New method for the synthesis of cage and polymeric metallosiloxanes

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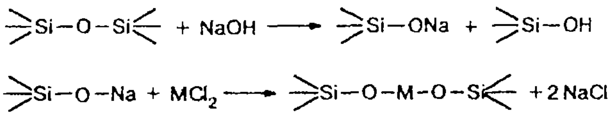
Cage organometallosiloxanes were synthesized according to a new procedure using monomeric organoalkoxysilanes as the starting compounds. The latter were subjected to hydrolysis immediately before the exchange reaction of sodium silanolate with metal halides. Difficultly accessible metallovinylsiloxanes, metallomethylsiloxanes, and metallosiloxanes containing a functional group in the organic radical at the silicon atom can be readily prepared according to the method proposed.

Key words: cage metallosiloxanes, trialkoxyalkyl(aryl)silanes, metallovinylsiloxanes, metallo-γ-aminopropylsiloxanes.

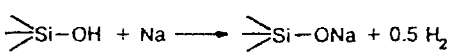
Previously,[1] a two-stage procedure has been reported for the synthesis of cage metallosiloxanes. This method involved the synthesis of sodium organosilanolate by cleavage of the corresponding organopolysiloxane with alkali in butanol in the first stage. The second stage involved the exchange reaction of sodium silanolate with metal halide.



$$\equiv Si-O-Si\equiv + NaOH \longrightarrow \equiv Si-ONa + \equiv Si-OH$$

$$\equiv Si-O-Na + MCl_2 \longrightarrow \equiv Si-O-M-O-Si\equiv + 2\,NaCl$$

Water that formed upon condensation of the silanol groups reversibly hydrolyzes silanolate. Sodium hydroxide liberated in this reaction interacts with metal halide and removes the latter from the reaction mixture as the corresponding hydroxide. Hence, it is desirable to eliminate the silanol groups from the system by adding metallic sodium, which results in the formation of a silanolate.



$$\equiv Si-OH + Na \longrightarrow \equiv Si-ONa + 0.5\,H_2$$

Manganese phenylsiloxane,[1] nickel phenylsiloxane,[2] copper sodium phenylsiloxane,[3] and some other metallosiloxanes were first prepared from polyphenylsiloxane, sodium hydroxide, metallic sodium, and the corresponding metal chloride according to the above-described procedure.

However, this procedure is not general because, unlike sodium phenylsilanolate, which is readily soluble in butanol, sodium ethyl-, vinyl-, and methylsilanolates are very poorly soluble in butanol. For this reason, we first attempted to perform the synthesis of copper sodium vinylsiloxanes with the use of potassium vinyl- and ethylsilanolates, which are more readily soluble in butanol. However, it appeared that these compounds reacted with copper chloride to form products[4] that differed in structure from those prepared by the reactions of sodium silanolates with $CuCl_2$.

Results and Discussion

In this work, we demonstrated that it is much more practical to use monomeric organotrialkoxysilanes rather than sodium silanolates, which are prepared by alkaline cleavage of preliminarily synthesized polyorganosiloxanes, for the successful preparation of organometallosiloxanes.

It is known[5] that the reactions of alkyltrialkoxysilanes with alkalis are accompanied by elimination of one alkoxy group.

$$MeSi(OEt)_3 + NaOH \longrightarrow MeSi(OEt)_2ONa + EtOH$$

The essence of the method proposed consists of treatment of organotrialkoxysilanes, in particular, of triethoxyphenylsilane, with an aqueous-methanolic solution of sodium hydroxide. In this case, the amount of water used should provide complete hydrolysis of alkoxy groups.

$$n\,PhSi(OEt)_3 + n\,NaOH + n\,H_2O \longrightarrow$$
$$\longrightarrow 3n\,EtOH + [PhSiOONa]_n,$$

$n = 3-6.$

Under these conditions, sodium organosilanolates obtained from organoalkoxysilanes are readily soluble in the reaction medium and the subsequent reaction with metal chlorides proceeds smoothly without complications.

