

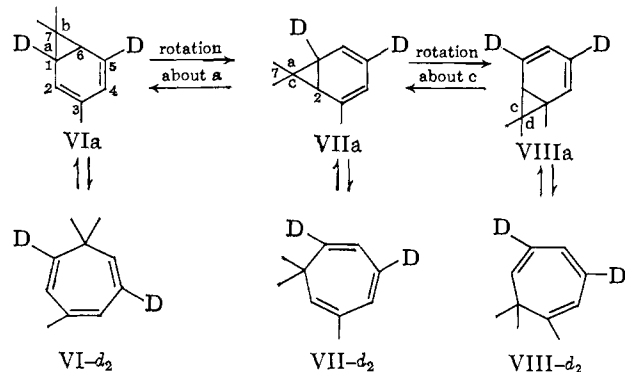
copy. Like VI- d_2 , both VII- d_2 and VIII- d_2 show three broadened singlets each of intensity 1 in the olefinic region, in contrast to the patterns with intensity ratios 2:1:2 and 2:2:1 shown² by undeuterated VII and VIII, respectively. Both IX- d_2 and X- d_2 show intact isopropenyl and methyl group absorptions in the n.m.r., but IX- d_2 has lost the absorption at 3.2 p.p.m. of the triply allylic proton as well as one olefinic proton absorption of IX; X- d_2 has lost half of the intensity of the doubly allylic proton resonance at 2.6 p.p.m. and one olefinic proton resonance of X. The doubly allylic proton resonance at 2.6 p.p.m. appears as a broad doublet in IX but is simplified to a slightly broadened singlet in IX- d_2 .⁵ These data are uniquely consistent with the formulation of VI-X- d_2 as shown.

In compound XI- d_2 , the presence of the group $(\text{CH}_3)_2\text{CD}$ instead of $(\text{CH}_3)_2\text{CH}$ is evident from the disappearance of the benzylic proton resonance and the collapse of the methyl doublet of XI ($J = 7$ c.p.s.) to a singlet of intensity 6. The lone methyl resonance is intact, but one-fourth of the intensity of the aromatic proton resonance is lost. The precise position of the aromatically bound deuterium of XI- d_2 cannot be directly deduced from the n.m.r. spectrum and is assigned here for consistency with the rest of the series. Compound XII- d_2 shows typical isopropyl and methyl absorptions, but the aromatic proton pattern is only half as intense as that of XII.

The formation of the cyclohexadienes IX and X from norcaradiene intermediates would be analogous to previously observed⁶⁻⁹ reactions of 1-alkyl-2-vinylcyclopropanes, although direct hydrogen transfers from one of the pair of geminal methyl groups to C-4 in the stable nonplanar form of any of the tropilidenes also could lead to IX and X with the proper labeling pattern.

The changes leading from VI- d_2 to VII- d_2 and VIII- d_2 are encompassed by a formalism in which C-1 and C-6 are joined and the isopropylidene group consisting of C-7 and its pair of methyls is allowed to wander over the six-membered ring. Reattachment at C-1-C-2 or C-4-C-5 (numbering as in VI) generates VII- d_2 , at C-2-C-3 or C-3-C-4 generates VIII- d_2 , and at C-1-C-6 or C-5-C-6 regenerates VI- d_2 . In detail, this might well involve the corresponding norcaradienes (VIa,

VIIa, VIIIa) as intermediates which are interconverted by a sequence in which rupture of one of the cyclopropane bonds alternates with a pivoting motion around the unbroken bond and recyclization at the next available site.^{10,11}



(10) The possibility that the rearrangements involve an intermediate in which *both* isopropylidene ring bonds are weakened (for example, some kind of complex between dimethylcarbene and the aromatic ring cannot be excluded formally, but seems unlikely). In this connection, W. G. Woods (*J. Org. Chem.*, 23, 110 (1958)) has considered the possibility that toluene is formed from cycloheptatriene or norbornadiene by dissociation and reinsertion of CH_2 .

