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

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Silyl-substituted o-carboranes $1-R-2-Me_3Si(CH_2)_n-1,2-C_2B_{10}H_{10}$ (R=Me, Ph; n=0, 1) undergo transmetallation on treatment with Bu^nLi to form lithium derivatives of o-carboranes, $1-R-2-Li(CH_2)_n-1,2-C_2B_{10}H_{10}$, where n=0, 1. A silicon derivative of o-carborane, $1-Ph-2-(Me_3SiCHPh)-1,2-C_2B_{10}H_{10}$, undergoes neither transmetallation nor metallation at the benzyl CH-group on treatment with Bu^nLi 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:

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

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

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. 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 $1\text{-R-2-Me}_3\text{SiCH}_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ compounds, where R=Ph (5) or Me (6), obtained by treatment of Me₃SiCH₂I with $1\text{-R-2-Li-1},2\text{-}C_2B_{10}H_{10}$ 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 $1\text{-R-2-Me}_3\text{SiCH}_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ 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 $1\text{-R-2-XCH}_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ (X = OCH₃, Cl).^{10,11}

However, the effect of the Me_3Si group on the acidity of methylene protons in compounds 5 and 6 was found to be insignificant. Therefore, metallation on the CH_2 group on treatment with Bu^nLi in an ether-benzene solution does not occur. Only transmetallation takes place according to the scheme

In this case, transmetallation occurs slowly and requires a prolonged heating of the reaction mixture. The structure of lithium derivatives of carboranes was confirmed by obtaining the corresponding acids 7 and 8 on treatment of the reaction mixture with CO₂. Evidently, in this case transmetallation occurs owing to the electron-withdrawing effect of the 1-o-carboranylmethylene group, which causes such polarization of the Si—C σ -bond that the silicon atom obtains a partial positive charge.

Unlike compounds 1 and 2, compounds 5 and 6 are stable against the hydrolysis of the C-Si σ -bond on treatment with aqueous or alcoholic solutions of bases. The mechanism of C-Si bond breaking on treatment with organolithium compounds has not yet been discovered. $^{\rm I}$

We have shown previously 12 that 1-benzyl-o-carboranes are strong CH-acids (p $K_a = 19.5$). They are readily metallated with BuⁿLi in an ether-benzene solution at 10-15 °C. We carried out the reaction of 2-benzyl-1-phenyl-o-carborane (9) with Me₃SiCl to give 1-phenyl-2-trimethylsilylbenzyl-o-carborane (10), assuming that the latter would be a stronger CH-acid than the starting benzyl derivative 9 due to the strong electron-withdrawing effect of the Me₃Si group. 6

One could expect that, unlike compound 5, compound 10 would undergo transmetallation and metallation on the CH group. However, it was found 12 that on treatment of compound 10 with BuⁿLi in an etherbenzene solution under the conditions used for metallation of compound 9 and with prolonged heating, compound 10 underwent neither transmetallation nor metallation but was recovered unchanged.

The absence of metallation was confirmed by two methods: (a) treatment with CO_2 did not give the corresponding carboxylic acid, and (b) on treatment with D_2O , deuterium did not enter the molecule, as shown by

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$$\xrightarrow{\text{Bi}_2\text{O}-\text{C}_6\text{H}_6}$$
 $\xrightarrow{\text{PhC}-\text{C}-\text{CHPh}}$ $\xrightarrow{\text{Bi}_1\text{O}+\text{I}_1\text{O}}$ $\xrightarrow{\text{Ph}}$ $\xrightarrow{\text{Ei}_2\text{O}-\text{C}_6\text{H}_6}$ $\xrightarrow{\text{PhC}-\text{C}}$ $\xrightarrow{\text{C}}$ $\xrightarrow{\text{SiMe}_3}$ $\xrightarrow{\text{Bi}_1\text{O}+\text{I}_1\text{O}}$ $\xrightarrow{\text{Li}}$

¹H NMR spectroscopy. We explain such an unexpected result by assuming that the CH group in compound 10 cannot react with BuⁿLi because of significant steric hindrance.

