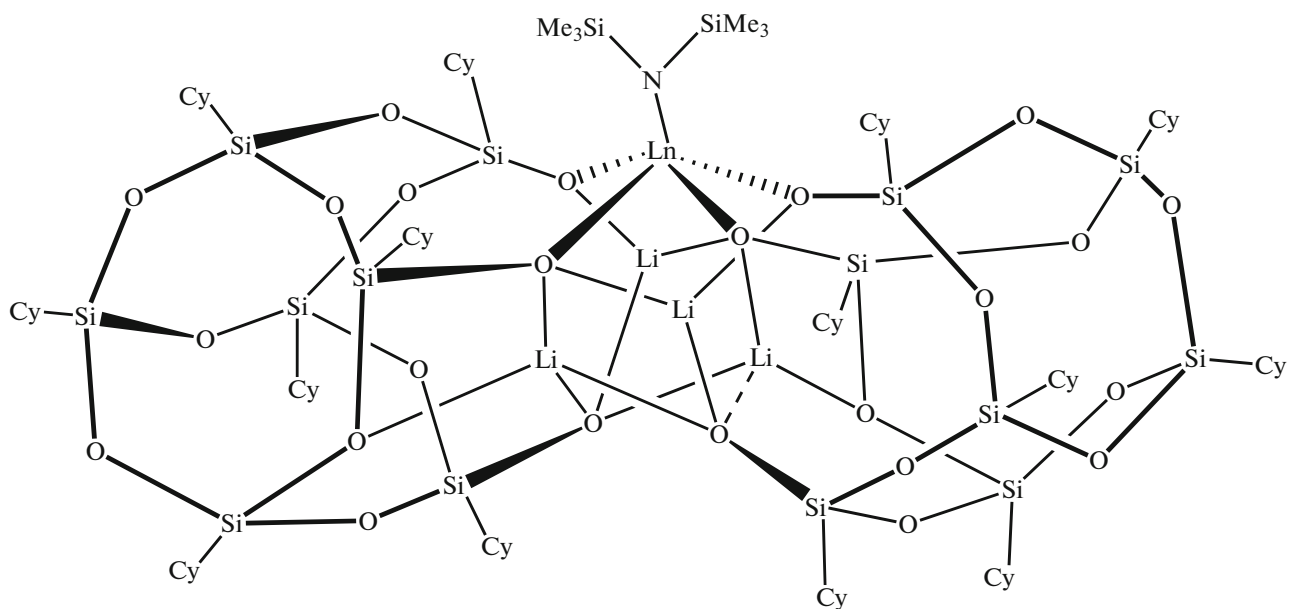
Of particular interest are organometallasilsesquioxanes of rare earth metals, which can act as homogeneous analogs of silica-supported rare earth compounds and can be potentially interesting materials for

optoelectronics. They are mostly synthesized from various rare earth compounds but also via the "silylamide" approach. For example, organometallasilsesquioxanes of various molecular structures ranging from monomeric [85] to dimeric [86], three-dimensional [87], and tetrameric [88] were prepared. Molecules of some compounds were bimetallic (contained ions of both rare earth and alkali metals).

The schematic synthesis and structure of a lanthanide-containing complex can be depicted as [85]:



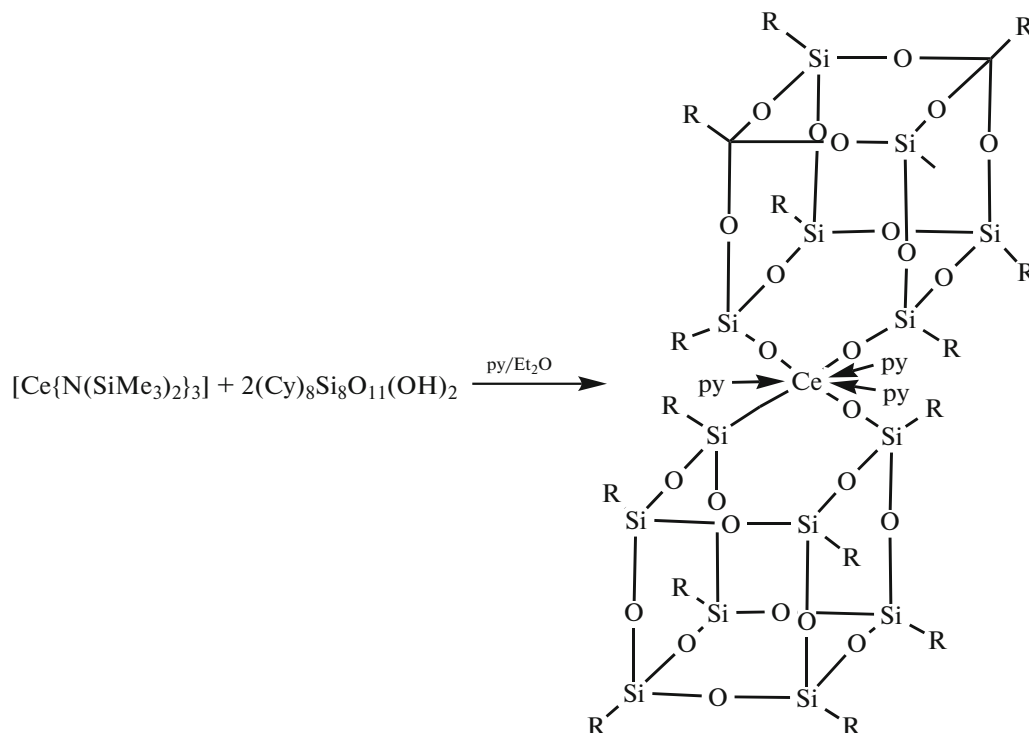
The structure of a polyhedral dimeric molecule containing ions of Gd or Yb and lithium (Cy = cyclohexyl) can be depicted as [86]:



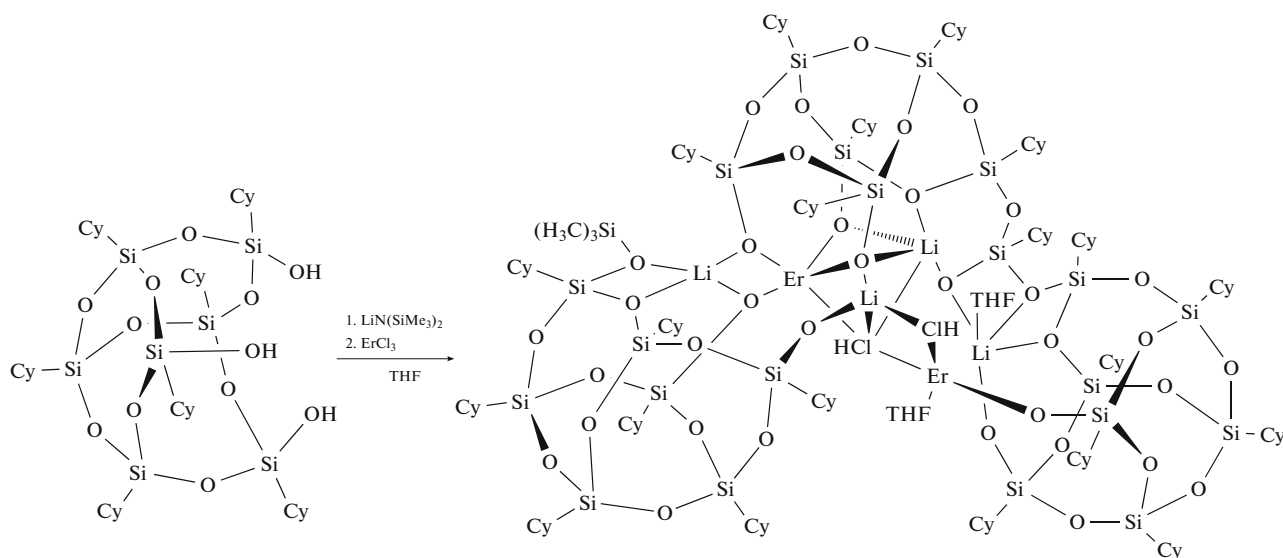
The interaction of $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3$ with two equivalents of incompletely condensed cubic disilanol $\text{Cy}_8\text{Si}_8\text{O}_{11}(\text{OH})_2$ containing only two silanol groups carried out in diethyl ether in the presence of excess pyridine affords monometallic dimeric com-

plex $(\text{Cy}_8\text{Si}_8\text{O}_{13})_2\text{Ce}(\text{Py})_3$ (Cy = cyclohexyl) [87].

