

Synthesis and thermal decomposition of cobalt-containing oligosilanes

V. V. Semenov,^{a*} N. F. Cherepennikova,^a A. N. Kornev,^a E. V. Naumova,^a N. P. Makarenko,^a S. Ya. Khorshev,^a G. A. Domrachev,^a and O. A. Bochkova^b

^aG. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, 49 ul. Tropinina, 603600 Nizhnii Novgorod, Russian Federation.

Fax: 007 (813 2) 66 1497

^bInstitute of Biochemical Physics, Russian Academy of Sciences, 4 ul. Kosygina, 117977 Moscow, Russian Federation.

Fax: 007 (095) 938 2156

Oligo(phenylcobaltcarbonylsilane) was prepared from oligo(phenylsilane) and dicobalt octacarbonyl. The reaction proceeds with elimination of H₂ and CO and insertion of cobalt carbonyl fragments into the silicone backbone of oligosilane. Oligosilane containing cobalt carbonyl groups in side organic substituents was obtained from oligo[methyl(phenylethynyl)silane and Co₂(CO)₈]. The reaction of 1,2-bis(phenylethynyl)tetramethyldisilane with Co₂(CO)₈ proceeds with the sequential attachment of cobalt carbonyl fragments to ethynyl groups to form disilane derivatives [η^2 -C≡CPhCo₂(CO)₆]. Thermal decomposition of cobalt-containing oligosilanes affords a mixture of paramagnets and ferromagnets.

Key words: organosilicon oligomers, silicon hydrides, organodisilanes, ethynylsilanes, dicobalt octacarbonyl; thermal decomposition, paramagnets, ferromagnets.

Organosilicon polymers and oligomers containing transition-metal atoms are attracting particular interest because these compounds can be used for preparing ceramic and magnetic materials as well as catalysts. A rather wide range of metal-containing siloxane and carbosilane polymers are known.¹ Analogous organopolysilane derivatives are still poorly studied. Previously,² a polymer has been prepared in which disilanyl groups alternate with metalloethynyl groups (M = Pt). Polysilanes with side ferrocenyl groups³ and with heteroatoms (Ge, Sn, As, or Te) in the main chain⁴ were synthesized by the Wurtz reaction. Polysilane derivatives with titanium and zirconium atoms in the silicon chain were synthesized by pyrolysis of polydimethylsilylene in the presence of halides of these metals.⁵ In this work, we studied reactions of oligoorganohydro- and ethynylsilanes with dicobalt octacarbonyl, which yielded cobalt-containing organosilicon oligomers.

Experimental

HPLC analysis was carried out on a Milikhrom-1A liquid chromatograph (UV detector, 250 nm, 64×2-mm column packed with a Separon-SGX sorbent with 5- μ m particles). Gases were analyzed on a Tsvet-530 gas chromatograph equipped with a vacuum pump, a mercury manometer, and a three-way cock (stainless steel 0.3×100-cm column, NaX molecular sieves). This device made it possible to measure the pressure in the reaction tube and to introduce a gas sample,

while excluding air. The use of a thermal conductivity detector and argon as the carrier gas allowed simultaneous determination of H₂, CO, and CH₄. The composition of the gas phase was calculated taking into account the tabulated values of thermal conductivities of gases.⁶ Prior to analysis, the sorbent was activated at 250 °C for 2 h. Analysis was carried out at 20–25 °C.

The molecular-weight characteristics were determined on a gel-chromatographic instrument containing three Styrogel columns with pore sizes of 25, 25, and 8 μ m, respectively. THF was used as the eluent. An RIDK-101 differential refractometer was used as a detector. Calibration was carried out with the use of polypropylene glycol standards.

The IR spectra were recorded on a Perkin-Elmer 577 spectrometer. The ¹H NMR spectra were obtained on a Tesla-BS-567A spectrometer (100 MHz). The UV spectra were recorded on a Specord-M40 spectrophotometer.

X-ray phase analysis was carried out on an IRIS instrument equipped with a Debye-Sherrer camera (the diameter of the camera was 53.7 cm, Cu-K α radiation, nickel filter). X-ray data were collected with rotation of the sample. The diameter of the sample was 1 mm.