The procedure proposed can successfully be used for the preparation of various cage and polymeric metallosiloxanes, *e.g.*, of copper sodium vinylsiloxane (**1**) and

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manganese vinylsiloxane (**2**) from trimethoxyvinylsilane with the use of $CuCl_2$ and $MnCl_2$, respectively, and copper sodium γ-aminopropylsiloxane (**3**), which is the first representative of metallosiloxanes containing the functional group in the organic radical.

$$12\ \mathrm{VinSi(OMe)_3} + 12\ \mathrm{NaOH} + 12\ \mathrm{H_2O} + 4\ \mathrm{CuCl_2} \longrightarrow$$
$$\xrightarrow{\mathrm{BuOH}} \underset{\mathbf{1}}{\mathrm{(VinSiO_{1.5})_{12}(CuO)_4(NaO_{0.5})_4}} + 8\ \mathrm{NaCl} +$$
$$+ 36\ \mathrm{MeOH}$$

$$12\ \mathrm{VinSi(OMe)_3} + 12\ \mathrm{NaOH} + 12\ \mathrm{H_2O} +$$
$$+ 6\ \mathrm{MnCl_2} \xrightarrow{\mathrm{BuOH}} \underset{\mathbf{2}}{\mathrm{(VinSiO_{1.5})_{12}(MnO)_6 \cdot NaCl}} +$$
$$+ 11\ \mathrm{NaCl} + 36\ \mathrm{MeOH}$$

Metallic sodium, which reacts with the known amount of water present in an alcohol to give the required amount of NaOH, can be used instead of sodium hydroxide. Thus, there is no need for thorough drying of alcohol, in particular, of ethanol.

Copper sodium vinylsiloxane (**1**), copper sodium phenylsiloxane (**4**), manganese phenylsiloxane (**5**), and copper sodium methylsiloxane (**6**) were prepared according to this version of the method.

The reaction can be performed in butanol, ethanol, or methanol. In methanol, the reaction proceeds somewhat faster in spite of the lower boiling temperature of the mixture. NaCl that forms in the reaction is virtually insoluble in butanol, very poorly soluble in ethanol, and noticeably soluble in methanol (1.4 g per 100 mL). Hence, it is necessary to exchange methanol for butanol to completely remove NaCl from the reaction mixture.

The crystal structures of compounds **1**, **4**, and **5** reported previously[1,2] were established by X-ray diffraction analysis. We believe that the structures of metallosiloxanes **2**, **3**, and **6**, which were prepared for the first time by us, are similar in general to those of **1**, **4**, and **5**.

The analytical characteristics of the synthesized compounds are given in the Experimental section. All compounds contain variable amounts of water and alcohol of crystallization.

Experimental

Copper sodium vinylsiloxane (1). *A.* A solution of NaOH (4 g, 0.1 mol) in water (5 mL) was added to a solution of $VinSi(OMe)_3$ (14.82 g, 0.1 mol) in MeOH (100 mL). The reaction mixture was refluxed for 1 h. Then a solution of $CuCl_2$ (4.48 g, 0.033 mol) in MeOH (20 mL) was added. The mixture was refluxed for 15 min and MeOH was distilled off with simultaneous addition of BuOH (120 mL) using a dropping funnel. The precipitate of NaCl that formed was filtered off. The solvent was evaporated from the filtrate until crystallization started. A compound of composition $(VinSiO_{1.5})_{12}(CuO)_4(NaO_{0.5})_4 \cdot 0.5BuOH \cdot 4H_2O$ was isolated in a yield of 6.37 g (53.7%). The mother liquor was concentrated to dryness and a polymer was obtained in a yield of 2.0 g (16.7%). The precipitate of NaCl (5.05 g) was washed with acetone and dissolved in water and the solution was filtered and concentrated on a water bath. The theoretical amount of NaCl (3.86 g) was obtained. A precipitate insoluble in water was obtained in a yield of 1.19 g. When metallosiloxane **1** was dried in air, the solvate butanol of crystallization gradually volatilized and the crystals eroded and became shapeless. Found (%): C, 19.87; H, 3.05; Cu, 15.39; Na, 5.57; Si, 21.85. $C_{24}H_{36}Cu_4Na_4O_{24}Si_{12} \cdot 0.5C_4H_{10}O \cdot 4H_2O$. Calculated (%): C, 20.20; H, 3.49; Cu, 16.44; Na, 5.95; Si, 21.80.

