

A facile route for the syntheses of trisilanes containing *C*-mono-substituted carborane

LUO, Yu-Mei(骆玉美) LIU, Fei(刘菲) WU, Shi-Hui*(吴世晖)

Department of Chemistry, Fudan University, Shanghai 200433, China

The syntheses of trisilanes containing *C*-monosubstituted *o*-carborane are described. The intermediate compound, 2-chloro-2-phenyl-hexamethyltrisilane, was prepared by elimination reaction between 2, 2-diphenylhexamethyltrisilane and hydrogen chloride with a catalytic amount of aluminum chloride in chloroform solution.

Keywords Synthesis, trisilane, carborane

Introduction

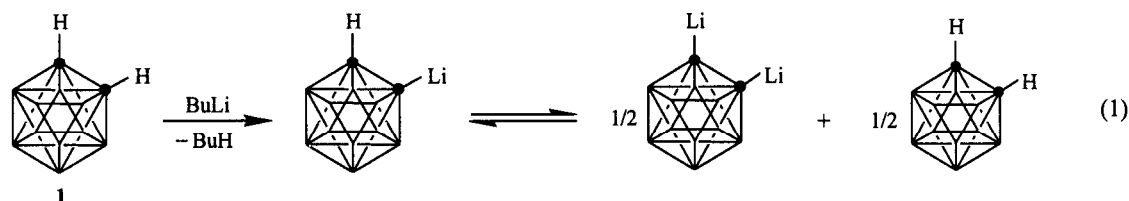
Linear trisilanes, $RR'Si(SiMe_3)_2$, are convenient photochemical precursors for the generation of silylenes.¹ Many trisilanes have been synthesized, and some of them contain bulky groups (The trisilanes containing bulky groups may generate new kind of silylenes-triplet silylenes),^{2,4} but there is no example of a trisilane containing a *C*-monosubstituted carborane. Carboranes have

been often described as three-dimensionally aromatic in analogy to the two-dimensional benzene rings, and have been characterized as "superaromatic". Carboranes show both electronwithdrawing character and bulky steric effect in many reactions.⁵ For the exploration of new silylenes, the hexamethyltrisilanes containing mono- and di-carboranyl groups were designed and synthesized.

Results and discussion

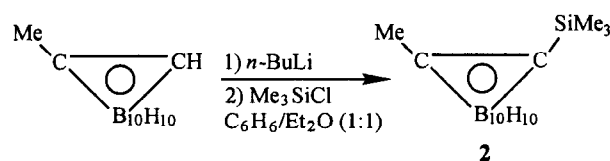
Silanes containing *o*-carboranyl group, such as dimethyldi(*o*-carboranyl)-silane,⁶ trimethylsilyl-*o*-carborane⁷ and 1-trimethylsilyl-2-methoxy(di-methyl)-silyl-methyl-*o*-carborane,⁸ have been reported. In general, organosilicon compounds with carboranyl groups have received little attention. The conventional syntheses of *C*-monosubstituted *o*-carboranes lead to the undesired di-*C*-substituted product as well.⁵

Scheme 1



In our laboratory, 1-methyl-2-trimethylsilyl-*o*-carborane (**2**) was prepared as a model compound in the yield of 85% by the reaction of 1-methyl-*o*-carborane with *n*-BuLi, followed by treatment with chlorotrimethylsilane (Scheme 2). The structure of **2** could be readily confirmed by spectrometric analysis.

Scheme 2



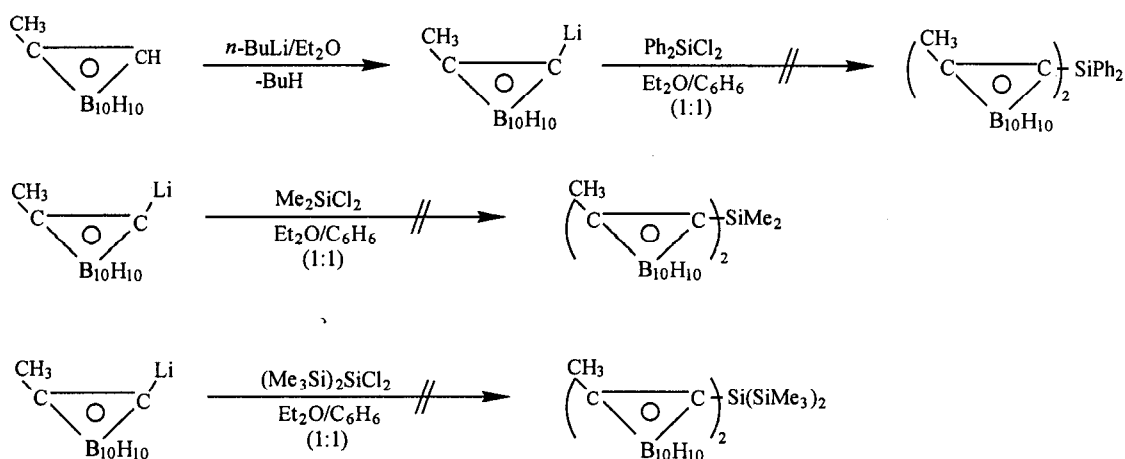
Received March 8, 2000; accepted June 9, 2000.

