

A novel synthetic route to peralkylated carborane anions, 1-H-CB₉Me₉⁻ and 1-H-CB₁₁R₁₁⁻ (R = Me, Et)

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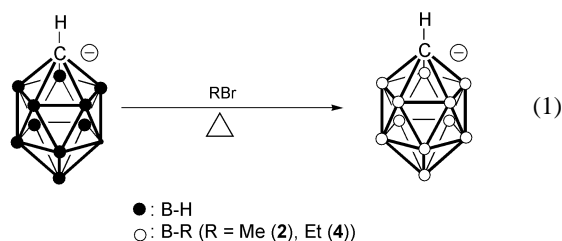
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Treatment of carborane anions with excess RBr (R = Me, Et) in a sealed Pyrex tube at 200 °C gives peralkylated carborane anions in quantitative yields, which represents the most convenient and the most economic method so far reported in the literature for the preparation of peralkylcarborane anions.

As a class of the robust and weakly coordinating anions, carborane anions have found many applications in catalysis, metathesis, and oxidation chemistry as well as in stabilizing highly reactive cations.¹ Many derivatives of carborane anions have recently been reported; among these, the polymethylated species have received much attention.^{2–7} Two main methods have been developed for the transformation of B–H or B–I vertices to B–C ones; they include palladium-catalyzed alkylation of B–I vertices of iodocarboranes with Grignard reagents,^{2–5} and electrophilic substitution of B–H vertices by strong methylating reagents such as methyl triflate or trimethylaluminum/MeI.^{6,7} These methods often involve complicated workup procedures, and sometimes a mixture of products, which lead to a lower yield. We report herein a very facile synthesis of peralkylated carborane anions.

Treatment of [Me₃NH][1-H-CB₉H₉] or [Me₃NH][1-R-CB₁₁H₁₁] with excess MeBr in a sealed Pyrex tube at 200 °C for 5 days gives permethylated products [Me₃NH][1-H-CB₉Me₉] (**1**) or [Me₃NH][1-R-CB₁₁Me₁₁] [R = H (**2**), CH₃ (**3**)] in almost quantitative yields.† The first perethylated carborane anion, [Me₃NH][1-H-CB₁₁Et₁₁] (**4**), can also be prepared quantitatively in the same manner by using EtBr as a reagent [eqn. (1)].



No organic solvent is involved and no workup procedures are needed. After the reaction is complete, the Pyrex tube is opened and excess RBr is immediately evaporated leaving a pure product. These compounds have been fully characterized by ¹H, ¹³C and ¹¹B NMR, MS and IR spectroscopy. The complete conversion of B–H vertices into B–R (R = Me, Et) vertices is indicated by the absence of the characteristic B–H absorption (*ca.* 2600 cm⁻¹) in the IR spectra and identical proton-coupled and proton-decoupled ¹¹B NMR spectra. The formation of the B–C bonds is also reflected in the broadening and upfield shifted carbon chemical shifts in their ¹³C NMR spectra due to the close proximity of carbon nuclei to both ¹¹B and ¹⁰B nuclei.^{3,8}

Reaction of [Me₃NH][1-H-CB₁₁H₁₁] with excess ⁱPrBr under the same or more rigorous reaction conditions, however, affords a mixture of polyalkylated carboranes [Me₃NH][1-H-CB₁₁H_{11-n}Pr_n] (*n* = 4–7) on the basis of MS analyses. The

reasons for that are probably due to the steric effects of the isopropyl groups. It is noteworthy that no brown Br₂ is produced and only HBr gas is detected in the above-mentioned reactions. If the permethylation is carried out in a (MeO)₃P(O) solution or the perethylation is performed in a (EtO)₃P(O) solution, both the reaction temperature and reaction time are reduced.⁹

In contrast, reaction of [Me₃NH][1-H-CB₁₁H₁₁] with excess MeI, under the same reaction condition, yields a mixture of products [Me₃NH][1-H-CB₁₁Me_{11-n}I_n] (*n* = 3–5) on the basis of MS analyses, along with the formation of HI and purple I₂. These results indicate that MeI may undergo both heterolytic and homolytic reactions generating Me⁺, Me[•], I⁻ and I[•]. Coupling of I[•] yields purple I₂. Both Me⁺ and I₂ are electrophiles, which react with carborane to form a mixture of [1-H-CB₁₁Me_{11-n}I_n]⁻.

In summary, a very facile and economic method has been developed for the first time for the synthesis of permethylated and perethylated carborane anions. Applications of this novel methodology to other carborane and borane molecules are under investigation.