B. Metallic Na (0.46 g, 0.02 g-at.) was added to a solution of $VinSi(OMe)_3$ (2.96 g, 0.02 mol) in a mixture of MeOH (15 mL) and 96% EtOH (25 mL). The reaction mixture was refluxed for 1 h. Then a solution of $CuCl_2$ (0.9 g, 6.6 mmol) in MeOH (5 mL) was added. The mixture was refluxed for 2 h and MeOH was distilled off with simultaneous addition of BuOH (25 mL). The mixture was refluxed for an additional 15 min and NaCl that precipitated was filtered off. The solvent was evaporated from the filtrate until crystallization started. After 48 h, the crystals were filtered off and dried at 20 °C. Product **1** of composition $(VinSiO_{1.5})_{12}(CuO)_4(NaO_{0.5})_4 \cdot BuOH \cdot 4H_2O$ was obtained as a crystalline compound in a yield of 2.15 g (92%). Concentration of the mother liquor gave an additional amount of crystals in a yield of 0.13 g (5.6%). The yield of NaCl was 0.66 g (98%). The weight of an insoluble residue was 0.18 g. Found (%): C, 21.21; H, 3.56; Cu, 15.58; Na, 5.34; Si, 21.63. $C_{24}H_{36}Cu_4Na_4O_{24}Si_{12} \cdot C_4H_{10}O \cdot 4H_2O$. Calculated (%): C, 21.36; H, 3.54; Cu, 16.52; Na, 5.98; Si, 21.92.

Manganese vinylsiloxane (2) was prepared according to procedure *A* from $VinSi(OMe)_3$ (7.41 g, 0.05 mol), NaOH (2 g, 0.05 mol), and $MnCl_2$ (3.17 g, 0.025 mol). Product **2** of composition $(VinSiO_{1.5})_{12}(MnO)_6 \cdot NaCl \cdot 3BuOH \cdot 2H_2O$ was isolated as a dark-brown compound in a yield of 5 g (87%). NaCl and an insoluble precipitate were obtained in yields of 2.8 g (95.5%) and 0.05 g (2.82% with respect to MnO), respectively. Found (%): C, 24.82; H, 3.96; Mn, 19.18; Si, 19.87. $C_{24}H_{36}Mn_6O_{24}Si_{12} \cdot NaCl \cdot 3C_4H_{10}O \cdot 2H_2O$. Calculated (%): C, 25.55; H, 4.17; Mn, 19.48; Si, 19.92.

Copper sodium γ-aminopropylsiloxane (3). $H_2N(CH_2)_3Si(OEt)_3$ (11.07 g, 0.05 mol) was dissolved in MeOH (50 mL). A solution of NaOH (2 g, 0.05 mol) in a mixture of MeOH (15 mL) and water (2.5 mL) was added. The reaction mixture was refluxed for 1 h. Then a solution of $CuCl_2$ (2.28 g, 0.017 mol) in MeOH (10 mL) was added. The mixture was refluxed for 30 min and MeOH was distilled off with simultaneous addition of EtOH (100 mL). The mixture was cooled, NaCl was filtered off, and the solvent was removed. Product **3** of composition $(H_2NC_3H_6SiO_{1.5})_{12}(CuO)_4(NaO_{0.5})_4 \cdot 4EtOH \cdot 6H_2O$ was isolated as a dark-blue compound in a yield of 6.85 g (93%); NaCl and an insoluble precipitate were obtained in yields of 1.95 g (98%) and 0.5 g (3.67%), respectively. Metallosiloxane **3** is readily soluble in water. Product **3** was hydrolyzed upon prolonged storage of its aqueous solutions to give a precipitate of $Cu(OH)_2$. Found (%): C, 25.36; H, 6.16; Cu, 11.99; Na, 3.65; N, 7.79; Si, 16.54. $C_{36}H_{96}Cu_4N_{12}Na_4O_{24}Si_{12} \cdot 4C_2H_6O \cdot 6H_2O$. Calculated (%): C, 25.69; H, 6.47; Cu, 12.36; Na, 4.47; N, 8.17; Si, 16.39.