Magnetochemical measurements were carried out on a Bruker B-E15 Faraday balance at 25 °C. The field was stabilized with a Hall Stabilizer for Field Control B-H15. The cobalt content of oligomers was determined photocolometrically on an SF-46 spectrophotometer according to the known procedure.⁷

Sample preparation for analysis. A weighed sample of an oligomer (0.03–0.06 g) was dissolved in a mixture (3 mL) of CCl₄ and MeOH (6:1, v/v), and three drops of Br₂ were added. The mixture was shaken and kept at 25 °C for 20 min.

Concentrated HCl (1 mL) was added. The upper layer was removed, and the bottom layer was twice extracted with concentrated HCl until the blue color disappeared. The extracts were combined and concentrated in a porcelain dish. Then the salt was transferred into a 250-mL volumetric flask and diluted to the mark with distilled water. The concentration of cobalt in the aqueous solution was determined from the calibration curve.

Oligo(phenylcobaltcarbonylsilane) (2). A solution of oligo(phenylsilane) **1** (1.45 g) in toluene (10 mL) and a solution of $\text{Co}_2(\text{CO})_8$ (2.34 g, 6.9 mmol) in toluene (10 mL) were placed separately in reaction tubes. The solutions were degassed by repeated freezing-thawing *in vacuo*, cooled to -15°C , and mixed. Gases that evolved were removed periodically *in vacuo*, and the temperature was maintained at $-10\pm 15^\circ\text{C}$ for 2 h. Then the mixture was heated to 25°C , kept for 20 h, and cooled to 0°C . The solution was decanted, and toluene was removed *in vacuo* at $25\text{--}30^\circ\text{C}$. Hexane (20 mL) was distilled to the product obtained. Then the solution was decanted and concentrated. Oligomer **2** was obtained in a yield of 2.73 g as a brown resin. M_w 740 (cryoscopy in benzene). The composition was as follows (%): C, 51.25; H, 3.86; Co, 18.6 (photocolorimetry). UV (hexane), λ/nm : 307, 405. ^1H NMR (CDCl_3), δ : 8.1, 7.65, 7.39, 7.34 (5 H, C_6H_5). The yield of a hexane-insoluble fraction was 0.62 g.

Thermal decomposition of oligo(phenylcobaltcarbonylsilane) (2). **Method A.** Oligomer **2** (0.23 g) was heated in a quartz tube connected with a mercury burette under an atmosphere of argon. The temperature was gradually increased (over 3 h) from 25 to 400°C . The volume of gas that evolved was 38.3 mL. Its composition (%) was as follows: H_2 , 2.1; CO, 87.1; CH_4 , 10.8. The weight loss was 0.05 g (21.7%).

Method B. A solution of **2** (0.5 g) in hexane (5 mL) was divided over five tubes *in vacuo*. The tubes were sealed off, weighed, and heated at 125, 150, 200, 250, and 300°C for 2 h. The pressure in tubes was measured with the use of a mercury manometer. The gas composition was determined by GLC. The results are given in Table 1.

1,2-Bis(phenylethynyl)tetramethyldisilane (3). A solution of $\text{ClMe}_2\text{SiSiMe}_2\text{Cl}$ (30.3 g, 0.16 mol) in THF (50 mL) was added dropwise with stirring and cooling to a solution of $\text{PhC}\equiv\text{CMgBr}$ (410 mL, 0.49 mol). The mixture was heated for 12 h. Hexane (400 mL) was added, and then 1 M HCl (200 mL) was added with stirring and cooling. The organic layer was separated, washed with water, and dried with CaCl_2 . The solvent was removed by distillation. Sublimation of the residue yielded 6.2 g (12%) of compound **3** as white crystals, m.p. $74\text{--}75^\circ\text{C}$. Found (%): C, 75.30; H, 6.90; Si, 18.02. $\text{C}_{20}\text{H}_{22}\text{Si}_2$. Calculated (%): C, 75.41; H, 6.96; Si, 17.63. IR, ν/cm^{-1} : 2140 ($\text{C}\equiv\text{C}$); 1240, 840, 785, 770 (Si—Me); 3050, 1580, 1480, 1430, 1215, 1070, 1030, 815, 750, 680, 650, 600, 540 (Ph).

