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Reaction of the framework 3d-organometallosiloxanes with acetylacetone

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A reaction of acetylacetone with the framework sandwich-type metallosiloxanes (MOS) of general formula $[PhSiO_2]_6M_6[PhSiO_2]_6$, where M = Cu, Ni, Mn, was studied by GPC, ^{1}H and ^{29}Si NMR spectroscopy, X-ray diffraction, elemental and functional analysis. The reaction involved replacement of the metal atoms with the hydrogen atoms and is accompanied by the formation of the corresponding chelate complexes $M(acac)_2$. Displacement of the metal from the framework MOS leads to the destruction of molecular skeleton and formation of phenylsiloxanes containing Si—OH groups. The yield and composition of the reaction products considerably depend on the nature of the metal in $[PhSiO_2]_6M_6[PhSiO_2]_6$. A selective substitution of the metal leads to the stereoregular hexahydroxyhexaphenylcyclohexasiloxane, $[PhSiO(OH)]_6$, *cis*-isomer. The structure and composition of the crystalline hexahydroxyhexaphenylcyclohexasiloxane obtained were confirmed by ^{29}Si NMR spectroscopy, X-ray diffraction study, and functional analysis, while its TMS derivative was studied with ^{1}H NMR spectroscopy and GPC. Using a framework manganese phenylsiloxane as an example, a reversible character of the process has been established and an alternative synthesis of this compound from hexahydroxyhexaphenylcyclohexasiloxane and $Mn(acac)_2$ has been accomplished for the first time.

Key words: framework copper-, nickel-, and manganese-containing organometallosiloxanes, 3d metal complexes, destructive substitution of metals, reaction with β-diketones, acetylacetonates, organometallic synthesis, stereoregular organo(hydroxy)cyclosiloxanes.

Lately, organometallosiloxanes (MOS) attract increasing interest due to their specific structure and reactivity.[1—7] Unusal chemical properties of MOS are due to the presence of differing (Si)O—Si and (Si)O—M bonds, the former of which is susceptible to nucleophilic agents, whereas the latter is easily destroyed upon the action of electrophiles.

Upon preparation of MOS with trifunctional (organosilsesquioxane) structural units $RSiO_{3/2}$, a mixture of individual crystalline MOS with polymeric metallosiloxanes is formed. In the case of individual MOS, the architecture of metal complexes formed has a complex spatial structure in the form of cellular three-dimensional network, whose formation is determined by a decisive role of coordination properties of the transition metal ions[1,2] forming the metal clusters.

The most acquainted representatives of individual framework-type MOS containing 3d transition metals are the sandwich-structure metal complexes, in which metal atoms are placed in the central plane as the $[M_n]$ clusters flanked by two cyclosiloxane ligands bound with the M^{II} ions by covalent and coordination metallosiloxane bonds.

A unique structural organization of the framework MOS is responsible for the possibility of their application as synthons for the organoelement synthesis,[3] as well as metal-containing precursors in the synthesis of new catalysts,[4] preparation of metalloceramic materials,[5] and for development of metal-containing nanocomposites.[6,7]

When we started our work, information on the reactivity of MOS in the disintegration reactions based on the cleavage of the metal-oxide (Si)O—M bonds was rather limited and was basically on the reactions of MOS with electrophilic reagents (acids, anhydrides, organochlorosilanes). It is known that the reactions of this type are very characteristic of metallosilicates,[8] which are the closest inorganic analogs of MOS. These reactions were successfully used not only for the study of the silicate structures by destructive silylation with trimethylchlorosilane[9] (the Lentz method), but also for the development of convenient methods for obtaining organo-inorganic polymers

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and polyorganosiloxane resins based on mineral raw materials.[8] In the series of the framework MOS, this is the destruction of SiO—M metal-oxide bonds which was used for the preparation of stereoregular cyclosiloxanes of different structures,[6,10,11] including mesomorphous organocyclosiloxane hydroxy derivatives of stereoregular structure. For example, disintegration of the framework metallophenylsiloxanes containing the 3d transition metal atoms upon the action of acids (HCl, H_2S) leads to stereoregular cyclosiloxanols $[PhSiO(OH)]_n$, where $n = 4$, 6, and 12 (see Refs 6 and 10). Other types of transformations of MOS involving metal-oxide bonds virtually are not studied so far. For development of controlled methods for the synthesis based on MOS, chemical transformations observed in the reactions with complexation agents are of special interest.

