

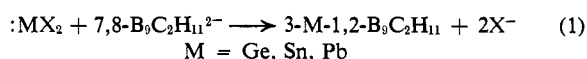
Reactions Involving the
Undecahydro-7,9-dicarba-*nido*-undecaborate(2-) Ion,
7,9-B₉C₂H₁₁²⁻. Insertion, Oxidative Closure, and Addition

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Abstract: The carbametallic borane 3-Ge-1,7-B₉C₂H₁₁ was prepared from a reaction between GeI₂ and the 7,9-B₉C₂H₁₁²⁻ ion. However, attempts to prepare 3-Sn-1,7-B₉C₂H₁₁ by the corresponding reaction with SnCl₂ led to a facile oxidative closure of the anion to give high yields of 2,3-B₉C₂H₁₁ and tin. If the oxidative closure is followed by treatment with ligands, B₉C₂H₁₁·L adducts are formed. The adducts are believed to be isomers of those which can be formed by an oxidative substitution involving the 7,8-B₉C₂H₁₂⁻ ion. The present path to B₉C₂H₁₁·L species is not an oxidative substitution but involves the distinct steps of oxidative closure followed by addition. Evidence is presented which shows that the addition reaction results in asymmetric substitution but not necessarily at the facial 10 position as found for the reaction between 2,3-B₉C₂H₁₁ and certain carbanions. Rather, the adducts studied here are suggested to have a 3-L-7,9-B₉C₂H₁₁ structure (L = N(CH₃)₃, P(C₆H₅)₃, OC₂H₅⁻).

We previously reported the preparation and characterization of carbametallic boranes¹ analogous to the unknown tricarbaborane B₉C₃H₁₁. Their preparation involved the treatment of 7,8-B₉C₂H₁₁²⁻ with carbenoid reagents (eq 1). Attempts to expand



the scope of this chemistry with the preparation of new MB₉C₂H₁₁ isomers gave some unexpected results. Based on the comparison of the mass spectra for the 3-M-1,2-B₉C₂H₁₁ molecules, thermal isomerization without destruction of the icosahedral structure was anticipated only for 3-Ge-1,2-B₉C₂H₁₁.¹ The latter prognosis was borne out in the present study; however, the expectation of a routine extension of the carbenoid synthesis to 7,9-B₉C₂H₁₁²⁻ was not. Instead, a new oxidative closure reaction was discovered. The formation of ligand adducts with the closure product was also investigated.

Results and Discussion

Insertion. As anticipated by analogy to the preparation of 3-Ge-1,2-B₉C₂H₁₁ from 7,8-B₉C₂H₁₁²⁻ and the carbenoid, treatment of 7,9-B₉C₂H₁₁²⁻ with GeI₂ gives the new isomer 3-Ge-1,7-B₉C₂H₁₁ which can also be prepared by thermal isomerization of 3-Ge-1,2-B₉C₂H₁₁ at 600°. This volatile solid sublimes at 80° *in vacuo*. The mass spectrum shows a sharp cutoff at *m/e* 210 corresponding to ⁷⁶Ge¹²C₂¹¹B₉¹H₁₁⁺. As in the case of the 3-Ge-1,2-B₉C₂H₁₁¹ the infrared spectrum of 3-Ge-1,7-B₉C₂H₁₁ gives a peak at 280 cm⁻¹, probably a Ge-C cage motion, and no evidence for a hydrogen pendent from Ge (Table I). The single broad resonance observed at 1.47 ppm downfield from TMS in the ¹H nmr spectrum of a benzene

(1) R. W. Rudolph, R. L. Voorhees, and R. E. Cochoy, *J. Amer. Chem. Soc.*, **92**, 3351 (1970); R. L. Voorhees and R. W. Rudolph, *ibid.*, **91**, 2713 (1969).

(2) M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. C. Schwerin, F. N. Tebbe, and P. A. Wegner, *ibid.*, **90**, 862 (1968).

(3) The nomenclature used in this report is that most recently suggested for polyhedral heteroboranes by IUPAC, *Pure Appl. Chem.*, **30**, 681 (1972); it may differ from that used in previous reports concerning the same compounds. To avoid confusion, the reader should consult Figures 1, 3, and 4.

Table I. Infrared Spectra^a

3-Ge-1,7-B ₉ C ₂ H ₁₁ ^b	3030 w, 2576 vs, 2548 vs, 1158 m, 1116 w, 1078 vw, 1054 w, 1035 vw, 1002 s, 980 m, 931 w, 921 vw, 902 m, 875 w, 855 vw, 770 w, 740 br, m, 697 w, 630 m, 281 br, m
2,3-B ₉ C ₂ H ₁₁ ^c	3077 w, 2590 vs, 2565 s, 1149 s, 1094 s, 1039 vw, 991 w, 943 w, 922 w, 903 w, 886 vw, 835 m, 798 w, 768 m, 709 m, 695 w, 688 w, 660 vw, 485 vw, 427 vw
7,9-B ₉ C ₂ H ₁₁ ·P(C ₆ H ₅) ₃ ^b	3081 vw, 3060 w, 3035 vw, 2520 br, vvs, 1979 vw, 1958 vw, 1886 w, 1808 w, 1583 w, 1566 vvw, 1481 s, 1434 vs, 1395 br, m, 1332 w, 1313 w, 1187 br, m, 1160 w, 1120 br, s, 1101 vs, 1070 vw, 1054 m, 1028 s, 998 s, 966 m, 926 s, 820 w, 846 w, 816 w, 746 vs, 713 s, 690 vs, 639 m, 604 w, 595 m, 568 w, 556 vw, 535 s, 515 vs, 501 vs, 458 w, 450 m, 417 m
7,9-B ₉ C ₂ H ₁₁ ·N(CH ₃) ₃ ^b	3020 m, 2956 w, 2530 br, vvs, 1482 vs, 1461 vs, 1413 s, 1275 w, 1237 m, 1181 br, w, 1122 s, 1103 s, 1060 s, 1031 s, 1013 m, 968 vs, 928 vs, 895 sh, m, 883 m, 840 vw, 825 w, 798 vw, 759 sh, w, 739 w, 645 vw, 627 vw, 600 w, 572 vw, 557 vw, 460 w, 448 vw, 295 w, 279 sh, vw
(CH ₃) ₃ N ⁺ ·7,9-(CH ₃) ₂ -7,9-B ₉ C ₂ H ₉ ·OC ₂ H ₅ ⁻ ^b	3030 m, 2965 s, 2920 s, 2860 s, 2550 vs, 2510 vs, 2460 vs, 1484 s, 1450 m, 1415 w, 1386 w, 1372 w, 1360 vw, 1286 w, 1180 vs, br, 1150 s, sh, 1085 w, 1046 w, 1035 w, 1008 m, sh, 998 s, 946 vs, 930 m, sh, 892 m, 862 m, 822 s, 800 w, 770 vw, 746 m, 716 w, br, 685 vw, 662 m, 620 m, 608 m, 550 vw, 535 vw, 480 vw, 436 m