Table 1. Volume and composition of gas evolved upon thermal decomposition of **2** in evacuated tubes.

Number of tubes	$T/^\circ\text{C}$	V^*/mL	Composition of the gas phase (mol.%)		
			H_2	CO	CH_4
1	100	29	16	84	—
2	150	109	—	100	—
3	200	202	—	100	—
4	250	171	—	73	27
5	300	140	—	—	100

*Per 1 g of oligomer **2**.

Reaction of disilane 3 with dicobalt octacarbonyl. A solution of $\text{Co}_2(\text{CO})_8$ (3.42 g, 0.01 mol) in CH_2Cl_2 was added to a solution of disilane **3** (1.59 g, 0.005 mol) in CH_2Cl_2 (10 mL). The mixture was stirred for 12 h. It was demonstrated by HPLC, taking into account the quantity of CO evolved, that virtually all $\text{Co}_2(\text{CO})_8$ reacted with ethynyldisilane. The solvent was removed *in vacuo*. 1,1,2,2-Tetramethyl-1,2-bis(phenylethynyldicobalthexacarbonyl)-1,2-disilane (**4**) was obtained in a yield of 4.19 g (94%) as a brown powder. Found (%): C, 43.20; H, 2.63; Co, 27.80. $\text{C}_{32}\text{H}_{22}\text{Co}_4\text{O}_{12}\text{Si}_2$. Calculated (%): C, 43.15; H, 2.49; Co, 26.50. IR, ν/cm^{-1} : 2940, 2880, 1240, 840, 785, 770, 750 (Si—Me); 3050, 1580, 1550, 1475, 1465, 1430, 1215, 1070, 1020, 820, 730, 680, 660, 600 (Ph); 2070, 2040, 1980, 510, 490, 450 (Co—CO).

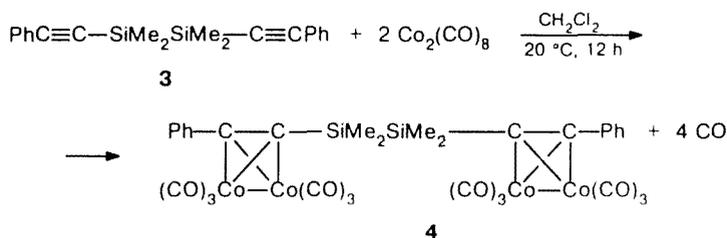
Oligo[methyl(phenylethynyl)]silane (7). A solution of oligo(methylchlorosilane) **6** (0.35 g-at. Cl, 27.7 g) in THF (50 mL) was added dropwise to a 1.78 M solution of phenylethynylmagnesium chloride (207 mL, 0.37 mol) obtained from $\text{PhC}\equiv\text{CH}$ and MeMgCl in THF. After completion of the exothermic reaction, the mixture was refluxed for 10 h and filtered. The solvent was removed by distillation. Benzene (150 mL) was added, and the mixture was filtered. The filtrate was washed with a saturated solution of NH_4Cl at low temperature and dried with Na_2SO_4 . The major portion of benzene was removed by distillation. The viscous residue was evacuated *in vacuo* (0.1 Torr) at $80\text{--}100^\circ\text{C}$ for 5 h. Oligomer **7** was obtained in a yield of 28.9 g (57%) as a yellow-brown glassy compound, M_w 705, M_n 410, M_w/M_n 1.7. Found (%): C, 73.55; H, 6.03; Si, 18.72. $\text{C}_9\text{H}_8\text{Si}$. Calculated (%): C, 74.94; H, 5.59; Si, 19.47. IR, ν/cm^{-1} : 2140 ($\text{C}\equiv\text{C}$); 1240, 830, 750 (Si—Me); 3040, 1580, 1560, 1470, 1430, 1070, 750, 690, 600, 540 (Ph). ^1H NMR (CDCl_3), δ : 0.6 (s, 3 H, MeSi); 7.0—7.5 (m, 5 H, Ph). UV, λ/nm : 220.