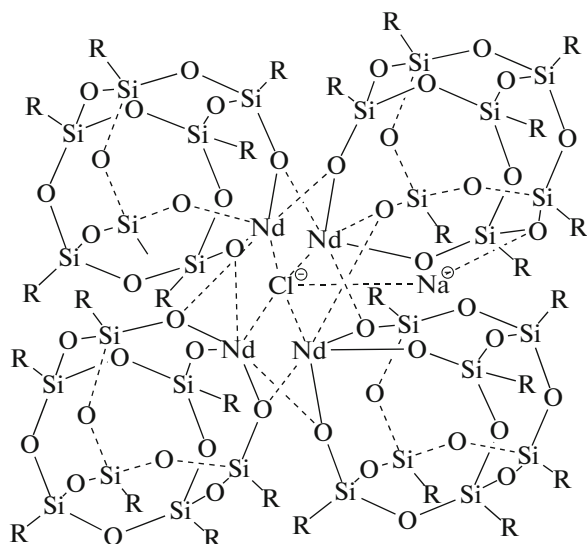
The synthesis and structure of cerium-containing compound $[\text{Ce}\{(\text{Cy})_8\text{Si}_8\text{O}_{13}\}_2(\text{Py})_3]$, (R = Cy = cyclohexyl) can be depicted as [87]:



The synthesis and structure of $(c\text{-C}_6\text{H}_{11})_{21}\text{Si}_{21}\text{O}_{36}(\text{SiMe}_3)\text{Er}_2(\text{THF})_2\text{Li}_4\text{Cl}_2$ (Cy = cyclohexyl) can be depicted as [88]:



Neodymium-containing tetrameric silsesquioxane was prepared by the interaction of NdCl_3 with $i\text{-PrONa}$ followed by the addition of trisilanol [$(i\text{-C}_4\text{H}_9)_7(\text{Si}_7\text{O}_9)(\text{OH})_3$] in the reaction mixture in toluene, $\{[(i\text{-C}_4\text{H}_9)_7(\text{Si}_7\text{O}_{12})\text{Nd}]_4\text{NaCl}\}$ [89]:



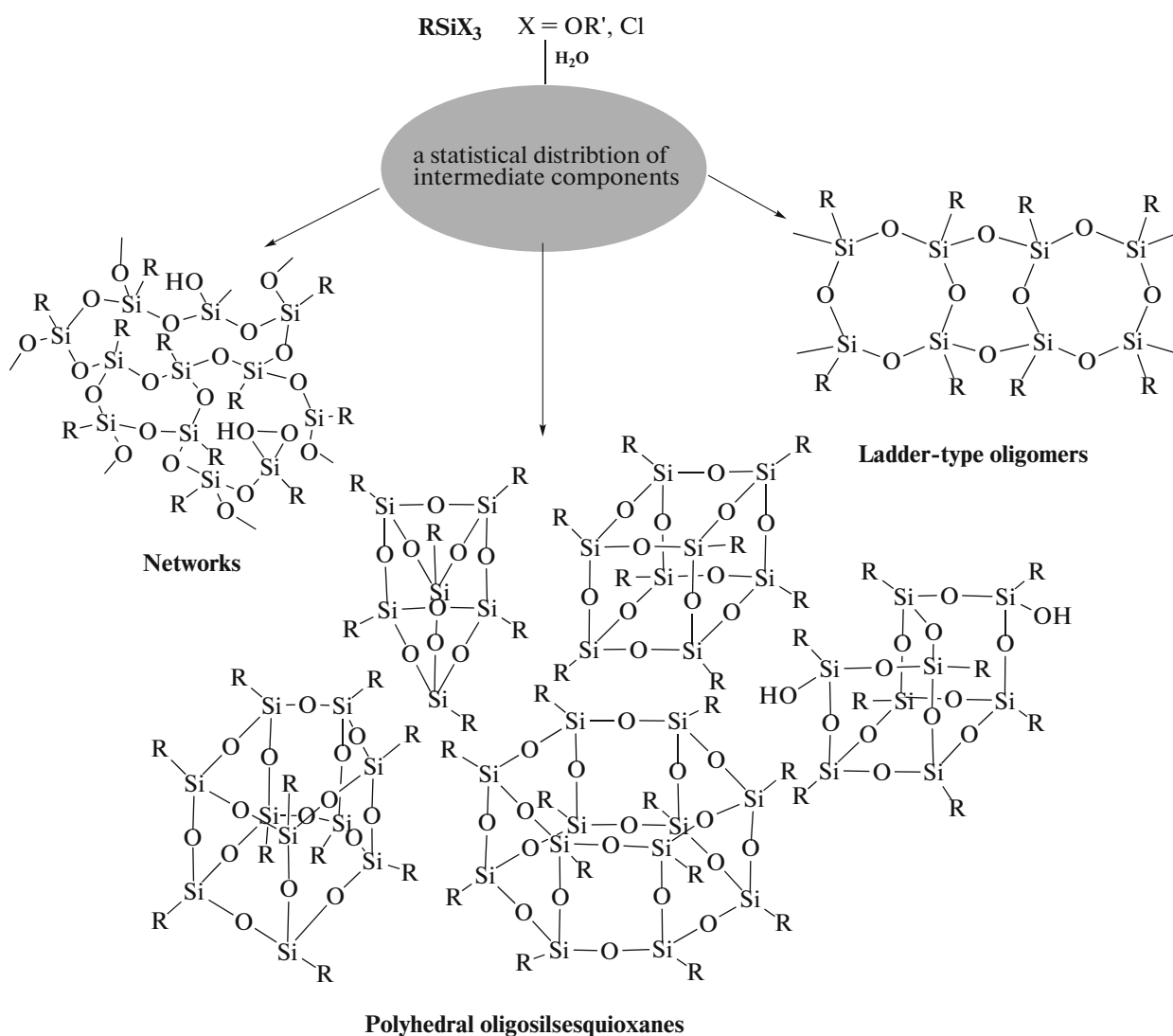
Thus, a large number of diverse organometal-lasilsesquioxanes with a wide range of various molecular structures is available, many of which were described in [61–73, 83, 89, 90]. The review

[91] covered in detail the application of silsesquioxane metal-containing complexes as molecular models of catalytic sites grafted onto silica, and it was shown that the complexes of organometal-lasilsesquioxanes based on IPOSS can help in understanding reactions occurring on the catalyst surface at the molecular level.

Summing up the foregoing it can be supposed that the search for novel structures suitable for the synthesis of individual organometal-lasiloxanes and their preparation methods, in our opinion, will provide a powerful impetus for further development of this chemistry realm. Possibility to strictly control the structure of target organometal-lasiloxanes at the stage of organosilicon and metal-containing precursors will make it possible to considerably expand application fields of the given organometal-lasiloxanes.

Precursors Based on Trifunctional Organochloro- and Organoalkoxysilanes

It is well known that the hydrolytic condensation of trifunctional chloro- or alkoxysilanes is a complex multistep process that is very sensitive to even slight changes in reaction conditions. Therefore, the resulting mixtures contain a wide set of products spanning from small oligomers and polyhedral silsesquioxanes to complex mixtures of low molecular weight resins and gels:



In the 1990s, Zhdanov et al. isolated several individual polyhedral organometallasiloxanes (**POMS**) with molecular weight up to 3.0×10^3 which contained ions of alkali and transition metals and lanthanides [92–100] (Fig. 2). The general synthetic technique included three steps: the first step involved the hydrolytic condensation of organotrichlorosilane in an aromatic solvent to yield a low molecular weight organosilsesquioxane oligomer; at the second step the alkaline cleavage of this oligomer by sodium or potassium hydroxides in an alcohol medium ($\text{Si} : \text{M} = 1$) occurred; and the third step was the exchange reaction of alkali metal organosiloxanolate formed in situ with $\text{M}'\text{Cl}_n$ ($\text{Si} : \text{M}' = 3$ and $n = 2$ for transition metals; $\text{Si} : \text{M}' = 4$ and $n = 3$ for lanthanides).

As evidenced by X-ray diffraction analysis, the molecules of individual polyhedral organometallasiloxanes feature a sandwich (Figs. 2a–2c) or globular structure (Fig. 2d) based on one or two stereoregular organosi-

loxanolate cyclic fragments coordinated by metal ions. The size of the cyclic organosiloxanolate fragment is determined by the metal coordination geometry. Sandwich-type molecules also contain encapsulated bridging anionic ligands (OH^- , Cl^- , O^{2-}).

This selectivity was not observed previously in organosilicon chemistry. It is presumably associated with the organizing role of a metal in an organosilicon intermediate formed via the alkaline cleavage of the silsesquioxane resin in an alcohol medium. Later, it was shown that this intermediate may be alkali metal organosiloxanolate of the formula $\{[\text{RSi}(\text{OR}')(\text{OH})\text{O}^-](\text{Na}^+)\}$ ($\text{R}' = \text{alkyl}, \text{H}$). This compound can result from the simultaneous occurrence of at least six reversible and irreversible reactions [97] and proton-cation exchange between silanolate and silanol groups [92] during the cleavage of the silsesquioxane resin by alkali metal hydroxide in the alcohol medium (Scheme 2a).

