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Ammonolysis of boron-substituted chlorosilylmethyl *ortho*-carborane derivatives*

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We studied the ammonolysis of boron-substituted chlorosilylmethyl *ortho*-carborane derivatives and co-ammonolysis with trimethylchlorosilane. The reaction affords carboranylmethyl(organo)silanes with terminal aminosilane or trimethylsilyl groups. During ammonolysis, the bulky carboranylmethyl groups hinder the intermolecular condensation of intermediate products with aminosilane groups and favors the formation of low-molecular-weight organosilazanes not only from mono- and dichlorosilanes, but also from carboranylmethyltrichlorosilane. The $C_{carborane}$—H groups having the acidic nature were found to be possibly involved in the formation of oligo(carboranylmethyl)silsesquiazane structure and its room-temperature structuring products.

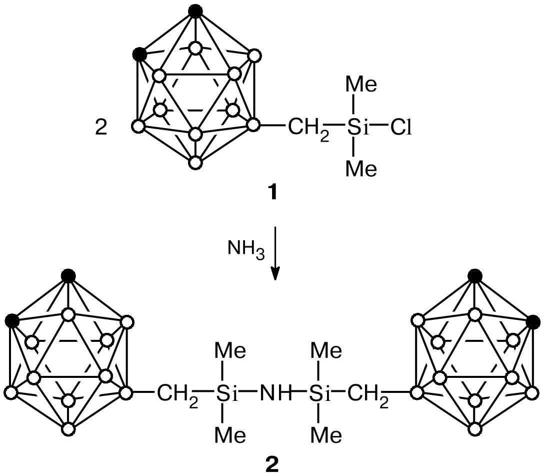
Key words: boron-substituted chlorosilylmethyl *ortho*-carborane derivatives, ammonolysis, organosilazanes.

One of the most important and interesting trends in the chemistry of carborane system is the study of boron-substituted chlorosilylmethyl derivatives. A higher coordination number of boron in carboranes-12 equal to 6 changes dramatically the properties of thereto-bound functional groups compared to those of three-coordinated boron compounds. The boron-substituted chlorosilylmethyl derivatives of carboranes exhibit a high chemical stability to the boron—carbon—silicon bond cleavage and are similar from the chemical viewpoint to the corresponding aliphatic and aromatic derivatives.

The presence of the carboranylmethyl substituent containing the bulky carborane nucleus at the silicon atom would have a considerable effect on the composition and structure of organosilazanes that form upon ammonolysis.

We studied the ammonolysis of carboranylmethyl(organo)chlorosilanes of different functionality (mono-, di-, and trichlorosilanes) in the medium of diethyl ether and toluene. It was found that, depending on the organochlorosilane used, organosilazanes of linear, cyclic, and cyclic spatial structure are produced. For example, ammonolysis of carboranylmethyl(dimethyl)chlorosilane (**1**) yields quantitatively 1,3-di(carboranylmethyl)-1,1,3,3-tetramethyldisilazane (**2**) (Scheme 1).

Scheme 1



A high yield of compound **1** suggests that condensation of intermediate organoaminosilanes with each other proceeds at higher rate than that of organochlorosilane with ammonia.

The presence of two chlorine atoms in carboranylmethyl(methyl)dichlorosilane (**3**) allows the formation of