Reaction of silane 7 with dicobalt octacarbonyl. A solution of $\text{Co}_2(\text{CO})_8$ (1.17 g, 3.4 mmol) in CH_2Cl_2 (10 mL) was added to a solution of oligosilane **7** (0.50 g) in CH_2Cl_2 (10 mL). The course of the reaction was monitored by IR spectroscopy (a decrease in the intensity of the absorption band $\nu(\text{C}\equiv\text{C})$ at 2140 cm^{-1}) and volumetrically (CO evolution). The mixture was stirred at 25°C for 12 h, and then CH_2Cl_2 was removed *in vacuo*. The residue was washed with pentane, and then pentane was removed *in vacuo*. Oligo[methyl(phenylethynyldicobalthexacarbonyl)]silane (**8**) was obtained in a yield of 1.45 g (97%) as a dark-brown powder. Found (%): C, 40.34; H, 2.35; Co, 28.54 (photocolorimetry). $\text{C}_{15}\text{H}_8\text{Co}_2\text{O}_6\text{Si}$. Calculated (%): C, 41.87; H, 1.87; Co, 27.42. IR, ν/cm^{-1} : 1250, 830, 750 (Si—Me); 3040, 1580, 1070, 720, 680, 600 (Ph); 2060, 2040, 2010, 510, 490 (Co—CO).

Results and Discussion

Reaction of oligo(phenylsilane) with dicobalt octacarbonyl. Oligosiloxanes containing cobalt carbonyl groups were prepared by the reaction of oligo(methylhydrosiloxanes) ($\text{MeHSiO})_n$ or $\text{Me}_3\text{Si}(\text{OSiMeH})_n\text{OSiMe}_3$ with dicobalt octacarbonyl.⁸ Analogous reactions of oligo(organohydrosilanes) $\text{H}(\text{RHSi})_n\text{H}$ have not been studied yet. However, it is known that the reaction of the model compound, 1,1,2,2-tetramethyldisilane, did not stop at the stage of attachment of one or two cobalt tetracarbonyl groups. Further transformation of primary silylcobalt derivatives to the final product with two bridging dimethylsilylene fragments occurs⁹ (Scheme 1).

Scheme 2



carried out with equimolar amounts of the reagents, the amount of hydrogen that evolved indicated that no less than 55% of silicon-hydride groups of oligomer **1** entered into the reaction with $\text{Co}_2(\text{CO})_8$ and $\text{HCo}(\text{CO})_4$. The actual degree of substitution should be somewhat higher because some hydrogen remains in the form of $\text{HCo}(\text{CO})_4$. Therefore, product **2** is a mixture of oligomers containing structural units **A**, **B**, and (PhSiH) . The cobalt content of oligomer **2** was 18.6%.

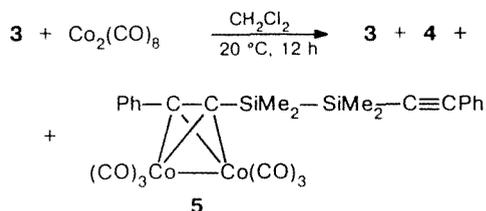
Oligo(phenylcobaltcarbonylsilane) **2** is rather stable to oxygen and moisture. A short-term exposure to air (15–20 min) leaves the IR spectrum unchanged. However, a more prolonged exposure to air (3–5 h) results in the appearance of a broad band at 1030 cm^{-1} , which is indicative of the presence of siloxane bonds. In this case, the oligomer becomes insoluble in toluene.

Reaction of oligo[methyl(phenylethynyl)]silane with dicobalt octacarbonyl. It is known¹¹ that phenylethynylsilanes $\text{PhC}\equiv\text{CSiR}_3$ react with $\text{Co}_2(\text{CO})_8$ to produce $[\eta^2\text{-C}\equiv\text{CPhCo}_2(\text{CO})_6]\text{SiR}_3$. In the $\text{PhC}\equiv\text{CSiMe}_2\text{H}$ compound, the ethynyl group reacts first followed by the silicon-hydride group to form $[\eta^2\text{-C}\equiv\text{CPhCo}_2(\text{CO})_6]\text{SiMe}_2\text{Co}(\text{CO})_4$.¹¹ We have established that when $\text{Co}_2(\text{CO})_8$ reacts with ethynylsilanes, the silicon–silicon bond is not cleaved. Thus, the reaction of 1,2-bis(phenylethynyl)tetramethyldisilane (**3**) with $\text{Co}_2(\text{CO})_8$ (2 mol) proceeds with a quantitative addition to both $\text{C}\equiv\text{CPh}$ groups (Scheme 2).

