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New preparative Grignard synthesis of (*m*-carboranylmethyl)siloxanes from chlorodimethylsiloxanes

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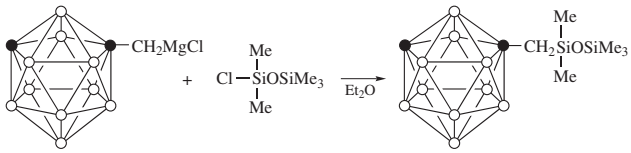
New *m*-carborane-containing siloxanes were obtained by the Grignard reaction based on chloromethyl-*m*-carboranes and chlorodimethylsiloxanes. In case of (7-methyl-*m*-carboran-1-yl)methyl chloride, side processes of isomerization and transmetalation do not occur, which provides the yield of the desired product as high as 87%.

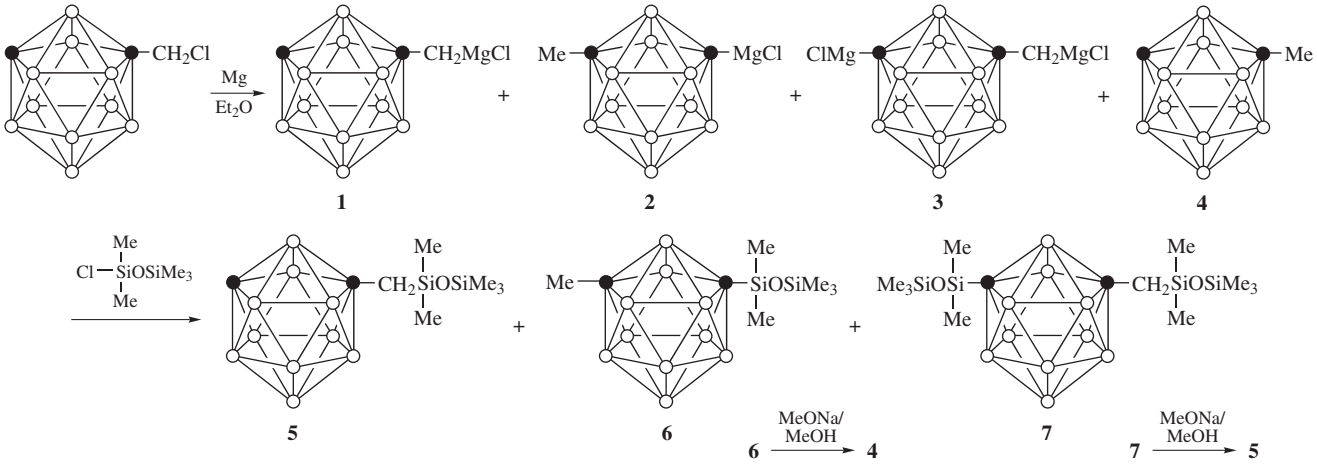


Carborane-containing organosiloxanes and polyorganosiloxanes[1] are prepared from carborane organometal derivatives, cross-coupling methods being successfully employed. Monomers of 1,7-bis[bromo(organo)silylmethyl]-*m*-carborane type were synthesized[2] as precursors for obtaining new organosiloxanes with 1,7-bis(dimethylsilylmethyl)-*m*-carborane units in the chain.[3] Precursors for carborane-containing polysiloxanes, such as *N*,*N*′-bis(3-trialkoxysilylpropyl)-*m*-carborane-1,7-dicarboxamides were synthesized from 3-aminopropyltrialkoxysilanes and *m*-carboranedicarboxylic acid or its chloride.[4,5] Boron-substituted carborane-containing siloxanes of linear or silsesquioxanes structure also look promising.[6,7]

Recently,[8,9] we have prepared carborane-containing siloxanes from alkoxysilanes and chlorosilanes by the Grignard reaction. In the present work, this reaction was employed for obtaining *m*-carborane-containing siloxanes from chlorodimethylsiloxanes. Previously, (*m*-carboran-1-yl)lithium and low-active carbofunctional chloromethyl(dimethyl)siloxanes were used for this purpose.[10] In such a reaction, the siloxane bond cleavage does actively occur, which causes formation of much by-products and decrease in the yield of the target compound by 30–40%.