^a Band positions are reported in cm⁻¹ with relative intensities given by s = strong, m = medium, w = weak, v = very, sh = shoulder, br = broad. ^b Determined in a KBr matrix. ^c Determined from a thin deposit of the solid sublimed onto a CsI window which was held at -196°.

solution is consistent with C_s point symmetry (Figure 1). Six doublets are expected in the ¹¹B nmr spectrum, three of intensity 2 and three of intensity 1. The spectrum determined at 70.6 Hz (Figure 2) gives doublets at 3.34 (150) 1, 6.21 (173) 2, 6.95 (160) 1, 10.42 (157) 4, and 17.45 (162) 1 ppm;⁴ the signal at 10.42 ppm appears to be due to the overlap of two separate resonances. Although the ¹¹B spectrum is not completely resolved, evidence in support of the proposed structure of 3-Ge-1,7-B₉C₂H₁₁ comes from the known position of the carbon atoms in the starting material.⁵ Thus, 26 electrons are assigned to the bonding of the icosahedral framework in accord with empirical and theoretical observations regarding the

(4) Reported in ppm upfield from F₃B·O(C₂H₅)₂ followed by the doublet splitting in parentheses (Hz) and the relative intensity.

(5) D. V. Howe, C. J. Jones, R. J. Wiersma, and M. F. Hawthorne, *Inorg. Chem.*, **10**, 2516 (1971).

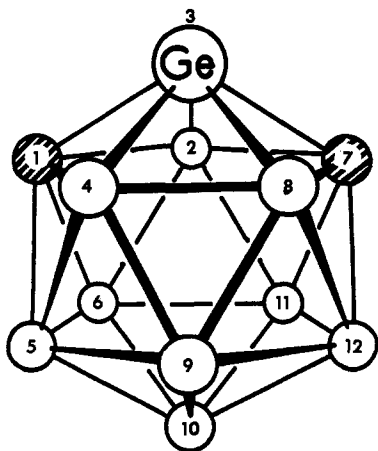
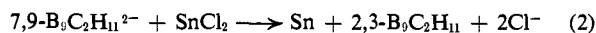


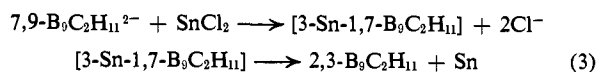
Figure 1. The proposed structure and numbering convention for 3-Ge-1,7-B₉C₂H₁₁. Carbon atoms are shaded; all vertices except Ge actually have exodeltahedral hydrogens attached.

correlation of electron count and structure in heteroboranes.⁶⁻⁸

Oxidative Closure. Surprisingly, when the 7,9-B₉C₂H₁₁²⁻ ion was treated with SnCl₂ in the same manner as for GeI₂, insertion did not occur. Rather than undergoing insertion to form a stannacarborane the carbenoid effects an *oxidation* as vividly demonstrated by a rapid blackening of the reaction mixture upon the addition of SnCl₂ to a solution of 7,9-B₉C₂H₁₁²⁻. Although SnCl₂ is not usually thought of as an oxidizing agent, the meta dicarbollide ion apparently is a relatively strong reducing agent and oxidative closure results (eq 2). Removal of two to the 26 "framework



electrons" in the *nido*-7,9-B₉C₂H₁₁²⁻ ion gives the requisite number^{9a} for an 11 atom deltahedron^{9b} as found in 2,3-B₉C₂H₁₁.¹⁰ The particular meta relationship of the carbons in the only known isomer of B₉C₂H₁₁ places them at the lowest order vertices of the deltahedron, in accord with empirical observations for the "preferred" placement of "electron-rich" heteroatoms.^{6b} Apparently the meta relationship of the carbons in 7,9-B₉C₂H₁₁²⁻ renders the closure facile compared to 7,8-B₉C₂H₁₁²⁻ where closure would not place the ortho carbon atoms at low order vertices without a major rearrangement of the polyhedron (see Figure 3). Although we have been unable to isolate the stannacarborane 3-Sn-1,7-B₉C₂H₁₁, the *detailed* mechanism of closure probably involves its formation followed by disproportionation to metallic Sn and 2,3-B₉C₂H₁₁ (eq 3). In fact, when sufficient energy is



supplied to the rather stable 3-Sn-1,2-B₉C₂H₁₁, it too

(6) (a) R. E. Williams, *Inorg. Chem.*, **10**, 210 (1971); (b) R. E. Williams, *Progr. Boron Chem.*, **2**, 37 (1970).

(7) K. Wade, *Chem. Commun.*, 792 (1971).

(8) R. W. Rudolph and W. R. Pretzer, *Inorg. Chem.*, **11**, 1974 (1972).

(9) (a) As discussed in ref 8 this number is $2n + 2$, $2n + 4$, or $2n + 6$ for *closo*, *nido*, and *aracho* structures, respectively, where n = the number of polyhedral vertices in the framework. (b) A polyhedron whose faces are triangular as in the case of *closo* boranes and heteroboranes.

(10) (a) F. N. Tebbe, P. M. Garret, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **90**, 869 (1968); (b) C. D. Tsai and W. E. Streib, *ibid.*, **88**, 4413 (1966).

