Dynamical Processes in Boranes, Borane Complexes, Carboranes, and Related Compounds

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Contents

I. Introduction 465
II. The Tetrahydroborate Ion (BH_4^-) 466
III. Amine-Boranes and Aminoboranes 470
IV. Diboranes and Diborohydrides 471
V. Triborane (B_3H_7) 472
VI. Triborohydride Ion ($B_3H_8^-$) 473
VII. Tetraborane Derivatives 475
  A. $B_4H_8 \cdot$ (*N,N,N',N*-Tetramethylethylenediamine) 475
  B. Nonahydrotetraborate (1−) Ion ($B_4H_9^-$) 475
  C. $F_2XP \cdot B_4H_8$ 476
VIII. Pentaborane Derivatives 477
  A. Octahydropentaborate (1−) Ion ($B_5H_8^-$) 477
  B. $C_3B_5H_7$ 477
  C. CB_5H_7 478
  D. Pentaborane(11) (B_5H_{11}) 479
  E. Dodecahydropentaborate (1−) Ion ($B_5H_{12}^-$) 479
  F. Pentaborane(9) (B_5H_9) 479
IX. Hexaborane Derivatives 479
  A. Hexaborane(10) (B_6H_{10}) 479
  B. Nonahydrohexaborate(1−) Ion ($B_6H_9^-$) 480
  C. Undecahydrohexaborate (1−) Ion ($B_6H_{11}^-$) 480
  D. μ-[$(CH_3)_2B$]B_5H_8 481
X. Octaborane Derivatives 482
  A. Octahydrooctaborate (2−) Ion ($B_8H_8^{2-}$) 482
  B. Octahydrooctaborate (1−) Ion ($B_8H_8^-$) 482
  C. Octaborane(12) (B_8H_{12}) 482
XI. Nonaborane Derivatives 483
  A. $B_9H_{14}^-$ 483
  B. $B_9H_{13}L$ Compounds 483
  C. Metal Complexes of $B_9H_{14}^-$ and $B_9H_{12}S^-$ 484
  D. $B_9C_2H_{12}^-$ Ions 484
  E. Alkylaluminum and Alkylgallium Derivatives of (3)-1,2-$B_9C_2H_{13}$ 484
XII. Decaborane Derivatives 485
  A. $B_{10}H_{12}(NCCH_3)_2$ 485
  B. $B_{10}H_{15}^-$ Ion 485
  C. Metal Complexes of $B_{10}H_{13}^-$ 485
  D. Icosahedral Carboranes 486
XIII. Undecaborane Derivatives 486
  A. $B_{11}H_{14}^-$ Ion 486
  B. $B_{11}H_{13}^{2-}$ Ion 486
  C. Metal Complexes of $B_{11}H_{14}^-$ 486
  D. Undecahydroundecaborate(2−) Ion ($B_{11}H_{11}^{2-}$) 486

I. Introduction

The general synthetic utility and unusual bonding associated with boron hydrides and derivatives have prompted a recent intense effort in definitive structure elucidation. X-Ray diffraction, electron diffraction, nuclear magnetic resonance (nmr) spectroscopy, electron spin resonance (esr) spectroscopy, and dipole moment studies have been applied to the problem.

In several instances, there exists an apparent discrepancy between the structure indicated by the solution nmr spectrum (at room temperature) and the X-ray crystallographic structure. In essentially every case for which the apparent discrepancy exists, the nmr spectrum suggests a greater structural symmetry than that revealed in the crystal structure.[2] In attempting to define the source of this apparent discrepancy, variable-temperature nmr (dnmr) spectroscopy has revealed two fundamentally different rate processes which occur in many boron hydrides. In one case, lower temperatures result in elimination of the $^{10,11}B-^{1}H$ spin-spin coupling (*e.g.*, as observed in the ^1H dnmr spectrum) and an eventual simplification of the spectrum.[3] This phenomenon is caused by more rapid ^{11}B and ^{10}B quadrupolar relaxation at lower temperatures and increasing viscosity inducing more rapid interconversion between respective ^{11}B and ^{10}B nuclear spin states and effective decoupling of boron from hydrogen. This *in situ* heteronuclear spin decoupling has been treated theoretically in a quantitative fashion.[4] For a nucleus with spin $I > \frac{1}{2}$, interaction of the nuclear quadrupole moment with a fluctuating electric field gradient at the nucleus provides an efficient spin relaxation mechanism under certain conditions. In solution, molecular reorientation (tumbling) occurs rapidly, and interaction of the quadrupolar nucleus with the lattice leads to a rapidly fluctuating electric field gradient at the nucleus. The rate of molecular tumbling is characterized by a correlation time (τ_c) which generally is directly proportional to the viscosity of a solution and inversely proportional to the absolute temperature.[5] For a quadrupolar nucleus, the nuclear spin-lattice relaxation time (T_1) can be related to τ_c by eq 1.[4,5]

$$\frac{1}{T_1} = \left(\frac{3}{40}\right)\frac{2I + 3}{I^2(2I - 1)}(1 + \eta^2/3)(e^2qQ/h)^2\tau_c \qquad (1)$$

I = nuclear spin, eq = electric field gradient at quadrupolar nucleus, eQ = nuclear quadrupole moment, e^2qQ

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(1) Alfred P. Sloan Research Fellow, 1971–1974; Camille and Henry Dreyfus Teacher-Scholar, 1972–present.

