

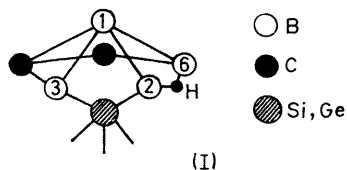
A New Class of Small *nido*-Carborane Compounds Containing a Stable B-MMe₃-B (M=Si or Ge) Three-centre Bond

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Summary The preparation of 2,3- μ -trimethylsilyl (and germyl)-*CC'*-dimethyl-4,5-dicarba-*nido*-hexaborane(8), 2,3- μ -Me₃MC₂Me₂B₄H₅, (M = Si or Ge), has been achieved by the action of the trimethylchloro-compounds, Me₃MCl, on the anion, C₂Me₂B₄H₅⁻; the compounds do not isomerise at room temperature to the terminal isomers.

ALTHOUGH several lower carborane compounds have been characterised relatively little is known of their properties. Thus for the pentagonal-pyramidal *nido*-4,5-C₂R₂B₄H₆ (R = H or Me) series substitution of the terminal B-H bonds with both halogen¹ and alkyl² has been achieved, and a Ga-Me group has been claimed to be inserted into the



basal B₃C₂ face,³ but the only other reported reaction is the removal of *one* of the two basal bridging hydrogen atoms (in B-H-B bonds) by nucleophiles yielding the anion, 4,5-C₂R₂B₄H₅⁻.⁴ The carborane is regenerated on addition of a proton donor (*e.g.* HCl, DCl, B₁₀H₁₄), and deuteration studies have shown that the proton is inserted exclusively into the vacant bridge position.⁴

During our studies on the C₂Me₂B₄H₅⁻ anion we have found that other groups (Me₃Si and Me₃Ge) are readily inserted into the vacant bridge position yielding a new class of stable *nido*-carborane compounds. The volatile liquid compounds, 2,3- μ -Me₃MC₂Me₂B₄H₅ (I),[†] are obtained in high yield from the action of the trimethyl compounds, Me₃MCl, on the sodium salt, Na⁺C₂Me₂B₄H₅⁻, in ethereal solution at 25°. The Me₃M groups have been identified as being 2,3- (or the equivalent 2,6-) bridge substituted from the ¹¹B n.m.r. spectra which are similar for the two compounds consisting of a high-field doublet (area 1.0), and three low-field doublets (area 3.0) assignable to the apical and basal boron atoms, respectively. The doublet at lowest field is both well separated from the other signals and rather broad, and exhibits only terminal B-H coupling indicating that it arises from the 2-B atom (other results have shown that basal boron atoms with *two* adjacent bridging groups show similar characteristics⁵⁻⁸). The two other low-field doublets are sharp and overlap, and may be assigned to the 3- and 6-B atoms, in that the former shows only terminal B-H coupling, while for the latter both terminal B-H and B-H-B bridge coupling are observed. The ¹H n.m.r. spectra are also consistent with the above assignments since in each case the integrated ratio for the bridge and terminal protons is 1:4, and both spectra show the further significant feature of the separation of the two singlets due to the C-CH₃ groups by *ca.* 5 Hz, arising from the asymmetry introduced into the molecule by the bridging M(CH₃)₃

[†] These compounds have been characterised by elemental analysis and high-resolution mass spectrometry. The nomenclature used for these compounds follows that recommended in *Inorg. Chem.*, 1968, 7, 1945.

groups. It is relevant that such a separation has not previously been observed where it has been expected, *e.g.* in the 3-B terminally substituted alkyl² and halogen^{1,8} derivatives.

An interesting property of these compounds is the absence of any isomerisation process in ethereal solution at 25° over 24 h, because under similar conditions the bridge substituted μ -Me₃SiB₅H₈ isomerises rapidly to the terminal isomer.⁹ The ¹¹B n.m.r. spectra of μ -Me₃SiB₅H₈, and the

structurally related B₅H₈⁻¹⁰ and B₆H₁₀^{11,12} are consistent with a rapid exchange (tautomerism) of the bridging hydrogen atoms. However, the bridging hydrogen atom(s) in the μ -Me₃MC₂Me₃B₄H₅ compounds, and the parent carborane,⁵ C₂Me₂B₄H₆, do not exhibit such tautomerism suggesting that other bridge-substituted derivatives of these carboranes would also possess a similar stability towards isomerisation.

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