Metalation of 1-R-2-benzyl-*o*-carboranes with lithium aluminum hydride

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Carboranes with the general formula 1-R-2-$PhCH_2$-1,2-$C_2B_{10}H_{10}$ (R = Me, Pr^i, Ph, $PhCH_2$) are readily metalated with lithium aluminum hydride in a THF solution at the CH_2 group. In this case only one hydrogen atom in $LiAlH_4$ is substituted, and trihydride complexes 1-R-2-PhCH(AlH_3Li)-1,2-$C_2B_{10}H_{10}$, are formed, which are stable in a solution.

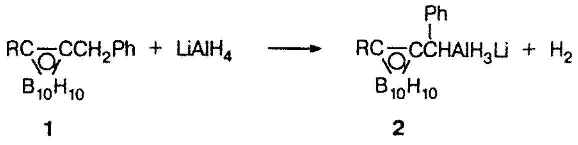
Key words: 1-R-2-benzyl-*o*-carboranes, lithium aluminum hydride, metalation; lithium organotrihydridoaluminates.

Earlier it was reported[1] that 1-R-2-benzyl-*o*-carboranes are strong CH-acids due to the benzyl CH_2 group attached to the carbon atom of *o*-carborane moiety. For example, 1-methyl-2-benzyl-*o*-carborane has pK_a 19.5 (MSED scale). These compounds are readily metalated with *n*-butyl lithium either in a THF or in an ether—benzene mixture to yield 1-R-2-lithiumbenzyl-*o*-carboranes.[1,2] It is well known that aluminum hydrides of alkaline metals in ether[3] or THF[4] metalate 1-alkynes (pK_a 18.5—23.2) to form $(RC{\equiv}C)_4AlM$ (M = Li, Na, and K).[4] Because the acidities of 1-R-2-benzyl-*o*-carboranes and 1-alkynes are approximately equal, we suggested that these carborane derivatives would also be metalated with $LiAlH_4$. However, it should be noted that the ease of metalation of CH-acids with alkaline metal aluminum hydrides is not always determined by their acidity. Thus, cyclopentadiene (pK_a 15.0) reacts with $MAlH_4$ to give $MAlCp_4$ only at 140—160 °C in diglyme,[5] indene (pK_a 18.5) is not metalated with lithium aluminum hydride in ether solutions, and fluorene (pK_a 22.9) is not metalated with $LiAlH_4$ in diethyl ether,[6] but it is metalated in THF.[7] At the same time the reaction of carboranes of the 1,2-, 1,7- и 1,12-$C_2H_2B_{10}H_{10}$ type (pK_a 23.3, 27.9 and 30.0, respectively[8]) with $MAlH_4$ readily occurs in a THF solution to give (1,2-, 1,7-, and 1,12-$B_{10}H_{10}C_2H)_2AlH_2M$ (M = Li, Na).[9] The differences in metalation of CH-acids were supposed to be associated with the mechanism of negative charge stabilization in conjugated carbanions.[10]

Results and Discussion

In this study we have shown that carboranes of general formula 1-R-2-($PhCH_2$)-1,2-$C_2B_{10}H_{10}$ (**1**) can be metalated with lithium aluminum hydride (THF, 20 °C) according to Scheme 1.

Scheme 1



R = Me, Pr^i, Ph

The reaction leads to lemon-colored solutions of trihydride complexes **2**. Further metalation of benzylcarboranes **1** with complexes **2** does not occur even at a prolonged heating of the solution. Thus, the second molecule of carborane **1** cannot substitute the second hydrogen atom in the trihydride complex **2** because of the significant steric hindrances resulting from the bulky *o*-carborane moiety.

The steric hindrances in benzylcarboranes are so great that metalation of 1,2-dibenzyl-*o*-carborane (**3**) with an excess of lithium aluminum hydride in THF proceeds with involvement of only one methylene group to yield trihydride complex **4** (Scheme 2).