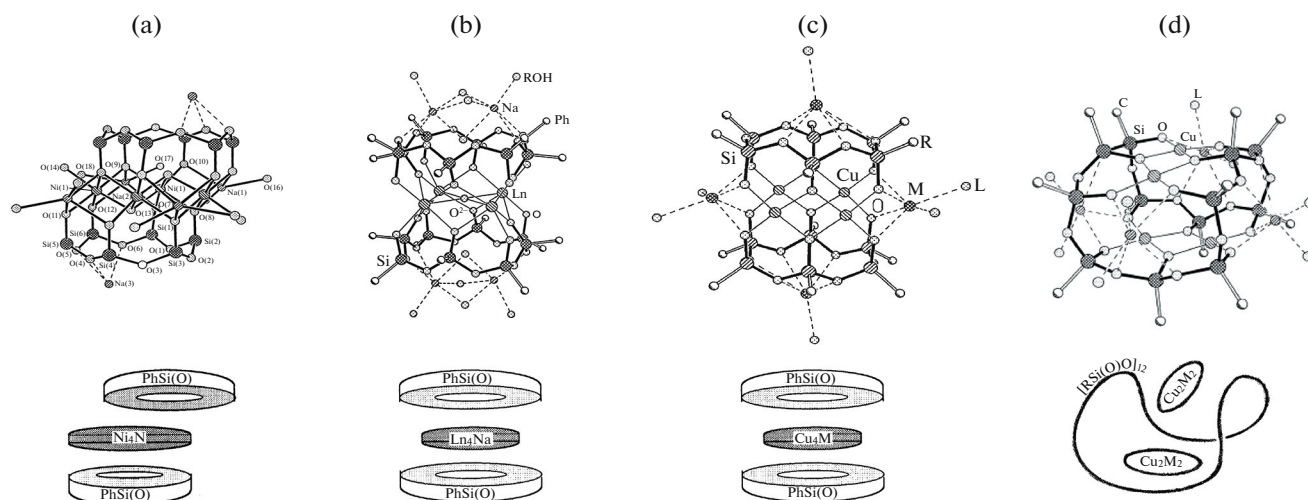
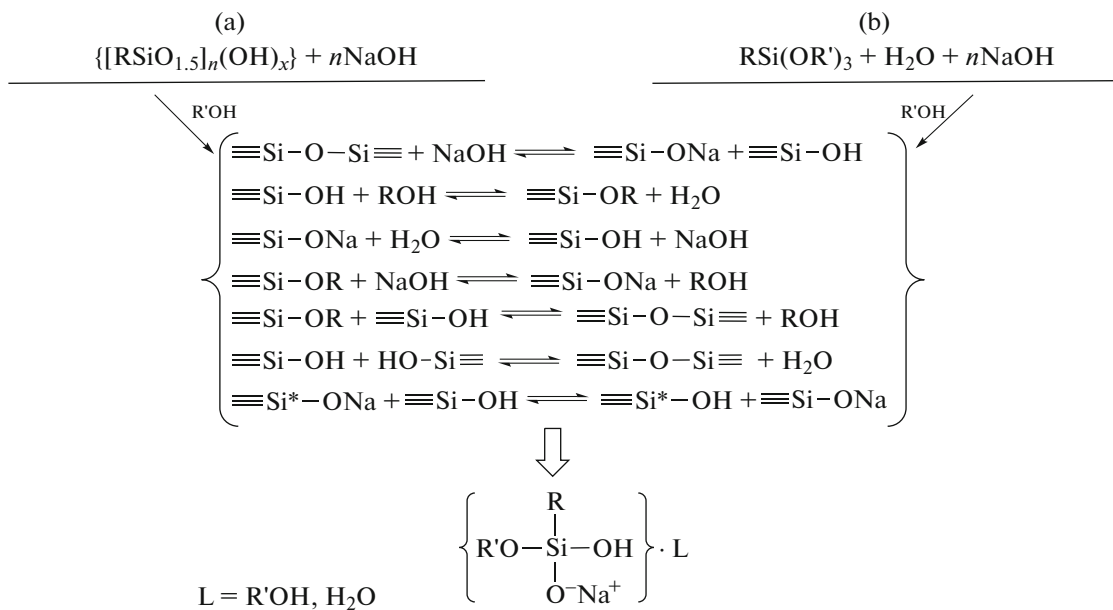


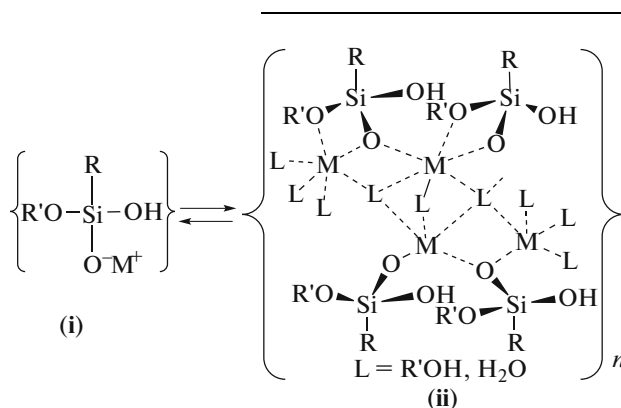
Fig. 2. Polyhedral phenylmetallasiloxanes of (a–c) sandwich and (d) globular molecular structure.

Therefore, later, it was suggested [101–106] that similar reactions, although in a different order, should also occur during the hydrolysis of organotrialkoxysilanes in an alcohol medium in the presence of the equimolar amount of alkaline (Scheme 2b):



Scheme 2

Alkaline intermediates (i) containing solvated ion pairs show the tendency toward association in an organic medium giving rise to complex aggregates (ii), in which the ionic matrix solvated by alcohol and water molecules is surrounded by organosilicon fragments with functional hydroxyl and alkoxy groups. It is shown that there is equilibrium between dissociated ion pairs (i) and ion aggregates (ii):



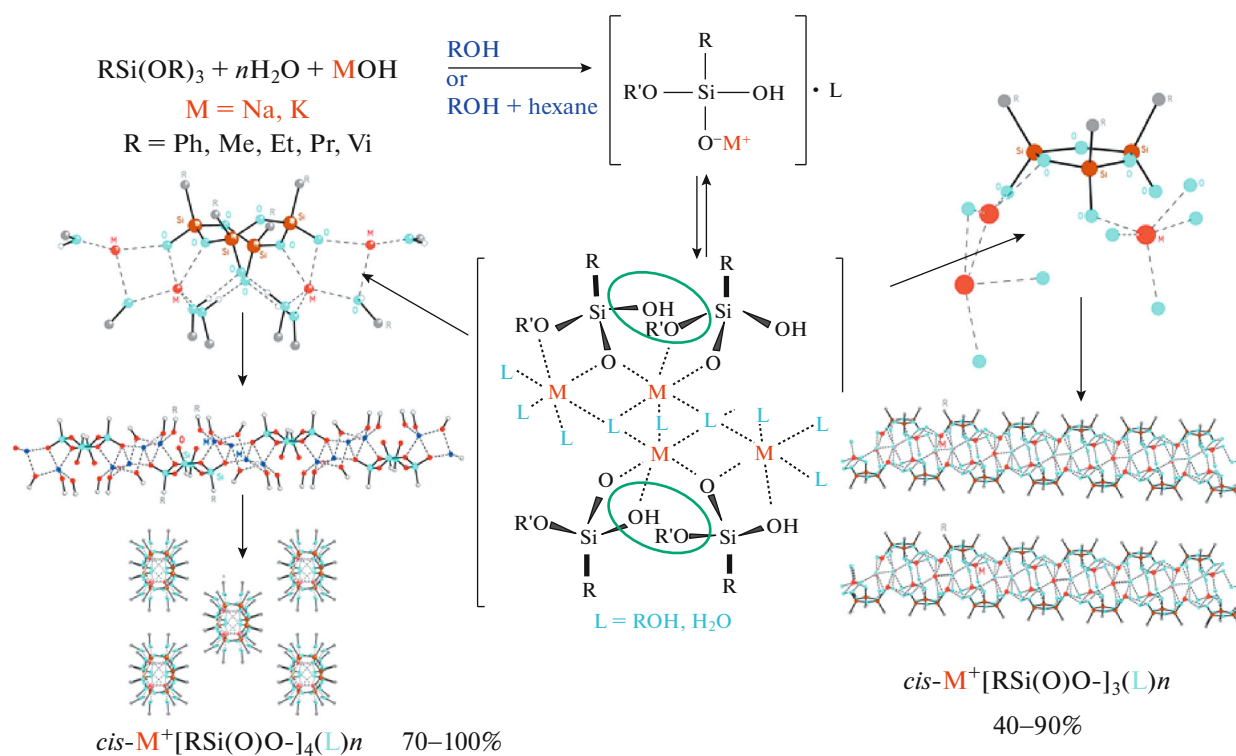


Fig. 3. Synthesis of sodium or potassium organosiloxanates from organotrialkoxysilanes.