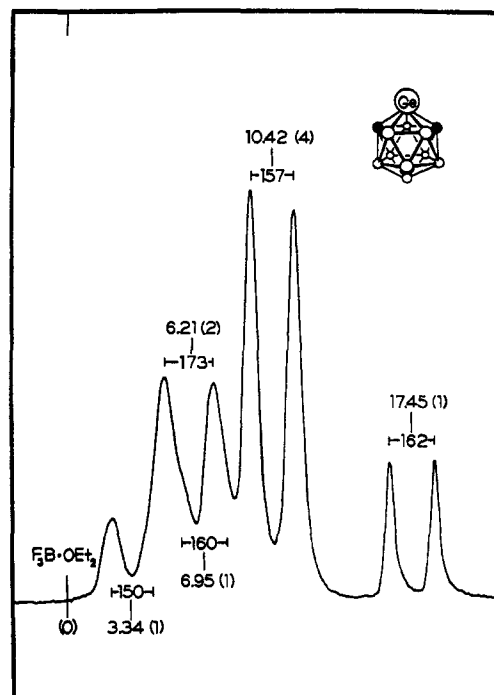


Figure 2. The 70.6-MHz ¹¹B nmr spectrum of 3-Ge-1,7-B₉C₂H₁₁. The chemical shift of each doublet is followed by the relative intensity in parentheses; the ¹¹B-¹H coupling is given in Hz inside the brackets denoting each doublet; determined in benzene.

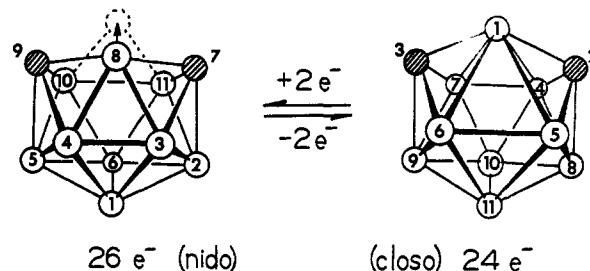
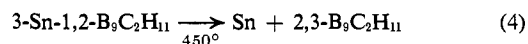


Figure 3. The interconversion of *nido* and *closo* 11-atom frameworks and the numbering conventions for each.

undergoes disproportionation and rearrangement to give Sn and 2,3-B₉C₂H₁₁ in 98% yield (eq 4), providing



a convenient route to the dicarbaundecaborane. By comparison, 3-(GaC₂H₅)-1,2-B₉C₂H₁₁ gives a 74% yield of 2,3-B₉C₂H₁₁ upon pyrolysis.¹¹ The 2,3-B₉C₂H₁₁ formed by either pyrolysis or oxidative closure (*vide supra*) was spectroscopically shown to be the same isomer as previously reported.¹⁰ However, it should be noted that the previous characterization includes ¹¹B chemical shifts which are in error.¹² Our observed spectrum is in complete agreement in every

(11) D. A. T. Young, R. J. Wiersema, and M. F. Hawthorne, *ibid.*, **93**, 5687 (1971).

(12) The error can be detected by calculating an "internal" chemical shift between two peaks in the published spectrum using the published coupling constants as a calibration and then checking for self-consistency. For example, the internal shift calculated in this manner for the separation between the lowest field and highest field doublets is 11.1 ppm; the reported shift is $17.3 - 1.2 = 16.1$ ppm; we observe 11.6 ppm. Our complete set of values for 2,3-B₉C₂H₁₁ in benzene referenced to the external standard (C₂H₅)₂O·BF₃ is (chemical shift (ppm) followed by coupling constant (Hz) and relative intensity): 4.07 (170) 4; 8.53 (172) 2; 10.06 (150) 2; 15.61 (173) 1.

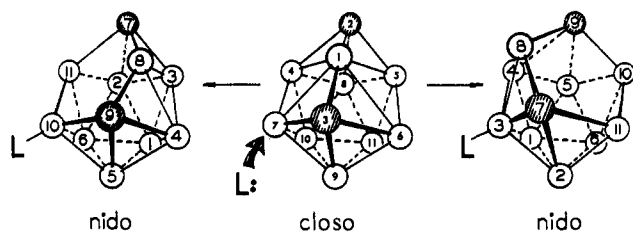


Figure 4. Possible manners for the opening of the $2,3\text{-B}_9\text{C}_2\text{H}_{11}$ deltahedron subsequent to nucleophilic attack. Note that the numbering conventions are not intended to indicate atom rearrangement but merely represent the accepted numbering scheme for each polyhedron.

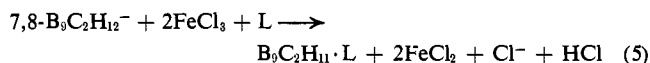
other respect with the previously published spectrum which is consistent with the X-ray structure of the dimethyl derivative.^{10b}

The ir spectrum of $2,3\text{-B}_9\text{C}_2\text{H}_{11}$ was obtained by subliming a thin film of the compound onto a CsI window maintained at -196° . The spectrum is tabulated in Table I.

The facility of this closure reaction with a weak oxidizing agent like SnCl_2 points to the fact that careful attention must be paid to the oxidizing strength of any reagent which might be employed in an insertion reaction involving nido or arachno boranes and heteroboranes.

Addition. The convenient formation of $2,3\text{-B}_9\text{C}_2\text{H}_{11}$ by pyrolysis of $3\text{-Sn-1,2-}\text{B}_9\text{C}_2\text{H}_{11}$ or oxidative closure of $7,9\text{-B}_9\text{C}_2\text{H}_{11}^{2-}$ prompted an investigation of some of its reaction chemistry. We chose to investigate a characteristic reaction of $2,3\text{-B}_9\text{C}_2\text{H}_{11}$ with electron-pair donors to form $\text{B}_9\text{C}_2\text{H}_{11}\cdot\text{L}$ adducts.^{10,13} If the ligand, L, is regarded to donate an electron pair to the framework, the 26 electrons characteristic of a nido^{6,8} structure for an 11-atom skeleton are obtained, and $\text{B}_9\text{C}_2\text{H}_{11}\cdot\text{L}$ molecules would be expected to have an open structure similar to that shown in Figure 3. Existing spectroscopic evidence indicates that the $\text{B}_9\text{C}_2\text{H}_{11}\cdot\text{L}$ molecules are structurally similar to the *nido-7,9- $\text{B}_9\text{C}_2\text{H}_{11}^{2-}$* ion which can in fact be formed from $2,3\text{-B}_9\text{C}_2\text{H}_{11}$ and $\text{H}^- = \text{L}$.¹³ Although a nido framework appears to be well established as a general structural feature for $\text{B}_9\text{C}_2\text{H}_{11}\cdot\text{L}$ molecules, the position of the L substituent is not so clear cut. Although all the boron atoms in $2,3\text{-B}_9\text{C}_2\text{H}_{11}$ are electropositive relative to the carbon atoms, the unique boron is the only one with two carbon atoms as nearest neighbors and inductive withdrawal renders it the most positive. Thus, it was first proposed without spectroscopic evidence, in cases where $\text{L} = (\text{C}_6\text{H}_5)_3\text{P}$, $(\text{C}_2\text{H}_5)_3\text{N}$, OH^- , and $\text{C}_2\text{H}_5\text{NC}$, that ligand attack occurred at the unique boron site (position 1).¹⁰ Such attack would give a symmetrical *nido- $\text{B}_9\text{C}_2\text{H}_{11}\cdot\text{L}$* molecule, *i.e.*, one in which the mirror plane defined by atoms 1, 10, and 11 of $2,3\text{-B}_9\text{C}_2\text{H}_{11}$ was preserved in the product (atoms 1, 6, and 8, Figure 3). Subsequent investigation¹³ in cases where $\text{L} = \text{H}^-$, CH_3^- , C_4H_9^- , $\text{CH}(\text{CN})_2^-$, $\text{B}_{10}\text{C}_2\text{H}_{10}\text{R}^-$, and $\text{B}_8\text{C}_2\text{H}_8\text{R}^-$ included spectroscopic evidence which showed that the adducts were in fact asymmetric and it was proposed that nucleophilic attack occurred at one of the four equivalent 4, 5, 6,