(11) Whether these acts are concerted or stepwise cannot yet be answered, nor can a decision yet be reached on whether the rotations occur in a specific direction. If the symmetry of the highest occupied molecular orbital (HOMO) is as influential here as in the cases of electrocyclic additions,¹² and if it is permissible to use as a crude model of the process VIa \rightarrow VIIa a transition state in which the C-2-C-6 system is treated as a pentadienyl radical, a concerted change would require that bond c in VIIIa be formed between C-2 and the *same* face of C-7 as was used to form bond b in VIa, since the HOMO has *two* nodes. Corollary conclusions are that the norbornadiene \rightarrow norcaradiene and vinylcyclopropane \rightarrow cyclopentene rearrangements are stepwise. Although these considerations must be taken as merely suggestive at present, it will be of interest to observe the extent of their concordance with more detailed calculations or experiment.

(12) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 87, 395 (1965).

(13) National Institutes of Health Postdoctoral Fellow, 1964-1965.

Jerome A. Berson, M. Robert Willcott, III¹³

Department of Chemistry, University of Wisconsin
Madison, Wisconsin

Received April 17, 1965

A New Type of Electron-Deficient Compound. A Polyborane Hydridomanganese Carbonyl, $\text{HMn}_3(\text{CO})_{10}(\text{BH}_3)_2^1$

Sir:

We wish to report the preparation, properties, and structure (Figure 1) of $\text{HMn}_3(\text{CO})_{10}(\text{BH}_3)_2$, the first known example of a polyborane-transition metal carbonyl complex. This compound containing a $(\text{BH}_3)_2$ fragment with a B-B bond also represents the first known case in which all three hydrogens of a BH_3 group are coordinated to other atoms *via* three-center bonds. The X-ray structural determination not only substantiates the existence of transition metal-hydrogen-boron bridging systems²⁻⁵ but also confirms the

(1) H. D. K. and W. F. acknowledge the financial support of the National Science Foundation, G. P. 4175; G. R. W. and L. F. D. acknowledge the financial support of the National Science Foundation, G. P. 1523, and the use of the CDC 1604 computer at the Computing Center (University of Wisconsin).

(2) R. Nöth and R. Hartwimmer, *Chem. Ber.*, 93, 2238 (1960).

(3) R. B. King, *Z. Naturforsch.*, 18b, 157 (1963).

(4) R. K. Nanda and M. G. H. Wallbridge, *Inorg. Chem.*, 3, 1798 (1964).

(5) J. M. Davidson, *Chem. Ind. (London)*, 2021 (1964).

(5) The triply allylic proton resonance at 3.2 p.p.m., which appears as a broad doublet in X, is still a doublet in X- d_2 , apparently because of long-range coupling.

(6) W. von E. Doering and W. Grimme, unpublished observations, cited by W. von E. Doering and W. R. Roth, *Angew. Chem.*, 75, 27 (1963); W. Grimme, *Chem. Ber.*, 98, 756 (1965).

(7) W. R. Roth, *Ann.*, 671, 10 (1964).

(8) D. S. Glass, J. Zirner, and S. Winstein, *Proc. Chem. Soc.*, 276 (1963).

(9) R. J. Ellis and H. M. Frey, *ibid.*, 221 (1964).

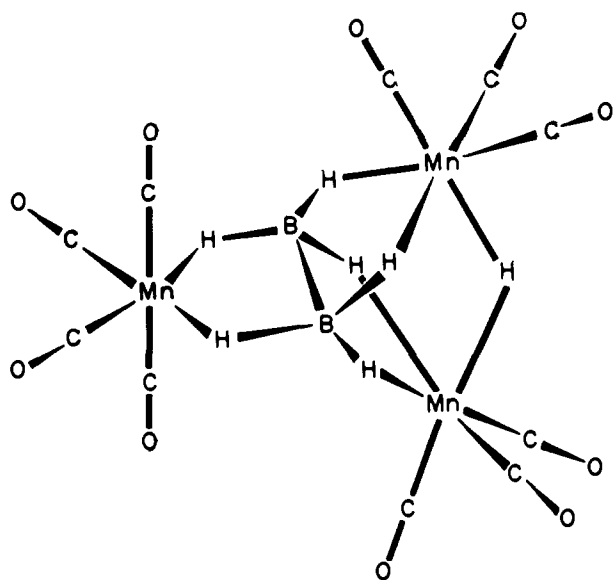


Figure 1. Molecular configuration of $\text{HMn}_2(\text{CO})_{10}(\text{BH}_3)_2$. The four independent Mn-B distances are equivalent with a mean value of 2.30 Å. (individual e.s.d., 0.02 Å.). The B-B distance of 1.76 ± 0.03 Å. compares favorably with those in the boron hydrides: Cf. W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin Inc., New York, N. Y., 1963. For the $\text{HMn}_2(\text{CO})_6$ moiety the observed Mn...Mn distance of 2.845 ± 0.003 Å. is significantly shorter than the value of 2.923 ± 0.003 Å. found for the direct Mn-Mn bond in $\text{Mn}_2(\text{CO})_{10}$: L. F. Dahl and R. E. Rundle, *Acta Cryst.*, **16**, 419 (1963).