Copper sodium phenylsiloxane (4) was prepared according to procedure *B* from $PhSi(OEt)_3$ (4.8 g, 0.02 mol), metallic Na (0.46 g, 0.02 mol), and $CuCl_2$ (0.9 g, 0.066 mol) in a mixture of 96% EtOH (25 mL) and MeOH (5 mL). Product **4** of composition $(PhSiO_{1.5})_{12}(CuO)_4(NaO_{0.5})_4 \cdot (H_2O)_{12}$ was isolated as a bright-blue crystalline compound in a yield of 3 g (90.3%) and NaCl was obtained in a yield of 0.75 g (96%). An insoluble residue was obtained in an insignificant amount. Found (%): C, 39.85; H, 3.92; Cu, 11.17; Na, 4.28; Si, 15.58.

$C_{72}H_{60}Cu_4Na_4O_{24}Si_{12} \cdot 12H_2O$. Calculated (%): C, 39.15; H, 3.83; Cu, 11.51; Na, 4.16; Si, 15.26.

Manganese phenylsiloxane (5) was prepared according to procedure *B* from $PhSi(OEt)_3$ (4.8 g, 0.02 mol), Na (0.46 g, 0.02 mol), and $MnCl_2$ (1.26 g, 0.01 mol) in a mixture of 96% EtOH (25 mL) and MeOH (5 mL). Product 5 of composition $(PhSiO_{1.5})_{12}(MnO)_6 \cdot NaCl \cdot BuOH \cdot 12H_2O$ was isolated as a dark-brown crystalline compound in a yield of 1.4 g (42.5%); NaCl and an insoluble precipitate were obtained in yields of 1.1 g (94%), and 0.05 g (7.1%), respectively. Found (%): C, 38.33; H, 3.81; Mn, 13.71; Si, 14.45. $C_{72}H_{60}Mn_6O_{24}Si_{12} \cdot NaCl \cdot C_4H_{10}O \cdot 12H_2O$. Calculated (%): C, 39.26; H, 4,08; Mn, 14.18; Si, 14.50.

Copper sodium methylsiloxane (6). Water (0.72 g, 0.04 mol) and Na (0.46 g, 0.02 mol) were added to a solution of $MeSi(OMe)_3$ (3.56 g, 0.02 mol) in MeOH (20 mL). The mixture was refluxed for 2 h and then a solution of $CuCl_2$ (0.9 g, 6.6 mmol) in MeOH (5 mL) was added. The mixture was refluxed for an additional 3 h and MeOH was distilled off by replacing it with BuOH (50 mL). After cooling, NaCl was rapidly filtered off (0.85 g) and the filtrate was concentrated until crystallization started. The mixture was kept for 10 h. Bright-blue crystals of compound **6** of composition $(MeSiO_{1.5})_{12}(CuO)_4(NaO_{0.5})_4 \cdot 4BuOH \cdot 8H_2O$ were obtained in a yield of 1.35 g (64.9%). Found (%): C, 20.01; H, 5.31; Cu, 14.87; Na, 5.77; Si, 19.43. $C_{12}H_{36}Cu_4Na_4O_{24}Si_{12} \cdot 4C_4H_{10}O \cdot 8H_2O$. Calculated (%): C, 19.92; H, 5.49; Cu, 15.05; Na, 5.45; Si, 19.97. The product is readily soluble in BuOH upon heating and is soluble in cold water.

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