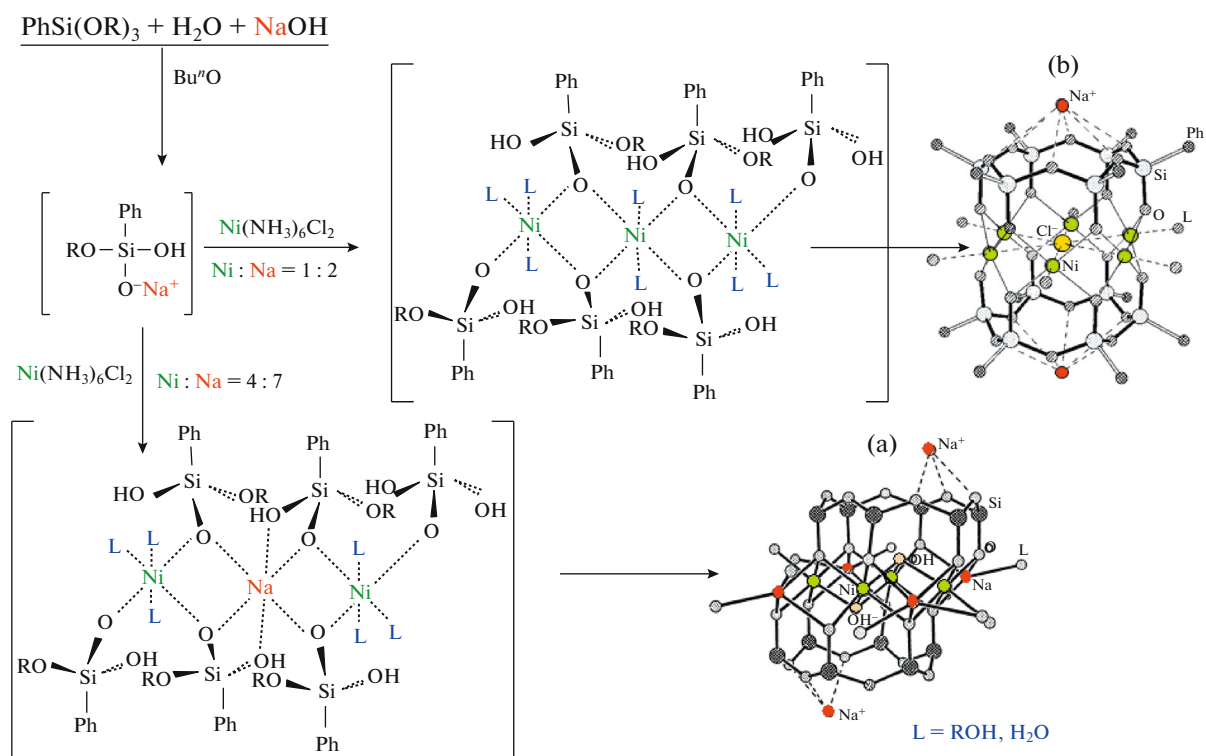


Fig. 4. Synthesis of nickel-containing polyhedral phenylmetallasiloxanes from phenyltrialkoxysilanes (PhSi(OR)₃) (a) (Na)₂{[PhSi(O)O]₆(Ni)₂(Na)₄(μ₃-OH)₂[PhSi(O)O]₆}·L and (b) [PhSi(O)O]₆(Ni)₆(μ₆-Cl)(PhSi(O)O)₆]·L_n (L = ROH, R = Buⁿ, Et, H).

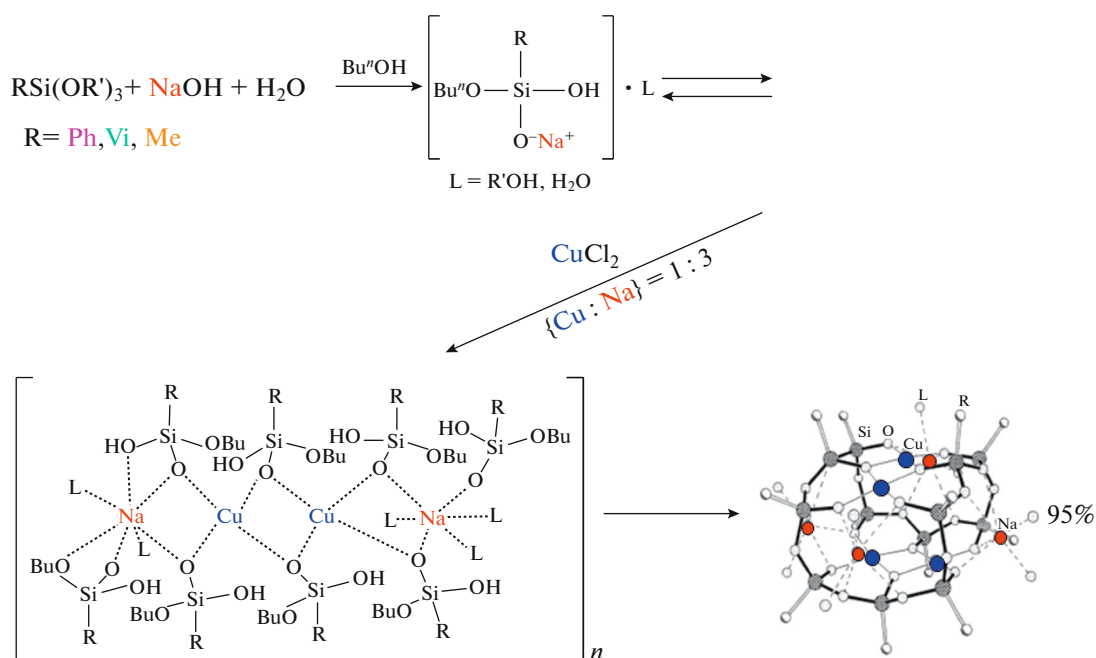


Fig. 5. Schematic self-assembly of coppersodiumorganosiloxane $\{(\text{Na})_4[\text{RSi}(\text{O})\text{O}]_{12}(\text{Cu})_4\} \cdot \text{L}_n$, (R = Me, Vi, Et, Pr; L = R'OH, R' = Bu_n, Et, H) from organotrialkoxysilanes.

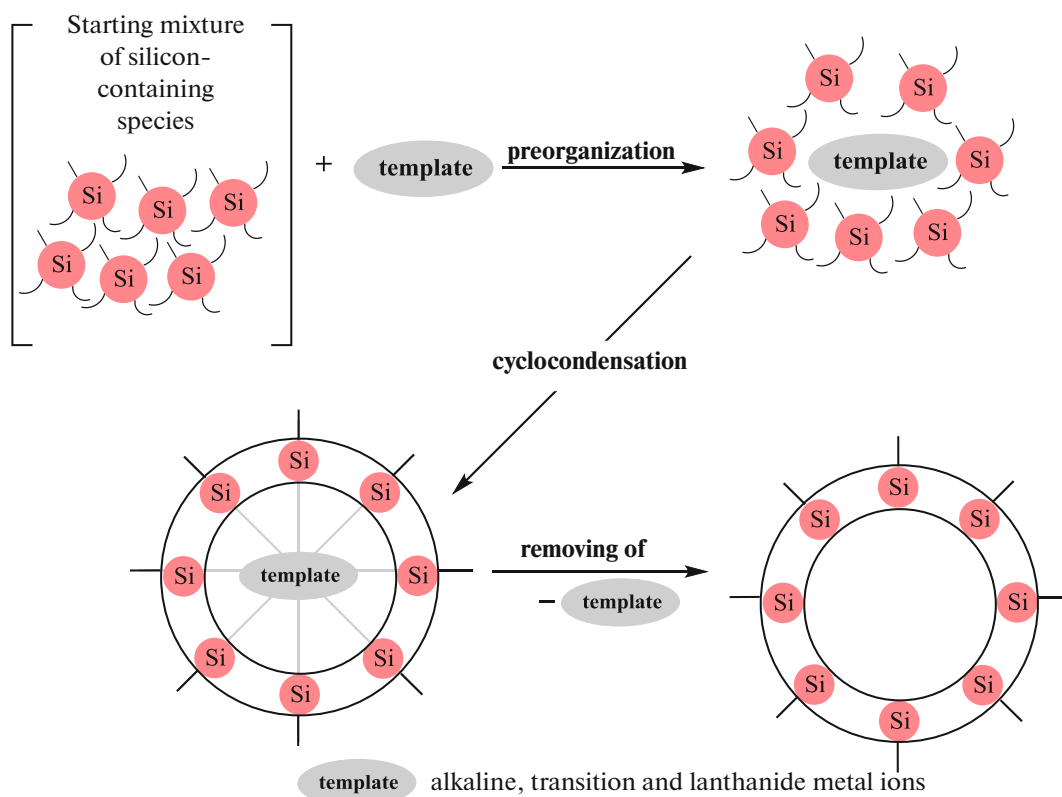


Fig. 6. Simplified scheme of the directed hydrolytic condensation of trifunctional organosilanes in the presence of template (matrix).

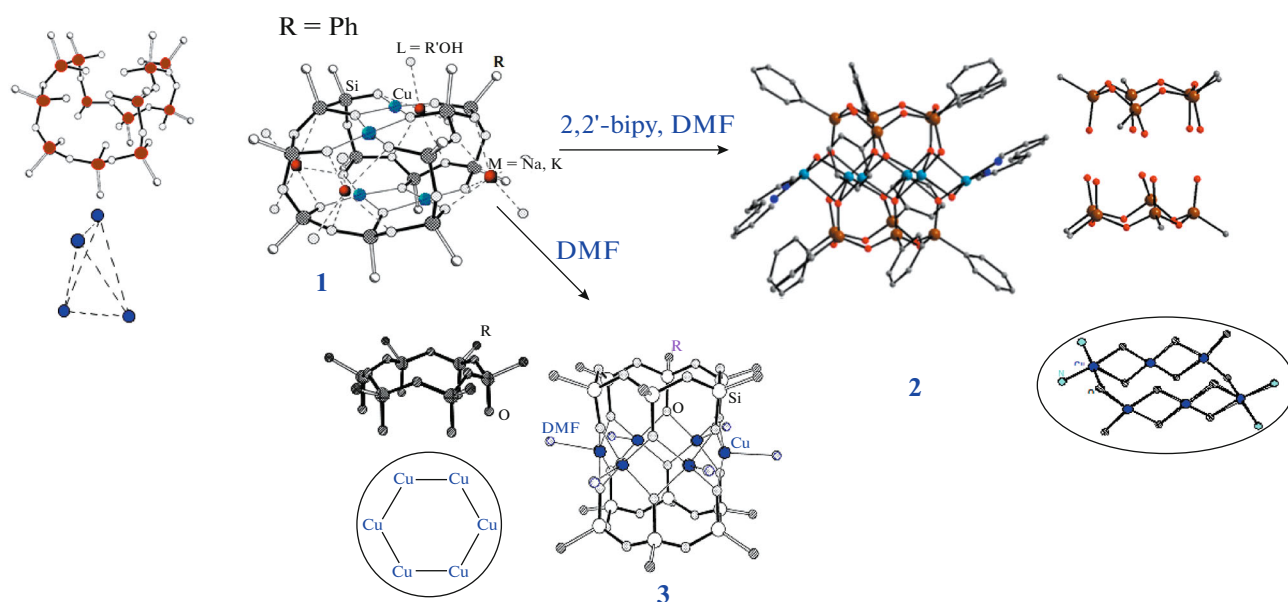


Fig. 7. Rearrangement of (1) a molecule of globular phenylcoppersodiumsiloxane $\{[\text{PhSi}(\text{O})\text{O}^-]_{12}(\text{Cu}^{2+})_4(\text{Na}^+)_4(\text{BuOH})_x\}$ into molecules of phenylcoppersiloxanes of the sandwich structure containing no alkali metal ions (2) $\{[\text{PhSi}(\text{O})\text{O}]_5(\text{Cu})_6[\text{PhSi}(\text{O})\text{O}]_5\} \cdot 2\text{bipy} \cdot \text{L}$ ($\text{L} = \text{DMF}, \text{H}_2\text{O}$) and (3) $\text{Cu}_6\{[\text{PhSi}(\text{O})_2\text{O}]_2\} \cdot 6(\text{DMF})$.