or 7 sites (Figure 3) in $2,3\text{-B}_9\text{C}_2\text{H}_{11}$ ¹³ to give a nido molecule with L at the 10 position (Figure 3). The proposed 10 substitution (facial substitution) was well substantiated in the cases of $\text{L} = [-\text{CH}(\text{CN})_2]^-$ and $[-\text{OC}(\text{OCH}_3)\text{CHCOOCH}_3]^-$ by ¹¹B nmr data published subsequently.^{13b} We give here nmr data which were formerly lacking for typical neutral ligand adducts of $2,3\text{-B}_9\text{C}_2\text{H}_{11}$. Although the data show that substitution is asymmetric in all cases, they also suggest that facial substitution does not occur (*vide infra*). In the present case, $\text{B}_9\text{C}_2\text{H}_{11}\cdot\text{L}$ species were found to be identical when the ligand was added subsequent to closure of $7,9\text{-B}_9\text{C}_2\text{H}_{11}^{2-}$ by SnCl_2 or when $7,9\text{-B}_9\text{C}_2\text{H}_{11}^{2-}$ was simultaneously treated with SnCl_2 and L. Thus, both the latter and the former procedures are thought to involve distinct steps of closure and addition even though the latter more closely resembles another report of $\text{B}_9\text{C}_2\text{H}_{11}\cdot\text{L}$ species formed by an oxidative substitution reaction (eq 5).¹⁴



Since the oxidative substitution reaction and the direct interaction of $2,3\text{-B}_9\text{C}_2\text{H}_{11}$ with a ligand involve reactants in which the carbon atoms are ortho and meta, respectively, and since both reactions involve relatively mild conditions, it seems likely that different $\text{B}_9\text{C}_2\text{H}_{11}\cdot\text{L}$ isomers are formed by these two routes.

We have supported the latter implication with the preparation of $7,9\text{-B}_9\text{C}_2\text{H}_{11}\cdot\text{P}(\text{C}_6\text{H}_5)_3$ by the direct interaction of $\text{P}(\text{C}_6\text{H}_5)_3$ with $2,3\text{-B}_9\text{C}_2\text{H}_{11}$ and a comparison of the resulting product with the asymmetric $7,8\text{-B}_9\text{C}_2\text{H}_{11}\cdot\text{P}(\text{C}_6\text{H}_5)_3$ isomer reported by Young.¹⁵ Both $\text{B}_9\text{C}_2\text{H}_{11}\cdot\text{P}(\text{C}_6\text{H}_5)_3$ isomers are asymmetrically substituted as shown by the ¹H nmr spectra in DCCl_3 : $7,9\text{-B}_9\text{C}_2\text{H}_{11}\cdot\text{P}(\text{C}_6\text{H}_5)_3$ displays two broad singlets each of relative intensity 1 at δ 1.30 and 1.72 for the H-C-(cage) protons and a multiplet of relative intensity 15 centered at δ 7.5 (prominent peaks at δ 7.34, 7.54, 7.59, and 7.64) for the phenyl protons; the corresponding peaks for $7,8\text{-B}_9\text{C}_2\text{H}_{11}\cdot\text{P}(\text{C}_6\text{H}_5)_3$ are reported at δ 1.25, 1.51, and 7.47.¹⁵ The latter data indicate distinctly different isomers as does a comparison of infrared spectra and melting points. Particularly diagnostic is the $830\text{--}990\text{-cm}^{-1}$ region which is free of any strong absorptions in $7,8\text{-B}_9\text{C}_2\text{H}_{11}\cdot\text{P}(\text{C}_6\text{H}_5)_3$,¹⁵ but where among others a band of strong intensity is found at 926 cm^{-1} for $7,9\text{-B}_9\text{C}_2\text{H}_{11}\cdot\text{P}(\text{C}_6\text{H}_5)_3$ (Table I). The 7,8 and 7,9 isomers give melting points of $178\text{--}179^\circ$ ¹⁵ and $188\text{--}189^\circ$, respectively. The ¹¹B nmr spectrum of the asymmetric 7,8 isomer was not reported; that of the 7,9 isomer is compared to those of other $7,9\text{-B}_9\text{C}_2\text{H}_{11}\cdot\text{L}$ adducts below.

Nucleophilic Attack of $2,3\text{-B}_9\text{C}_2\text{H}_{11}$. As a prelude to the assignment of the position of L substitution in $7,9\text{-B}_9\text{C}_2\text{H}_{11}\cdot\text{L}$ molecules from nmr evidence, the nature of nucleophilic attack on $2,3\text{-B}_9\text{C}_2\text{H}_{11}$ will be discussed. Here we (1) attempt to establish the position of attack, (2) assume that the nucleophile does not migrate subsequent to attack, and (3) propose that the deltahedron opens as shown in Figure 4.

Hawthorne previously recognized that the unique

(14) D. C. Young, D. V. Howe, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **91**, 859 (1969).