presence of symmetrical hydrogen bridging between two transition metal atoms.^{6,7}

The complex is obtained as a by-product in the synthesis of $[\text{HMn}(\text{CO})_4]_3$ ⁸ by a method similar to that which afforded $[\text{HM}(\text{CO})_4]_3$, $\text{M} = \text{Tc}$ ⁹ and Re .¹⁰ The gross reaction products are subjected to sublimation under high vacuum for 40 hr. at 50° in order to remove $\text{Mn}_2(\text{CO})_{10}$ and $[\text{HMn}(\text{CO})_4]_3$. The residue then is dissolved at 35° in a mixture of cyclohexane-methylcyclohexane (80:20), filtered, and crystallized overnight at 0° to give dark red needles of $\text{HMn}_2(\text{CO})_{10}(\text{BH}_3)_2$ in yields of about 15% of $\text{Mn}_2(\text{CO})_{10}$ starting material. The compound is moderately air stable in the crystalline state, but in solution it decomposes very quickly when exposed to air.

Anal. Calcd. for $\text{H}_7\text{Mn}_2\text{B}_2(\text{CO})_{10}$: Mn, 34.80; C, 25.36; H, 1.49; B, 4.57; mol. wt., 473.6. Found: Mn, 34.60; C, 25.51; H, 1.41; B, 4.79; mol. wt., 440 (vapor pressure osmometer in cyclohexane solution under argon).

The compound in the solid state is diamagnetic.¹¹ Proton magnetic resonance in solution gives a weak, broad resonance at τ 29, which is in the region expected for transition metal-bonded hydrogen atoms.¹²

(6) X-Ray evidence for a symmetrical, bent three-center metal-hydrogen-metal bond was obtained from a recent three-dimensional structural investigation of $[(\text{C}_6\text{H}_5)_2\text{Mo}_2\text{H}\{\text{P}(\text{CH}_3)_2\}(\text{CO})_4]^-$.

(7) R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2576 (1965).

(8) (a) D. K. Huggins, Dissertation, University of California, Los Angeles, Oct. 1963; (b) W. Fellmann, D. K. Huggins, and H. D. Kaesz, "Proceedings of the VIIIth International Conference on Coordination Chemistry," V. Gutmann, Ed., Springer-Verlag, Berlin, 1964, pp. 255-257.

(9) H. D. Kaesz and D. K. Huggins, *Can. J. Chem.*, **41**, 1250 (1963).

(10) D. K. Huggins, W. Fellmann, J. M. Smith, and H. D. Kaesz, *J. Am. Chem. Soc.*, **86**, 4341 (1964).

(11) We are indebted to M. L. Maddox at U.C.L.A. for magnetic measurements; found: χ_{mole} (293°K.) = $(+33.6 \pm 18) \times 10^{-6}$ cm.³/mole. We also are grateful to M. L. Maddox and Dr. C. G. Kreiter for proton magnetic resonance measurements.

In cyclohexane solution its infrared spectrum with LiF optics shows seven principal maxima in the terminal carbonyl region in agreement with the total expected from the structure (*vide infra*) containing a $\text{cis-Mn}(\text{CO})_4$ group (four bands) and a $\text{Mn}_2(\text{CO})_6$ group (three resolvable bands). Other infrared regions also were investigated for KBr pellets with a grating instrument. No absorptions occur above the carbonyl region and, particularly, none in the region 2400-2600 cm.⁻¹ in which terminal B-H stretching frequencies have been reported.¹³ Two weak bands which appear at approximately 1000 cm.⁻¹ and which shift on deuteration may be assigned to the Mn-H-Mn system.¹⁴ Although the infrared spectrum of the fully deuterated derivative reveals essentially no changes in the maxima of the carbonyl bands, a somewhat broad absorption of medium intensity at 1400-1500 cm.⁻¹ (maxima, 1425 and 1447 cm.⁻¹) may be ascribed to Mn-D-B modes, since the isotopic shift is that expected for the corresponding Mn-H-B modes which would be buried under the carbonyl absorptions of the undeuterated sample.