Under certain conditions condensation occurring via hydroxyl and alkoxy groups is accompanied by oligocyclization. Alkali metal ions fix condensing silicon fragments in the specified order and contribute to the formation of well-defined structures (Fig. 3).

Upon partial or complete exchange of alkali metal ions for transition metal or lanthanide ions more complex molecules can be synthesized (Figs. 4, 5).

Thus, it can be concluded that a template (matrix) introduced into the reaction medium can play the organizing role. The template can gather around itself organosilicon intermediates via noncovalent bonds and bring functional groups attached to the silicon atom into contacts, facilitating the cyclization reaction and the formation of the well-organized architecture. Subsequent removal of the template also affords an individual organocyclosiloxane molecule with the well-defined structure (Fig. 6).

Thus, the method of hydrolytic condensation of trifunctional organoalkoxysilanes was developed, in which the selective self-assembly of polyhedral organometallasiloxanes occurred in the presence of ions of various metals that acted simultaneously as templating units and structural elements. The coordination saturation of metal ions forming the matrix framework is achieved due to the solvate molecules of solvents, in which the self-assembly of POMS proceeds. If the first method was used for the synthesis of primarily phenylmetallasiloxanes, then the new

method allowed the preparation of organometallasiloxanes with both phenyl and other organic substituents at the silicon atom, namely, vinyl-, methyl-, ethyl-, propyl-, tolyl-, etc. [102, 103, 107–114].

As a result, a large number of diverse polyhedral organometallasiloxanes containing copper ions was synthesized by both new and old methods [93, 94, 97, 102, 103, 107, 108, 112, 115–120]. The combination of stereochemical features of Cu(II) [121] and specifics of the siloxane bond (its nature, properties, and transformations) [122] offers the possibility to prepare a great structural diversity of copper-containing organosiloxanes; therefore, a separate study on the development of methods for the selective synthesis of Cu-containing organometallasiloxanes was performed [123].

Of special interest are polyhedral organometallasiloxanes containing simultaneously ions of transition and alkali metals. Specifically, this is associated with the ability of these compounds to undergo various cage rearrangements depending on donor properties of the solvate environment. For example, we first showed [124] that during recrystallization of globular phenylcoppersodiumsiloxane $\{[\text{PhSi}(\text{O})\text{O}^-]_{12}(\text{Cu}^{2+})_4(\text{Na}^+)_4(\text{BuOH})_x\}$ in DMF in the presence of 2,2'-bipyridyl the globular structure of a molecule with a 24-membered phenylsiloxanolate cycle rearranges into the sandwich one $\{[\text{PhSi}(\text{O})\text{O}]_5(\text{Cu})_6[\text{PhSi}(\text{O})\text{O}]_5\} \cdot 2\text{bipy} \cdot \text{L}$ ($\text{L} = \text{DMF}, \text{H}_2\text{O}$), in which the CuO cluster coordinates two

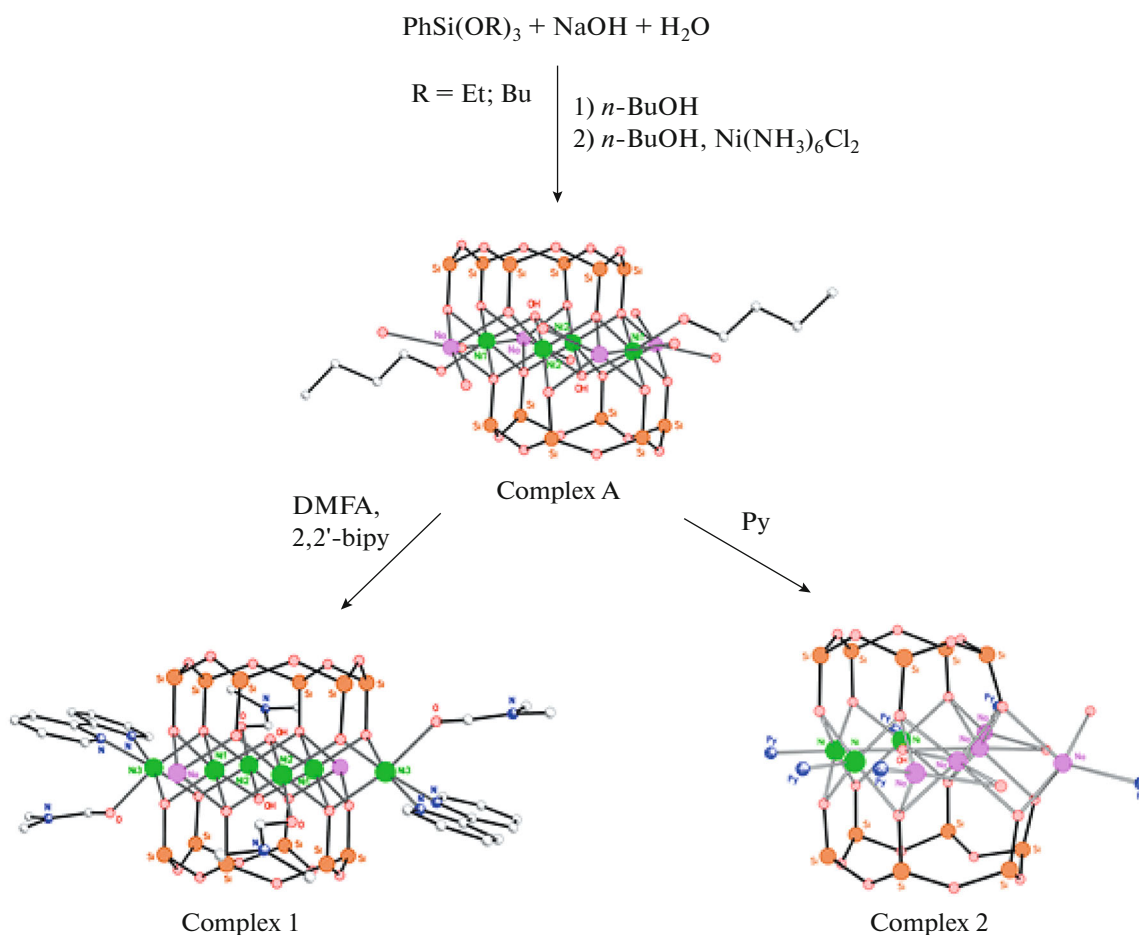


Fig. 8. Synthesis of organometallasiloxane complex A and its rearrangement into complexes $\{[\text{PhSi}(\text{O})\text{O}^-]_6(\text{Ni}^{2+})_6(\text{Na}^+)_2(\mu_3\text{-OH})_2[\text{PhSi}(\text{O})\text{O}^-]_6\} \cdot 2(\text{BIPY}) \cdot 4(\text{DMF})$ (complex 1) and $\{[\text{PhSi}(\text{O})\text{O}^-]_6(\text{Ni}^{2+})_3(\text{Na}^+)_6(\mu_5\text{-OH})_2[\text{PhSi}(\text{O})\text{O}^-]_5\} \cdot 7(\text{PY}) \cdot 2(n\text{-BuOH}) \cdot 2(\text{H}_2\text{O})$ (complex 2).

10-membered phenylsiloxanolate cycles (Fig. 7). Meanwhile, the molecule of the resulting compound no longer contains sodium ions.

