A new way of introducing metal oxide fragments into polysilane chains

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When permethyl-α,ω-dichlorooligosilanes undergo heterofunctional condensation with metal acetates, the formation of a metallosiloxane fragment is the predominant process, whereas the formation of cyclosilane-siloxane resulting from the exchange of functional groups between the silicon and metal atoms is a side reaction. The scheme of these transformations is proposed.

Key words: metal-containing polysilanes, heterofunctional condensation, exchange reaction.

Metal oxide fragments M—O (M is a polyvalent metal) have previously[1] been introduced into the polysilane chain by the exchange reaction

$$-SiR_2-SiR_2-ONa + Hal-M- \longrightarrow$$

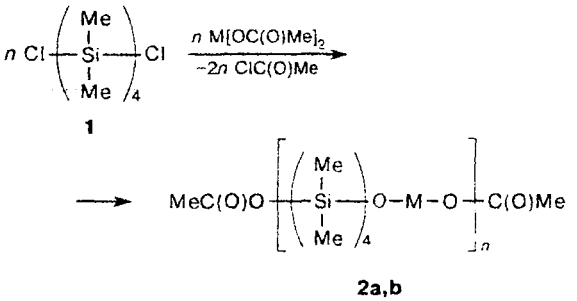
$$\longrightarrow -SiR_2-SiR_2-O-M- + NaHal.$$

In some cases, for compounds containing branched polysilane fragments, this route results in the formation of metalloxanepolysilane complexes with starting silanolate. In this work, we propose a different way of formation of the metallosiloxane fragment in the polysilane chain.

Results and Discussion

We established that the reaction of 1,4-dichlorooctamethyltetrasilane (**1**) with acetates of bivalent metals results in the formation of polysilanemetalloxanes (Scheme 1).

Scheme 1



M = Cu (**a**), Co (**b**)

The composition of oligomers obtained is presented in Table 1. The chain length (n) of oligomer was calculated from the results of analysis of the content of terminal acetate groups.

The formation of polysilanemetalloxanes due to the side reaction of exchange of functional groups between silicon and metal atoms is accompanied by the appearance of minor amounts (10—12%) of octamethyloxatetrasilacyclopentane. Exchange of functional groups (Scheme 2) resulting in mixed metal acetate-chloride and intermediate compound **4** occurs through the six-membered cyclic transition state (**3**). Subsequent transformation of polysilane **4** can occur *via* two competing directions: by intramolecular cyclization to form cyclosilane-siloxane **5** and due to the reaction with metal acetate affording compound **6**. The studies showed that the second direction, which explains the presence of terminal acetate groups at the silicon atom in the oligomer structure, is predominant.

Metal acetates differ in behavior from metal hydroxides studied in a similar reaction[2] where the exchange of functional groups between silicon and metal atoms is predominant.

Experimental

Starting dichlorotetrasilane **1** was synthesized by the procedure described previously.[3] All reactions were carried out in a dry nitrogen atmosphere.

Table 1. Composition of synthesized oligomers **2a,b**

Compound	M	Found (%)			Si/M	n
		Si	M	OAc		
2a	Cu	31.92	18.54	6.22	3.89	5.46
2b	Co	33.04	16.95	6.81	4.09	5.03

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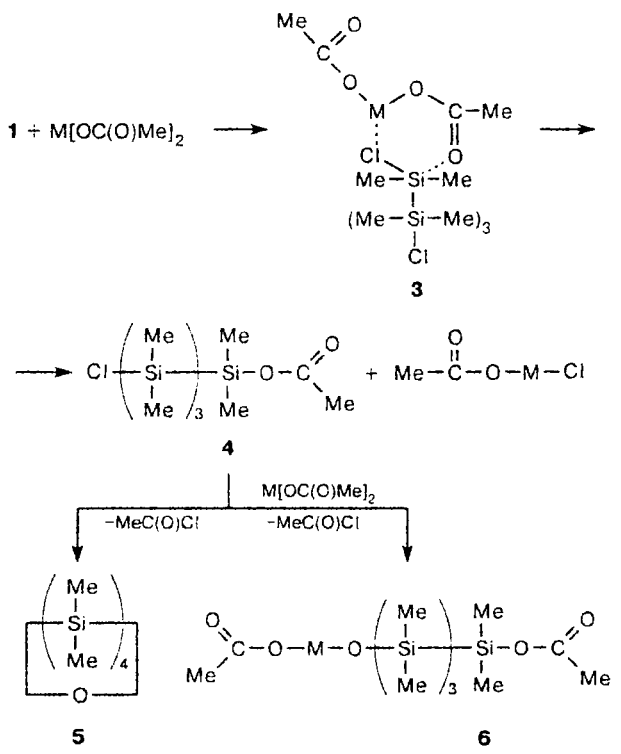
Scheme 2