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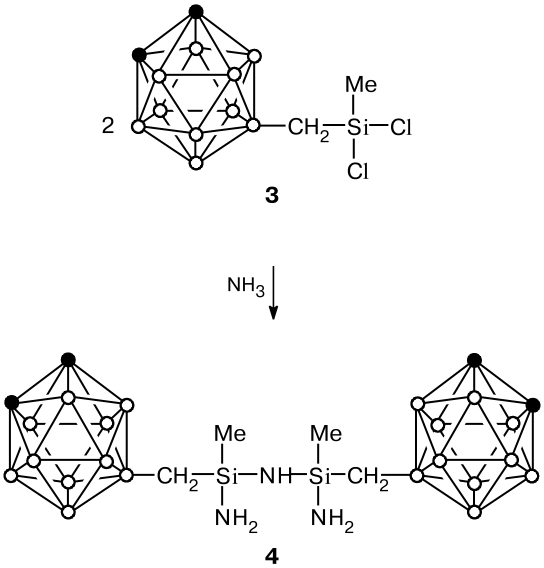
compounds with linear or cyclic silazane bridges. But since the bulky carboranylmethyl group, apparently, hinders the intermolecular condensation of intermediate ammonolysis products, the ammonolysis results in high-yield formation of 1,3-diamino-1,3-di(carboranylmethyl)-1,3-dimethyldisilazane (**4**) (Scheme 2).

Scheme 2

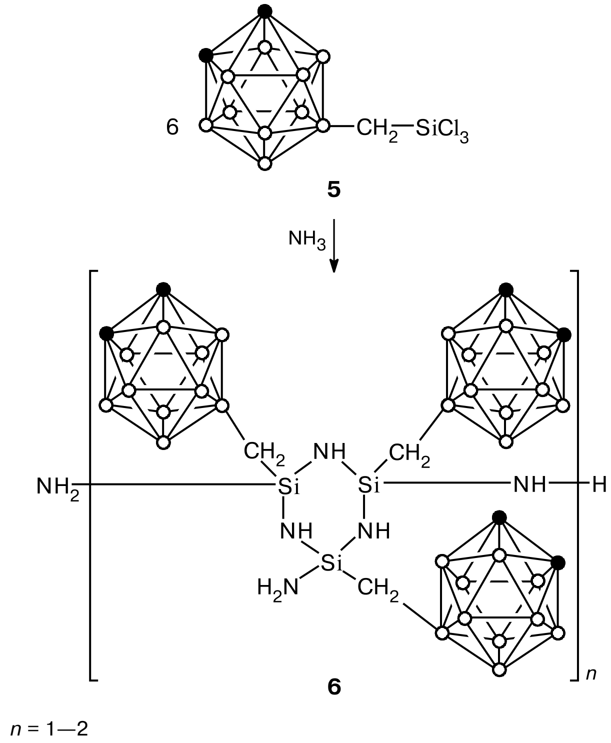


The ammonolysis of carboranylmethyltrichlorosilane (**5**) proceeds by a more complex pathway, since there is a possibility of cross-linking between the chains of products through the silazane bridges, which results in the quantitative formation of oligo(carboranylmethyl)silsesquiazane **6** (Scheme 3).

The distinctive feature of product **6** compared to known oligoorganosilsesquiazanes[1] is its high solubility in diethyl ether, benzene, toluene, chloroform and other solvents, which is caused by a high liophilicity of the carborane core. It should be noted that upon storage of product **6** for one month at room temperature, the aminosilane groups undergo condensation with each other to evolve ammonia. One cannot exclude that due to the acidic nature of the $C_{carborane}$—H hydrogen atoms, there are also chemical bonding between the silazanes and the carborane carbon atoms. As a result of the condensation processes mentioned above, the softening point of product **6** increases by 40—45 °C to reach 180—195 °C.

Based on the behavior of carboranylmethyl(organo)chlorosilanes in the ammonolysis reaction and the structures of products that formed, one can conclude that a specific effect of the carborane core is embodied in the formation of lower-molecular-weight products compared to the ammonolysis of normal organochlorosilanes.[1,2]