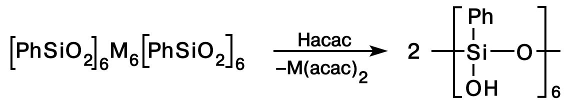
The present work is devoted to the study of reactions of the framework MOS of general formula $[PhSiO_2]_6M_6[PhSiO_2]_6$ (M = Cu, Ni, Mn) with β-diketones, forming stable complexes almost with all the transition and nontransition metals.[12] Taking into account that the very possibility of obtaining stereoregular cyclosiloxanes is determined by the presence in the structure of the framework MOS of polydentate cyclic ligands of strictly determined spatial structure,[1,2,13] during study of the reactions of MOS with β-diketones it seemed interesting to find synthetic scope of these reactions, in particular, to establish whether the ligands retain their configuration during destruction of the framework MOS.

Results and Discussion

The study was devoted to the reaction of the framework MOS containing the 3d transition metal atoms with typical representative of β-diketones, acetylacetone (Hacac). The sandwich-type metal complexes of general formula $[PhSiO_2]_6M_6[PhSiO_2]_6$, where M = Cu (**1a**), Ni (**1b**), Mn (**1c**), have been chosen as the objects for the study. These compounds have similar sandwich-type structure, which is based on two six-membered siloxane rings with six metal atoms placed between them. The difference is that in the nickel (**1b**) and manganese (**1c**) compounds a chlorine anion is encapsulated inside the framework with the counterion (Na^+) being placed in the outer sphere of the molecule.

The reaction of the framework MOS with Hacac is generally described by Scheme 1.

Scheme 1



$$[PhSiO_2]_6M_6[PhSiO_2]_6 \xrightarrow[-M(acac)_2]{Hacac} 2\left[\overset{Ph}{\underset{OH}{Si}}-O\right]_6$$

1a—c **2**

1: M = Cu (**a**), Ni (**b**), Mn (**c**)

Extraction of metal from the metallosiloxane framework of MOS with diketones can result in the appearance of silanol Si—OH groups in the reaction products. Firstly, the scheme given resembles cleavage of MOS with acids,[6,10] also leading to the formation of silanol derivatives. However, there are significant differences, too.

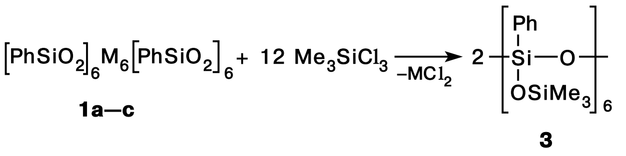
As it is known, decomposition of MOS with acids is accompanied by the side processes.[9] Due to the tendency of Si—OH groups to ion-catalytic dehydrocondensation and, as a result, high susceptibility to the effects of ionic impurities, the silanol derivatives obtained by traditional methods are unstable and can undergo spontaneous polycondensation to high-molecular-weight products. This is the reason why methods for the preparation of cyclosiloxanols of given structure by acidic decomposition of MOS, especially upon the action of strong acids, have significant limitations. To suppress polycondensation, it is necessary to use low starting concentrations of MOS, thoroughly controlled reaction conditions, which affect the dehydrocondensation rate (the pH value, temperature, the ratio, order, and rate of addition of reagents, and *etc*).

Therefore, the reaction of MOS with diketones, in principle, can be considered as an alternative method for obtaining siloxanols, including also cyclosiloxanols of the general formula $[RSiO(OH)]_n$. It is important that aliphatic β-diketones are very weak acids. It is known[12] that acetylacetone (one of the most acidic aliphatic diketones, $pK_a = 8.95$) is a considerable inferior in acidity even to such weak acids as H_2S ($pK_{a_1} = 7.2$; $pK_{a_2} = 14$) and H_2CO_3 ($pK_{a_1} = 6.4$; $pK_{a_2} = 10.3$).[14] In this connection, one can expect that the reaction products of MOS with β-diketones, *i.e.*, silanols, formed according to Scheme 1, would be more stable even in the presence of considerable excess of β-diketone or at higher concentrations of reagents as compared to the products of the MOS cleavage by traditional methods, for example, by mineral acids.