Project (No. 29272040) supported by the National Natural Science Foundation of China

The syntheses of diphenyldi(1-methyl-*o*-carboranyl)silane and dimethyl-di(1-methyl-*o*-carboranyl)silane by a similar method failed. And the attempts to prepare 2,2-di(2-methyl-*o*-carboranyl)hexamethyltri-

silane using the same approach were also in vain, since the Si—Si bond length (0.234 nm) is longer than the C—Si distance (0.186—0.190 nm) (Scheme 3).

Scheme 3



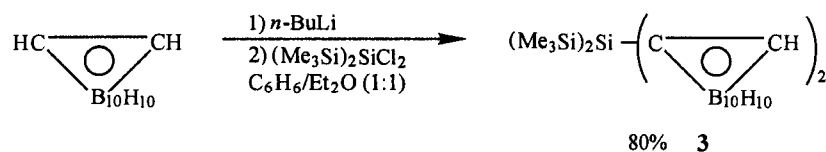
The above synthesis may illustrate that the presence of the *ortho*-methyl group in 1-methyl-*o*-carborane hinders the reaction between the lithiated substrate and the chlorosilanes.

For the synthesis of monosubstituted *o*-carborane, Hawthorne *et al.*⁹ reported an approach that protected one carbon atom of *o*-carborane with a *t*-butyldimethylsilyl (TBDMS) group. In our laboratory, a facile route

for the synthesis of trisilane containing *C*-monosubstituted *o*-carborane was attained using steric effect.

By the reaction of lithiated *o*-carborane and 2,2-dichlorohexamethyl-*t*risilane, 2,2-di(*o*-carboranyl)hexamethyltrisilane (**3**) was obtained in 80% yield (Scheme 4). It could be recrystallized from hexane, to give a pure sample, mp 79—80°C.

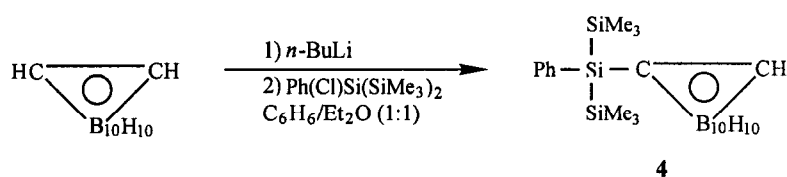
Scheme 4



The 2-phenyl-2-(*o*-carboranyl) hexamethyltrisilane (**4**) was synthesized similarly. The substrate, 2-chloro-2-phenylhexamethyltrisilane, was obtained by the elimination reaction between 2,2-diphenylhexamethyltri-

lane^{10,11} and hydrogen chloride with aluminum chloride in chloroform solution.¹² The yield of this chlorosilane was 74% (Scheme 5).

Scheme 5



Compounds **2** and **4** are stable. Compound **3** is not stable at room temperature, as time went on, some of **3** decomposed. Therefore good results of elemental analysis and mass spectrum can not be obtained for compound **3**.

We tried to generate the carborane containing silylene by irradiation of **4**. In the presence of cyclohexene and methanol, the main photolytic product was *o*-carborane. It might come from the decomposition of **4** itself.

Conclusion

2-Phenyl-2-(*o*-carboranyl) hexamethyltrisilane and 2,2-di(*o*-carboranyl)-hexamethyltrisilane have been synthesized by the reaction of 2-chloro-2-phenyl-hexamethyltrisilane and 2,2-dichlorohexamethyltrisilane with carboranyl lithium, respectively. The intermediate compound, 2-chloro-2-phenylhexamethyltrisilane, was prepared by elimination reaction between 2, 2-diphenylhexamethyltrisilane and hydrogen chloride with a catalytic amount of aluminum chloride in chloroform solution. Moreover this result suggests that other highly hindered trisilane containing *C-o*-carboranyl group may be prepared by this method.

Experimental

Anhydrous ether and benzene were heated with sodium and distilled under nitrogen atmosphere before use. 2, 2-Dichlorohexamethyltrisilane^{3, 10} and 2, 2-diphenylmethyl-trisilane^{10, 11} were prepared by literature procedures.

