siders the crystal field and coupling effect to be weak as a result of the shielding of the 4f electrons by the 5s and 5p electrons. The results of magnetic studies (Faraday method) over the temperature range 300–23°K on the nicotinates of Pr(III), Nd(III), and Gd(III) are given in Table I. The moments of the Pr(III) and Nd(III) compounds are temperature dependent; the greatly reduced magnetic moments at 23°K for the Pr(III) and Nd(III) complexes as compared with their normal paramagnetic room temperature moments might be attributed to antiferromagnetic coupling between the two metal ions in the dimeric species. The absence of such a decrease in moment in the Gd(III) complex (with the $^8S_{7/2}$ ground state for the metal ion), however, suggests that the decrease results from crystal field effects. Further detailed susceptibility studies of these and other lanthanide complexes are in progress.

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# Carboranes Containing Gallium and Indium Cage Heteroatoms. Synthesis, Molecular Structure, and Reactions

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**Abstract:** The reaction of trimethylgallium or trimethylindium with 2,3-dicarba-*nido*-hexaborane(8) yields the closed polyhedral species $1\text{-}CH_3GaC_2B_4H_6$ and $1\text{-}CH_3InC_2B_4H_6$, respectively, in which the metal atom in each case forms one apex of a pentagonal-bipyramidal cage. These carboranes have been structurally characterized by boron-11 and proton nmr, mass spectra, and infrared spectra, and by a single-crystal X-ray diffraction study of the gallium compound. The X-ray results have disclosed two distinctive features: (1) the gallium atom is closer to the boron atoms than to the carbon atoms in the five-membered equatorial ring, in contrast to other related carborane structures, and (2) the $Ga\text{-}CH_3$ axis is tilted by 20° with respect to the perpendicular to the equatorial plane. These findings are interpreted in terms of a qualitative molecular orbital model which assumes back-donation of electrons from the $d_{yz}$ orbital of the metal atom to the $e_2$ antibonding orbital of the carborane ligand. The gallium and indium compounds are thermally stable to at least 100°, but pyrolysis at high temperatures generates $2,3\text{-}C_2B_4H_8$. Both materials react readily with HCl, the gallium compound generating $2,3\text{-}C_2B_4H_8$. Bromine attacks both metallocarboranes at room temperature, destroying the cage structure and forming the dimer of $(CH_3)_2GaBr$ and presumably the indium analog, respectively.

The remarkable variety of stable carborane cage compounds is illustrated by the many known families of isoelectronic and isostructural species. For example, the well-known icosahedral carborane isomers *o*-, *m*-, and *p*- carborane (1,2- 1,7-, and 1,12-$C_2B_{10}H_{12}$) are isoelectronic analogs of a number of other icosahedral cage systems containing transition metal or main group heteroatoms in addition to boron and carbon. Among the main group heterocarboranes are such recent discoveries as $BeC_2B_9H_{12}^-$,[1] $RAlC_2B_9H_{11}$[2] ($R = CH_3$ or $C_2H_5$), $M^{IV}C_2B_9H_{11}$[3] ($M^{IV}$ = Ge, Sn, or Pb), $CH_3GeCB_{10}H_{11}$,[4] and $M^V$-$CB_{10}H_{11}$[5] ($M^V$ = P, As, or Sb), in all of which the heteroatom formally replaces an isoelectronic BH or CH group in $C_2B_{10}H_{12}$. In addition, a large number of transition metal π complexes and other species have been derived from several of the compounds listed.[6]

Few examples are known of heteroatom insertion into small carboranes, a fact which reflects the heretofore limited research effort in this area rather than inherent problems of synthesis or stability in these systems. Several recent communications from this laboratory have reported the synthesis of small carborane–transition metal π complexes[7] and of $1\text{-}CH_3GaC_2B_4H_6$,[8] an analog of the polyhedral $2,4\text{-}C_2B_5H_7$ system. In this paper we describe in detail the preparation, structural characterization, and some chemistry of $1\text{-}CH_3\text{-}GaC_2B_4H_6$ and $1\text{-}CH_3InC_2B_4H_6$, as well as the results

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(1) (a) G. Popp and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 90, 6553 (1968); (b) G. Popp and M. F. Hawthorne, *Inorg. Chem.*, 10, 391 (1971).

(2) (a) B. M. Mikhailov and T. V. Potapova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1153 (1968); (b) D. A. T. Young, G. R. Willey, M. F. Hawthorne, M. R. Churchill, and A. H. Reis, Jr., *J. Amer. Chem. Soc.*, **92**, 6663 (1970).

(3) (a) R. L. Voorhees and R. W. Rudolph, *ibid.*, **91**, 2173 (1969); (b) R. W. Rudolph, R. L. Voorhees, and R. E. Cochoy, *ibid.*, **92**, 3351 (1970).