Composition and structure of the reaction products were studied by GPC, ^1H and ^{29}Si NMR spectroscopy, X-ray diffraction, as well as by elemental and functional analysis (to determine amount of the silanol Si—OH groups).[15] In addition, Me_3SiO-derivatives were used to study composition of the reaction products, which can be obtained by both destructive trimethylsilylation of the starting MOS[11,16] (Scheme 2) and protection of the silanol groups in the reaction products upon the action of trimethylchlorosilane (Scheme 3).

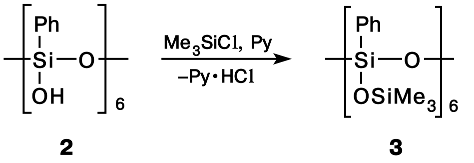
Applicability of the silylation method, developed earlier for the protection of terminal Si—OH groups in the linear polydimethylsiloxanes,[17] for the analysis of oligomeric polyol systems (siloxanols) was confirmed in the model reaction of $[PhSi(OH)O]_6$ (**2**) with trimethylchlorosilane, Me_3SiCl. This reaction resulted in the high yield (75%) of

Scheme 2



M = Cu, Ni, Mn

Scheme 3



the corresponding TMS-derivative **3**, whose silanol Si—OH groups are completely substituted for Me_3SiO groups.

The study of the reaction systems showed that both the framework and polymeric MOS react with acetylacetone under mild conditions (at 25 °C). The color of the reaction mixture changed right after addition of Hacac into the suspension of the framework copperphenylsiloxane (**1a**) in diethyl ether with the appearance of strong blue color characteristic of the copper acetylacetonate complex. After separation of a $Cu(acac)_2$ precipitate and subsequent reprecipitation with hexane from the ethereal filtrate, a colorless product was isolated as needle-like crystals, which were 1,3,5,7,9,11-hexahydroxy-1,3,5,7,9,11-hexaphenylcyclohexasiloxane (**2**) (see Scheme 1).

It was found that when the ratio Cu : Hacac = 1 : 2, the yield of compound **2** in this reaction is quantitative (≥92%).

The structure and composition of compound **2** were confirmed by independent methods: X-ray diffraction, ^{29}Si NMR spectroscopy, the elemental and functional analysis data (on amount of silanol Si—OH groups). The elemental analysis data and amount of the silanol groups correspond to the composition of the elementary unit [PhSi(OH)O]. The ^{29}Si NMR spectrum exhibits one signal at δ –70.59 related to the silicon atom of the fragment [PhSi(OH)O] in the six-membered ring.[10] X-ray study confirms that the compound obtained is identical to the known compound $[PhSi(OH)O]_6$ (see Ref. 10).

After silylation of compound **2**, the ^{1}H NMR spectrum of TMS-derivative **3** exhibits signals for the protons of the $SiMe_3$ groups (a singlet at δ 0.11) and phenyl groups (a multiplet in the region of δ 6.8—7.15) characteristic of the six-membered ring. Gel chromatography shows that the retained volumes of TMS-derivative **3** and standard compound $[PhSiO(OSiMe_3)]_6$ (**2**) are the same.

