Synthesis of bimetallic cage-like metalloorganosiloxanes from polymeric metallosiloxanes

B. G. Zavin, N. V. Sergienko, N. V. Cherkun, A. N. Bilyachenko, O. M. Starikova, A. A. Korlyukov, M. S. Dronova, M. M. Levitskii, and G. I. Timofeeva*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow, Russian Federation.
E-mail: zavin@ineos.ac.ru

A new approach to the synthesis of the cage-like metalloorganosiloxanes (MOS) was developed. Unlike existing schemes for the synthesis of the cage-like MOS from monomeric structural units, regular polyhedral structures were formed from irregular polymeric MOS by their reaction with sodium phenylsilanolate. Efficiency of the method suggested was confirmed by directed synthesis of the earlier described bimetallic cage-like (Cu^{II},Na)- and (Fe^{III},Na)-phenylsiloxanes in 69 and 47% yields, respectively. Compounds that obtained were identified by destructive trimethylsilylation, GPC, ^{1}H NMR, and X-ray crystallography.

Key words: cage-like and polymeric metalloorganosiloxanes, bimetallic metallosiloxanes; (copper,sodium)phenylsiloxane, (iron,sodium)phenylsiloxane, sodium phenylsilanolate.

Polymeric and cage-like metalloorganosiloxanes (MOS) containing atoms of transition and nontransition metals attract increased interest as potential starting substances in development of new nanocomposite ceramic and high-performance materials. By now, different methods have been developed for the synthesis of the cage-like MOS containing clusters of transition metals bound to the siloxane fragments through the M—O bonds. Various representatives of this class of compounds are characterized not only by different nature of metals involved,[1] but also by a great variety of structures of the cage-like molecules. Despite differences that present, the known methods for the preparation of the cage-like MOS are characterized by the fact that the synthesis of the cage-like structure ("assembling" the polyhedral molecules) is accomplished involving low-molecular-weight compounds containing silicon atoms (organosilanolates, organosilanols, organoalkoxysilanes) and metal-containing compounds (usually halides or alkoxy derivatives).

In the present work, we studied a possibility of the synthesis of the cage-like MOS starting from MOS of polymeric structure. It is known that the siloxane Si—O bonds are sensitive to acids and bases.[2] Because of increased ionic character of the skeleton bonds in heterosiloxanes, they are very sensitive to ionic agents[3,4] and are easy cleaved by acids. As to the reactions of MOS with nucleophilic agents, they are not virtually studied. Quantum mechanical calculations indicate higher basicity of oxygen atoms and increased polarity of the Si—O—M bonds in heterosiloxanes as compared to the siloxane Si—O—Si bonds (see Ref. 5). This allows us to suggest higher sensitivity of metal atoms in heterosiloxanes to nucleophilic agents.

Proceeding from the given suggestions, we have chosen sodium phenylsilanolate of the composition $C_6H_5Si(O)ONa$, which possesses highly basic oxygen atom, as a nucleophilic agent. This choice was determined not only by increased reactivity of the silanolate in the reactions of cleavage of polar Si—O—M bonds, but also by the known role of organosilanolates in the "assembling" of skeletons of polyhedral cage-like metallosiloxanes.

It is known that the reaction of polyorganosiloxanes with alkali metal silanolates leads to the cleavage of the siloxane SiOSi bonds and destruction of the macromolecules.[2] It was of interest to consider a possibility of formation of polyhedral cage-like structures while reorganization of the skeleton bonds of polymeric metallosiloxanes.

It is significant that the structural specific features of possible polyhedral structures resulted from the destruction are determined by differences in coordination properties of transition metals.[1] Therefore, for this process to be studied, it was necessary to consider polymeric MOS containing polyvalent metal ions of different nature.

Results and Discussion

We studied polymeric (copper)phenylsiloxane (**1**) of the composition $[(PhSiO_{1,5})_2(CuO)]_n$ ($n = 89$) and (iron)phenylsiloxane (**2**) of the composition $[(PhSiO_{1,5})_3(FeO_{1,5})]_n$ ($n = 68$) as the MOS objects. We considered different

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versions of the reactions of polymeric MOS **1** and **2** with phenylsilanolate, differing in the way how this reagent was introduced. Thus, in the reaction with **1**, silanolate PhSi(O)ONa was generated *in situ* according to the known procedure[6] (hydrolysis of alkoxysilane $PhSi(OEt)_3$ by measured amounts of water and metallic Na), whereas **2** reacted with hydrated phenylsilanolate of the composition $[PhSiO(ONa)]_3 \cdot 8H_2O$ obtained by traditional method.[7]

Reactions of indicated polymetallosiloxanes with organosilanolates were carried out in organic solvents (*n*-butanol/toluene) (Scheme 1).