(4) L. J. Todd, A. R. Burke, H. T. Silverstein, J. L. Little, and G. S. Wikholm, *ibid.*, **91**, 3376 (1969).

(5) (a) J. L. Little, J. T. Moran, and L. J. Todd, *ibid.*, **89**, 5495 (1967); (b) L. J. Todd, J. L. Little, and H. T. Silverstein, *Inorg. Chem.*, **8**, 1698 (1969); (c) L. J. Todd, A. R. Burke, H. T. Silverstein, J. L. Little, and G. S. Wikholm, *J. Amer. Chem. Soc.*, **91**, 3376 (1969); (d) L. J. Todd, A. R. Burke, A. R. Garber, H. T. Silverstein, and B. N. Storhoff, *Inorg. Chem.*, **9**, 2175 (1970); (e) A. I. Echeistova, Y. K. Syrikin, L. I. Zakharkin, and V. I. Kyskin, *Zh. Strukt. Khim.*, **11**, 552 (1970); (f) L. I. Zakharkin and V. I. Kyskin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2142 (1970).

(6) For recent reviews, see M. F. Hawthorne, *Accounts Chem. Res.*, **1**, 281 (1968); L. J. Todd, *Advan. Organometal. Chem.*, **8**, 87 (1970); R. N. Grimes, "Carboranes," Academic Press, New York, N. Y., 1970, Chapter 9.

(7) (a) J. W. Howard and R. N. Grimes, *J. Amer. Chem. Soc.*, **91**, 6499 (1969); (b) R. N. Grimes, *ibid.*, **93**, 261 (1971); (c) J. W. Howard and R. N. Grimes, *Inorg. Chem.*, **11**, 263 (1972).

(8) R. N. Grimes and W. J. Rademaker, *J. Amer. Chem. Soc.*, **91**, 6498 (1969).

Table I. Partial Mass Spectra of 1-$CH_3GaC_2B_4H_6$ and 1-$CH_3InC_2B_4H_6$

| | Relative intensities[a] | | | |
|---|---|---|---|---|
| *m/e* | 1-$CH_3GaC_2B_4H_6$ | Assignment | 1-$CH_3InC_2B_4H_6$ | Assignment |
| 205 | | | 3.4 | $^{13}C^{12}C_2{}^{115}In^{11}B_4{}^1H_9{}^+$ |
| 204 | | | 100.0 | $^{12}C_3{}^{115}In^{11}B_4{}^1H_9{}^+$ |
| 203 | | | 100.0 | *b* |
| 202 | | | 44.3 | *b* |
| 201 | | | 11.0 | *b* |
| 161 | 1.6 | $^{13}C^{12}C_2{}^{71}Ga^{11}B_4{}^1H_9{}^+$ | | |
| 160 | 53.8 | $^{12}C_3{}^{71}Ga^{11}B_4{}^1H_9{}^+$ | | |
| 159 | 54.3 | *b* | | |
| 158 | 100.0 | *b* | | |
| 157 | 81.2 | *b* | | |
| 156 | 30.5 | *b* | | |
| 155 | 5.0 | *b* | | |
| 130 | | | 106 | $^{115}In^{12}C^1H_3{}^+$ |
| 115 | | | 1880 | $^{115}In^+$ |
| 86 | 82.9 | $^{71}Ga^{12}C^1H_3{}^+$ | | |
| 84 | 121.0 | $^{69}Ga^{12}C^1H_3{}^+$ | | |
| 76 | 7.3 | $^{12}C_2{}^{11}B_4{}^1H_8{}^+$ | 86.5 | $^{12}C_2{}^{11}B_4{}^1H_8{}^+$ |
| 75 | 8.0 | *b* | 81.2 | *b* |
| 74 | 11.3 | *b* | 119 | *b* |
| 73 | 22.6 | *b* | 252 | *b* |
| 72 | 16.6 | *b* | 171 | *b* |
| 71 | 230 | $^{71}Ga^+$ [c] | 112 | *b* |
| 70 | 6.3 | *b* | 92.5 | *b* |
| 69 | 345 | $^{69}Ga^+$ [c] | 122 | *b* |

[a] Normalized to base peak in parent group = 100. [b] Assigned to more than one species due to statistical distribution of $^{11}B$ and $^{10}B$ isotopes. [c] Contains small contribution from fragments derived from $C_2B_4H_8{}^+$.

of a single-crystal X-ray diffraction study of the gallium compound.