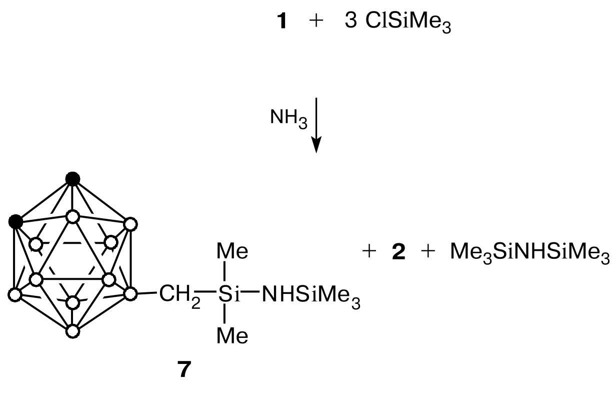
Scheme 3



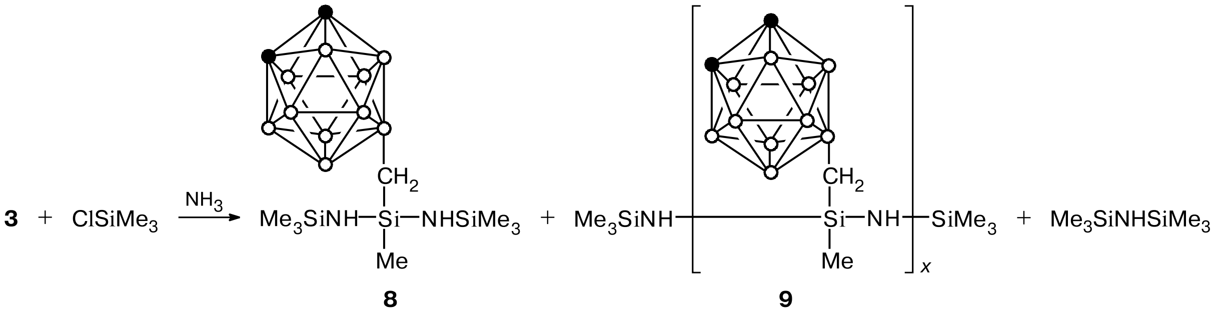
We assumed that ammonolysis of a mixture of carboranylmethyl(organo)chlorosilanes with trimethylchlorosilane will result in the formation of a higher amount of oligomers among the reaction products. For this purpose, we studied the coammonolysis of carboranylmethyl(organo)chlorosilanes with trimethylchlorosilane.

It was found that the coammonolysis of carboranylmethyl(dimethyl)chlorosilane and trimethylchlorosilane taken in equimolar amounts affords a mixture of 1-(carboranylmethyl)-1,1,3,3,3-pentamethyldisilazane (**7**) and 1,3-di(carboranylmethyl)-1,1,3,3-tetramethyldisilazane (**2**) (Scheme 4).

Scheme 4



Scheme 5



When trimethylchlorosilane is taken in the six- or ninefold molar excess, the content of compound **7** in the mixture increases up to 50% or 60%, respectively. Subsequent increase in the molar content of trimethylchlorosilane does not increase the yield of this compound. The fact that even the 18-fold molar excess of trimethylchlorosilane in the mixture does not suppress the formation of compound **2** allows conclusion of a high tendency of the intermediate carboranylmethyl(dimethyl)aminosilane to homocondensation.

The use of carboranylmethyl(methyl)dichorosilane with two chlorine atoms in the molecule results in a considerable complexation of the coammonolysis reaction with trimethylchlorosilane to form a mixture of carborane-containing products: 1,1,1,3,5,5,5-heptamethyl-3-carboranylmethyltrisilazane (**8**), oligocarboranylmethyl(methyl)silazanes (**9**), and hexamethyldisilazane (Scheme 5).

A considerable increase in the trimethylchlorosilane content in the starting mixture (up to 27 moles) had no significant effect on the formation of compound **8** whose yield reached the value of 40%.

The coammonolysis of carboranylmethyltrichlorosilane (**5**) with trimethylchlorosilane affords mainly a mixture of oligomers. When the starting molar ratio between carboranylmethyltrichlorosilane and trimethylchlorosilane was 1 : 30, we succeeded in isolation of a small amount (12%) of tris(trimethylsilylamino)carboranylmethylsilane (**10**) from the resulted mixture (Scheme 6).