Scheme 1

$$[(PhSiO_{1.5})_2(CuO)]_n \xrightarrow{PhSi(OEt)_3/H_2O/Na} \underset{\mathbf{1}}{}$$

$$\longrightarrow \underset{n = 90}{} \underset{\mathbf{3}}{(PhSiO_{1.5})_{12}(CuO)_4(Na_2O)_2 \cdot 8\ BuOH}, \quad (1)$$

$$(PhSiO_{1.5})_3(FeO_{1.5})_m \xrightarrow{[PhSi(O)ONa]_3 \cdot 8H_2O} \underset{\mathbf{2}}{}$$

$$\longrightarrow \underset{n = 70}{} \underset{\mathbf{4}}{(PhSiO_{1.5})_{20}(FeO_{1.5})_6(Na_2O)_4 \cdot 9\ BuOH \cdot C_7H_8}, \quad (2)$$

Reaction products were identified by comparison with individual compounds, *viz.*, polyhedral (cage-like) MOS (copper,sodium)phenylsiloxane **3** and (iron,sodium)-phenylsiloxane **4**, whose synthesis and structures were described earlier.[8,9] According to available data on compositions and structures of these compounds obtained by X-ray crystallography and elemental analysis, the ratio Si:Cu:Na for the crystalline cage-like (copper,sodium)-phenylsiloxane[8] is 3 : 1 : 1, whereas for the crystalline cage-like (iron,sodium)phenylsiloxane,[9] the ratio Si : Fe : Na is 10 : 3 : 4. These values strongly differ from the compositions of the starting polymeric MOS. Such a strong difference in the compositions of the starting MOS and final reaction products allows us to reliably establish the fact of the reaction of polymeric MOS with sodium organosilanolate, as well as to find effects of coordination properties of the metal on the composition of the cage-like compounds formed.

Synthesis of the cage-like MOS was accomplished with stoichiometric ratios of reagents according to the reactions (1) and (2).

Both systems with Cu- and Fe-MOS (polymers **1** and **2**) furnished colored crystalline products Cu- (**3**) or Fe-MOS (**4**). The yields of the products after crystallization from the reaction mixture were 69 and 47%, respectively.

The composition of the dark blue crystalline product synthesized by reaction (1) allowed us to suggest that it is a cage-like (copper,sodium)phenylsiloxane **3**. It is known that this compound exists in two isomeric forms:[10] a "sandwich" isomer of the structure $[PhSiO_2]_6[Cu_4Na_4][PhSiO_2]_6$, whose cage is built involving two hexasiloxane rings, and a "globular" ("saddle-shaped") isomer of the structure $[PhSiO_2]_{12}[Cu_4Na_4]$, whose cage forms a dodecasiloxane ring. The structure of (copper,sodium)phenylsiloxane **3** obtained by reaction (1) was established by traditional method of destructive trimethylsilylation[11] (upon treatment of compound **3** with chlorotrimethylsilane). This procedure resulted in the conversion of the cage-like MOS to the corresponding trimethylsilyl-substituted cyclosiloxanes and metal halide (Scheme 2).