The obtained results indicate that the extraction of metal from MOS with β-diketones can in principle serve as a convenient preparative method for the preparation of reactive polysiloxanols, which are of considerable interest. It was interesting to test this suggestion using a non-ordered MOS, *i.e.*, polymeric copperphenylsiloxane of the same composition, as an example. It turned out that in the case of polymeric copperphenylsiloxane (PCPS), $\{[PhSiO_2]_2Cu\}_n$, under analogous conditions (the ratio Cu : Hacac = 1 : 2), a complete cleavage of the SiO—Cu bonds also occurs with quantitative extraction of copper from PCPS as a chelate complex $Cu(acac)_2$. The IR spectroscopic data of the reaction products (after separation from a $Cu(acac)_2$ precipitate and precipitation from the solution) contain a certain amount of silanol groups, that is indicated by a broad absorption band of the OH groups with the absorption maximum at 3342 cm^{-1} (see Ref. 18). However, attempted quantitative determination of the OH groups content using Chugaev—Tserevitinov method failed, apparently, due to the too low content of the silanol groups in the reaction products.

The more detailed studies of the reaction of PCPS with Hacac using ^{1}H NMR spectroscopy confirmed the presence of secondary processes of polycondensation involving silanol Si—OH groups. In this connection, we accomplished trimethylsilylation of three samples taken at different stages of the process: the starting PCPS (**I**), the ethereal solution of the reaction products of PCPS with Hacac directly after removal of a $Cu(acac)_2$ precipitate (**II**), and the products in the final step obtained after precipitation from the ethereal solution with hexane and evaporation of the solvent (**III**).

Analysis of composition of the TMS derivatives obtained (based on the ratio of the integral intensities of the signals for the Ph and Me groups in the ^{1}H NMR spectra) shows that the content of the Me_3SiO groups gradually decreases going from sample **I** to **II** and especially to sample **III**. The ratio PhSi : $SiMe_3$ in samples **I**, **II**, and **III** is 1 : 1.37, 1 : 0.91, and 1 : 0.39, respectively. Results of the study of all the three samples of the trimethylsilyl derivatives by GPC serve as an additional evidence in favor of secondary condensation. A comparison of gel-chromatograms shows a broadening of the peak of the reaction product and shift of its maximum toward more high-molecular-weight region (Fig. 1). These data clearly indicate a polycondensation evolution, which is accompanied by the increase in the molecular weight and polydispersity of the oligomers formed. A probable reason of different stability of silanols formed upon decomposition of the framework and polymeric MOS with acetylacetone consists in the presence in PCPS of ionogenic impurities as terminal functional groups (presumably, SiONa or SiOCuCl).

The reaction of the framework nickelphenylsiloxane (**1b**) with acetylacetone proceeds similarly, rather at lower rate. Under analogous conditions (at the ratio Hacac : Ni = = 2 : 1), appearance of color is observed immediately after