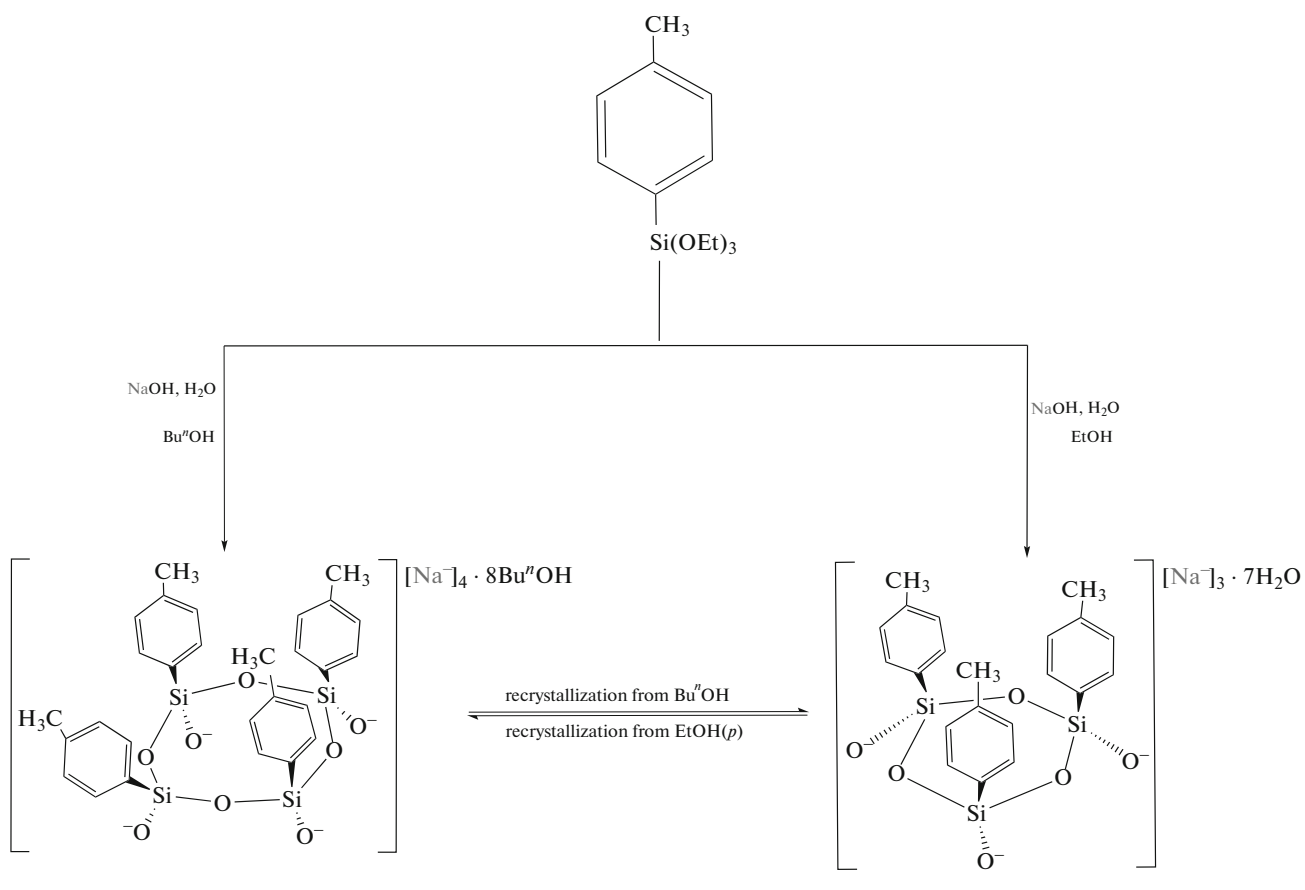
It should be noted that the rearrangement of globular phenylcoppersodiumsiloxane is strongly affected by reaction conditions. If it is recrystallized only from DMF, compound, $\text{Cu}_6\{[\text{PhSi}(\text{O})_2]_6\} \cdot 6(\text{DMF})$, is isolated after some time (about two months). Its molecule also has the sandwich structure, but here two six-membered phenylcyclosiloxanolate fragments are connected to six copper atoms which, in turn, are also coordinated with DMF molecules [93, 124].

The recrystallization of polyhedral phenylnickelsodiumsiloxane $(\text{Na})_2\{[\text{PhSi}(\text{O})\text{O}]_6(\text{Ni})_4(\text{Na})_4(\mu_3\text{-OH})_2[\text{PhSi}(\text{O})\text{O}]_6\} \cdot 16(\text{Bu}^n\text{OH})$ (complex A) [125] from DMF in the presence of 2,2-bipyridyl (complex 1)

or pyridine (complex 2) affords two novel polyhedral phenylmetallasiloxane complexes (Fig. 8).

As in the previous example, *p*-donor ligands of the pyridine series play the decisive role in the dissociation of the initial metallasiloxane cage and its repeated assembly on the new metal ion matrix. Not only the metal-containing cationic layer rearranges with a change in the number, ratio, and spatial arrangement of nickel and sodium cations but also the size of cyclic siloxanolate ligands changes [126].

Using the examples of sodium *cis*-tetra(*p*-tolyl)cyclotetrasiloxanolate, $\{(\text{Na}^+)_4[\text{ToSi}(\text{O})\text{O}^-]_4 \cdot 8(n\text{-BuOH})\}$, and sodium *cis*-tris(*p*-tolyl)trisiloxanolate, $\{(\text{Na}^+)_3[\text{ToSi}(\text{O})\text{O}^-]_3 \cdot 7\text{H}_2\text{O}\}$, which were synthesized from *p*-tolyltriethoxysilane, we demonstrated the possibility of their mutual transformation [113]:



Polyhedral organometallasiloxanes containing transition and alkali metal ions are also of interest since they can

be used for the synthesis of bimetallic compounds containing two types of transition metals (Fig. 9) [127–130].

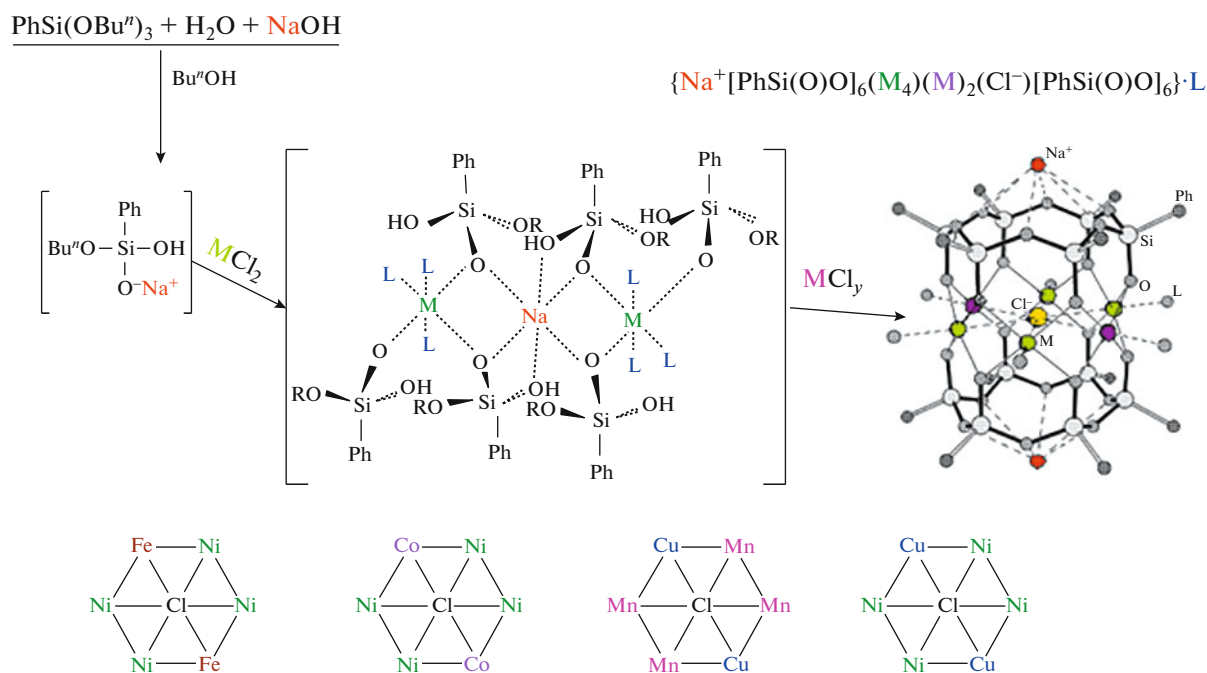


Fig. 9. Synthesis of bimetallic polyhedral organometallasiloxanes containing ions of various transition metals.