(15) D. C. Young, Ph.D. Dissertation, University of California, Riverside, 1966.

(13) (a) D. A. Owen and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **91**, 6002 (1969); (b) D. A. Owen, Ph.D. Dissertation, University of California, Los Angeles, 1969.

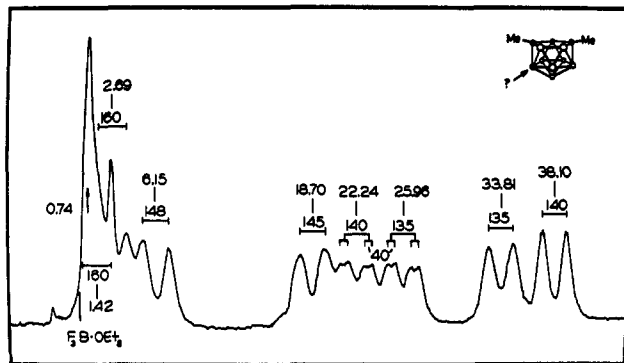


Figure 5. The 70.6-MHz ^{11}B nmr spectrum of $2\text{-C}_2\text{H}_5\text{O-7,9-(CH}_3)_2\text{-7,9-B}_9\text{C}_2\text{H}_9^-$. The chemical shift is given for the center of each doublet; the various ^{11}B - ^1H coupling features are given in Hz and appear near the brackets denoting the couplings; determined in acetone- d_6 for the $(\text{CH}_3)_4\text{N}^+$ salt.

boron atom (position 1, Figure 3) was the most positive in the 11-atom deltahedron.¹⁰ We have corroborated the latter recognition with EHMO estimations of the atom charges in $2,3\text{-B}_9\text{C}_2\text{H}_{11}$.¹⁶ Of the remaining ten borons, the EHMO calculations indicated that the set of four equivalent borons at positions 4, 5, 6, and 7 (Figure 3) was the most positively charged, the pair at positions 10 and 11 the least, and the pair 8 and 9 intermediate. The LUMO was localized mainly on borons 4, 5, 6, and 7, perhaps explaining why nucleophilic attack does not appear to occur at the most positively charged boron site (position 1) but at one of the four equivalent sites.

The structure of the product depends on the nature of the opening of the deltahedron subsequent to attack. If the deltahedron opens such that the unique boron moves toward the nucleophile, the substituent is found at position 3(4) in the nido product; if the movement is away, the substituent ends up at position 10(11) (Figure 4).¹⁷ Thus, the nature of the product is variable and depends on whether the deltahedral opening is toward or away from the site of nucleophilic attack. These alternative modes of opening are perhaps related to the nature of the nucleophile. The problem is under further investigation, but the data discussed below are indicative of $3\text{-L-7,9-B}_9\text{C}_2\text{H}_{11}$ structures for the cases where the adducts were formed by interaction of OC_2H_5^- with $2,3\text{-(CH}_3)_2\text{-2,3-B}_9\text{C}_2\text{H}_9$ and $\text{P}(\text{C}_6\text{H}_5)_3$ or $\text{N}(\text{CH}_3)_3$ with $2,3\text{-B}_9\text{C}_2\text{H}_{11}$.

Structure. The structural assignments build more cohesively if data are presented for yet another $7,9\text{-B}_9\text{C}_2\text{H}_{11}\cdot\text{L}$ molecule, one not formed *via* any of the methods discussed here. We have discovered that degradative substitution of $1,7\text{-(CH}_3)_2\text{-1,7-B}_{10}\text{C}_2\text{H}_{10}$ can lead to alkoxy derivatives of $7,9\text{-(CH}_3)_2\text{-7,9-B}_9\text{C}_2\text{H}_{10}^-$, e.g., $7,9\text{-(CH}_3)_2\text{-7,9-B}_9\text{C}_2\text{H}_9\cdot\text{OR}^-$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$, and $i\text{-C}_3\text{H}_7$).¹³ The ^{11}B nmr spectra of all of these alkoxy derivatives are practically superimposable; that of the ethoxy congener is shown in Figure 5. Since all nine boron environments are readily discernible, the ^{11}B nmr data for $7,9\text{-(CH}_3)_2\text{-7,9-B}_9\text{C}_2\text{H}_9\cdot\text{OC}_2\text{H}_5$ definitively

(16) W. R. Pretzer and R. W. Rudolph, unpublished results.

(17) Of course these considerations do not speak to the question of the mechanism of transfer of the H atom to the open face. However, an intramolecular H transfer appears to be easier in the "open-away" mechanism.

(18) V. Chowdhry, W. Pretzer, and R. W. Rudolph, unpublished results.

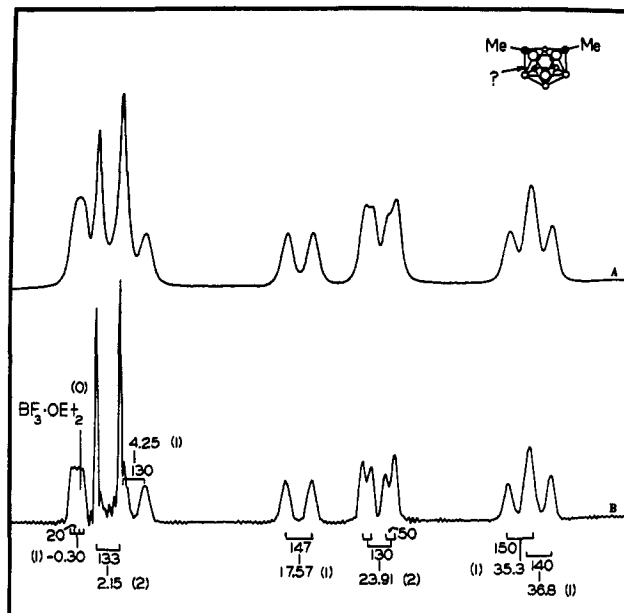


Figure 6. The 70.6-MHz ^{11}B nmr spectra of $3\text{-C}_2\text{H}_5\text{O-7,9-(CH}_3)_2\text{-7,9-B}_9\text{C}_2\text{H}_9^-$, (A) normal, (B) with line narrowing. The chemical shift is given for the center of each doublet; the various coupling features are given in Hz and appear near the brackets denoting the couplings; relative intensities are in parentheses; determined in acetone- d_6 for the $(\text{CH}_3)_4\text{N}^+$ salt.