## Results

**Synthesis of 1-$CH_3GaC_2B_4H_6$ and 1-$CH_3InC_2B_4H_6$.** The preparation of icosahedral heteroatom carboranes is typically accomplished *via* insertion of the heteroatom into an 11-atom fragment such as $C_2B_9H_{13}$ or the $C_2B_9H_{11}{}^{2-}$ ion.[6] An analogous route to the synthesis of small heteroatom carboranes of pentagonal-bipyramidal geometry was expected to involve the pyramidal species 2,3-$C_2B_4H_8$ or its anionic derivative, $C_2B_4H_7{}^-$. Accordingly, the gas-phase reaction of trimethylgallium or trimethylindium with $C_2B_4H_8$ yields the corresponding 1-methyl-1-galla- or 1-methyl-1-inda-2,4-dicarba-*closo*-heptaborane(7).

$$C_2B_4H_8 + Ga(CH_3)_3 \xrightarrow{215^\circ} \underset{20\text{–}30\%}{CH_3GaC_2B_4H_6} + B(CH_3)_3 + \text{solids}$$

$$C_2B_4H_8 + In(CH_3)_3 \xrightarrow{95\text{–}110^\circ} \underset{50\text{–}60\%}{CH_3InC_2B_4H_6} + B(CH_3)_3 + \text{solids}$$

The gallacarborane has been characterized from $^{11}B$ and $^1H$ nmr,[8] mass spectra (Table I), and infrared spectra (Table II), and a pentagonal-bipyramidal structure containing an apex gallium atom with an attached methyl group has been proposed.[8] Although the spectroscopic data alone do not reveal whether the carbon atoms in the equatorial belt are adjacent, the formation of 2,3-$C_2B_4H_8$ as the major pyrolysis product strongly indicated the adjacent-carbon structure (a conclusion subsequently confirmed by the X-ray study described below). It should be noted that this contrasts with the analogous carborane system, 2,4-$C_2B_5H_7$, in which the carbons are in nonadjacent equatorial positions.[9,10]

Table II. Infrared Intensities[a]

| 1-$CH_3GaC_2B_4H_6$ | 1-$CH_3InC_2B_4H_6$ |
|---|---|
| 3050 (m) | 3025 (m) |
| 2950 (s) | 2985 (s) |
| 2905 (m) | 2923 (s) |
| 2590 (vs) | 2590 (vs) |
| 1320 (m) | 1930 (m) |
| 1283 (s) | 1510 (s) |
| 1200 (s) | 1346 (m) |
| 1023 (vs) | 1290 (s) |
| 994 (vs) | 1155 (m) |
| 850 (m) | 1060 (s) |
| 618 (s) | 1022 (m) |

[a] Frequencies in $cm^{-1}$; in $CDCl_3$ solution *vs.* $CDCl_3$.

The similarity of the $^{11}B$ and $^1H$ nmr spectra, mass spectra (Table I), and infrared spectra (Table II) of the indacarborane to those of the gallium compound suggests an analogous polyhedral structure containing an apex In–$CH_3$ group. Again, the formation of 2,3-$C_2B_4H_8$ on pyrolysis of 1-$CH_3InC_2B_4H_6$ is taken as clear evidence that the carbon atoms are adjacent in the cage framework.

**Reactions of 1-$CH_3GaC_2B_4H_6$ and 1-$CH_3InC_2B_4H_6$.** Both compounds are colorless, slightly volatile crystalline solids which are thermally stable to at least 100° but are slowly degraded by air. Pyrolysis of either material generates 2,3-$C_2B_4H_8$ in 20–30% yield, but no other significant volatile products.

Bromine reacts rapidly with the gallacarborane under Friedel–Crafts conditions, destroying the cage structure and forming primarily dimethylbromogallane dimer. In the presence of aluminum bromide, mole ratios of bromine consumed to gallacarborane as high as 10:1 have been observed; in the absence of aluminum bromide, the same reaction is observed but less bromine is taken up. No volatile boron-containing products are obtained. Bromination of the indacarborane proceeds similarly in $CS_2$ at room temperature,

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(9) R. A. Beaudet and R. L. Poynter, *J. Chem. Phys.*, **43**, 2166 (1965).

(10) A *C,C'*-dimethyl derivative of a new isomer of $C_2B_5H_7$ having adjacent carbon atoms has been reported: R. R. Rietz and R. Schaeffer, *J. Amer. Chem. Soc.*, **93**, 1263 (1971).

$$CH_3GaC_2B_4H_6 + Br_2 \xrightarrow[CS_2,\ 25^\circ]{AlBr_3} \underset{\sim 30\%}{[(CH_3)_2GaBr]_2} + CH_3Br + HBr + \text{solids}$$

with bromine consumed in a 4:1 mole ratio. Again, the cage framework is evidently degraded.

Hydrogen chloride readily attacks both carboranes in a 2:1 stoichiometry, but with contrasting results. In the case of the gallacarborane the major products are 2,3-$C_2B_4H_8$ and a compound assumed to be the dimer of methyldichlorogallane. The reaction of $CH_3InC_2B_4H_6$ with HCl, on the other hand, yields no detectable $C_2B_4H_8$ or indeed any volatile product other than $H_2$.

$$CH_3GaC_2B_4H_6 + 2HCl \xrightarrow{25\text{–}50^\circ} \underset{40\text{–}53\%}{C_2B_4H_8} + 0.5(CH_3GaCl_2)_2 + \text{solids}$$

No reaction is observed between 1-$CH_3GaC_2B_4H_6$ and the electrophilic reagents $AlCl_3$ and $BF_3$.

