

Study of the transmetallation of silicon derivatives of *o*-carboranes on treatment with BuⁿLi

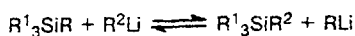
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Silyl-substituted *o*-carboranes 1-R-2-Me₃Si(CH₂)_n-1,2-C₂B₁₀H₁₀ (R = Me, Ph; *n* = 0, 1) undergo transmetallation on treatment with BuⁿLi to form lithium derivatives of *o*-carboranes, 1-R-2-Li(CH₂)_n-1,2-C₂B₁₀H₁₀, where *n* = 0, 1. A silicon derivative of *o*-carborane, 1-Ph-2-(Me₃SiCHPh)-1,2-C₂B₁₀H₁₀, undergoes neither transmetallation nor metallation at the benzyl CH-group on treatment with BuⁿLi due to significant steric hindrance.

Key words: silyl-substituted *o*-carboranes, transmetallation, *n*-butyllithium, lithium derivatives of *o*-carboranes.

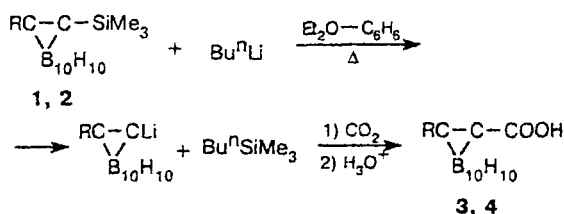
The transmetallation method is used rather widely in the synthesis of organolithium compounds. In particular, it is used for the synthesis of vinyl and acetylene derivatives of lithium from vinyl and acetylene derivatives of silicon.¹



R = CH=CHR³, C≡CR³

Under ordinary conditions, arylsilanes do not undergo exchange reactions with aliphatic lithium compounds.^{2,3} The transmetallation of organosilicon derivatives of carboranes with organolithium compounds has not yet been studied.⁴

We found that trimethylsilyl derivatives of *o*-carboranes (1, 2), in which the silicon atom is bound to the six-coordinate carbon atom of the *o*-carborane ring, undergo transmetallation with BuⁿLi in an ether-benzene solution according to the scheme:



R = Ph (1, 3); R = Me (2, 4)

Transmetallation occurs rather slowly on heating the reaction mixture, and the behavior of silylcarboranes in this reaction is similar to that of silylacetylene

PhC≡CSiPh₃.⁵ The structure of lithiocarboranes in the reaction products was confirmed by obtaining the corresponding carboranecarboxylic acids 3 and 4 on treatment of the reaction mixture with CO₂.

It should be noted that the C—Si bond in 1-silyl-*o*-carborane derivatives readily undergoes hydrolysis on treatment with aqueous and alcoholic solutions of bases to give *o*-carborane and R₃SiOH.⁴ In this case, the ease of cleavage of the C—Si bond is caused not only by the strong electron-withdrawing properties of the 1-*o*-carboranyl group but also by the high affinity of the oxygen atom to the silicon atom.⁴

The transmetallation of aliphatic silicon compounds, containing the Si—C_{sp}³ σ-bond, with organolithium compounds is not known.¹ Such transmetallation has only been reported for derivatives of highly strained three- and four-membered silacycloalkanes.^{6,7}

We also studied the reaction of butyllithium with 1-R-2-Me₃SiCH₂-1,2-C₂B₁₀H₁₀ compounds, where R = Ph (5) or Me (6), obtained by treatment of Me₃SiCH₂I with 1-R-2-Li-1,2-C₂B₁₀H₁₀ in an ether-benzene solution. It could be anticipated that not only transmetallation but also metallation on the CH₂ group would occur, because the CH-acidity of the compounds 1-R-2-Me₃SiCH₂-1,2-C₂B₁₀H₁₀ is much higher due to the stabilization of the carbanion by the Me₃Si group.^{8,9} Such metallation has been observed in the case of 1-R-2-XCH₂-1,2-C₂B₁₀H₁₀ (X = OCH₃, Cl).^{10,11}