The resulted organosilazane products **2**, **4**, **6**—**8**, and **10** are very soluble in diethyl ether, acetone, benzene,

Scheme 6

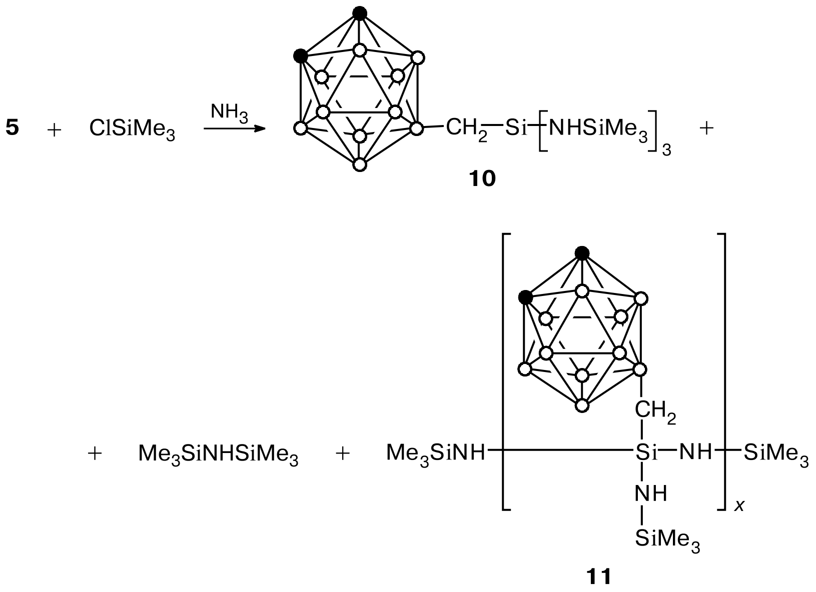


Table 1. Elemental analysis and spectral data for silazanes **2**, **4**, **6**—**8**, and **10**

Silazana	Molecular formula	Found/Calculated (%)					Molecular weight Found*/Calculated	IR, ν/cm^{-1}		
		C	H	B	N	Si		SiNSi	B—H	C_{carb}—H
2	$C_{10}H_{39}B_{20}NSi_2$	26.83	8.72	47.93	3.00	12.11	440	930—945	2610	3090
		26.94	8.81	48.49	3.14	12.59	445			
4	$C_8H_{37}B_{20}N_3Si_2$	22.00	7.99	48.00	9.00	12.00	450	940—950	2610	3090
		21.45	8.32	48.28	9.37	12.54	448			
6	$C_{18}H_{93}B_{60}N_{11}Si_6$	17.11	7.00	51.10	10.30	13.10	1300	950—960	2610	3090
		16.87	7.31	50.63	12.02	13.15	1280			
7	$C_8H_{25}B_{10}NSi_2$	32.00	9.78	35.63	4.28	18.00	300	945	2610	3090
		31.75	9.32	35.72	4.62	18.35	303			
8	$C_{10}H_{36}B_{10}N_2Si_3$	31.02	9.52	29.10	7.00	22.19	370	945	2610	3090
		31.88	9.63	28.70	7.43	22.37	377			
10	$C_{12}H_{43}B_{10}N_3Si_4$	31.89	9.45	24.30	9.35	24.38	450	945	2610	3090
		32.03	9.63	24.02	9.33	24.96	450			

* Ebullioscopy in toluene.

toluene, and other solvents. Some characteristics of these products are given in Table 1.

Thus, upon ammonolysis of boron-substituted chlorosilylmethyl *o*-carborane derivatives and their coammonolysis with trimethylchlorosilane, new carboranylmethyl(organo)silazanes with terminal aminosilane or trimethylsilyl groups were obtained. It was established that, during ammonolysis, the bulky carboranylmethyl groups hinder the intermolecular condensation of intermediate products with aminosilane groups and favor the formation of low-molecular-weight organosilazanes not only from mono- and dichlorosilanes, but also from carboranylmethyltrichlorosilane. The possibility of the $C_{carborane}$—H groups having the acidic nature to be involved in the formation of oligo(carboranylmethyl)silsesquiazane (**6**) and its room-temperature structuring products was found.