Previously,¹³ we have already observed a steric effect in the metallation of compound 9 with lithium aluminum hydride in THF. In that reaction, metallation of only one hydrogen atom of the CH group took place, and the resulting trihydride aluminum complex of the type RAIH₃Li was stable and did not tend to disproportionate, which is characteristic of ordinary trihydride aluminum complexes, due to significant steric hindrance.¹³

Thus, it is believed that in compounds of the structure $1-R-2-CHR'Ph-1,2-C_2B_{10}H_{10}$ (R' being an organic or organometallic residue), the R' group can cause significant steric hindrance of the CH group, and in this case the hydrogen atom of this group cannot be replaced by a lithium atom. We confirmed this by the fact that $2-(\alpha-\text{allylbenzyl})-1-\text{isopropyl}-o-\text{carborane}$ (11), which is formed upon replacement of a hydrogen atom in the CH₂ group of compound 9 by an allyl group, cannot be metallated at the CH group on treatment with BuⁿLi in an ether-benzene solution on prolonged heating under the conditions used for the metallation of compound 10.

Experimental

¹H NMR spectra were recorded on a Bruker WP-200SY instrument in a C_6D_6 solution relative to HMDS. All reactions with BuⁿLi were carried out in a pure argon atmosphere in dry solvents. 1-Phenyl-2-trimethylsilyl-o-carborane was obtained according to the procedure in Ref. 4.

1-Methyl-2-trimethylsilyl-o-carborane (2). A 1.77 M solution of BuⁿLi in benzene (6 mL, 0.01 mol) was added at 20 °C with stirring in an argon atmosphere to a solution of 1-methylo-carborane (1.6 g, 0.01 mol) in dry ether (7 mL). The solution was heated at 40 °C for 30 min, cooled to 20 °C, and a solution of Me₃SiCl (1.1 g, 0.01 mol) in 5 mL of benzene was added to it. The reaction mixture was refluxed for 1 h, cooled, and poured into 5% HCl. The organic layer was separated from the aqueous layer, washed with water, and dried with CaCl₂. The solvent was removed, and the residue was recrystallized from hexane to give 2.1 g (91%) of compound 2, m.p. 82-83 °C. ¹H NMR (C_6D_6), δ : -0.14 (s, 9 H, (C_{13})₃Si); 1.16 (s, 3 H, C_{13}). Found (%): C, 31.49; H, 9.63; B, 46.81; Si, 12.22. $C_6H_{22}B_{10}$ Si. Calculated (%): C, 31.30; H, 9.56; B, 46.95; Si, 12.17.

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

(s, 9 H, $(CH_3)_3Si)$; 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. $C_{12}H_{26}B_{10}Si$. 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 Me₃SiCH₂I (2.2 g, 0.01 mol) gave 2 g (80%) of compound 6, m.p. 68-69 °C (hexane). ¹H NMR (C₆D₆), δ : -0.15 (s, 9 H, (CH₃)₃Si); 0.81 (s, 3 H, CH₃); 1.22 (s, 2 H, CH₂). Found (%): C, 35.08; H, 9.78; Si, 11.25. C₇H₂₄B₁₀Si. Calculated (%): C, 34.42; H, 9.83; Si, 11.47.

1-Phenyl-2-(\alpha-trimethylsilylbenzyl)-o-carborane (10). A 1.77 M solution of BuⁿLi 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 Me₃SiCl (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 CaCl2. 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, (CH_3)₃Si); 2.5 (s, 1 H, CH); 5.11-7.29 (m, 10 H, Ph). Found (%): 57.88; H, 8.45; Si, 6.97. $C_{18}H_{30}B_{10}Si$. Calculated (%): 56.54; H, 7.85; Si, 7.32.

Transmetallation of 1-phenyl-2-trimethylsilyl-o-carborane on treatment with BuⁿLi. A 1.57 M solution of BuⁿLi 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 CO₂. 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 CaCl₂. 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 BuⁿSiMe₃, which was identical to that obtained from BuⁿLi and Me₃SiCl.

Transmetallation of 1-methyl-2-trimethylsilyl-o-carborane on treatment with Bu^aLi. Similarly to the above procedure, the reaction of compound 2 (1.6 g, 0.007 mol) and Bu^aLi 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 BuⁿLi. A 1.57 M solution of BuⁿLi 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 CO₂. 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 BuⁿLi. Similarly to the above procedure, the reaction of compound 6 (0.5 g, 0.006 mol) and BuⁿLi 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 BuⁿLi. A. A 1.2 M solution of BuⁿLi (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 BuⁿLi, the reaction mixture remained homogeneous throughout 2 h of refluxing. The usual carboxylation by treatment with a mixture of solid CO₂ 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 BuⁿLi 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, (CH₃)₃Si); 2.5 (s, 1 H, CH); 5.11—7.29 (m, 10 H, Ph).

Treatment of 2-(α -allylbenzyl)-1-isopropyl- α -carborane (11) with BuⁿLi. A 1.44 M solution of BuⁿLi (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 CO₂. Ordinary workup 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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