Scheme 2

$$\{[PhSi(O)O]_2Cu\}_x + 2x\ MeSiCl \xrightarrow[-CuCl_2]{}$$

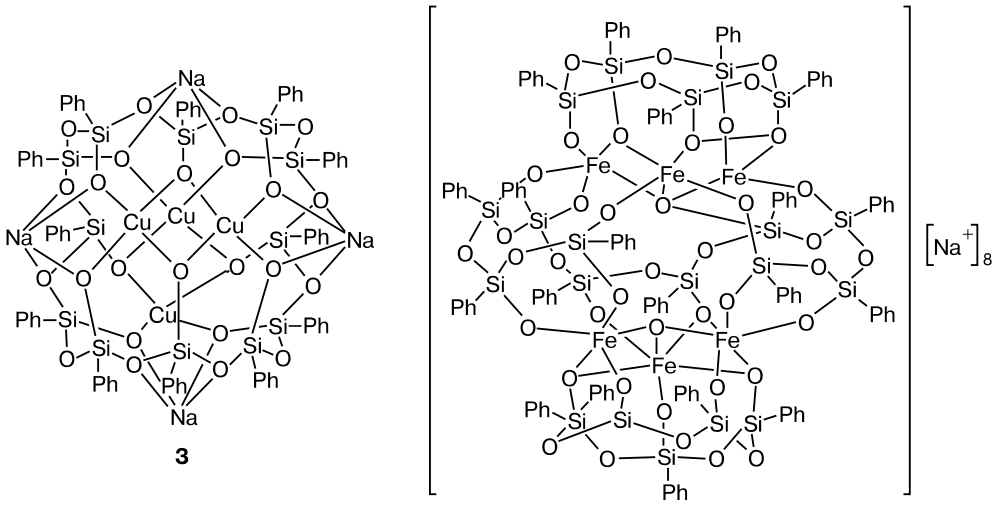
$$\longrightarrow 2 \left[\begin{array}{c} Ph \\ | \\ -Si-O- \\ | \\ OSi(Me)_3 \end{array} \right]_x$$

According to the GPC and ^1H NMR data, the trimethylsilylated cylcyclosiloxane that obtained is identical to the cycle $[PhSiO(OSiMe_3)]_{12}$ described earlier, which is formed by destructive trimethylsilylation of the standard cage-like (copper,sodium)phenylsiloxane $[PhSiO_2]_{12}[Cu_4Na_4]$ of the globular structure containing a dodecasiloxane ring in it[11] (Fig. 1).

The data from elemental analysis and IR spectroscopy showed that the light brown crystals isolated from the products of reaction (2) corresponded to (iron,sodium)-phenylsiloxane **4** described earlier.[9] Since (iron,sodium)-phenylsiloxane that obtained was isolated in the same solvent system (toluene/*n*-butanol) as the mentioned above (iron,sodium)siloxane of the lantern structure,[9] we determined and compared parameters of crystallographic cells of the product obtained and the model compound.

The cell parameters were determined for several monocrystals of the obtained compound at 100 K. Results of the measurements confirmed that the compound synthesized is isostructural to the model one, that allows us to reliably assign a lantern structure of compound **4** to the product obtained (see Fig. 1).

In conclusion, it was found that the cage-like (polyhedral) MOS can be obtained not only by the exchange decomposition of organosilanolates with metal chlorides, but also by the reaction of organosilanolates with preprepared irregular polymeric MOS.



3 **4**

Fig. 1. Structures of the cage-like MOS: the globular (copper,sodium)phenylsiloxane $[PhSiO_2]_{12}[Cu_4Na_4]$ (**3**) and the lantern (iron,sodium)phenylsiloxane $[PhSiO_2]_{20}[Fe_6Na_8]$ (**4**) (molecules of the solvate solvents are not shown in the cage structural formulas).

Experimental

Gel permeation chromatographic (GPC) curves were recorded on a Waters-510 instrument equipped with a detector-refractometer and Ultrastyragel 10^2, 10^3, 10^4 Å columns. THF was used as an eluent (the flow rate was 1 mL min^{-1}, 35 °C).

Parameters of crystallographic cell were determined on a Bruker Smart APEX II diffractometer.

^1H NMR spectra were recorded on a Bruker Avance-400 spectrometer in $CDCl_3$.

IR spectra were recorded on a Specord M-82 spectrograph in Nujol between KBr plates.

Molecular masses of polymeric heterosiloxanes were determined by sedimentation equilibrium method on a MOM 3180 analytical ultracentrifuge in 0.5% toluene solutions (the rate of rotor rotation was 50000 rpm, 25 °C).

Polymeric MOS such as copperphenylsiloxane **1** and ironphenylsiloxane **2** (n = 68) were used in experiments.

Poly(copperphenylsiloxane) (1), $[(PhSiO_{1,5})_2(CuO)]_n$, was obtained according to the procedure described earlier[12] and had the following composition (wt.%): Cu, 18.20; Si, 17.21 (Si : Cu = 2.13). The molecular weight of the polymer is M_{sd} = = 30000 (n = 89).

Poly(ironphenylsiloxane) (2), $[(PhSiO_{1,5})_3(FeO_{1,5})]_n$, was obtained according to the known procedure[13] and had the composition (wt.%): Fe, 12.2; Si, 17.9 (Si : Fe = 2.92). The molecular weight of the polymer is M_{sd} = 32000 (n = 68).