Experimental

Boron-containing chlorosilylmethyl derivatives of *o*-carborane were prepared from chloromethyl(organo)chlorosilanes and *o*-carborane according to a known procedure.[3]

1,3-Di(*o*-caboranyl-9-methyl)-1,1,3,3-tetramethyldisilazane (2). A flask equipped with a reflux condenser, stirrer, thermometer, and bubbler for NH_3 supply and cooled with an acetone—dry ice mixture was loaded with carboranylmethyl(dimethyl)chlorosilane (**1**) (15 g, 0.059 mol) in dry diethyl ether (100 mL) and cooled to –50 °C. NH_3 gas was passed with stirring through the mixture so that the reaction temperature was not higher than –30 °C. At pH 10, NH_3 supply was stopped, the reaction mixture was warmed to room temperature, NH_4Cl was separated on a glass filter, and diethyl ether was evaporated. Heptane (30 mL) was added to the residue and the resulted solution was cooled to –20 °C to precipitate crystals of compound **2** (12.2 g, 91.5%). After recrystallization from heptane, the melting point was 150—152 °C.

1,3-Diamino-1,3-di(*o*-caboranyl-9-methyl)-1,3-dimethyldisilazane (4) was obtained according to the analogous procedure from carboranylmethyl(methyl)dichlorosilane (**3**) (16.24 g, 0.059 mol) in yield of 11 g (82%) as a colorless oily liquid.

Oligo(*o*-caboranyl-9-methyl)silsesquiazane (6) was obtained according to the analogous procedure from (carboranylmethyl)trichlorosilane (17.5 g, 0.059 mol) in yield of 10.4 g (81%) as a white amorphous powder with a softening point of 140—150 °C.

1-(*o*-Caboranyl-9-methyl)-1,1,3,3,3-pentamethyldisilazane (7). A flask equipped with a reflux condenser, stirrer, thermometer, and bubbler for NH_3 supply and cooled with a acetone—dry ice mixture was loaded with carboranylmethyl(dimethyl)chlorosilane (**1**) (15 g, 0.059 mol), trimethylchlorosilane (6.5 g, 0.059 mol), and dry diethyl ether (160 mL) and cooled to –50 °C. NH_3 gas was passed with stirring through the mixture so that the reaction temperature was not higher than –40 °C. At pH 10, the NH_3 supply was stopped, the reaction mixture was warmed to room temperature, and NH_4Cl was separated on a glass filter. Distillation at 145—146 °C (2 Torr) yielded compound **7** (4.53 g, 25%) as a heavy-bodied liquid with n_D^{20} = 1.500. Heptane (30 mL) was added to the residue and the resulted solution was cooled to –20 °C to precipitate crystals of compound **2** (2.4 g, 18%).

1,1,1,3,5,5,5-Heptamethyl-3-(*o*-caboranyl-9-methyl)trisilazane (8) was prepared according to the analogous procedure from carboranylmethyl(methyl)dichlorosilane (**3**) (16.26 g, 0.059 mol) and trimethylchlorosilane (8.68 g, 0.059 mol). After distillation at 160—161 °C (2 Torr), compound **8** (4.4 g, 19.5 %) was obtained as a colorless viscous liquid with n_D^{20} = 1.5135.

Tris(trimethylsilylamino)-*o*-caboranyl-9-methylsilane (10) was prepared according to the analogous procedure from (carboranylmethyl)trichlorosilane (**5**) (17.5 g, 0.059 mol) and trimethylchlorosilane (10.86 g, 0.059 mol). After distillation at 175—176 °C (2 Torr), compound **10** (1.62 g, 6%) was obtained as a colorless viscous liquid with n_D^{20} = 14934.

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