The course of the reaction is conveniently monitored by HPLC. As in the case of oligophenylsilane **1**, the cobalt carbonyl fragments decrease retention volumes. The initial disilane **3** is readily separated from $\text{Co}_2(\text{CO})_8$ and from the addition products. Addition of $\text{Co}_2(\text{CO})_8$ (2 equiv.) to disilane **3** resulted in an almost complete transformation of these compounds to 1,1,2,2-tetramethyl-1,2-bis(phenylethynyl)dicobalthexacarbonyl-1,2-disilane **4**. When the reaction was carried out with equimolar amounts of the reagents, $\text{Co}_2(\text{CO})_8$ was consumed completely and disilane **3** remained in an amount of 11 mol.%. Besides compound **4**, the mixture contained product **5** with a smaller retention volume as compared to **3**. The molar ratio of **3** : **4** : **5** was 11 : 39 : 50. After the addition of 1 equivalent of $\text{Co}_2(\text{CO})_8$, compound **5** and disilane **3** transformed to one final product

4. These results suggest that the intermediate compound **5** is 1,1,2,2-tetramethyl-1-phenylethynyl-2-phenylethynylcobalthexacarbonyl-1,2-disilane, which is a product of the addition of $\text{Co}_2(\text{CO})_8$ to only one of two ethynyl groups (Scheme 3). However, we failed to isolate this compound.

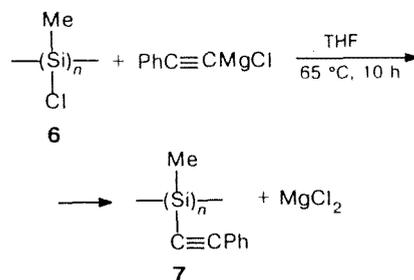
Scheme 3



Ethynyl groups act as two virtually independent reaction centers. It is also known¹² that in organosilicon polymers of the $-\text{[SiR}_2\text{-C}\equiv\text{C-C}\equiv\text{C]}_n-$ type, $\text{Co}_2(\text{CO})_8$ adds predominantly to only one ethynyl group of the diethynyl fragment for steric reasons.

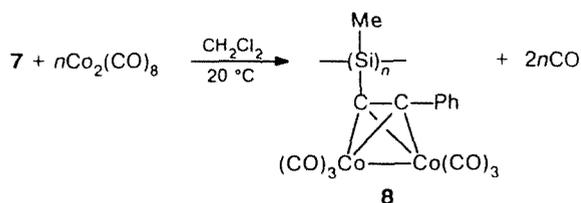
Oligo[methyl(phenylethynyl)]silane (**7**) was prepared from oligomethylchlorosilane (**6**)¹³ and phenylethynylmagnesium chloride.

Scheme 4



Compound **7** is a pale-brown glassy substance, which softens in the temperature range of 95–105 °C. Treatment of **7** with dicobalt octacarbonyl yields oligo[methyl(phenylethynyl)dicobalthexacarbonyl]silane (**8**) as a brown powder.

Scheme 5



Oligomer **8** is rather stable to oxygen and moisture, readily soluble in benzene, THF, and CH_2Cl_2 , and poorly soluble in saturated hydrocarbons.

Thermal decomposition. Thermal decomposition of oligomer **2** was studied by two methods: first, by heating the oligomer under an atmosphere of argon in a tube connected with a mercury burette used to collect the gas phase (Fig. 1) and, second, by heating in sealed evacuated tubes (see Table 1). When the temperature was slowly increased (during 3 h) to 400°C , gradual accumulation of gas was observed, which was virtually completed at 250°C . The gas phase had the following composition (%): H_2 , 2.1; CO , 87.1; CH_4 , 10.8. The weight loss was 21.7%. The data of IR spectroscopy demonstrated that in the product obtained by heating compound **2** to 250°C , carbonyl groups still remained (four medium intensity bands at 2005, 1990, 1960, and 1945 cm^{-1}). Heating to 400°C resulted in complete destruction of the compound. The IR spectrum showed no bands corresponding to carbonyl groups and even to Si—Ph fragments. The solid products (250 and 400°C) are X-ray-amorphous. A fine-crystalline phase (cobalt and its silicides) appeared only when the sample was heated to 600°C .