However, the effect of the Me₃Si group on the acidity of methylene protons in compounds 5 and 6 was found to be insignificant. Therefore, metallation on the CH₂ group on treatment with BuⁿLi in an ether-benzene solution does not occur. Only transmetallation takes place according to the scheme

1-Phenyl-2-(trimethylsilylmethyl)-*o*-carborane (5) was obtained similarly. ^1H NMR for compound 5 (C_6D_6), δ : -0.28

(s, 9 H, $(\text{CH}_3)_3\text{Si}$); 1.01 (s, 2 H, CH_2); 6.82–7.36 (m, 5 H, Ph). Found (%): C, 47.11; H, 8.62; Si, 9.21. $\text{C}_{12}\text{H}_{26}\text{B}_{10}\text{Si}$. Calculated (%): C, 47.05; H, 9.49; Si, 9.15.

1-Methyl-2-(trimethylsilylmethyl)-o-carborane (6). Similarly to the experiment above, the reaction of 1-methyl-o-carborane (1.6 g, 0.01 mol) and $\text{Me}_3\text{SiCH}_2\text{I}$ (2.2 g, 0.01 mol) gave 2 g (80%) of compound 6, m.p. 68–69 °C (hexane). ^1H NMR (C_6D_6), δ : -0.15 (s, 9 H, $(\text{CH}_3)_3\text{Si}$); 0.81 (s, 3 H, CH_3); 1.22 (s, 2 H, CH_2). Found (%): C, 35.08; H, 9.78; Si, 11.25. $\text{C}_7\text{H}_{24}\text{B}_{10}\text{Si}$. Calculated (%): C, 34.42; H, 9.83; Si, 11.47.

1-Phenyl-2-(α -trimethylsilylbenzyl)-o-carborane (10). A 1.77 M solution of Bu^nLi in benzene (6 mL, 0.01 mol) was added at 15 °C with stirring to a solution of compound 9 (3.1 g, 0.01 mol) in dry ether (10 mL). As a result, two liquid layers were formed, the lower of which was orange. The mixture was stirred for 30 min at 20 °C and then for 10 min with refluxing. The mixture was cooled to 20 °C, a solution of Me_3SiCl (1.1 g, 0.01 mol) in benzene (5 mL) was gradually added with stirring, and the reaction mixture was refluxed for 6 h. The orange layer disappeared, and precipitation of LiCl was observed. After cooling to 20 °C, the reaction mixture was poured into water, and the organic layer was separated from the aqueous layer and dried with CaCl_2 . The solvent was removed to give 3.1 g (81%) of compound 10, m.p. 133–134 °C (hexane). ^1H NMR (C_6D_6), δ : 0.15 (s, 9 H, $(\text{CH}_3)_3\text{Si}$); 2.5 (s, 1 H, CH); 5.11–7.29 (m, 10 H, Ph). Found (%): C, 57.88; H, 8.45; Si, 6.97. $\text{C}_{18}\text{H}_{30}\text{B}_{10}\text{Si}$. Calculated (%): C, 56.54; H, 7.85; Si, 7.32.

Transmetallation of 1-phenyl-2-trimethylsilyl-o-carborane on treatment with Bu^nLi . A 1.57 M solution of Bu^nLi in benzene (5 mL, 0.008 mol) was added at 20 °C to a solution of compound 1 (2 g, 0.007 mol) in dry ether (10 mL). At once, the reaction mixture turned light-yellow. The solution was refluxed for 2 h, cooled to 20 °C, and poured into a mixture of ether and solid CO_2 . After the temperature increased to 20 °C, 2% KOH was added to the mixture. The alkaline solution was separated and acidified with HCl. The carboxylic acid 3 that precipitated was extracted with ether and dried with CaCl_2 . The ether was removed to give 1.1 g (60%) of acid 3, m.p. 142–143 °C (heptane) (cf. Ref. 4: m.p. 142–143 °C). GLC showed that the organic layer remaining after removal of the alkaline layer contained Bu^nSiMe_3 , which was identical to that obtained from Bu^nLi and Me_3SiCl .