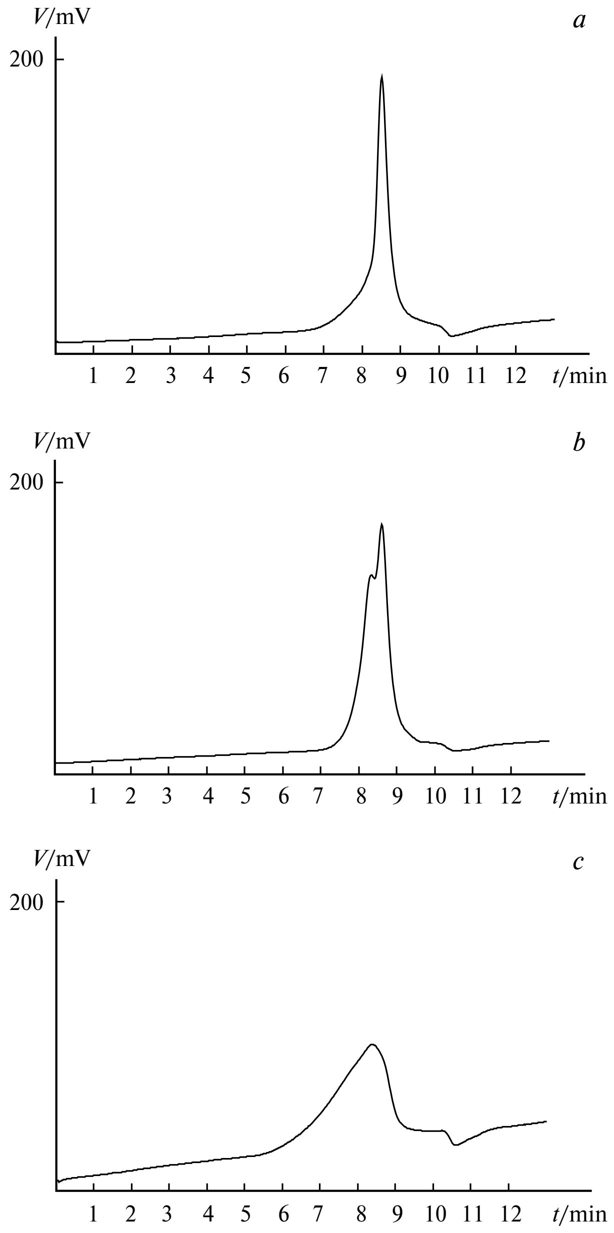


Fig. 1. Gel-chromatograms of the samples of PCPS trimethylsilyl derivative : **I** (*a*), **II** (*b*), and **III** (*c*).

addition of nickelphenylsiloxane into the suspension begins, which is due to the formation of a $Ni(acac)_2$ chelate complex. After extraction of ~2/3 of the total amount of metal the reaction is retarded. The elemental analysis data show that the soluble reaction products, in addition to compound **2**, contain at this stage also compounds formed as a result of incomplete extraction of the Ni atoms from the starting framework nickelsiloxane **1b**. Nevertheless, the yield of compound **2** reaches 64% after the reaction is completed. When the amount of Hacac increases (with respect to the ratio Hacac : Ni = 2 : 1), the yield of compound **2** increases insignificantly, however, the character of the reaction described is retained (Table 1). The data obtained indicate that the reaction of the framework MOS with β-diketones, probably, proceeds through the step-wise replacement of the ligand surrounding of the metal atoms in the structure of molecular framework.

Table 1. The yields of compound **2** in the reaction of the framework MOS **1a—c** with acetylacetone depending on the ratio Hacac : M

Compound	Yield of **2** (%) for Hacac : M		
	2 : 1	4 : 1	8 : 1
1a	92	—*	—*
1b	64	67	—*
1c	—**	—**	8

* No experiment was performed.
** No compound **2** was detected.

Manganesephenylsiloxane (**1c**) exhibits the lowest reactivity in the series of compounds studied. In this case, the product of complete substitution of the metal **2** is successfully isolated in the about 8% yield only at a fourfold excess of acetylacetone (Hacac : Mn = 8 : 1).

To sum up, reactivity of the framework MOS decreases with the change in the nature of metal in the order Cu ≥ Ni > Mn.

The results obtained agree on the qualitative level with stability constants of the corresponding metal acetylacetonates: the higher is the stability constant of the metal acetylacetonate, the higher is the yield of compound **2** (Table 2). Though there are no literature data on the stability constants of compounds **1a—c**, the increase in the yield of product **2** in the reactions (see Scheme 1) with the increase in the content of acetylacetone in the starting mixture can indicate a reversible character of the process. To check a suggestion on a possibility of the reverse reaction, we attempted to accomplish an alternative synthesis of the framework MOS from hexasiloxanol **2** and metal acetylacetonates. As it was noted, the framework manganese- and nickelphenylsiloxanes have encapsulated chlorine ion. We have chosen lithium chloride as a source of this ion, since it possesses good solubility in ethanol, in which the reaction was run.

Table 2. Stability constants[12] of metal acetylacetonates formed in the reaction of the framework MOS **1a—c** with acetylacetone

Complex	$\log K_1$	$\log K_2$
$Cu(acac)_2$	11.85	10.74
$Ni(acac)_2$	9.70	8.15
$Mn(acac)_2$	8.15	6.87

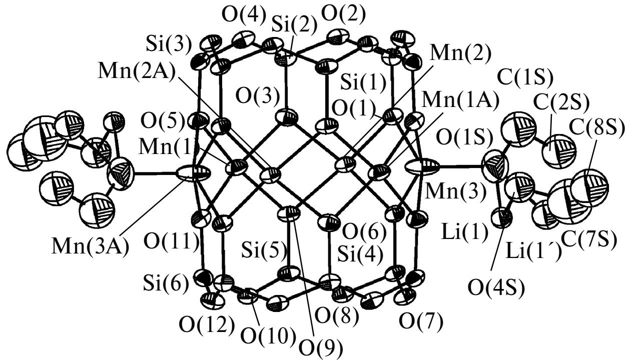


Fig. 2. Metallosiloxane framework of compound **1c** according to the X-ray diffraction data. Two positions of the disordered lithium atom and the solvate molecules of ethanol closest to them are shown, the chlorine atom inside the complex is not shown.