(Copper,sodium)phenylsiloxane (3) was synthesized using the *in situ* generation of silanolate by hydrolysis of $PhSi(OEt)_3$ with measured additions of water and metallic Na (see Ref. 6). Butanol (60 mL), triethoxyphenylsilane (5.06 g, 0.021 mol), and water (0.76 g, 0.042 mol) were placed into a flask equipped with a reflux condenser and a magnetic stirrer, the mixture was stirred for 1 h, followed by addition of metallic sodium (0.49 g, 0.021 mol). After sodium was completely dissolved, the solvents (butanol—ethanol—water) were partially evaporated (20 mL) from the reaction mixture, then, a solution of polymeric copperphenylsiloxane (4.90 g, containing 0.014 mol of Cu) in butanol (30 mL) was added. The reaction mixture was refluxed for 1 h. The cooled solution was filtered and gradually half concentrated to isolate a bright bluish violet crystalline product (6.25 g). The yield was 69%. A part of the product obtained was dried *in vacuo* (10 Torr, 100 °C) until the weight was constant. Found (%): C, 41.27; H, 3.38; Si, 15.39; Cu, 11.72; Na, 4.25. The ratio Si : Cu : Na = 3 : 1.01 : 1.01. $C_{72}H_{60}Si_{12}O_{24}Cu_4Na_4$. Calculated (%): C, 43.4; H, 3.03; Si, 16.92; Cu, 12.72; Na, 4,62.

(Iron,sodium)phenylsiloxane (4). A solution of polymeric ironphenylsiloxane (2.5 g, containing 0.0055 mol of Fe) in butanol (12 mL) and toluene (15 mL) was added dropwise to a solution of $[PhSi(O)ONa]_3 \cdot 8H_2O$ (4.9 g, 0.0078 mol, obtained by a traditional method[7]) in butanol (20 mL) with stirring. After reflux for 2 h, the reaction solution was cooled to room temperature and filtered. The filtrate was gradually half concentrated *in vacuo* (10 Torr, 100 °C) to obtain light brown crystals (1.74 g, 47%). The IR spectrum of the crystalline compound exhibited a set of signals characteristic of MOS, ν/cm^{-1}: 1120 (Ph—Si), 940—1100 (Si—O—Si). 900 (Si—O—Fe), 720, and 680 (monosubstituted phenyl ring). X-ray crystallographic measurements showed that the crystals have monoclinic crystal system with the following parameters of the cell a = 30.043(8) Å, b = 20.342(6) Å, c = 32.218(8) Å, β = 92.91(7)°, that agrees with analogous parameters for (ironsodium)phenylsiloxane having a cage of the lantern form.[9]

A part of the product obtained was dried *in vacuo* (10 Torr, 100 °C) until the weight was constant. Found (%): C, 44.13; H, 3.71; Si, 16.89; Fe, 10.01; Na, 5,51. The ratio Si : Fe : Na = = 20.22 : 6 : 1.34. $C_{120}H_{100}Si_{20}O_{43}Fe_6Na_8$. Calculated (%): C, 43.53; H, 3.04; Si, 16.97; Fe, 10.12; Na, 5,56.

Destructive trimethylsilylation of (copper,sodium)phenylsiloxane (3). A solution of chlorotrimethylsilane (1.13 g, 10.4 mmol) in toluene (15 mL) and pyridine (0.83 g, 10.4 mmol) were added to the crystalline (copper,sodium)phenylsiloxane (compound **3**) (1.5 g, 0.58 mmol) with subsequent isolation of organocyclo-

siloxane according to the described procedure.[11] The product obtained was further studied by GPC and ^{1}H NMR spectroscopy. The GPC measurements (a RIDK-102 refractometer, a Phenogel-75KD column, THF as an eluent, the flow rate of 10 mL min^{-1}, 40 °C) showed a signal with the retention time 8.446 min.

The ^{1}H NMR spectrum exhibited two singlets at δ −0.11 (Me_3SiO groups, *cis*,*cis*-conformation) and −0.32 (Me_3SiO groups, *cis*,*trans*-conformation) with the ratio of integral intensities 1 : 2, as well as multiplets for the protons of the PhSiO groups at δ 6.50—7.50 with the ratio of integral intensities for the signals of the Me and Ph protons 9 : 5.

The results obtained (GPC and NMR) completely correspond to the data for the standard compound $[PhSiO(OSiMe_3)]_{12}$ (see Ref. 11).

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