point to asymmetric substitution of the polyhedron. Furthermore, since the two doublets at 22.24 and 25.96 ppm show additional coupling to a bridge hydrogen, substitution on the pentagonal face is excluded (hydrogen always bridges between two borons on the non-trigonal face of a nido molecule). In corroboration of nonfacial substitution there is no evidence of bridge hydrogen coupling on the singlet at 0.74 ppm which is due to the substituted boron. The latter ethoxy derivative is isomeric with that prepared by treatment of $2,3\text{-(CH}_3)_2\text{-2,3-B}_9\text{C}_2\text{H}_9$ with OC_2H_5^- and whose ^{11}B nmr spectrum is shown in Figure 6. Since it is reasonable that nucleophilic attack at $2,3\text{-B}_9\text{C}_2\text{H}_{11}$ and derivatives can lead to 3 substitution (*vide supra*) and since a detailed examination of the ^{11}B nmr spectra given below also indicates asymmetric lower belt substitution for the latter ethoxy isomer, we assign the latter a $3\text{-C}_2\text{H}_5\text{O-7,9-(CH}_3)_2\text{-7,9-B}_9\text{C}_2\text{H}_9^-$ structure and, by process of elimination, the former a $2\text{-C}_2\text{H}_5\text{O-7,9-(CH}_3)_2\text{-7,9-B}_9\text{C}_2\text{H}_9^-$ structure. Although only seven of the nine environments expected for asymmetric substitution can be resolved in the spectrum of the 3 isomer, symmetric substitution would give six. The overall appearance of the spectrum is similar to that of the proposed 2 isomer except that certain doublets appear to have become superpositioned in the 3 isomer (compare Figures 5 and 6). The salient result of this superpositioning is that the two doublets showing additional bridge hydrogen coupling appear as one asymmetric doublet of doublets of relative intensity 2 at 23.91 ppm (Figure 6). The asymmetry and the magnitude of the bridge coupling feature are identical at 32.1 and 70.6 MHz which indicate that the asymmetric doublet of doublets is due to the near chemical-shift equivalence of two signals split to a different extent by a bridge hydrogen. Furthermore, no other peak in the spectrum displays bridge hydrogen coupling even after the lines are

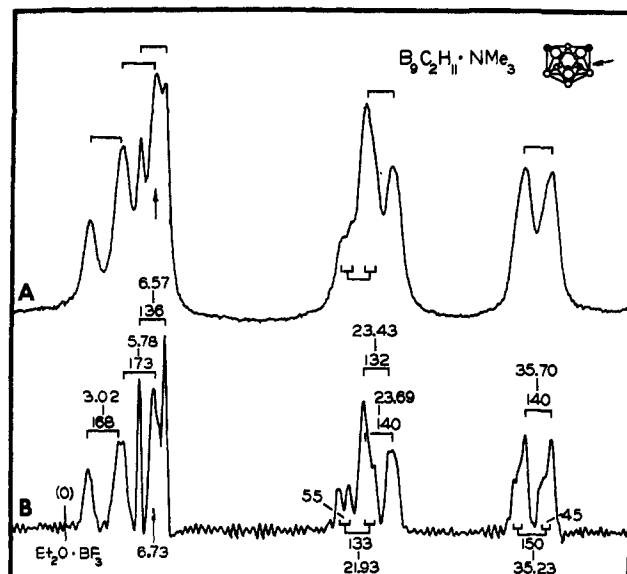


Figure 7. The 70.6-MHz ^{11}B nmr spectra of 3-(CH_3) $_3\text{N}$ -7,9- $\text{B}_9\text{C}_2\text{H}_{11}$, (A) normal, (B) with line narrowing. The chemical shift is given for the center of each doublet; the various ^{11}B - ^1H coupling features are given in Hz and appear near the brackets denoting the couplings; determined in benzene.

narrowed in an elegant manner recently described by Clouse, Moody, Rietz, Roseberry, and Schaeffer.¹⁹ After "line narrowing" the singlet at -0.30 ppm shows fine structure, but the 1:1:1:1 quartet is assignable to preferential ^{11}B - ^{11}B coupling of the substituted boron with a single other boron atom in the molecule. The "hash" in the 1-3-ppm region of Figure 6 is characteristic of a more drastic loss of signal-to-noise when inherently sharp peaks are "line narrowed."¹⁹

In the case of 7,9- $\text{B}_9\text{C}_2\text{H}_{11}\cdot\text{N}(\text{CH}_3)_3$, the normal 70.6 MHz ^{11}B nmr spectrum (Figure 7A) shows seven of the nine boron environments expected for asymmetric substitution. The proton spectrum in benzene corroborates the asymmetry of the substitution in that two equally intense H-C(cage) resonances are seen at δ 1.05 and 1.38 along with a sharp singlet, nine times more intense, assigned to the Me_3N protons, at δ 1.93. After "line narrowing," all nine of the boron environments are clearly discernible (Figure 7B), eight doublets and a singlet for the substituted boron. Although incipient resolution of the bridge hydrogen coupling (55 Hz) on the doublet at 21.93 ppm was evident in the normal spectrum (Figure 7A), it is clearly evident after line narrowing. Furthermore, a second doublet at 35.23 ppm also shows coupling with a bridge hydrogen (45 Hz).²⁰ Again, these salient observations demonstrate that two B-H moieties in the 7,9- $\text{B}_9\text{C}_2\text{H}_{11}\cdot\text{NMe}_3$ molecule are connected by a bridging hydrogen. The usual placement of the bridge hydrogen between borons 10 and 11 and the evidence for asymmetric substitution require that the substituent be placed on either atom 2 or 3 in the "lower tier" of the nido framework (Figure 3). Again, consideration of the probable nature of

(19) A. O. Clouse, D. C. Moody, R. R. Rietz, T. Roseberry, and R. Schaeffer, *J. Amer. Chem. Soc.*, **95**, 2496 (1973).

(20) We discount the possibility that this doublet is due to a complex multiplet arising from ^{11}B - ^{11}B coupling primarily on the basis of the magnitude of the effect and our inability to derive a doublet pattern using various sets of spin = $3/2$ nuclei.