Scheme 2

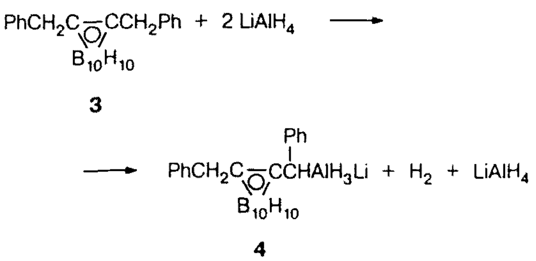


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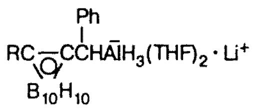
Table 1. Chemical shifts in ^{27}Al NMR spectra of trihydride aluminum complexes (in THF)

Complex	δ ^{27}Al (±2)	Other parameters
1-Me-2-PhCH(AlH$_3$Li)-1,2-C$_2$B$_{10}$H$_{10}$	67.6 (s)	
1-Pr^i-2-PhCH(AlH$_3$Li)-1,2-C$_2$B$_{10}$H$_{10}$	100.2 (s)	Line width Δ = 100 Hz
1-Ph-2-PhCH(AlH$_3$Li)-1,2-C$_2$B$_{10}$H$_{10}$	73.0 (s)	
1-PhCH$_2$-2-PhCH(AlH$_3$Li)-1,2-C$_2$B$_{10}$H$_{10}$	72.0 (s)	
1,2-HCB$_{10}$H$_{10}$CAlH$_3$Li	135.5 (s)	
LiAlH$_3$Et·	117.0 (s)	
LiAlH$_4$	96.0 (quint)	$J_{\text{Al—H}}$ = 180 Hz

The course of metalation of carboranes **1** and **3** was monitored by the amount of hydrogen liberated.

The structure of the trihydride complexes **2** and **4** in a solution is supported by ^{27}Al NMR spectra. In many cases the method of ^{27}Al NMR spectroscopy makes it possible to record the presence of complexes that differ in structure.[11] Replacement of the hydride-ion in anion AlH$_4^-$ by an alternative substituent affects the value of chemical shift, the line width, and multiplicity of the signal from the anion AlH$_4^-$ in the ^{27}Al NMR spectrum.[12]

The ^{27}Al NMR spectra of complexes **2** and **4** in THF are broadened singlets whose chemical shifts range from 67 to 100 ppm depending on substituent R (Table 1). For comparison Table 1 presents the parameters of ^{27}Al NMR spectra for complexes HCB$_{10}$H$_{10}$CAlH$_3$Li,[13] LiAlH$_3$Et, [14] and LiAlH$_4$.[12] We know[9] that the value of chemical shift in ^{27}Al NMR spectra may be a characteristic of electron density on the alumina atom in complex alumina compounds. Comparison of the values δ ^{27}Al in complexes 1,2-HCB$_{10}$H$_{10}$CAlH$_3$Li, and LiAlH$_3$Et with the chemical shifts in the spectra of organotrihydridoaluminates **2** and **4** indicates that the negative charge in anions of the latter complexes is concentrated on the Al atom to a greater extent. This can be explained by the fact that complexes **2** and **4** exist in the form of solvate-separated ion pairs because of the steric hindrances.

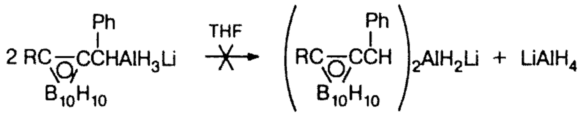


The chemical shift in the ^{27}Al NMR spectrum of 1-Pr^i-2-PhCH(AlH$_3$Li)-1,2-C$_2$B$_{10}$H$_{10}$ markedly differs from the δ ^{27}Al values observed for similar complexes containing other substituents R. This may be a consequence of the stronger electron-donor effect of the isopropyl group compared to Me, Ph, or PhCH$_2$ groups, which results in an increase in polarity of C—Al bonds and, therefore, a decrease in the negative charge on the Al atom. The presence of color in complexes **2** and **4** indicates the marked polarity of C—Al δ-bond and the delocalization of the negative charge on the carbon atom of the benzyl group.

Although trihydride aluminum complexes, such as LiAlEtH$_3$,[13] 1,2-HCB$_{10}$H$_{10}$CAlH$_3$Li,[9] and NaAlBu^{i}H$_3$,[14] were well known previously, they proved to be unstable in solutions and underwent disproportionation.

$$2\ \mathrm{MAlRH_3} \longrightarrow \mathrm{MAlH_4} + \mathrm{MAlR_2H_2}$$

Recently[15] the synthesis of the first trihydride aluminum complexes (Me$_2$PhSi)$_3$CAlH$_3$Li and (Me$_3$Si)$_3$CAlH$_3$Li has been reported, which did not undergo disproportionation because of the considerable steric hindrances caused by the bulky substituents. We have shown that complexes **2** and **4** are novel stable organotrihydride aluminum complexes which are not able to undergo disproportionation.