**X-Ray Structure Determination of 1-$CH_3GaC_2B_4H_6$.** A single-crystal X-ray diffraction study of the gallacarborane has established the molecular geometry indicated in Figure 1, in space group *Pn*$2_1$*a* with four molecules per unit cell. The bond distances and angles are given in Table III, and the carbon–carbon bond in the equatorial plane is identified from its uniquely short length of 1.47 Å. No abnormally close intermolecular contacts were found, the shortest being Ga···B, 3.69; B···$CH_3$, 3.93; C···$CH_3$, 3.97; and C···B, 3.87 Å.

Table III. Bond Lengths and Angles in 1-$CH_3GaC_2B_4H_6$[a]

| Bond lengths, Å | | Bond angles, deg | |
|---|---|---|---|
| Ga–B(5) | 2.11 (3) | B(4)–Ga–B(5) | 46 (2) |
| Ga–C(2) | 2.32 (3) | B(4)–Ga–B(6) | 75 (2) |
| C(2)–C(3) | 1.47 (4) | B(5)–Ga–$CH_3$ | 166 (2) |
| B(4)–B(7) | 1.77 (4) | B(6)–B(7)–B(4) | 99 (3) |
| Ga–B(4) | 2.22 (3) | B(4)–B(5)–B(6) | 105 (3) |
| Ga–$CH_3$ | 1.91 (3) | B(4)–C(3)–C(2) | 113 (3) |
| B(4)–B(5) | 1.70 (3) | B(4)–Ga–C(3) | 40 (2) |
| B(5)–B(7) | 1.74 (4) | C(2)–Ga–C(3) | 37 (2) |
| C(3)–B(4) | 1.57 (4) | C(2)–Ga–$CH_3$ | 122 (3) |
| C(3)–B(7) | 1.74 (4) | C(2)–B(7)–C(3) | 50 (3) |
| | | B(5)–B(4)–C(3) | 104 (3) |

[a] Estimated standard deviations given in parentheses.

## Discussion

The single-crystal X-ray diffraction study of 1-$CH_3GaC_2B_4H_6$, while confirming the essential features of the structure originally proposed,[8] has produced two unexpected findings: substantial displacement of the gallium away from the framework carbon atoms, and a large (23°) angle between the Ga–$CH_3$ bond and the Ga–B(7) axis. These structural anomalies contrast sharply with the X-ray determined structure[2b] of the related icosahedral molecule 1-$C_2H_5$-$AlC_2B_9H_{11}$, in which the nearest-neighbor Al–C and Al–B distances are essentially equal and the ethyl group is located directly above the cage aluminum atom. The structure of 1-$CH_3GaC_2B_4H_6$ also differs significantly from that of its isoelectronic carborane analog, 2,4-$C_2B_5H_7$, in which the apex–equatorial bond distances are the same within ~0.1 Å.[9] In the absence of quantitative molecular orbital studies, discussion of the bonding in this compound must be speculative in nature, but some tentative observations seem appropriate. Since gallium contains d electrons in its valence shell, in contrast to boron and aluminum, the distortions from pseudo-$C_5$ symmetry in the gallacarborane may be a consequence of d-orbital participation in the bonding. However, the filled $d^{10}$ subshell of gallium requires that d-orbital involvement be limited to back-donation from the metal to the carborane ligand; forward (ligand to metal) bonding can utilize only the empty or partially filled s and p orbitals of gallium. As a basis for constructing a qualitative molecular orbital description of the bonding, it is useful to consider the treatment of the pentagonal-bipyramidal $B_7H_7^{2-}$ ion by Lipscomb and Hoffmann.[11] In their analysis, the apex boron atoms are artificially separated from the five-membered equatorial belt, and the $p_z$ orbitals in the ring are used, as in the planar $C_5H_5^-$ system, to construct five molecular orbitals of which three are bonding. The bonding MO's are of the proper symmetry for overlap with the available $sp_z$, $p_x$, and $p_y$ orbitals on the apex borons, resulting in a filled-shell electronic structure for $B_7H_7^{2-}$ and, by analogy, for the isoelectronic $C_2B_5H_7$ system as well.