Transmetallation of 1-phenyl-2-(trimethylsilylmethyl)-o-carborane on treatment with Bu^nLi . Similarly to the above procedure, the reaction of compound 2 (1.6 g, 0.007 mol) and Bu^nLi in an ether-benzene solution with refluxing for 2 h gave 0.9 g (64%) of acid 4, m.p. 197–198 °C (cf. Ref. 4: m.p. 194–195 °C).

Transmetallation of 1-phenyl-2-(trimethylsilylmethyl)-o-carborane on treatment with Bu^nLi . A 1.57 M solution of Bu^nLi in benzene (5 mL, 0.008 mol) was added at 20 °C to a solution of compound 5 (2 g, 0.0065 mol) in dry ether (10 mL). The reaction mixture was refluxed for 4 h, cooled to 20 °C, and poured into a mixture of ether and solid CO_2 . Ordinary work-up gave 1.1 g (60%) of acid 7, m.p. 96–97 °C (cf. Ref. 4: m.p. 196–198 °C).

Transmetallation of 1-methyl-2-(trimethylsilylmethyl)-o-carborane on treatment with Bu^nLi . Similarly to the above procedure, the reaction of compound 6 (0.5 g, 0.006 mol) and Bu^nLi in an ether-benzene solution with refluxing for 4 h followed by ordinary treatment gave 0.7 g (52%) of acid 8, m.p. 119–120 °C (cf. Ref. 4: m.p. 121 °C).

Treatment of 1-phenyl-2-(α -trimethylsilylbenzyl)-o-carborane with Bu^nLi . A 1.2 M solution of Bu^nLi (4 mL, 0.004 mol) in benzene was added at 15 °C in a stream of argon to a

solution of compound 10 (1.6 g, 0.004 mol) in dry ether (12 mL). The solution color did not change, and two layers did not form. Unlike in the reaction of 2-benzyl-1-phenyl-o-carborane with Bu^nLi , the reaction mixture remained homogeneous throughout 2 h of refluxing. The usual carboxylation by treatment with a mixture of solid CO_2 and ether did not give a carboxylic acid. Instead, the original compound 10, m.p. 132–133 °C (hexane), was isolated in 95% yield.

B. A solution of compound 10 (0.3 g, 0.0008 mol) in dry ether (5 mL) and a 1.4 M Bu^nLi solution in benzene (0.6 mL, 0.0008 mol) was refluxed for 2 h. After cooling to 20 °C, 1 mL of D_2O was added, and the mixture was stirred for 30 min. Ordinary work-up gave 0.28 g of compound 10, m.p. 132–133 °C (hexane). ^1H NMR (C_6D_6), δ : 0.15 (s, 9 H, $(\text{CH}_3)_3\text{Si}$); 2.5 (s, 1 H, CH); 5.11–7.29 (m, 10 H, Ph).

Treatment of 2-(α -allylbenzyl)-1-isopropyl-o-carborane (11) with Bu^nLi . A 1.44 M solution of Bu^nLi (2 mL, 0.002 mol) in benzene was added at 15 °C to a solution of compound 11 (0.62 g, 0.002 mol) in dry ether (5 mL). The solution color did not change, and two layers did not form even after refluxing the reaction mixture for 1 h. The solution was cooled and poured into a mixture of ether and CO_2 . Ordinary work-up did not give a carboxylic acid. Instead, the original compound 11 was isolated in almost quantitative yield, m.p. 91–92 °C (cf. Ref. 12: m.p. 91–92 °C).

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Received December 6, 1996;
in revised form October 15, 1997