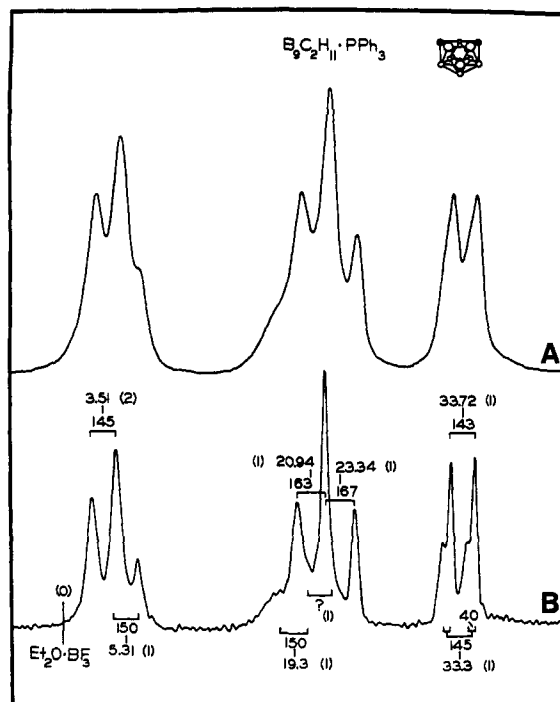


Figure 8. The 70.6-MHz ^{11}B nmr spectra of 7,9- $\text{B}_9\text{C}_2\text{H}_{11}\cdot\text{P}(\text{C}_6\text{H}_5)_3$, (A) normal, (B) with line narrowing. The chemical shift is given for the center of each doublet; the coupling features are given in Hz and appear near the brackets denoting the couplings; relative intensities are in parentheses; determined in chloroform- d_1 .

nucleophilic attack on the 2,3- $\text{B}_9\text{C}_2\text{H}_{11}$ molecule suggests a 3- Me_3N -7,9- $\text{B}_9\text{C}_2\text{H}_{11}$ structure.

The ^1H nmr data for 7,9- $\text{B}_9\text{C}_2\text{H}_{11}\cdot\text{P}(\text{C}_6\text{H}_5)_3$ indicate asymmetric substitution as discussed previously in comparison to 7,8- $\text{B}_9\text{C}_2\text{H}_{11}\cdot\text{P}(\text{C}_6\text{H}_5)_3$. The ^{11}B nmr data for 7,9- $\text{B}_9\text{C}_2\text{H}_{11}\cdot\text{P}(\text{C}_6\text{H}_5)_3$ are not as definitive as those just discussed. The line-narrowed spectrum corroborates asymmetric substitution, but only one doublet, that, at 33.3 ppm, clearly shows additional coupling with a bridge hydrogen (Figure 8). Even if a second doublet of doublets were discernible, since the substituent atom phosphorus has a nuclear spin of $1/2$, its mere observation would not necessarily indicate lower belt substitution unless ^{11}B - $\{^{31}\text{P}\}$ double-resonance experiments showed that some other doublet in the spectrum was due to P-B coupling. Nevertheless, because of the overall similarities between the spectrum for the $\text{N}(\text{CH}_3)_3$ adduct and that for the $\text{P}(\text{C}_6\text{H}_5)_3$ adduct (Figures 7 and 8), we speculate that the latter also has the 3-L-7,9- $\text{B}_9\text{C}_2\text{H}_{11}$ structure.

Experimental Section

General Procedure. Infrared spectra were determined on a Perkin Elmer 457 as KBr disks except for 2,3- $\text{B}_9\text{C}_2\text{H}_{11}$ in which case a cell similar to that described by Wagner and Hornig²¹ was used. The ^{11}B nmr spectra were recorded on Varian instruments operating at 32.1 or 70.6 MHz (Indiana University), proton nmr spectra on Varian T-60 and HA-100 spectrometers. Chemical shifts are reported relative to $(\text{C}_2\text{H}_5)_2\text{O}\cdot\text{BF}_3$ (external) and $\text{Si}(\text{CH}_3)_4$ (internal) for ^{11}B and ^1H , respectively. The mass spectra were obtained on an Associated Electronics Industries MS-902.

All preparations were conducted under an atmosphere of nitrogen. Benzene was dried by percolation through molecular sieves and then stored over fresh sieves. The $\text{Me}_3\text{NH}^+\cdot 7,9\text{-B}_9\text{C}_2\text{H}_{11}^{2-}$

(21) E. L. Wagner and D. F. Hornig, *J. Chem. Phys.*, **18**, 296 (1950).

and 3-Sn-1,2-B₉C₂H₁₁¹ were prepared according to literature procedures. Triphenylphosphine and SnCl₂ were obtained from Matheson Coleman and Bell; GeI₂, *n*-butyllithium, and trimethylamine were purchased from Rocky Mountain Research Chemicals, Alfa Inorganics, and Eastman Organics, respectively; these reagents were used without further purification.

3-Ge-1,7-B₉C₂H₁₁. In a 100-ml three-necked flask, equipped with a condenser, nitrogen inlet, rubber septum, magnetic stirrer, and heating mantle were placed 1.0 g (5.16 mmol) of Me₃NH⁺ 7,9-B₉C₂H₁₂⁻ and 50 ml of benzene. Before heating, 5.0 ml of 2.28 *M* *n*-butyllithium was added with a syringe through the septum. The mixture was then stirred at reflux for 12 hr with a slow purge of N₂ to remove NMe₃ and form the 7,9-B₉C₂H₁₁²⁻ ion. GeI₂ (1.83 g) was then added and the mixture stirred at reflux for an additional 54 hr before it was poured into a Soxhlet thimble and extracted with benzene for 24 hr. After rotary evaporation of the solvent the solid was further purified by vacuum sublimation at 55° to give 0.210 g of 3-Ge-1,7-B₉C₂H₁₁. *Anal.* Calcd for B₉C₂GeH₁₁: B, 47.44; C, 11.71; Ge, 35.43; H, 5.41. Found: B, 49.61; C, 11.21; Ge, 33.17; H, 5.48. The compound was not observed to melt when heated to 310° in a sealed capillary.

When 3-Ge-1,2-B₉C₂H₁₁ was vacuum sublimed through 20-mm o.d. Vycor tubing which was maintained at 600° for a 100-mm length, the sublimate was observed to be a mixture of 3-Ge-1,2-B₉C₂H₁₁ and 3-Ge-1,7-B₉C₂H₁₁ by infrared spectroscopy.