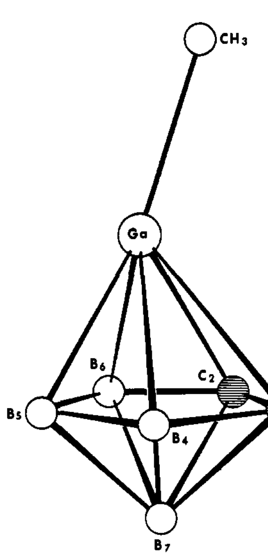

Figure 1. Structure of 1-$CH_3GaC_2B_4H_6$. Molecular parameters are listed in Table III.

Applying this reasoning to the present case, the replacement of an apex BH group in $C_2B_5H_7$ with a $GaCH_3$ unit permits a similar bonding description, except that the structural distortions in the gallium compound must also be accounted for. If the molecule is arbitrarily considered as a $CH_3Ga^{2+}$ group bonded to a pyramidal $C_2B_4H_6^{2-}$ ligand, the ligand will contain six delocalized electrons occupying an $a_1$ and two $e_1$ bonding MO's, with a pair of $e_2$ antibonding MO's at higher energy. The gallium atom may utilize a pair of $sp_z$ hybrid orbitals to bond to the methyl group and to receive an electron pair from the $a_1$ orbital of $C_2B_4H_6^{2-}$, while the empty $p_x$ and $p_y$ orbitals of gallium may each accept an additional pair from the $e_1$ degenerate MO's of the ligand, as shown in Figure 2a–c.

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(11) (a) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179 (1962); (b) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963; (c) W. N. Lipscomb, *Proc. Nat. Acad. Sci. U. S.*, 47, 1791 (1961).

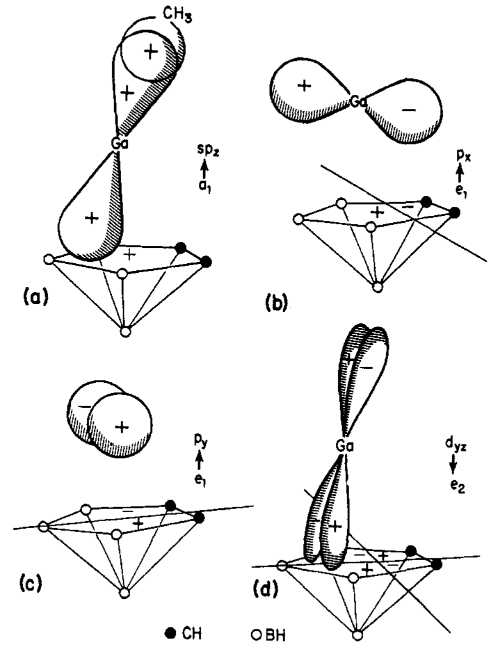

Figure 2. Suggested gallium–carborane ligand orbital interactions in 1-$CH_3GaC_2B_4H_6$.

The available $e_2$ antibonding MO's of $C_2B_4H_6^{2-}$ may receive two pairs of electrons *via* back-bonding from metal d orbitals of the correct symmetry. However, this cannot take place effectively unless the metal atom is shifted to one side of the open face of the ligand; with the metal in this position, the $d_{yz}$ orbital can overlap with an $e_2$ orbital as indicated in Figure 2d. Additional back-donation is possible from the $d_{x^2-y^2}$ orbital to the remaining $e_2$ ligand MO. Similar arguments have been invoked to account, in part, for the slip distortions in complexes of the dicarbollide ion ($C_2B_9H_{11}^{2-}$) with $d^8$ or $d^9$ metal atoms,[12] and in complexes of $Ag^+$ and $Cu^+$ with benzene.[13,14]

The foregoing considerations do not account for the bending of the methyl group away from the Ga–B(7) axis, which implies tilting of the $sp_z$, $p_x$, and the d orbitals on gallium with respect to the equatorial ring. A possible rationale for this tilting is that such a distortion increases the effective overlap of the gallium $p_x$ orbital with the carbon atoms in the ring (Figure 2b), and at the same time facilitates back-bonding from the $d_{x^2-y^2}$ orbital to the appropriate $e_2$ MO on the equatorial ring.

In summary, one factor distinguishing the gallacarborane from the more symmetrical carboranes containing only lighter group III elements in the cage may be the availability of filled d orbitals on gallium. The metal atom shift in the gallium compound is comparable in magnitude to that of the slip-distorted dicarbollyl complexes, and therefore is assumed to reflect a fairly general phenomenon rather than an isolated case. Consequently, similar structural distortions are expected in 1-$CH_3InC_2B_4H_6$ and in the corresponding (but presently unknown) thallium compound.

## Experimental Section

**General Procedure.** Except where otherwise stated, all work was conducted in Pyrex vacuum systems using standard techniques.