In our hands, the reaction of (*m*-carboran-1-yl)methylmagnesium chloride **1** with an excess of 1-chloro-1,1,3,3,3-pentamethyldisiloxane in diethyl ether (Scheme 1) gives rise to a mixture containing target (1,1,3,3,3-pentamethyldisiloxanylmethyl)-*m*-carborane **5** as the main component. Obviously, the reaction between (*m*-carboran-1-yl)methyl chloride and magnesium metal affords mainly species **1** which would partially transform into monomagnesium compound **2**, dimagnesium derivative **3** and 1-methyl-*o*-carborane **4**. The ratio between these species was determined by the bromination method.[9] 1-Chloro-1,1,3,3,3-pentamethyldisiloxane when reacted with the mixture of monomagnesium species **1** and **2** and dimagnesium one **3** gives the target compound **5** and by-products such as 1-(1,1,3,3.3-pentamethyldisiloxanyl)-7-methyl-*m*-carborane **6** and 1-(1,1,3,3,3-pentamethyldisiloxanylmethyl)-7-(1,1,3,3,3-pentamethyldisiloxanyl)-*m*-carborane **7** along with methylcarborane **4**. To increase the yield of the desired compound **5**, the final mixture of products was treated with catalytic amounts of sodium methoxide in methanol solution at room temperature to cause the cleavage of Si–carborane bond. As a result, by-product **6** transformed into compound **4**, and compound **7** provided an additional crop of the target product **5** (see Scheme 1).[†]

The preparative yield of compound **5** was 73%. The formation of silicon-containing mixture of products **5**–**7** indicates a moderate selectivity of formation of the initial Grignard reagent **1** in diethyl



Scheme 1

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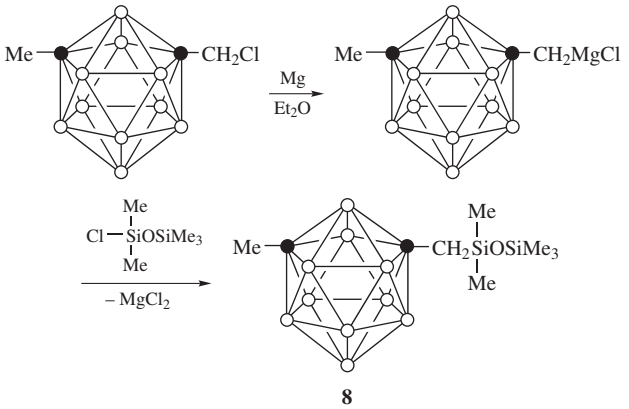
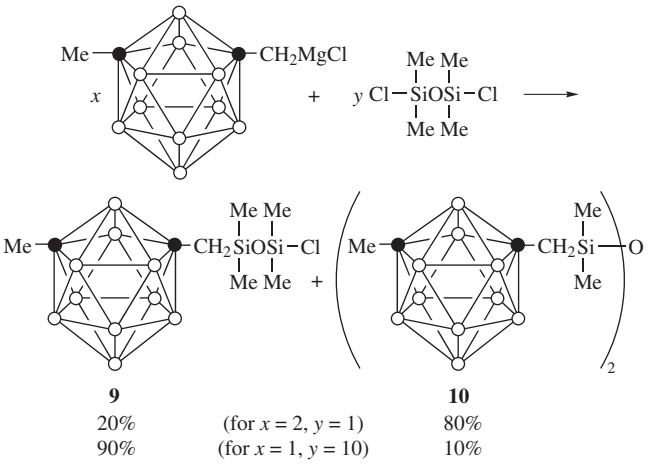


Scheme 2

ether. We reasoned that the use of 1-dichloromethyl-*m*-carboranes with blocked 7-CH position in the reaction with magnesium metal would allow us to avoid isomerization and transmetalation processes and thus improve the yield of the target Grignard reagent. In fact, (7-methyl-*m*-carboran-1-yl)methyl chloride afforded the corresponding organomagnesium compound in 93% yield, which upon treatment with 1-chloro-1,1,3,3,3-pentamethyldisiloxane gave 1-(1,1,3,3,3-pentamethyldisiloxanylmethyl)-7-methyl-*m*-carborane **8** in a yield up to 87% (Scheme 2).‡



Scheme 3

The reaction between the same Grignard reagent and 1,3-dichloro-1,1,3,3-tetramethyldisiloxane, depending on their ratio, leads to substitution products of one or two chlorine atoms, compounds **9** or **10**, respectively (Scheme 3). With raising the relative content of dichlorodisiloxane to 10 equiv., the quantity of monosubstituted product **9** increases up to 90%, whereas the percentage of disubstituted product **10** can reach 80% relying on stoichiometry.§

In summary, the new synthesis of *m*-carboranylmethyl-containing organosiloxanes from chlorodimethylsiloxanes by the Grignard reaction was accomplished. The high yields of the products provides a good prospect for the chemistry of carborane-containing organosilicon compounds.