The entire molecular configuration was found by a three-dimensional X-ray analysis which included anisotropic least-squares refinement; all independent hydrogen positions were revealed from three-dimensional difference maps. Discrepancy factors of $R_1 = 9.8\%$ and $R_2 = 9.4\%$ were obtained for the 1012 observed data collected photographically with Mo K α radiation. The crystals are monoclinic with symmetry $\text{P}2_1/\text{m}$ (C_{2h}^2) and lattice constants $a = 9.57$, $b = 14.03$, $c = 6.62$ Å., $\beta = 100^\circ 35'$; $\rho_{\text{obsd}} = 1.80$ g./cc. vs. $\rho_{\text{calcd}} = 1.80$ g./cc. for two formula species per unit cell. The centrosymmetric space group demands that each molecule possess a crystallographic mirror plane which passes through one manganese atom and two of its attached carbonyl groups, the two boron atoms and two of their Mn-coordinated hydrogen atoms, and the unique hydrido hydrogen atom. Hence, the crystallographic C_s -m symmetry requires the Mn-H-Mn bridging system to be symmetrical. Within experimental error the molecular configuration conforms to C_{2v} -2mm symmetry. Both kinds of manganese atoms possess octahedral-type valency. The molecular geometry with three-center Mn-H-B and Mn-H-Mn bridge bonds enables the electronic configuration of each of the two kinds of manganese atoms formally to obey the "inert gas rule" (*i.e.*, by which only the bonding MO's are utilized) in accord with the observed diamagnetism of the compound.¹⁵

(12) In particular, compare with $\text{HMn}_2\{\text{P}(\text{C}_6\text{H}_5)_2\}(\text{CO})_6$, τ 26.8: M. L. H. Green and J. T. Moelwyn-Hughes, *Z. Naturforsch.*, **17b**, 783 (1962); see also L. L. Lohr, Jr., and W. N. Lipscomb, *Inorg. Chem.*, **3**, 22 (1964), and A. D. Buckingham and P. J. Stephens, *J. Chem. Soc.*, 2747, 4583 (1964).

(13) As found in (a) boron hydrides and alkylboron hydrides: cf. W. J. Lehmann and I. Shapiro, *Spectrochim. Acta*, **17**, 396 (1961); (b) in the compound $\text{B}_{20}\text{H}_{14}$: cf. N. E. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, **85**, 3506 (1963); and in the ion $[(\text{CO})_5\text{MnBH}_3]^-$: cf. G. W. Parshall, *ibid.*, **86**, 361 (1964).

(14) For terminal metal-hydrogen infrared stretching frequencies see (a) J. Chatt, *Proc. Chem. Soc.*, 318 (1962), and references cited therein; (b) M. L. H. Green, *Angew. Chem.*, **72**, 719 (1960), and references cited therein; (c) L. Vaska, *J. Am. Chem. Soc.*, **86**, 1943 (1964).

(15) Since the bookkeeping of electrons involves a fractional charge distribution, it is briefly outlined. With the assumption of approximately tetrahedral hybridization for the two boron atoms by the assignment of a "normal" single bond between them, each of the boron atoms has left three orbitals and two valence electrons for bonding with the three manganese atoms *via* three three-center Mn-H-B bonds. The unique manganese atom (lying on the crystallographic mirror plane), which is surrounded by four carbonyl groups and two hydrogen atoms,