The volumes of the gas evolved after decomposition of oligomer **2** in sealed evacuated tubes and its composition are given in Table 1. As can be seen from Table 1 and Fig. 1, the gas phases obtained by heating **2** to 300 —

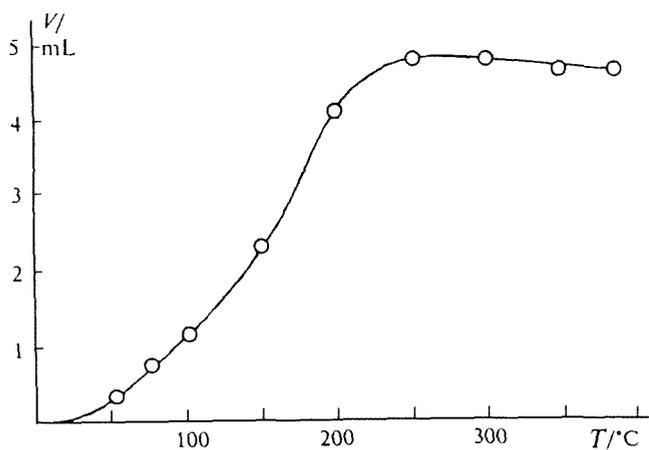


Fig. 1. Curve of gas evolution in the course of thermal decomposition of oligophenylcobaltcarbonylsilane **2** ($m = 0.23\text{ g}$).

400°C in a device equipped with a burette and in sealed tubes differ substantially in composition. In the tube, only CH_4 was detected, whereas in the burette, H_2 , CO , and CH_4 were found. The removal of the gas from the hot zone to the burette prevents the formation of methane, whereas in sealed tubes (in the presence of cobalt compounds at 250°C), carbon monoxide and hydrogen produce methane. Apparently, this is the cause of a certain decrease in the total volume of the gas evolved at 250 and 300°C as compared to that obtained at 200°C .

No organic compounds (benzene, biphenyl, etc.), which could be formed upon elimination of phenyl groups, were found (extraction with ether and analysis by GLC) in the products of thermal decomposition of **2** (both in tubes and in the device equipped with a burette). Apparently, organic compounds undergo graphitization, whereas hydrogen is consumed for the formation of methane in the presence of cobalt compounds at high temperature.

Prior to decomposition and after heating to 100°C , oligomer **2** appears as a brown resin. After heating to 150°C and above, **2** appears as a black brittle substance.

Figure 2 shows the relationships between the specific magnetization and the magnetic field intensity for the samples of oligomer, which were thermally treated in evacuated tubes at 125 , 150 , 200 , 250 , and 300°C for 2 h. It follows from Fig. 2 that the initial compound **2** and the products of its heating to 125 and 150°C are very weak paramagnets. In the temperature range of 25 — 150°C , the magnetic properties remain virtually

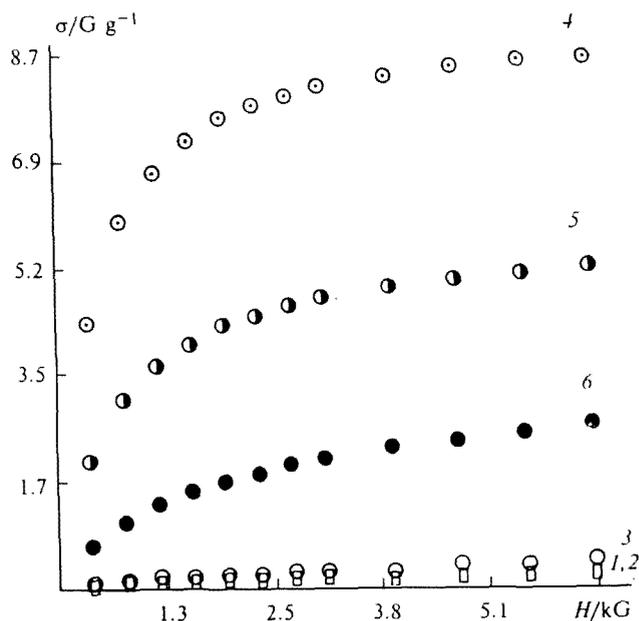


Fig. 2. Dependence of the specific magnetization on the magnetic field intensity (H) for oligophenylcobaltcarbonylsilane **2**: initial (**1**) and heated at the temperature ($^\circ\text{C}$): 125 (**2**), 150 (**3**), 200 (**4**), 250 (**5**), and 300 (**6**).