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† *Synthesis of (1,1,3,3,3-pentamethyldisiloxanylmethyl)*-m-*carborane* **5**. (*m*-Carboran-1-yl)methylmagnesium chloride (10.85 g, 0.05 mol) in absolute diethyl ether (70 ml) was added dropwise under stirring to a solution of 1-chloro-1,1,3,3,3-pentamethyldisiloxane (36.6 g, 0.2 mol) in absolute benzene (280 ml). The mixture was refluxed for 3 h and cooled. Then 1% sodium methoxide solution in methanol (10 ml) was added, and the mixture was refluxed with stirring for 1 h. After cooling, it was washed with distilled water, the organic layer was dried over $MgSO_4$ and concentrated on a rotary evaporator. 1-Methyl-*m*-carborane **4** was distilled off from the mixture *in vacuo* to leave (1,1,3,3,3-pentamethyldisiloxanylmethyl)-*m*-carborane **5** (11.1 g, 73%) in the residue; mp 118–119 °C. IR (KBr, ν/cm^{-1}): 2600, 3070 (B–H, H–CB), 2980, 2900 (Si–CH_2), 1120–1030 (Si–O–Si). ^{1}H NMR ($CDCl_3$) δ: 0.25 (s, 6H, MeSi), 1.40 (s, 2H, CH_2), 2.94 (s, 1H, H–CB). Found (%): C, 31.51; H, 9.15; B, 35.58; Si, 18.20. Calc. for $C_8H_{28}B_{10}OSi_2$ (%): C, 31.54; H, 9.26; B, 35.49; Si, 18.44.

‡ *Synthesis of 1-(1,1,3,3,3-pentamethyldisiloxanylmethyl)-7-methyl*-m-*carborane* **8**. (7-Methyl-*m*-carboran-1-yl)methylmagnesium chloride (11.55 g, 0.05 mol) in absolute diethyl ether (70 ml) was added dropwise under stirring to 1-chloro-1,1,3,3,3-pentamethyldisiloxane (18.3 g, 0.1 mol) in absolute benzene (70 ml). The mixture was refluxed for 3 h, cooled, washed with distilled water, the organic phase was dried over $MgSO_4$ and concentrated on a rotary evaporator. Then volatile products were distilled off *in vacuo* to leave product **8**; mp 138–139 °C. IR (KBr, ν/cm^{-1}): 2600 (B–H, H–CB), 2980, 2900 (Si–CH_2), 1120–1035 (Si–O–Si). ^{1}H NMR ($CDCl_3$) δ: 0.23 (s, 6H, MeSi), 1.54 (s, 2H, CH_2), 1.70 (s, 3H, Me–CB). Found (%): C, 34.10; H, 9.60; B, 34.60; Si, 17.10. Calc. for $C_9H_{30}B_{10}OSi_2$ (%): C, 33.92; H, 9.48; B, 33.93; Si, 17.63.

§ *Synthesis of 1-(chloro-1,1,3,3-tetramethyldisiloxanylmethyl)-7-methyl*-m-*carborane* **9** *and 1,3-bis(1-methyl*-m-*carboranylmethyl)-1,1,3,3-tetramethyldisiloxane* **10**. 1,3-Dichloro-1,1,3,3-tetradisiloxane (10.15 g, 0.05 mol) in absolute benzene (70 ml) was added dropwise under stirring to (7-methyl-*m*-carboran-1-yl)methylmagnesium chloride (23.1 g, 0.1 mol) in absolute diethyl ether (140 ml). The mixture was refluxed for 3 h, cooled, filtered through a glass filter and concentrated on a rotary evaporator. Distillation *in vacuo* afforded 6.78 g (20%) of product **9** (bp 45 °C/1 Torr, mp 166–168 °C). IR (KBr, ν/cm^{-1}): 2600 (B–H, H–CB), 2980, 2900 (Si–CH_2), 1120–1035 (Si–O–Si). ^{1}H NMR ($CDCl_3$) δ: 0.23 (s, 6H, C–Si–Me), 0.30 (s, 6H, Cl–Si–Me), 1.57 (s, 2H, CH_2), 1.73 (s, 3H, Me–CB). Found (%): C, 28.12; H, 8.00; B, 31.57; Si, 16.71. Calc. for $C_8H_{27}B_{10}OSi_2Cl$ (%): C, 28.33; H, 8.02; B, 31.88; Si, 16.56.

The further distillation of the residue at 61 °C (1 Torr) afforded 18.9 g (80%) of product **10** as an oil. IR (KBr, ν/cm^{-1}): 2600 (B–H, H–CB), 2980, 2900 (Si–CH_2), 1120–1035 (Si–O–Si). ^{1}H NMR ($CDCl_3$) δ: 0.27 (s, 12H, MeSi), 1.53 (s, 2H, CH_2), 1.77 (s, 3H, Me–CB). Found (%): C, 30.43; H, 8.73; B, 45.85; Si, 11.78. Calc. for $C_{12}H_{42}B_{20}OSi_2$ (%): C, 30.35; H, 8.91; B, 45.53; Si, 11.83.