When the solutions of the complexes **2** and **4** in THF were heated at 30—40 °C for 4 h, we did not observe the appearance of new signals in ^{27}Al NMR spectra including the signals from LiAlH$_4$. This fact indicates the stability of the compounds obtained under the experimental conditions.

The literature data[15] and the results of our experiments allows us to conclude that the presence of bulky organic moiety linked with the Al atom is required to obtain stable trihydride aluminum complexes.

Experimental

All the procedures including the purification of solvents and recording ^{27}Al NMR spectra were performed in an atmosphere of dry argon; THF was distilled over NaAlH$_4$ just before use. The ^{27}Al NMR spectra were recorded on a Bruker WP-200 (52.1 MHz) spectrometer. Chemical shifts were measured relative to an aqueous solution of $AlCl_3(H_2O)_6^{3+}$. A clarified solution of $LiAlH_4$ in THF (0.4 mol L^{-1}) was used. The hydride hydrogen was analyzed by gas volumetry. The aluminum content was determined by trilonometric method with Dithizone used as an indicator.

Metalation of 1-R-2-benzyl-*o*-carboranes (1) with lithium aluminum hydride (general procedure). ***A.*** A solution of $LiAlH_4$ (1 mmol) in THF was gradually added to a solution of carborane **1** (R = Me, Pr^i, and Ph) (1 mmol) in 5 mL of THF at 20 °C; the course of the reaction was monitored by gas volumetry. The reaction was conducted until the liberation of hydrogen was completed according to stoichiometry. The samples of the solutions of metalation products were then taken from the reaction mixture and placed into NMR tubes for recording ^{27}Al NMR spectra. After removing the solvent *in vacuo* at 20 °C, trihydride complexes **2** (R = Me, Pr^i, and Ph) were allowed to stand at 1 Torr and ~20 °C until their weight was constant. The compounds obtained were viscous lemon-colored liquids that were not crystallized under prolonged storage. Complex 1-Pr^i-2-$PhCH(AlH_3Li)$-1,2-$C_2B_{10}H_{10} \cdot 2C_4H_8O$ was crystallized under storage. Found (%): Al, 5.96; H(hydr.), 0.63; Al : H = 1.00 : 2.85. $C_{12}H_{26}AlLiB_{10} \cdot 2C_4H_8O$. Calculated (%): Al, 5.92; H(hydr..), 0.65; Al : H = 1: 3.

B. A solution of $LiAlH_4$ (1 mmol) in THF was added to a solution of carborane **1** (R = Me and Ph) (2 mmol) in 10 mL of THF at 20 °C; the course of the reaction was monitored by gas volumetry; in this case 1 mmol of H_2 was liberated. The reaction mixture was heated at 40 °C (for 2 h), and then refluxed for 1 h; the further liberation of hydrogen was not observed. The pattern of ^{27}Al NMR spectra was not changed in comparison with the corresponding spectra of complexes **2** (R = Me and Ph) before heating.

Metalation of 1,2-$(PhCH_2)_2$-1,2-$C_2B_{10}H_{10}$ with lithium aluminum hydride. ***A.*** A solution of $LiAlH_4$ (1 mmol) in THF was added to a solution of 1,2-dibenzyl-*o*-carborane **3** (1 mmol) in 5 mL of THF at 20 °C. The reaction was carried out until liberation of hydrogen was completed according to the stoichiometry. The signal from complex **4** was observed in the ^{27}Al NMR spectrum of the reaction mixture (see Table 1).

B. A solution of $LiAlH_4$ (2 mmol) in THF was added to a solution of 1,2-dibenzyl-*o*-carborane **3** (1 mmol) in 5 mL of THF at 20 °C. In this case only 1 mmol of H_2 was liberated. The signals of complex **4** and free $LiAlH_4$ were observed in the ^{27}Al NMR spectrum of the reaction mixture; no other signals were found.

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