unchanged. An increase in the temperature to 200 °C causes structural changes, which result in the occurrence of ferromagnetism. However, the contribution of the ferromagnetic component decreases as the temperature increases further. Oligomer **2** heated to 250 °C and particularly to 300 °C exhibits substantially weaker ferromagnetic characteristics than the sample treated at 200 °C. As follows from the results of X-ray phase analysis, these transformations occur in the amorphous state. The relationships observed $\sigma = f(H)$ reflect complex processes, which occur in the oligomer upon heating.

Thermal decomposition of oligo[methyl(phenylethynyl)silane **7** was carried out *in vacuo* by heating the sample slowly (over 4 h) from 20 to 400 °C. When the sample was heated to 200 °C, its IR spectrum remained unchanged. Further increase in the temperature (250–300 °C) caused a substantial degradation of the oligomer. In the IR spectrum, the absorption band at 2140 cm^{-1} ($\text{C}\equiv\text{C}$) disappears, and intensities of the bands at 1240 and 830 cm^{-1} ($\text{Si}-\text{Me}$), and 1580, 750, and 690 cm^{-1} (Ph) decrease. The IR spectrum of the sample of **7**, which was heated to 400 °C and kept at this temperature for 0.5 h, shows a broad band in the region of 1150–800 cm^{-1} . This sample is a cross-linked preceramic phase of silicon carbide.¹⁴

Cobalt-containing oligosilane **8** is stable up to 120 °C. At 150 °C, rapid elimination of CO was observed. The intensities of the absorption bands at 2060, 2040, and 2010 cm^{-1} ($\text{C}=\text{O}$) decrease, and these bands completely

disappear at 180 °C (0.5 h). The weight loss of the sample heated at 500 °C for 1 h and washed with hydrochloric acid (to remove cobalt) was 74%. Figure 3 shows the relationships between the specific magnetization and the magnetic field intensity of oligomer **8** heated at 85, 125, 155, and 180 °C for 2 h and at 500 °C for 1 h. It follows from Fig. 3 that substantial changes in the magnetic properties occur at about 150 °C. In this temperature range, intense elimination of carbon monoxide from the oligomer occurs. Samples heated at 85 and 125 °C are weak paramagnets. The character of curves 4 and 5 (see Fig. 3) indicates that the products of thermal decomposition (at 155 and 180 °C) are mixtures of paramagnets and ferromagnets. When compound **8** was kept at 500 °C for 1 h, the ferromagnetic properties were enhanced substantially. The character of curve 6 indicates that the contribution of the paramagnetic component is minimum. Analysis of the $\sigma = f(H)$ relationships shown in Figs. 2 and 3 demonstrates that the products of thermal decomposition of oligomers **2** and **8** exhibit comparable ferromagnetic properties. The limiting magnetization σ for oligomer **2** is approximately twice as large as that of oligomer **8**. This magnitude is achieved at lower temperature. The contribution of the paramagnetic component for the products of thermal decomposition (180–200 °C) of oligomer **8** is more significant than that for the corresponding products of decomposition of **2**. Heating of oligomer **8** caused a gradual increase in the limiting magnetization, whereas for **2** a more complex temperature dependence of σ was observed.

Therefore, our study demonstrated that two types of cobalt-containing organosilicon oligomers can be obtained by reactions of oligoorganosilanes with dicobalt octacarbonyl. Hydrosilane yields an oligomer in which cobalt carbonyl groups are incorporated into the main chain and form side substituents. Each cobalt atom is bonded to one or two silicon atoms. Ethynylsilane produces an oligomer containing cobalt carbonyl groups only in side organic substituents.

We thank I. L. Vasilevskaya for performing X-ray phase analysis, Yu. A. Kurskii for recording ^1H NMR spectra, and V. I. Kolegov for determining the molecular weight distribution of oligomers.