In fact, the reaction of $Mn(acac)_2$ with compound **2** in the presence of LiCl leads to a crystalline product in 62% yield, whose structure according to the X-ray diffraction data is identical to the framework manganesephenylsiloxane $[PhSiO_2]_6Mn_6[PhSiO_2]_6$, described earlier.[19] The structure of metallosiloxane framework of manganesephenylsiloxane (**1c**) synthesized by us is shown in Fig. 2. The molecule of **1c** is placed on the second order axis and the inside-cage chlorine atom occupies double particular position. In contrast to the copper complexes studied earlier, the lithium atom does not coordinate the oxygen atoms of the siloxane rings, rather it is placed in the outer sphere with respect to the metallosiloxane framework and is bound with the solvate molecules of EtOH.

In conclusion, successful accomplishment of an alternative synthesis of manganesephenylsiloxane from $Mn(acac)_2$ and hexahydroxyhexaphenylcyclohexasiloxane confirms reversible character of the reaction of the framework MOS with acetylacetone.

Experimental

^{1}H and ^{29}Si NMR spectra were recorded on a Bruker AV 300 spectrometer (300 MHz) in $CDCl_3$ using Me_4Si as an internal standard. Gel permeation chromatography was performed in a chromatographic system consisting of a HPP 5001 high pressure pump (Czech Republic), a RIDK 102 refractometric detector (Czech Republic), and a JETSTREAM 2 PLUS thermostat of columns (KNAUER, Germany). The thermostat temperature was 40 °C (±0.1 °C), tetrahydrofuran was an eluent, the flow rate was 1.0 mL min^{-1}, a 300×7.8-mm column filled with the Phenogel sorbent (Phenomenex, USA) with the particles size of 5 μm, and pores size of 500 Å. Recording and processing of the data were performed using the Mul′tiKhrom 1.6 GPC (Ampesand, Russia) and UniChrom 4.7 (Belarus) programs. IR spectra were recorded on a Specord M-82 spectrometer. Silanol groups were determined using the Chugaev—Tserevitinov method.[15]

The starting polymeric copperphenylsiloxane and framework copper-, nickel-, and manganesephenylsiloxanes were synthesized according to the procedures described earlier,[2,13] manganese acetylacetonate was synthesized according to the known procedure.[20]

Reaction of the framework copperphenylsiloxane (1a) with acetylacetone (the ratio Cu : Hacac = 1 : 2). Acetylacetone (1.89 g, 18.90 mmol) was added to copperphenylsiloxane (3.45 g, 1.43 mmol) in diethyl ether (50 mL) and the mixture was stirred at room temperature for 40 min. A precipitate of copper acetylacetonate was filtered off, washed on the filter with diethyl ether (30 mL), and dried at room temperature until the weight was constant to obtain copper acetylacetonate (2.25 g, 100%). Found (%): Cu, 24.2. $C_{10}H_{14}O_4Cu$. Calculated (%): Cu, 24.3. Si was not detected. Hexane (80 mL) was added to the filtrate, white needle-like crystals formed were filtered off and dried at room temperature until the weight was constant to obtain compound **2** (2.20 g, 92%). Found (%): C, 51.97; H, 4.56; Si, 20.20; OH, 13.1. $C_{36}H_{36}O_{12}Si_6$. Calculated (%): C, 52.15; H, 4.38; Si, 20.32; OH, 12.3. ^{29}Si NMR, δ: –70.59 (s, $Ph\underline{Si}O(OH)$).