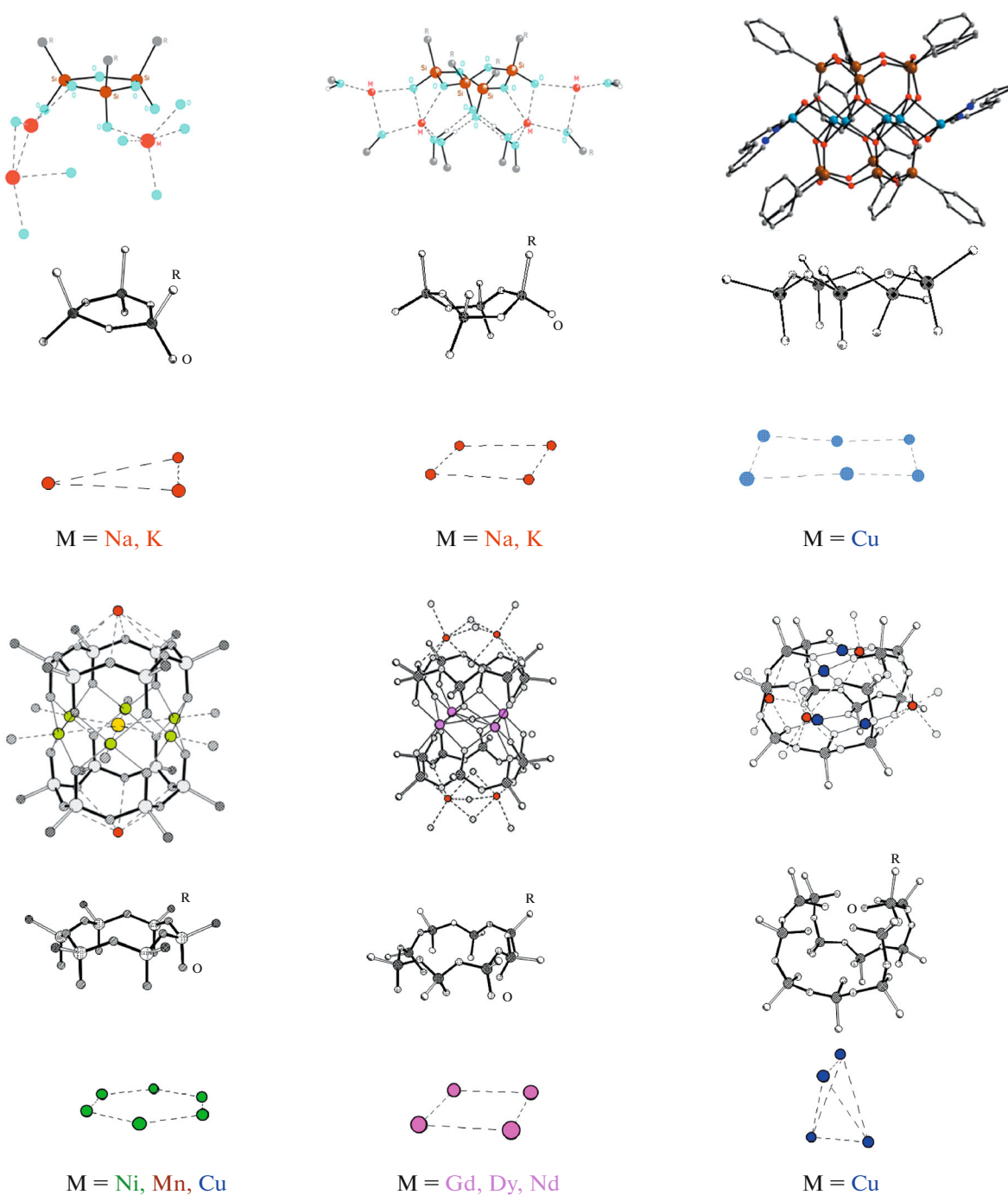


Fig. 10. Structures of polyhedral organometallasiloxanes and types of siloxanolate ligands and metal ion matrices in them.

For example, polyhedral organometallasiloxanes are unusual and unique polynuclear complexes, in which the “olate” oxygen atoms of cyclic siloxanolate ligands coordinate metal ions, usually acting as bridges between various metal “centers.” These compounds turned out to be deal candidates for studying magnetic properties. For the first time these studies were done by us jointly with Italian [131–134] and German researchers [107, 108, 135]. It was shown that the

bridging geometry of siloxanolate oxygen donors in many of the studied compounds is responsible for ferromagnetic intramolecular spin-spin interactions within the metal oxide ring (if angle M–O–M is close to 90°); in the case of other compounds, for antiferromagnetic interactions. Encapsulated anions, such as Cl^- , OH^- , and O^{2-} , present in an organometallasiloxane molecule also make their own contributions. It was demonstrated that small changes in bond angles of

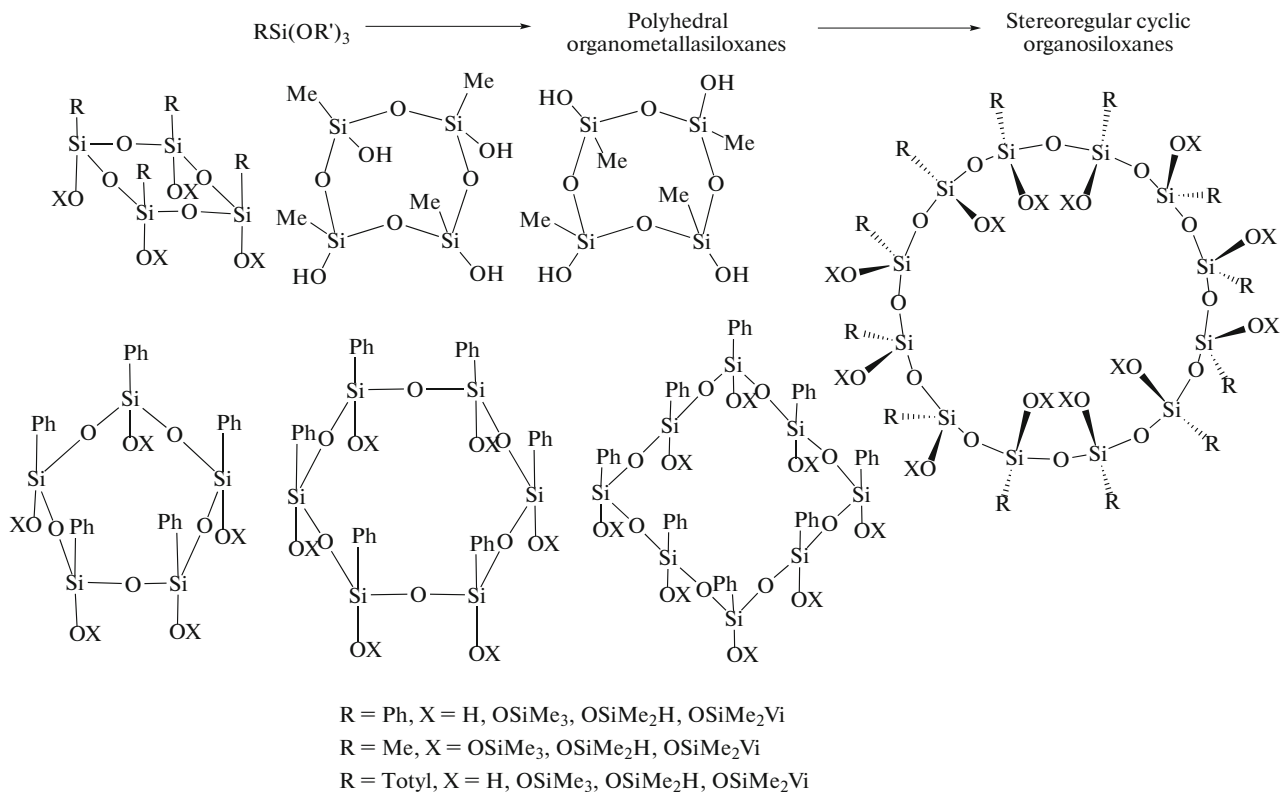
“oxygen-exchange” bridges may considerably influence exchange spin-spin interactions. It was revealed that even slight variations in molecular and crystalline structures can alternate ferro- and antiferromagnetic exchange interactions between magnetic ions [108].

It is necessary to highlight separately the direction elaborated by Levitsky's team. Combinatory opportunities of polyhedral organometallasiloxanes, in particular, possibility to combine ions of two metals of different chemical nature in a single structure and no less the chemical magnificence of these objects foreshadowed broad prospects for applying these compounds in catalysis [136]. Unfortunately, the researchers disregarded the chemical properties of organometallasiloxane polyhedrons, such as the silicate nature of these complexes [137], which they wrongly classified as organometallasilsesquioxanes based on covalent interactions. The coordination saturation of complexes, as opposed, for example, from branched organometallasiloxane oligomers, was responsible for poor solubility and low catalytic activity. Not surprising that in the case of these compounds the catalytic effect comparable with that of simple salts of the same metals was achieved if the authors used large amounts of a strong acid, which they called a cocatalyst (nitric acid [138–143], trifluoroacetic acid [144], and meta-chloroperoxybenzoic acid [137]). The only function of this cocatalyst, strictly speaking, is to break down the

metallasiloxane cage and to release metal ions introduced into it in the form of corresponding salts.

Another direction of applying polyhedral metallasiloxanes appeared to be more fruitful. Perfectly mastering the synthesis of a huge family of compounds of this class, the authors of this paper learned to use not only metal ions but first of all siloxane fragments of the molecules. When original and well reproducible methods of synthesizing metallasiloxanes were elaborated, we were the first to draw attention that the synthesized metallasiloxane polyhedrons contain one or two stereoregular organocyclosiloxanolate fragments bound to the ionic matrix containing from three to ten metal ions (Fig. 10). Their directed breakdown made it possible to obtain stereoregular siloxane cycles of various size in high yields.

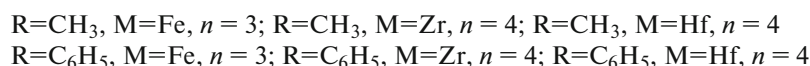
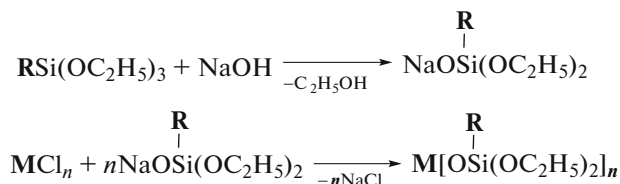
When these compounds were treated with trimethylchlorosilane, dimethylchlorosilane, vinyldimethylchlorosilane, or dilute aqueous solutions of hydrochloric, acetic, or carbonic acids, metal ions could be effectively removed in the form of their salts and mesomorphic trimethylsiloxycyclosiloxanes [109, 145–148] or various functional stereoregular organocyclosiloxanes and polyorganosiloxanols can be synthesized [125, 149–153]. This method has no analogs in organosilicon chemistry in reaction selectivity and target compound yields:



This class of cyclic compounds may compete with presently popular derivatives of calixarenes [154] and/or cyclodextrins [155] in designing novel supra-molecular systems. Stereoregular organocyclosiloxanes containing reactive groups ($-\text{OH}$, $-\text{H}$, vinyl) at the silicon atom may be used for the synthesis of organosilicon analogs of calixarenes [156] suitable for obtaining photoactive constructions [157, 158], as precursors in the synthesis of ladder-type polyphenylsilsesquioxanes with unique physicochemical properties [159, 160], as branching centers in the synthesis of star-shaped polymers, etc. [161–171].