IR spectra were recorded on a Specord M-80 spectrophotometer (a suspension in Nujol), and UV spectra were recorded on a Specord M-40 spectrophotometer in the 180—500 nm range in a 0.1-cm cell.

The content of acetate groups was determined by potentiometric titration with an ethanol solution of NaOH.

Polysilanecoppersiloxane (2a). A solution of dichlorooligosilane **1** (2 g, 6.6 mmol) in toluene (10 mL) was added with stirring to a suspension of anhydrous $Cu(OAc)_2$ (2.34 g, 13.2 mmol) in a MeCN—toluene (1 : 3) mixture (10 mL). The reaction mixture was heated during gradual distillation of solvents and simultaneous introduction of toluene to maintain a constant volume. When a temperature of 110 °C was achieved (after approximately 3 h), distillation of solvents was stopped, and the reaction mixture was filtered off. The filtrate was concentrated to give colorless crystalline compound **5** in a 12% yield (0.2 g) with m.p. 43—45°C (*cf.* Ref. 4: m.p. 45 °C). IR (KBr), ν/cm^{-1}: 1040 (SiOSi). UV (hexane), λ_{max}/nm: 233. The solid residue obtained after filtration was extracted using refluxing with a MeCN—toluene (1 : 1) mixture (10 mL). After the solvents were completely removed from the extract, light-yellow powdered compound **2a** was obtained in a 72% yield (1.64 g); the data of its elemental analysis are presented in Table 1. IR (KBr), ν/cm^{-1}: 920 (SiOM); 1720 (C=O); 1040 (SiOAc); 1260, 820 (SiMe). Recrystallization from water of the residue obtained after separation of compound **2a** gave a crystalline product, a mixture of copper acetate and halide in which Cl ions were found by argentometry. MeC(O)Cl (yield 0.78 g, 76%) was chromatographically determined in a mixture of solvents that were distilled-off during the reaction.

Polysilanecobaltsiloxane (2b). Cyclosilane-siloxane **5** (0.16 g, 10%), compound **2b** (1.72 g, 76%), and MeC(O)Cl (0.73 g, 72%) were obtained similarly from anhydrous $Co(OAc)_2$ (2.32 g, 13.2 mmol) and dichlorooligosilane **1** (2 g, 6.6 mmol). The elemental analysis data for compound **2b** are presented in Table 1. IR (KBr), ν/cm^{-1}: 930 (SiOM); 1740 (C=O); 1020 (SiOAc); 1265, 800 (SiMe). Absorption bands were assigned according to the data in Refs. 5 and 6.

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References

1. A. N. Kornev, T. A. Chesnokova, V. V. Semenov, E. V. Zhezlova, L. N. Zakharov, L. G. Klapshina, G. A. Domrachev, and V. S. Rusakov, *J. Organomet. Chem.*, 1997, **547**, 113.
2. M. M. Levitsky, B. G. Zavin, N. V. Karpilovskaya, and A. I. Chernyavskii, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 1658 [*Russ. Chem. Bull.*, 1998, **47**, 1615 (Engl. Transl.)].
3. A. I. Chernyavskii and B. G. Zavin, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1513 [*Russ. Chem. Bull.*, 1997, **46**, 1449 (Engl. Transl.)].
4. M. Kumada, M. Ishikawa, and B. Murai, *J. Chem. Soc. Jpn*, 1963, **66**, 637.
5. *Spektry i khromatogrammy elementoorganicheskikh soedinenii*, No. 2. *IK- i UF-spektry siloksanov i silazanov* [*Spectra and Chromatograms of Organoelement Compounds*, No. 2, *IR and UV Spectra of Siloxanes and Silazanes*], Khimiya, Moscow, 1976, 46 pp. (in Russian).
6. A. L. Smith, *Applied Infrared Spectroscopy*, Dow Corning Corporation, New York, 1979, 302 pp.

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