2,3-B₉C₂H₁₁. In a typical pyrolytic preparation a 20 mm o.d. Pyrex tube was charged with 730 mg of 3-Sn-1,2-B₉C₂H₁₁ and about 100 mm above the sample a 200 mm length of the tube was loosely packed with degreased glass wool. The tube was attached to a high vacuum system through a standard taper joint and outgassed at 300° by heating for 1 hr with a furnace placed around the packed portion. The furnace temperature was then raised to 450° and the 3-Sn-1,2-B₉C₂H₁₁ was sublimed up the tube by placing a 200° oil bath at the bottom. As the stannacarborane sublimed through the packed tube the 2,3-B₉C₂H₁₁ formed was pumped into a tared trap held at -196°. The yield was 380 mg (98%) [*m/e*] 134, ¹¹B₉¹²C₂¹H₁₁⁺].

The *in situ* preparation of 2,3-B₉C₂H₁₁ was effected in the following manner. A benzene solution of the 7,9-B₉C₂H₁₁²⁻ ion was generated from 1.0 g of Me₃NH⁺ 7,9-B₉C₂H₁₂⁻ (*vide supra*) before adding 1.07 g (5.65 mmol) of anhydrous SnCl₂. Within a few minutes the mixture showed incipient blackening and stirring was continued at reflux for 24 hr. The product could be recovered by removal of the Sn and NaCl by filtration and evaporation of the

filtrate *in vacuo*; however, rather than recover the 2,3-B₉C₂H₁₁, it was usually treated *in situ* with other reagents (*vide infra*).

7,9-B₉C₂H₁₁·P(C₆H₅)₃. A freshly prepared solution of 2,3-B₉C₂H₁₁ (*vide supra*) was cooled to 25° and 1.47 g (5.60 mmol) of (C₆H₅)₃P was added before continuing reflux and stirring for 24 hr. More conveniently, (C₆H₅)₃P was added to a freshly prepared benzene solution of 7,9-B₉C₂H₁₁²⁻ along with the SnCl₂. In this case, blackening was noted immediately and stirring was continued at reflux for 24 hr. Recovery of the crude product was accomplished by removal of Sn and NaCl by filtration and evaporation of the benzene. The crude product was extracted with heptane to remove unreacted (C₆H₅)₃P, dried, and finally either recrystallized from benzene-heptane or vacuum sublimed (180°) to give 1.57 g (4.01 mmol) of the pure material (78% yield). *Anal.* Calcd for B₉C₂₀H₂₆P: B, 24.67; C, 60.90; H, 6.59; P, 7.85. Found: B, 24.64; C, 60.10; H, 6.39; P, 7.62 [*m/e*] 396, B₉C₂₀H₂₆P⁺, mp 188-189°].

7,9-B₉C₂H₁₁·N(CH₃)₃. A reaction flask containing a fresh benzene solution of 7,9-B₉C₂H₁₁²⁻ prepared from 1.0 g of Me₃NH⁺ 7,9-B₉C₂H₁₂⁻ (*vide supra*) was fitted with a bubbler and anhydrous SnCl₂ (1.07 g) was added to the mixture. Anhydrous trimethylamine (7 g, 120 mmol) was then bubbled through the refluxing solution over a 1-hr period. After the addition was complete, stirring was continued at reflux for 3 hr. The work-up was the same as for (C₆H₅)₃P·B₉C₂H₁₁. The product sublimes at 170° *in vacuo*. *Anal.* Calcd for B₉C₅H₂₀N: B, 50.86, C, 31.38; H, 10.54; N, 7.31. Found: B, 50.01; C, 30.34, H, 10.11; N, 7.25 [*m/e*] 193, B₉C₅H₂₀N⁺, mp 264° dec].

7,9-(CH₃)₂-7,9-B₉C₂H₉·OC₂H₅⁻. Phosphoric acid (85%, 30 ml) was added to 1.33 g (4.5 mmol) of Cs⁺ 7,8-(CH₃)₂-7,8-B₉C₂H₁₀⁻ in 30 ml of toluene and the mixture stirred at reflux under nitrogen for 6 hr. The toluene layer was then decanted and the solvent removed on a rotary evaporator until a thick oil remained. The oil was treated, under nitrogen, with 50 ml of 1 *M* ethanolic KOH and stirred for 10 min before adding 15 ml of aqueous saturated (CH₃)₄N⁺Cl⁻ to precipitate the product. Pure product was obtained upon recrystallization from ethanol-water by slow evaporation of the ethanol (yield 0.40 g, 32%).

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Synthesis of Metallo-carboranes by Polyhedral Expansion¹

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Abstract: The reduction of the closo carboranes 1,7-C₂B₈H₈, 4,5-C₂B₇H₉, 1,6-C₂B₈H₁₀, 1,10-C₂B₈H₁₀, and 2,3-C₂B₉H₁₁ with Na followed by complexation with CoCl₂ and NaC₅H₅ produces metalloboranes of the following types: C₅H₅CoC₂B_nH_{n+2}, (C₅H₅Co)₂C₂B_nH_{n+2}, and C₅H₅CoC₂B_nH_{n+1}(C₂B_nH_{n+1}). Similarly, addition of FeCl₂ and NaC₅H₅ to the anions derived from the reduction of 1,7-C₂B₈H₈ and 1,6-C₂B₈H₁₀ results in new ferracarboranes. The preparation, characterization, and proposed structures of these metalloboranes are discussed.

Since 1965 a large number of metallo-carboranes have been prepared *via* the following three steps carried out in succession: (1) basic or oxidative degradation of a carborane, (2) deprotonation of the degradation product with a base such as sodium hydride, and (3) complexation of the resulting anion with a transition metal ion. In this manner metallo-carboranes con-

taining the C₂B₉H₁₁²⁻,² C₂B₇H₉²⁻,³ and C₂B₆H₈²⁻ moieties have been prepared. This work has been recently reviewed,⁵ and the following equations serve as an example.²

- (2) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *J. Amer. Chem. Soc.*, **90**, 879 (1968).
- (3) T. A. George and M. F. Hawthorne, *ibid.*, **91**, 5475 (1969).
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- (5) M. F. Hawthorne, *Accounts Chem. Res.*, **1**, 281 (1968); M. F. Hawthorne and G. B. Dunks, *Science*, **178**, 462 (1972).

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