Reaction of polycopperphenylsiloxane $\{[PhSiO_2]_2Cu\}_n$ with acetylacetone (the ratio Cu : Hacac = 1 : 2). Acetylacetone (1.58 g, 15.80 mmol) was added to polycopperphenylsiloxane (3.00 g, 7.90 mmol) in diethyl ether (60 mL) and the mixture was stirred at room temperature for 40 min. A blue precipitate was filtered off to obtain copper acetylacetonate (1.95 g, 95%). The filtrate was concentrated to 15 mL, followed by addition of hexane (70 mL), a precipitate of a polymer formed was dried *in vacuo* at room temperature until the weight was constant to obtain polyphenylsiloxane (1.88 g, 85.6%) as a viscous resin. Found (%): C, 51.4; H, 4.7; Si, 18.9. $C_{36}H_{36}O_{12}Si_6$. Calculated (%): C, 52.15; H, 4.38; Si, 20.32. The Si—OH groups were not detected by the Chugaev—Tserevitinov method,[15] the IR spectrum (a solution in hexachlorobutadiene) exhibits a broad band with the maximum at 3342 cm^{-1}.

Reaction of the framework nickelphenylsiloxane (1b) with acetylacetone. *A*. The ratio Ni : Hacac = 1 : 2. Acetylacetone (0.94 g, 9.43 mmol) was added to nickelphenylsiloxane (**1b**) (2.00 g, 0.79 mmol) in diethyl ether (30 mL) and the mixture was stirred at room temperature for 50 min. A pistachio-green precipitate was filtered off, washed on the filter with diethyl ether (10 mL) to obtain a precipitate (1.64 g), which was a mixture of the starting nickelphenylsiloxane and nickel acetylacetonate. The ethereal filtrate was concentrated to 10 mL, followed by addition of benzene (20 mL). After several minutes, needle-like crystals began to form in the solution. The crystals were filtered off and dried in air at room temperature until the weight was constant to obtain compound **2** (0.89 g, 64%) as white crystals. Found (%): C, 52.82; H, 4.88; Si, 19.06; OH, 12.5. The solvent from the mother solution was removed to dryness, the residue was dried *in vacuo* until the weight was constant to obtain polynickelphenylsiloxane (0.12 g, 7.8%) as a pale green polymeric product. Found (%): Si, 17.27; Ni, 5.0.

B*. The ratio Ni : Hacac = 1 : 4.** Compound **2** (0.91 g, 67%) was obtained as white crystals similarly to procedure ***A from nickelphenylsiloxane (**1b**) (2.00 g, 0.79 mmol) and acetylacetone (1.89 g, 18.87 mmol). Found (%): C, 52.35; H, 4.3; Si, 19.55; OH, 12.5. A pistachio-green precipitate (1.67 g), a mixture of the starting nickelphenylsiloxane and nickel acetylacetonate, was formed and polynickelphenylsiloxane (0.13 g, 8.8%) was isolated as a pale green polymeric product. Found (%): Si, 17.87; Ni, 1.15.

Reaction of the framework manganesephenylsiloxane (1c) with acetylacetone (the ratio Mn : Hacac = 1 : 8). Acetylacetone

(3.50 g, 35.40 mmol) was added to the framework manganesephenylsiloxane (1.60 g, 0.74 mmol) in diethyl ether (30 mL), the mixture was stirred at room temperature for 24 h and a precipitate was filtered off. The brown precipitate (1.5 g) was a mixture of the starting manganesephenylsiloxane and manganese acetylacetonate. The filtrate was concentrated to 10 mL and diluted with benzene (40 mL), followed by the formation of needle-like crystals in the solution. The crystals were filtered off, and the filtrate was again diluted with benzene (50 mL). The crystalline precipitate formed was combined with that isolated earlier and dried in air until the weight was constant to obtain compound **2** (0.10 g, 8%) as white crystals. Found (%): C, 52.80; H, 4.86; Si, 18.47.