The work was supported by the International Science Center (Grant 015-94); analyses were carried out in the Analytical Center of the Institute of Organometallic Chemistry of the Russian Academy of Science and were supported by the Russian Foundation for Basic Research (Project No. 95-03-10729g).

References

1. *Uspekhi v oblasti sinteza elementoorganicheskikh polimerov*, [Advances in the Synthesis of Organoelement Compounds], Ed. V. V. Korshak, Nauka, Moscow, 1988, 320 pp. (in Russian).

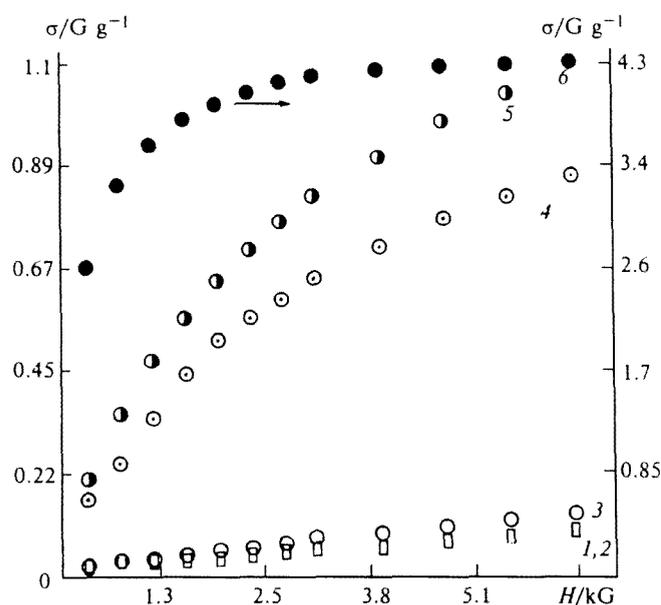


Fig. 3. Dependence of the specific magnetization on the magnetic field intensity (H) for oligomer **8**: initial (**1**) and heated at the temperature (°C): 85 (**2**), 125 (**3**), 155 (**4**), 180 (**5**), and 500 (**6**).

2. S. Kotani, K. Shiina, and K. Sonogashira, *Appl. Organometal. Chem.*, 1991, **5**, 417.
3. K. H. Pannell, J. M. Rozell, and S. Vincenti, in *Silicon-Based Polymer Science. A. Comprehensive Resource, Advan. Chem. Ser.*, **224**, Eds. J. M. Zeigler and F. M. Gordon, Am. Chem. Soc., Washington, DC, 1990, 329.
4. J. M. Zeigler, US. Pat. 4761464, 1989, **61**, No. 7, 50.
5. Jap. Pat. 61-58086, 1986.
6. D. A. Vyakhirev and A. F. Shushunova, *Rukovodstvo po gazovoi khromatografii [Manual on Gas Chromatography]*, Vysshaya Shkola, Moscow, 1987 (in Russian).
7. Z. Marchenko, *Fotometricheskoe opredelenie elementov [Photometrical Determination of Elements]*, Mir, Moscow, 1971, 455 pp. (in Russian).
8. J. F. Harrod and E. Pelletier, *Organometallics*, 1984, **3**, 1064.
9. R. C. Kerber and T. Pakkanen, *Inorg. Chim. Acta*, 1979, **37**, 61.
10. C. Aitken and J. F. Harrod, *J. Organomet. Chem.*, 1985, **279**, C11.
11. R. J. P. Corriu, J. J. E. Moreau, and H. Pract, *Organometallics*, 1989, **8**, 2779.
12. R. J. Corriu, N. Devylder, C. Guerin, B. Henner, and A. Jean, *Organometallics*, 1994, **13**, 3194.
13. V. N. Talanov, E. N. Timofeev, D. Shter, and S. A. Shamshina, *Metalloorg. Khim.*, 1991, **4**, 1036 [*Organomet. Chem. USSR*, 1991, **4** (Engl. Transl.)].
14. R. J. Corriu, C. Guerin, B. Henner, A. Jean, and H. Mutin, *J. Organomet. Chem.*, 1990, **396**, C35.

Received February 14, 1996;
in revised form May 12, 1996