**Materials.** Trimethylgallium was obtained from Alfa Inorganics, Inc., and used as received. Trimethylindium was prepared from indium metal and dimethylmercury (Alfa) by the method of Dennis, *et al.*,[15] and identified from its infrared[16] and mass spectra. 2,3-Dicarbahexaborane(8) was prepared by the reaction of pentaborane(9) with a ninefold excess of acetylene at 215°.[17] Bromine (Baker reagent) was distilled *in vacuo* before use. Hydrogen chloride was prepared from sodium chloride and concentrated sulfuric acid, and was purified by vacuum-line distillation through a −128° trap. Aluminum chloride, boron trifluoride, and boron trifluoride etherate were reagent grade and used as received.

**Instrumentation.** Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6D spectrometer, $^{11}B$ and $^1H$ nmr spectra on Varian HA-100 and Hitachi Perkin-Elmer R-20 spectrometers, and infrared spectra on a Beckman IR-8 grating spectrophotometer.

**Preparation of 1-Methyl-1-galla-2,4-dicarba-*closo*-heptaborane(7).** Typically, 3.0 mmol of 2,3-$C_2B_4H_8$ and 3.0 mmol of $Ga(CH_3)_3$ were sealed into a 100-ml Pyrex bulb equipped with a breakoff tip and pyrolyzed at 215° for 24 hr, during which the interior of the bulb was coated with gray solids. The volatile contents were fractionated on the vacuum line through a −45° trap for 1 hr. The material passing −45° consisted of unreacted $C_2B_4H_8$ and trimethylboron, while the −45° condensate was nearly pure crystalline 1-$CH_3GaC_2B_4H_6$. Final purification was achieved by pumping on the gallacarborane for a few minutes at 0°, which removed the last traces of $C_2B_4H_8$. The yield of 1-$CH_3GaC_2B_4H_6$ was 50 mg (20% yield based on $C_2B_4H_8$ consumed).

**Preparation of 1-Methyl-1-inda-2,4-dicarba-*closo*-heptaborane(7).** The reaction of 3.0 mmol of 2,3-$C_2B_4H_6$ with 3.6 mmol of $In(CH_3)_3$ was conducted at 100° for 8 hr. Vacuum distillation of the contents of the reactor at 25° removed all volatile materials other than the indacarborane; pure crystalline 1-$CH_3InC_2B_4H_6$ (339 mg, 60% yield) was obtained by sublimation *in vacuo* at 100° into a trap at −196°.

The 32.1-MHz $^{11}B$ nmr spectrum of 1-$CH_3InC_2B_4H_6$ in $CDCl_3$ solution very closely resembles the spectrum of 1-$CH_3GaC_2B_4H_6$ presented earlier,[8] and contains doublets at $\delta$ −4.5 ppm relative to external $BF_3 \cdot O(C_2H_5)_2$ ($J$ = 131 Hz), area 2; −0.31 (143), area 1; and +46.3 (173), area 1, assigned to B(4,6)–H, B(5)–H, and B(7)–H, respectively. The 60-MHz $^1H$ nmr spectrum in $CDCl_3$ contains single resonances at $\tau$ 3.60, area 2, and 9.75, area 3, assigned to the cage C–H and methyl C–H groups, respectively. The B–H quartets are not well defined.

**Pyrolysis of 1-Methyl-1-galla-2,4-dicarba-*closo*-heptaborane(7).** A 40-mg sample of pure gallacarborane was sealed into a 100-ml Pyrex bulb and heated at 285° for 12 hr, after which separation of the volatiles by vacuum fractionation gave 0.013 mmol of 2,3-$C_2B_4H_8$ (30% yield based on 1-$CH_3GaC_2B_4H_6$ consumed), $B(CH_3)_3$, and 34 mg of unreacted starting material. Dark solid deposits formed during the reaction were not investigated.

**Pyrolysis of 1-Methyl-1-inda-2,4-dicarba-*closo*-heptaborane(7).** A 7-mg sample of the indacarborane was heated at 215° in a sealed Pyrex reactor for 72 hr. The only volatile product was 2,3-$C_2B_4H_8$ (0.0073 mmol, 20% yield), and no starting material was recovered. Again, dark nonvolatile materials were produced.

**Bromination of 1-Methyl-1-galla-2,4-dicarba-*closo*-heptaborane(7).** The reaction was conducted under a variety of conditions, of which the following are typical. (a) Carbon disulfide (3 ml), 22.1 mg (0.14 mmol) of the gallacarborane, and 0.55 mmol of $Br_2$ were distilled into an evacuated reactor at −196° containing 0.27 mmol of aluminum powder. On warming to room temperature with stirring, the bromine was decolorized within seconds. Analysis of the volatile products by glpc gave 0.01 mmol of $CH_3Br$, 0.01 mmol of HBr, and 0.02 mmol of $[(CH_3)_2GaBr]_2$ (identified from its mass spectrum). Assuming the total conversion of Al to $AlBr_3$, the mole ratio of $Br_2$ to gallacarborane consumed was 1:1. (b) An identical procedure was followed, using 0.91 mmol of Al, 1.82 mmol of $Br_2$, and 13.0 mg (0.08 mmol) of 1-$CH_3GaC_2B_4H_6$. The $Br_2$ was not immediately decolorized, but after stirring for 48 hr at room temperature the solution was light yellow. The volatile products consisted of $[(CH_3)_2GaBr]_2$ (0.03 mmol) and traces of HBr and $CH_3Br$. The $Br_2$:$CH_3GaC_2B_4H_6$ mole ratio was 6:1

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[12] L. F. Warren, Jr., and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **90**, 4823 (1968).