Reaction of hexahydroxyhexaphenylcyclohexasiloxane (2) with manganese acetylacetonate. A solution of LiCl in ethanol (5 mL, 1.44 mmol mL^{-1}) was added to a solution of $Mn(acac)_2 \cdot 2H_2O$ (1.40 g, 4.34 mmol) in anhydrous ethanol (30 mL), followed by addition of a solution of compound **2** (1.20 g, 8.68 mmol) in anhydrous ethanol (30 mL). The mixture was stirred at room temperature for 24 h. A crystalline precipitate formed was filtered off and dried in air until the weight was constant to obtain the framework manganesephenylsiloxane (**1c**) (1.05 g, 62%) as light-brown crystals. Found (%): Si, 14.10; Mn, 14.18; Cl, 2.30. The ratio Si : Mn : Cl = 12.0 : 6.2 : 1.5. $C_{72}H_{60}O_{24}Mn_6LiCl$. Calculated (%): Si, 16.70; Mn, 16.33; Cl, 1.76. The ratio Si : Mn : Cl = 12 : 6 : 1.

Trimethylsilylation of hexahydroxyhexaphenylcyclohexasiloxane (2). A solution of compound **2** (0.85 g, 10.00 mmol) in diethyl ether (15 mL) was added to a mixture of trimethylchlorosilane (2.90 g, 26.70 mmol) and pyridine (2.43 g, 30.72 mmol). The mixture was stirred for 30 min at room temperature, and then was refluxed for 2 h. After cooling, DI water (20 mL) and concentrated hydrochloric acid (0.5 mL) were added to the mixture obtained. The mixture was separated using a separatory funnel. The aqueous phase was extracted with diethyl ether (15 mL). The ethereal extracts were combined and washed with water until the reaction for the chlorine ions was negative. The organic layer was dried with anhydrous sodium sulfate. Concentration of the ethereal solution yielded compound $[PhSiO(OSi(Me)_3)]_6$ (**3**) (0.95 g). ^1H NMR, δ: 0.11 (s, 9 H, $SiMe_3$); 6.80—7,15 (m, 5 H, Ph). According to the data of ^1H NMR spectrum, the ratio of integral intensities of the protons $SiC_6\underline{H}_5 : Si(C\underline{H}_3)_3 = 5 : 9$, according to the calculated data, 5 : 9. The yield was 75%.

X-ray study of compound **1c** obtained by alternative synthesis was performed on a SMART APEX II CCD diffractometer (Mo-Kα radiation, graphite monochromator, ω-scanning). The structure was solved by the direct method and refined by the least squares method in anisotropic full-matrix approximation on F_{2hkl}. Analysis of differential Fourier-syntheses of electron density showed that almost all the phenyl groups and some solvate molecules of ethanol are disordered, further refinement of these fragments was performed using limitations set on the C—C and O—C bond distances. The lithium atom is also disordered over two positions with equal population. The hydrogen atoms of the methyl, methylene, and phenyl groups are calculated geometrically. The hydrogen atoms of the hydroxy groups were not found. The principal crystallografic data and parameters of refinement are given in Table 3.

Atom coordinates, bond distances, and bond angles were deposited with the Cambridge Structural Database.

Table 3. Crystallografic data and parameters of refinement of structure **1c**

Parameter	Value
Molecular formula	$C_{87}H_{91.40}ClLi_2Mn_6O_{34}Si_{12}$
Molecular weight	2507.59
T/K	100
Crystal system	Monoclinic
Space group	$C2/c$
Z	4
a/Å	30.6166(17)
b/Å	18.8431(10)
c/Å	20.5336(12)
α/deg	90.00
β/deg	98.7780(10)
γ/deg	90.00
V/Å^3	11707.3(11)
d_{calc}/g cm^{-3}	1.360
μ/cm^{-1}	8.43
F(000)	4905.6
$2\theta_{max}$/deg	52
Number of measured/ independent reflections	56453/11541
Number of reflections with $I > 2\sigma(I)$	5641
Number of refining parameters	442
R-Factors on $I>2\sigma(I)$	$R_1 = 0.0884$
on all the reflections	$wR_2 = 0.2821$
GOF	0.985
Residual electron density (min/max)/e Å^{-3}	0.999/–0.677

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