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Notes and references

† Preparation of **4**: Method A. A thick-walled Pyrex tube was charged with [Me₃NH][1-H-CB₁₁H₁₁] (0.10 g, 0.49 mmol) and ethyl bromide (0.5 mL, 6.70 mmol) at 0 °C. This tube was then cooled with liquid N₂, sealed under vacuum and placed in a furnace. The temperature of the furnace was gradually increased to 160 °C, and this temperature was maintained for 2 days. The temperature was then slowly raised to 220 °C, and this temperature was maintained for 3 days. The tube was opened and excess ethyl bromide was evaporated, leaving a pale yellow solid. The ¹¹B NMR showed that it is a pure compound. This pale yellow solid can be further recrystallized from a water/acetone solution to give **4** as a white crystalline solid (0.23 g, 92%). ¹H NMR (acetone-*d*₆): δ 2.96 [s, (CH₃)₃NH], 0.96 [br s, B-CH₂CH₃], 0.87 [br s, B-CH₂CH₃]; ¹³C NMR (acetone-*d*₆): δ 45.48 [(CH₃)₃NH], 12.24 [s, B-CH₂CH₃(2–6)], 10.95 [s, B-CH₂CH₃(7–12)], 6.94 [br, B-CH₂CH₃(2–12)]; ¹¹B NMR (acetone-*d*₆): δ 2.95 (s, 1B), -4.05 (s, 5B), -7.78 (s, 5B); IR (cm⁻¹, KBr): ν 2953 (s), 2908 (s), 2874 (s), 1457 (m), 1156 (m), 1034 (w), 956 (m), 521(s); Negative-ion MALDI MS, *m/z* (isotopic abundance): calcd. for [1-H-CB₁₁(CH₂CH₃)₁₁]⁻ 449(34), 450(70), 451(100), 452(90), 453(45); found 449(32), 450(67), 451(100), 452(91), 453(43).

Method B. A thick-walled Pyrex tube was charged with [Me₃NH][1-H-CB₁₁H₁₁] (0.10 g, 0.49 mmol), ethyl bromide (0.5 mL, 6.70 mmol), and triethylphosphate (1.5 mL, 8.83 mmol) at 0 °C. This tube was then cooled with liquid N₂, sealed under vacuum and placed in a furnace. The temperature of the furnace was gradually increased to 180 °C, and this temperature was maintained for 3 days. The tube was opened and excess ethyl bromide was evaporated. The residue was dissolved in hot water and the precipitate formed was immediately filtered off. This solid was washed with CH₂Cl₂ and then hexane to give a white crystalline solid (0.21 g, 84%) that was identified as **4** by spectroscopic data.

Compounds **1–3** were prepared as white crystalline solids in the same manner in >95% yield.

Spectroscopic data for **1**: ¹H NMR (acetone-*d*₆): δ 2.90 [s, (CH₃)₃NH], -0.29 [br s, B-CH₃(2–5)], -0.55 [br s, B-CH₃(6–10)]; ¹³C NMR (acetone-

d_6): δ 52.62 [cage C], 45.00 [(CH₃)₃NH], -4.10 [br, CH₃(2-10)]; ¹¹B NMR (acetone- d_6): δ 37.04 (s, 1B), -4.19 (s, 4B), -8.24 (s, 4B); IR (cm⁻¹, KBr): ν 2919 (br s), 2863 (m), 1623 (m), 1456 (m), 1384 (s), 1093 (s), 1032 (s), 804 (w); these data are identical with those reported in the literature.⁵

Spectroscopic data for 2: ¹H NMR (acetone- d_6): δ 3.08 [s, (CH₃)₃NH], -0.21 [s, B-CH₃(2-6)], -0.44 [s, B-CH₃(7-12)]; ¹³C-NMR (acetone- d_6): δ 60.49 [cage C], 45.00 [(CH₃)₃NH], -3.05 [v br, B-CH₃(2-12)]; ¹¹B NMR (acetone- d_6): δ 4.24 (s, 1B), -3.91 (s, 5B), -7.36 (s, 5B); IR (cm⁻¹, KBr): ν 2927 (s), 2896 (s), 2831 (s), 1476 (m), 1458 (m), 1303 (m), 1226 (m), 1050 (s), 523 (m); Negative-ion MALDI MS, m/z (isotopic abundance): calcd. for [1-H-CB₁₁(CH₃)₁₁]⁻ 294(12), 295(36), 296(74), 297(100), 298(87), 299(38), 300(24); found 294(28), 295(61), 296(91), 297(100), 298(92), 299(57), 300(23).

Spectroscopic data for 3: ¹H NMR (acetone- d_6): δ 3.16 [s, (CH₃)₃NH], 0.80 [s, C-CH₃], -0.19 [s, B-CH₃(2-6)], -0.29 [s, B-CH₃(7-12)]; ¹³C NMR (acetone- d_6): δ 45.00 [(CH₃)₃NH], 14.30 [C-CH₃], -2.67 [v br, B-CH₃(2-12)]; ¹¹B NMR (acetone- d_6): δ 0.53 (s, 1B), -8.86 (s, 5B), -10.85 (s, 5B); IR (cm⁻¹, KBr): ν 2953 (s), 2913 (s), 2848 (m), 1640 (w), 1476 (m), 980 (s), 937 (s), 774 (s), 512 (vs); these data are identical with those reported in the literature.⁶

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