Spectroscopic measurements

Melting points were uncorrected. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. Infrared spectra were recorded on a Nicolet 5DX FT-IR spectrophotometer. Nuclear magnetic resonance spectra were recorded on a JNM-PMX 60 SI (60 MHz, JEOL) spectrometer and a Bruker MSL-300 spectrometer. Mass spectra were obtained on a Finnigan-MAT 4501 GC/MS spectrometer. Preparative gas chromatography was performed on a Shanghai 102 gas chromatograph with a thermal conductivity detector, hydrogen being used as carrier gas. The collections were conducted on a 6.3mm × 3m 20% SE-30 aluminum column.

*Synthesis of 2-chloro-2-phenylhexamethyltrisilane*¹³

In a 100-mL three-necked flask equipped with a magnetic stirring bar, condenser and inlet tube for hydrogen chloride, was placed a mixture of 2,2-diphenylhexamethyltrisilane (9.0 g, 37 mmol) dissolved in 40 mL of dry chloroform and 0.5 g of anhydrous aluminum chloride. Dry hydrogen chloride was introduced into the stirred solution at room temperature. After 3 h, the starting 2,2-diphenylhexamethyltrisilane was transformed into 2-chloro-2-phenylhexamethyltrisilane. Dry acetone (1 mL) was then added to the mixture in order to deactivate the catalyst. Solvent was removed under vacuum with a rotary evaporator, followed by distillation under reduced pressure to give 5.8 g (72.8%) of 2-chloro-2-phenylhexamethyltrisilane, a colorless liquid, bp 124—126°C/0.6 mm Hg. IR (KBr, cm⁻¹): 3062, 2957, 2901, 1992, 1903, 1872, 1647, 1443, 1430, 1402, 1320, 1249, 1120, 1111, 1061, 841, 785, 744, 697. ¹H NMR (δ, CCl₄, CH₂Cl₂ as inner standard): 0.30 (s, 18H, Me₃Si), 7.20—7.70 (m, 5H, ring protons).

Synthesis of 1-methyl-2-trimethylsilyl-o-carborane (2)

To a solution of 1-methyl-*o*-carborane (0.154 g, 0.97 mmol) in a dry benzene/diethyl ether (1:1) mixture (10 mL) at 0°C was added dropwise 1.2 mL (0.97 mmol) of a 0.8 M solution of *n*-BuLi in hexane with stirring. The mixture was continued to stir for 1 h at ambient temperature. The solution was cooled to 0°C again and trimethylchlorosilane (0.105 g, 0.97 mmol) in 10 mL of mixture of benzene/diethyl ether (1:1) was added dropwise. After being refluxed overnight, the solution was quenched with 5 mL of water and transferred to a separatory funnel and diluted with 10 mL of diethyl ether. The layers were separated and the aqueous layer was extracted with additional Et₂O (3 × 30 mL). The combined extracts were then dried over anhydrous MgSO₄. Solvent was removed under vacuum with a rotary evaporator, and gave 0.190 g (85%) of **2**, a light yellow solid. A pure sample was collected from a 3m 20% SE-30 chromatographic column, mp 70—71°C. IR (KBr, cm⁻¹): 2966, 2960, 2614, 2590, 2541, 2355, 2325, 1559, 1540, 1255, 867, 849. ¹H NMR (δ in CDCl₃): 0.32 (s, 9H), 2.00 (s, 3H), 1.10—3.50

(m, 10H). MS m/z (relative intensity): 232 (M^+ ($C_6H_{22}B_{10}Si$), 1.27), 73(100). Anal. $C_6H_{22}B_{10}Si$. Calcd: C, 31.28, H, 9.62. Found: C, 31.78, H, 9.76.

Synthesis of 2,2-di(*o*-carboranyl) hexamethyltrisilane (3)

To a solution of *o*-carborane (1.0 g, 7.7 mmol) in a dry benzene/diethyl ether (1:1) mixture (10 mL) at 0°C was added dropwise 9.6 mL (7.7 mmol) of a 0.8 M solution of *n*-BuLi in hexane with stirring. The mixture was allowed to warm to ambient temperature and stir for 1 h. The solution was cooled to 0°C again and 2,2-dichlorohexamethyltrisilane (0.9 g, 0.35 mmol) in 10 mL mixture of benzene/diethyl ether (1:1) was added dropwise. The solution was refluxed overnight and then quenched with 10 mL of water, transferred to a separatory funnel, and diluted with 20 mL of diethyl ether. The layers were separated and the aqueous layer was extracted with additional Et_2O (3×30 mL). The combined extracts were then dried over anhydrous $MgSO_4$. Solvent was removed under vacuum with a rotary evaporator. The residue was recrystallized from *n*-hexane to give 1.6 g (80%) of **3**, a colorless crystalline solid. mp 79—80°C. IR (KBr, cm^{-1}): 2966, 2603, 2572, 2355, 2325, 1716, 1698, 1559, 1540, 1255, 867, 849. 1H NMR (δ in $CDCl_3$): 0.22(s, 18H), 3.30(s, 2H), 1.10—3.36(m, 20H). MS m/z : 216 ($C_2B_{10}H_{11}Si_2$, 4.64), 739 (Me_3Si , 100). Precise mass for $C_2B_{10}H_{11}SiSiCH_3$: 216.1565, found: 216.2155; for $C_2B_{10}H_{11}SiSi$: 201.1330, found: 201.1885.