[13] R. S. Mulliken, *ibid.*, **74**, 811 (1952).

[14] M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C79 (1951).

[15] L. M. Dennis, R. W. Work, E. G. Rochow, and E. M. Chamot, *J. Amer. Chem. Soc.*, **56**, 1047 (1934).

[16] J. R. Hall, L. A. Woodward, and E. A. V. Ebsworth, *Spectrochim. Acta*, 20, 1249 (1964).

[17] T. P. Onak, R. P. Drake, and G. B. Dunks, *Inorg. Chem.*, **3**, 1686 (1964).

based on reactants consumed. (c) Following the same procedure, 10.8 mg (0.06 mmol) of 1-$CH_3GaC_2B_4H_6$ was allowed to react with a large excess (1.07 mmol) of $Br_2$ over 0.27 mmol of Al powder. After 5 days at 25° the red color of $Br_2$ persisted. The volatile materials consisted of 0.07 mmol of $Br_2$ (measured by vapor phase titration with $C_2H_4$), 0.05 mmol of a mixture of $CH_3Br$ and HBr which was not separated, and a trace of $H_2$. No 1-$CH_3GaC_2B_4H_6$ or $[(CH_3)_2GaBr]_2$ was detected, and the calculated $Br_2$:$CH_3GaC_2B_4H_6$ mole ratio was 10:1. (d) A reaction of 18.8 mg (0.12 mmol) of $CH_3GaC_2B_4H_6$ with 0.55 mmol $Br_2$ in $CS_2$, in the *absence* of Al, was continued for 4 days at 25°. The volatiles consisted of $[(CH_3)_2GaBr]_2$ (0.08 mmol), $CH_3Br$ and HBr (total of 0.02 mmol), and a trace of $H_2$. The $Br_2$:$CH_3GaC_2B_4H_6$ mole ratio was 4.6:1.

**Bromination of 1-Methyl-1-inda-2,4-dicarba-*closo*-heptaborane(7).** Following the procedure employed for bromination of the gallacarborane, 36.2 mg (0.18 mmol) of 1-$CH_3InC_2B_4H_6$ in 0.3 ml of $CS_2$ with 0.91 mmol of $Br_2$ was stirred for 2 days. The reaction appeared sluggish, partly due to limited solubility of the indacarborane. The volatile materials consisted of 0.04 mmol of $H_2$ and 0.22 mmol of $Br_2$, which was titrated with $C_2H_4$ in the gas phase. The calculated mole ratio of $Br_2$ consumed to indacarborane was ~4:1. The remaining solid was nonvolatile and contained no unreacted starting material.

**Reaction of 1-Methyl-1-galla-2,4-dicarba-*closo*-heptaborane(7) with Hydrogen Chloride.** The reaction of 0.14 mmol of the gallacarborane with 0.30 mmol of HCl in the absence of solvent proceeded rapidly, as evidenced by the disappearance of the gallacarborane crystals and the appearance of a volatile liquid. After 20 min at 25° the reactor was heated to 50° for 10 min. The volatile materials consisted of 2,3-$C_2B_4H_8$ (0.07 mmol, 50% yield), and a trace (<0.01 mmol) of HCl, but no $H_2$ was detected.

**Reaction of 1-Methyl-1-inda-2,4-dicarba-*closo*-heptaborane(7) with Hydrogen Chloride.** Indacarborane (0.31 mmol) was condensed with 0.68 mmol of HCl into an evacuated bulb at −196°. After warming to room temperature for 40 min, the reactor contained 0.06 mmol of $H_2$ and 0.25 mmol of HCl remained. The unreacted HCl was returned to the reactor and the reaction was continued for an additional 12 hr, after which only 0.09 mmol of HCl remained. Other than $H_2$, no volatile products were detected.

**Attempted Reactions of 1-Methyl-1-galla-2,4-dicarba-*closo*-heptaborane(7) with Boron Trifluoride and Aluminum Chloride.** A mixture of 0.29 mmol of the gallacarborane and 0.80 mmol of $BF_3$ gave no reaction at 50° over a 2-day period, as shown by the recovery of all starting materials. A solution of 9.2 mg of $AlCl_3$ with 3.0 mg of 1-$CH_3GaC_2B_4H_6$ in $CS_2$ gave no reaction in 2 days, and all of the original gallium compound was recovered.