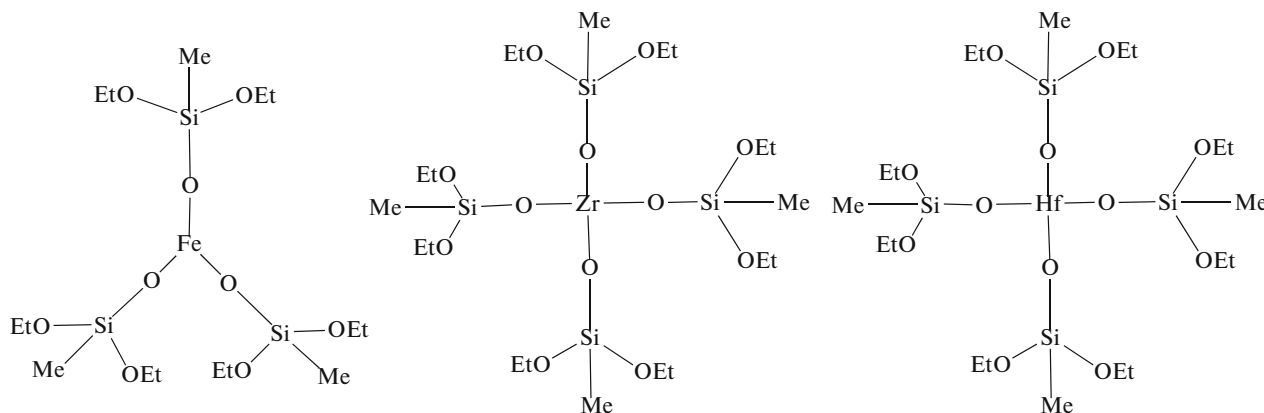
POLYFUNCTIONAL METALLASILOXANE OLIGOMERS

A new step in the synthesis of tailor-made organometallasiloxane structures is associated with the use of Rebrov's salts—sodium organoalkoxysilanolates [172, 173]. These salts enabled the synthesis of branched functional metallasiloxane oligomers [174]. These organometallaalkoxysiloxanes were prepared from sodium organodiethoxysilanolates through its subsequent treatment with corresponding metal chlorides:

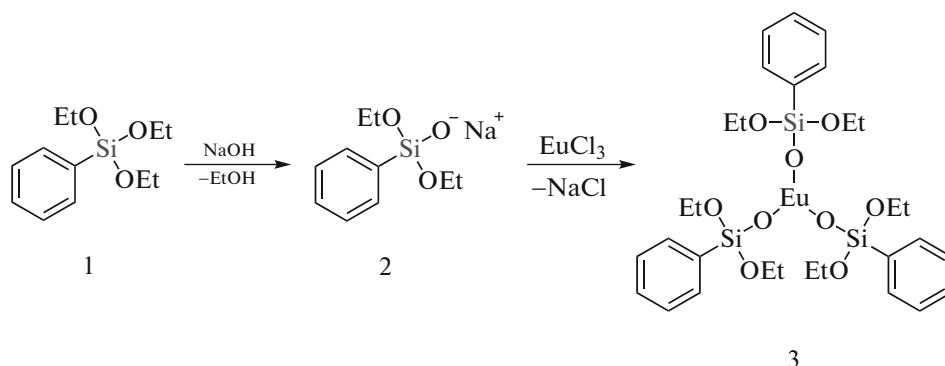


These compounds are distinguished by the metal type, the number of siloxane units corresponding to its valence, and substituents at the silicon atom. The

examples of molecular structures of functional oligomeric metallasiloxanes containing iron, zirconium, or hafnium atoms are outlined below [175]:



Later, using the same technique the authors of [176] synthesized polyfunctional europium-containing siloxane [176]:



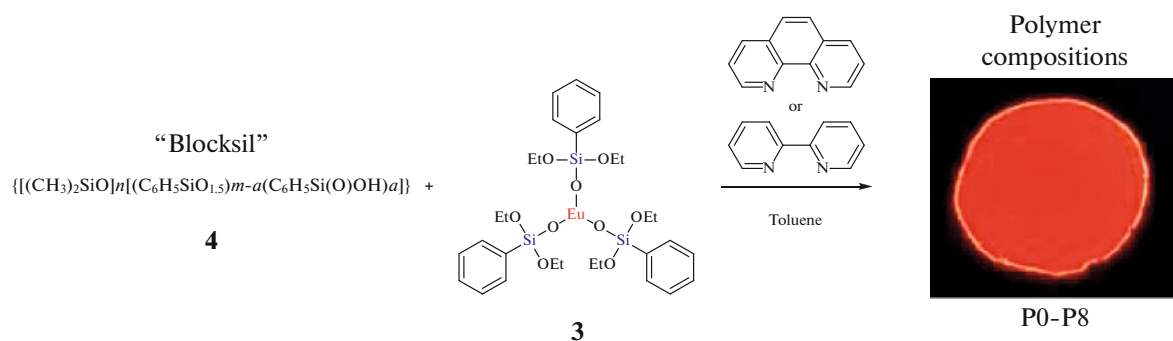


Fig. 11. Schematic synthesis of polymer compositions from “blocksil” and polyfunctional phenyleneuropiumsloxane [176].

Owing to a high reactivity of functional groups these oligomers were never isolated individually, since their isolation was always accompanied by the partial hydrolysis of functional groups. Therefore, after solvent removal the reaction mixture contained, along with the major product, the impurities of products resulting from the partial hydrolysis of target oligomers. The specific feature of these compounds is that they exhibit excellent solubility in most anhydrous organic solvents and contain a considerable number of reactive groups and coordinatively unsaturated metal ions which renders them extremely active reagents as modifying crosslinking agents. These functional organometallasiloxanes containing iron, zirconium, aluminum, niobium, or hafnium ions, are successfully used for curing various polymer matrices (poly(arylene ether ketone), polyimide, polyorganosiloxane, and epoxy resins [177–184]) to afford nanogels uniformly distributed in them. Polyfunctional phenyleneuropiumsloxane is also good for introducing indicator centers into various polymer matrices. For example, blocksil siloxane copolymer-based transparent luminescent polymer films containing uniformly distributed luminescent nanogels of the hybrid structure with Eu-O-Si and Si-O-Si fragments as molecular nanofillers were obtained (Fig. 11) [176].

CONCLUSIONS

This review was prepared for the special issue of the journal dedicated to the memory of professor Zhdanov on his 100th birthday.

Zhdanov made a considerable contribution to advancement of the chemistry of organometallasiloxanes and actively participated in all three time periods of their evolution. The present review written in historical perspective as well as possible reflects the value of his pioneering works. The review covered three historical periods of the chemistry of organometallasiloxanes both polymeric and individual and each period was marked by its own methodological approach. The first period, empirical, was characterized by a great

diversity of methods and pathways, as is natural for the initial period. During that time the data on product composition and very approximate ideas about the structure of polyorganometallasiloxanes were generally accessible for researchers. However, polyorganometallasiloxanes of that time found wide application as components of thermally stable binders and impregnating compositions.

The second period was marked by the development of methods for the synthesis of individual polyorganometallasiloxane structures of various chemical nature. It was a peculiar response to the request to govern the structure of polyorganometallasiloxanes of the early period. Polyhedral organometallasiloxanes emerged. Zhdanov et al. were at the origin of new approach. Subsequently they have long determined the advancement of this direction relying on the use of alkali metal siloxanates. The practical importance of this line of research is distinguished first of all by the simple and accessible synthesis of complex spatial structures, a huge variety of which was obtained over more than three decades. If “empirical” organometallasiloxanes were components of binders and modifiers, then novel “polyhedrons” were unique in their stereoregular macrocyclic organosiloxanolate ligands that were easily converted into corresponding macrocycles during the mild “disassembly” of metallasiloxane polyhedrons. Here, Zhdanov’s successors were divided into two groups, the first of which (Levitsky et al.) was more interested in the internal content of cages, the metallasilicate component, while the second group (Shchegolikhina et al.) placed emphasis on the use of macrocyclic ligands. Meanwhile, both groups continued to improve methods for the synthesis of novel structures, sorting out a significant number of metal ions, which expanded the base of initial compounds for both directions.

Against this background emergence of the third direction remained largely unnoticed. Using already famous “Rebrov’s salts,” N.A. Tebenev et al. suggested a simple alternative to the synthesis of organometallasiloxane oligomers. The ease of synthesis and visual diversity of practical applications as well as the

absence of rigid crystalline frameworks made it possible to unveil their relation to empirical organometallosiloxanes of the initial period, whereas silanolate precursors and the silicate nature of bonds shared equally strong “similarity” with “polyhedrons” of the second period. With all the dissimilarity of branched polyfunctional organometallosiloxane oligomers with strict crystalline forms similar to polyhedrons in nature, it is clear that this is their more flexible synthetic reincarnation. Due to the excellent solubility and accessibility of the coordination sphere of metal ions the mentioned oligomers are actually far superior all results of the catalytic studies of polyhedrons and their importance for practice. Nevertheless, it is clear that polyfunctional organometallosiloxanes are excellent synthetic precursors of novel polyhedrons, especially taking into account recent forms with partially substituted metal-ion branching centers. A matter of time when a high potential of novel organometallosiloxane forms will turn from expanding the diversity of metal-ion branching centers and choice of suitable organic decoration at silicon atoms to new catalytic systems and novel polyhedral forms of organometallosiloxanes, thus providing synthetic chemists with new unique macrocycles.

Thus, it can be stated that organometallosiloxanes are on the ascending branch of their research, their further development promises the design of novel catalytic architectures, molecular fillers, and highly functional macrocyclic structures offering great potential for the synthesis of novel polymer forms.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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