Synthesis of 2-phenyl-2-(*o*-carboranyl) hexamethyltrisilane (4)

To a solution of *o*-carborane (2.0 g, 13.9 mmol) in a dry benzene/diethyl ether (1:1) mixture (10 mL) at 0°C was added dropwise 17.3 mL (13.9 mmol) of a 0.8 M solution of *n*-BuLi in hexane with stirring. The mixture was allowed to warm to ambient temperature and stir for 1 h. The solution was cooled to 0°C again and 2-chloro-2-phenylhexamethyltrisilane (4.0 g, 13.7 mmol) in 10 mL mixture of benzene/diethyl ether (1:1) was added dropwise. After being refluxed overnight the solution was quenched with 10 mL of water and transferred to a separatory funnel and diluted with 10 mL of diethyl ether. The layers were separated and the aqueous layer

was extracted with additional Et_2O (3×20 mL). The combined extracts were then dried over anhydrous $MgSO_4$. Solvent was removed under vacuum with a rotary evaporator. The residue was recrystallized from *n*-hexane to give 4.6 g (83.7%) of **4**, a colorless crystalline solid. The melting point of compound **4** is 145—146°C. UV (in cyclohexane): $\lambda_{max} = 233$ nm. IR (KBr, cm^{-1}): 3050, 2960, 2954, 2899, 2590, 2355, 2325, 1698, 1686, 1540, 1522, 1243, 837, 734, 697. 1H NMR (δ in $CDCl_3$): 0.34(s, 18H), 2.88(s, 1H), 1.25—3.18(m, 10H), 7.39—7.51(m, 5H). MS m/z (relative intensity): 396 (M^+ ($C_{14}H_{34}B_{10}Si_3$), 1.18), 73(100). Anal. $C_{14}H_{34}B_{10}Si_3$. Calcd: C, 42.59; H, 8.68. Found: C, 42.38; H, 9.02.

Acknowledgments

We thank professor Maitland Jones, Jr. (Princeton University) for the gifts of *o*-carborane and 1-methyl-*o*-carborane, and helpful discussions.

References

1. For a review see: Ishikawa, M.; Kumada, M., *Adv. Organomet. Chem.*, **19**, 51(1981).
2. Ando, W.; Fujita, M.; Yoshita H.; Sekiguchi, A., *J. Am. Chem. Soc.*, **110**, 3310(1988).
3. Pae, D.H.; Xiao, M.; Chiang, M.Y.; Gaspar, P.P., *J. Am. Chem. Soc.*, **113**, 1281(1991).
4. Zhang, S.; Glnseller, P.E.; Colin, R.T., *J. Am. Chem. Soc.*, **113**, 4278(1991).
5. Bregradze, V.I., *Chem. Rev.*, **92**, 209(1992).
6. Zakharkin, L.I.; Shemyakin, N.F., *Zh. Obshch. Khim.*, **44**, 1085(1974).
7. Papetti, S., *U. S.*, **3**, 137, 719 [*Chem. Abstr.*, **61**, 5692 (1964)].
8. Kalinin, V.N.; Izmailov, B.A.; Kazantsev, A.A.; Myakushev, V.D.; Zhdanov A.A.; Zakharkin, L.I., *J. Organomet. Chem.*, **216**, 295(1981).
9. Gomez, F.A.; Hawthorne, M.F., *J. Org. Chem.*, **57**, 1384(1992).
10. Jackson, R.A.; Rhodes, C.J., *J. Organomet. Chem.*, **336**, 45(1987).
11. Tortorelli, V.J.; Jones, M.Jr.; Wu, S.-H.; Li, Z.-H., *Organometallics*, **2**, 759(1983).
12. Ishikawa, M., *Organometallic Syntheses*, Ed. King, R.B.; Eisch, J.J., Vol. 3, Elsevier Science Publishers B.V., Amsterdam, 1986, p.498.
13. Oka, K.; Nakao, R., *Chem. Express*, **4**, 789(1989).