**X-Ray Diffraction Study of 1-Methyl-1-galla-2,4-dicarba-*closo*-heptaborane(7).** An irregularly shaped crystal (0.3 × 0.2 × 0.2 mm) was sealed under nitrogen in a thin-walled capillary tube. Preliminary cell dimensions were obtained from precession photographs and refined by a least-squares fit to the values of $\pm 2\theta$ for 12 general, high-order reflections as measured on the diffractometer ($\lambda_{\mathrm{Mo}\,K\alpha}$ 0.71069 Å). Intensity measurements were made with a Picker four-circle diffractometer with Mo $K\alpha$ radiation, using techniques previously described.[18] Scattered intensity significantly above background was observed at 262 out of 601 reciprocal lattice points surveyed. Crystal decomposition was indicated by a uniform linear drop of 15% in the measured structure amplitudes of three reference reflections over the course of the experiment. An appropriate correction was applied to compensate for this effect, but no absorption corrections were made. Crystal data are as follows: mol wt 158.06; space group $Pn2_1a$ ($Pnma$ excluded by trial); $Z = 4$, $a = 12.226$ (3), $b = 7.412$ (1), $c = 7.971$ (1) Å; $D_{\mathrm{calcd}} = 1.45$ g cm$^{-3}$ (no measurement possible); $\mu(\mathrm{Mo}\,K\alpha) = 37$ cm$^{-1}$.

From the systematic absences, $Pnma$ and $Pn2_1a$ are possible space groups. No density determination was possible, but the observed volume of the unit cell suggests $Z = 4$. If the space group were $Pnma$ the molecule would be required to have a mirror plane of symmetry. The three-dimensional Patterson function could be interpreted to yield vectors corresponding to those for a molecule having a mirror plane of symmetry at $y = {}^1/_4$, and the structure was determined assuming the centrosymmetric space group. However, least-squares refinement of this model was unsatisfactory, giving unreasonably low thermal parameters for atoms off the mirror plane. In addition, even with anisotropic thermal parameters assumed for all atoms, $R$ did not fall below 0.12, and the agreement between observed and calculated structure amplitudes for several low-order reflections was very poor. The same positional parameters and an overall isotropic thermal parameter of 4.0 Å$^2$ gave $R = 0.10$ when the space group was taken as $Pn2_1a$, and refinement of this model with anisotropic thermal parameters assumed only for gallium gave $R = 0.05$ at convergence. No unacceptable discrepancies between observed and calculated structure amplitudes exist for this model, so that the space group is evidently $Pn2_1a$.

No convincing difference in $R$ for the two possible enantiomeric structures emerged when the anomalous dispersion terms for gallium were included in the refinement. For this reason, the absolute configuration of the molecule is not determined. A final three-dimensional difference electron-density synthesis showed no structurally significant features. The atomic parameters obtained from the least-squares refinement do not differ significantly from those for a model having a mirror plane of symmetry at $y = {}^1/_4$. The positional parameters for this model are given in Table IV.[19]

**Table IV.** Fractional Coordinates for the Idealized Model of 1-$CH_3GaC_2B_4H_6$[a]

| Atom | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| Ga | 0.0856 (2) | 0.2500 | 0.0994 (3) |
| C(2) | 0.250 (2) | 0.349 (3) | −0.013 (3) |
| C(3) | 0.250 (2) | 0.151 (3) | −0.013 (3) |
| $CH_3$ | 0.059 (2) | 0.250 | 0.336 (3) |
| B(4) | 0.147 (2) | 0.068 (4) | −0.101 (4) |
| B(5) | 0.074 (2) | 0.250 | −0.165 (3) |
| B(6) | 0.147 (2) | 0.432 (4) | −0.101 (4) |
| B(7) | 0.214 (2) | 0.250 | −0.202 (3) |

[a] Estimated standard deviations are given in parentheses.

Bond lengths and angles for the model, presented in Table III, are unremarkable except for the observed angle B(5)–Ga–$CH_3$ of 166°, which shows that the Ga–$CH_3$ axis is significantly displaced from a direction perpendicular to the central ring plane defined by C(2), C(3), B(4), B(5), and B(6).

The five-membered equatorial ring is coplanar within experimental error. The equation of the least-squares mean plane through the five atoms is $-0.489x + 0.872z + 1.583 = 0$, where $x$ and $z$ are measured, in ångströms, along the $a$ and $c$ axes, respectively. The mean displacement of atoms from this plane is 0.001 Å, the maximum 0.002 Å. The gallium atom lies 1.76 Å from the plane, with B(7) 1.10 Å from the plane on the opposite side.

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(18) R. F. Bryan, P. T. Greene, P. F. Stokely, and E. W. Wilson, Jr., *Inorg. Chem.*, 10, 1468 (1971).

(19) The observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.