The $\text{HMn}_2(\text{CO})_6\text{B}_2$ group in $\text{HMn}_3(\text{CO})_{10}(\text{BH}_3)_2$ possesses a configuration similar to that found in $\text{S}_2\text{Fe}_2(\text{CO})_6$ ¹⁶ for which a bent metal-metal bond arising from the overlap of octahedral-type iron orbitals is presumed to be mainly responsible for the molecular geometry with a resulting nonplanar S_2Fe_2 system. Furthermore, the coordination site of the binuclear hydride atom in $\text{HMn}_3(\text{CO})_{10}(\text{BH}_3)_2$ corresponds within experimental error to the intersection of the octahedral-type manganese orbitals as determined by the apical carbonyl groups of the $\text{HMn}_2(\text{CO})_6\text{B}_2$ fragment. The similar localized environments of the metal atoms in the $\text{HMn}_2(\text{CO})_6\text{B}_2$ group and the $\text{S}_2\text{Fe}_2(\text{CO})_6$ molecule with the hydrogen in the former compound substituted in place of the bent metal-metal bond in the thio-iron carbonyl complex may be considered as support for the existence of a bent metal-metal bond occupying a regular coordination site in $\text{S}_2\text{Fe}_2(\text{CO})_6$ (and in the structurally related complexes $[\text{C}_2\text{H}_5\text{SF}(\text{CO})_3]_2$ ¹⁷ and $[(\text{C}_6\text{H}_5)_2\text{PCoC}_5\text{H}_5]_2$ ¹⁸). Other borane metal carbonyl complexes of the type described above are being sought.

needs only $1/2$ electron from each boron to fill the two three-center bonding Mn-H-B orbitals and thereby to obtain the closed-shell configuration. Consequently, each of the two boron atoms has $1 1/2$ electrons remaining, of which $3/4$ electron is contributed *via* three-center Mn-H-B bonds to each of the symmetry-related manganese atoms. Since the three carbonyl groups together with the two hydrogen and two boron atoms can be considered as "effectively" donating $9 1/2$ electrons to each of these zerovalent manganese atoms, the binuclear hydrido Mn-H-Mn interaction also may be described in terms of bent three-center MO's (with each of the three MO's constructed from a σ -type metal orbital and the bridging 1s hydrogen orbital), of which again only the bonding one is occupied with $1/2$ electron from each of the two manganese atoms and one from the hydrogen atom. By this electron-counting scheme, in which the electrons in the three-center bonds are delocalized, the symmetry-related manganese atoms also conform to the closed-shell configuration.

(16) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **4**, 1 (1965).

(17) L. F. Dahl and C. H. Wei, *ibid.*, **2**, 328 (1963).

(18) J. M. Coleman and L. F. Dahl, to be published.

(19) Publication No. 1807.

(20) Alfred P. Sloan Research Fellow.

Herbert D. Kesz, Werner Fellmann

Department of Chemistry,¹⁹ University of California
Los Angeles, California 90024

Glenn R. Wilkes, Lawrence F. Dahl²⁰

Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received March 15, 1965

Unsymmetrical Cleavage of Diborane by Methylamine and Dimethylamine

Sir:

Most of the known reactions of diborane with Lewis bases appear, or are believed, to result in symmetrical cleavage of the boron-hydrogen bridge system.¹ Relatively few examples of unsymmetrical cleavage have been reported. Direct reaction of ammonia with diborane produces $\text{H}_2\text{B}(\text{NH}_3)_2^+\text{BH}_4^-$, the best documented example of unsymmetrical cleavage by a nitrogen base.² Conversely, reactions of diborane with methylamines have been reported to produce symmetrical cleavage products, amine boranes.^{3,4}

(1) H. I. Schlesinger and A. B. Burg, *Chem. Rev.*, **31**, 1 (1942); F. G. A. Stone, *Advan. Inorg. Chem. Radiochem.*, **2**, 279 (1960).

(2) R. W. Parry in collaboration with D. R. Schultz, S. G. Shore, and P. R. Girardot, *J. Am. Chem. Soc.*, **80**, 4 (1958); R. C. Taylor, D. R. Schultz, and A. R. Emery, *ibid.*, **80**, 27 (1958); T. P. Onak and I. Shapiro, *J. Chem. Phys.*, **32**, 952 (1960).

(3) E. Wiberg, A. Bolz, and P. Buchheit, *Z. anorg. Chem.*, **256**, 285 (1948); E. Wiberg, K. Hertwig, and A. Bolz, *ibid.*, **256**, 177 (1948).

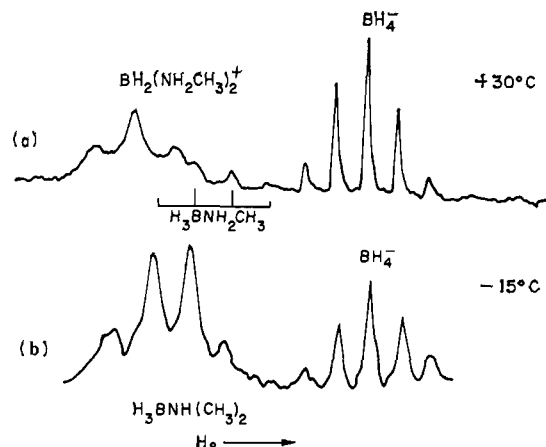


Figure 1. B^{11} n.m.r. spectra of cleavage products: (a) reaction of B_2H_6 with CH_3NH_2 in liquid CH_3NH_2 ; (b) reaction of B_2H_6 with $(\text{CH}_3)_2\text{NH}$ in liquid $(\text{CH}_3)_2\text{NH}$.

We have found that procedures equivalent to those used to prepare $\text{H}_2\text{B}(\text{NH}_3)_2^+\text{BH}_4^-$ ^{2,5} can produce unsymmetrical as well as symmetrical cleavage when B_2H_6 reacts directly with excess CH_3NH_2 or $(\text{CH}_3)_2\text{NH}$ at low temperature (-80 to -90°). Relative yields of cleavage products (estimated from B^{11} n.m.r. spectra) from individual reactions of diborane with CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$, and $(\text{CH}_3)_3\text{N}$ were found to be: $\text{H}_2\text{B}(\text{NH}_2\text{CH}_3)_2^+\text{BH}_4^- \gg \text{H}_3\text{BNH}_2\text{CH}_3$; $\text{H}_3\text{BNH}(\text{CH}_3)_2 > \text{H}_2\text{B}(\text{NH}(\text{CH}_3)_2)_2^+\text{BH}_4^-$; $\text{H}_3\text{BN}(\text{CH}_3)_3$, only detectable product.

Figure 1a shows B^{11} n.m.r. spectra of products of direct reaction of B_2H_6 with CH_3NH_2 under conditions cited in ref. 2 and 5. The predominant product, $\text{H}_2\text{B}(\text{NH}_2\text{CH}_3)_2^+\text{BH}_4^-$, is that of unsymmetrical cleavage. Only a barely detectable amount of symmetrical cleavage product, $\text{H}_3\text{BNH}_2\text{CH}_3$, is formed. The coupling constant ($J_{\text{BH}} = 82$ c.p.s.) and the chemical shift ($\delta = 40.5$ p.p.m., with respect to $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$) for the quintet are in agreement with reported values for BH_4^- .⁶ The triplet assigned to $\text{H}_2\text{B}(\text{NH}_2\text{CH}_3)_2^+$ has peak heights in the expected ratio 1:2:1, with $J_{\text{BH}} = 104$ c.p.s. and $\delta = 9.2$ p.p.m. Peaks assigned to the symmetrical cleavage product, $\text{H}_3\text{BNH}_2\text{CH}_3$, were duplicated by an authentic sample of this compound⁷; J_{BH} and δ were in agreement with reported values.⁸

Figure 1b presents B^{11} n.m.r. spectra of products of direct reaction of B_2H_6 with $(\text{CH}_3)_2\text{NH}$ under conditions cited in ref. 2 and 5; J_{BH} and δ of the quartet assigned to the symmetrical cleavage product were in agreement with reported values.⁸ Of the unsymmetrical cleavage product, only BH_4^- could be detected with certainty. In addition to the possibility that the spectrum of $\text{H}_2\text{B}(\text{NH}(\text{CH}_3)_2)_2^+$ most likely overlaps that of $\text{H}_3\text{BNH}(\text{CH}_3)_2$, results discussed below suggest that the spectrum of this ion would not be detected easily at the temperature at which the spectra were obtained.

The spectrum of $\text{H}_2\text{B}(\text{NH}_2\text{CH}_3)_2^+$ is markedly temperature dependent. Below -5° , this ion could not be detected at radiofrequency transmitter powers which produced the well-resolved quintet of BH_4^- . Only at a

(4) R. W. Parry, G. Kodama, and D. R. Schultz, *J. Am. Chem. Soc.*, **80**, 24 (1958).

(5) S. G. Shore and K. W. Boddeker, *Inorg. Chem.*, **3**, 914 (1964).

(6) T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).

(7) E. R. Alton, R. D. Brown, J. C. Carter, and R. C. Taylor, *J. Am. Chem. Soc.*, **81**, 3550 (1959).

(8) D. F. Gaines and R. Schaeffer, *ibid.*, **86**, 1505 (1964).