(2) G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969.

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(4) J. A. Pople, *Mol. Phys.*, **1**, 168 (1958); A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, London, 1961; A. Allerhand, J. D. Odom, and R. E. Moll, *J. Chem. Phys.*, **50**, 5037 (1969); see also N. C. Pyper, *Mol. Phys.*, **21**, 977 (1971).

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= nuclear quadrupole coupling constant, and η = nuclear asymmetry parameter.

For ^{11}B

$$\frac{1}{T_1} = \left(\frac{1}{10}\right)\frac{e^2qQ^2}{h}\tau_c \qquad Q = 0.0355 \times 10^{-24}\ \text{cm}^2$$

For ^{10}B

$$\frac{1}{T_1} = \left(\frac{3}{200}\right)\frac{e^2qQ^2}{h}\tau_c \qquad Q = 0.074 \times 10^{-24}\ \text{cm}^2$$

It is clear from eq 1, and specifically for ^{10}B and ^{11}B, that as τ_c increases owing to increasing viscosity, decreasing temperature, or increasing molecular volume,[5] T_1 decreases. A decreasing T_1 means decreasing lifetimes for the various ^{11}B ($m_I = -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}$) and ^{10}B ($m_I = -3, -2, -1, 0, +1, +2, +3$) spin states, *i.e.*, an increasing rate of interconversion between these spin states. If the rate of spin state interconversion in ^{10}B and ^{11}B becomes fast enough, other magnetic nuclei ($I \neq 0$) coupled to ^{10}B or ^{11}B will experience a single time-averaged environment due to the various ^{10}B and ^{11}B spin states, and spin-spin coupling will be eliminated. In a large number of diamagnetic boron hydrides[4] and other compounds,[5] it is usually assumed that quadrupolar coupling as described above is the dominant mechanism for ^{10}B and ^{11}B spin-lattice relaxation,[6] although intramolecular dipole-dipole and other interactions probably make small contributions. The effects of quadrupole-induced spin-lattice relaxation have been demonstrated experimentally by varying the temperature or the viscosity of nmr samples.[3,7]

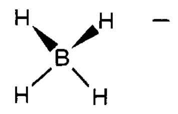
The other important effect which may be observed in the dnmr spectrum of a boron hydride is the separation of a time-averaged dnmr resonance at high temperatures into two or more peaks at lower temperatures, indicating the slowing of an intramolecular or intermolecular rate process.[8]

If dnmr spectroscopy is to be used in the structure elucidation of boron hydrides, it is important to realize that both boron quadrupolar relaxation and intramolecular or intermolecular chemical exchange processes can cause dramatic changes in the spectrum, and these two types of effect must be distinguished.

The intent of this report is to review all those papers through 1972 dealing with the observation of quadrupole-induced spin decoupling and nondestructive rate processes in boron hydrides and related compounds. The review will deal primarily with results obtained from dnmr studies.

II. The Tetrahydroborate Ion (BH_4^-)

In the free, uncomplexed BH_4^- ion, the tetrahedral array of the four protons (**1**) as demonstrated by infrared spectroscopic[9a] and X-ray powder diffraction[9b] studies renders all four protons chemically and magnetically equivalent. This equivalence was shown in early nmr studies of $NaBH_4$ in water or deuterium oxide by the observation of a dominant 1:1:1:1 quartet for the ^1H spectrum ($J(^{11}B,^1H)$ = 82 Hz)[9c-e] with the less intense ^{10}B coupling superimposed and a 1:4:6:4:1 quintet for the ^{11}B spectrum. The sharp lines observed in the ^1H and ^{11}B nmr spectra of uncomplexed BH_4^- are also compatible with a small angular dependence of the electric field gradients at the boron nucleus due to T_d symmetry. This, of course, will lead to a very small or zero quadrupole coupling constant (eq 1) and relatively slow quadrupole relaxation. Thus, spin-spin coupling is observed and the lines are sharp. The observed magnetic equivalence of the four protons in free BH_4^- would be consistent also with a square-planar (**2**) or square-pyramidal (**3**) geometry, but the angular dependence of the electric field gradients at the boron nucleus would be large. Significantly broadened nmr signals would be expected and are not observed.



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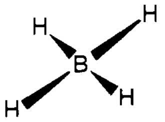

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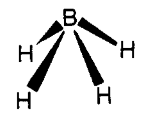

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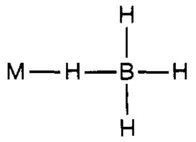
The observation of ^{11}B–^1H and ^{10}B–^1H spin-spin coupling for aqueous $NaBH_4$ in addition to ^1H–^2H coupling in randomly deuterated (37% ^2H) tetrahydroborate ($J(^1H,^2H)$ = 1.7 Hz)[10] indicates clearly that hydrogen exchange (B–H bond scission) is not occurring at a rate which is rapid on the nmr time scale at room temperature. From the established dependence of spin-spin coupling constants on the magnetogyric ratio,[11] the $J(^1H,^1H)$ in BH_4^- is calculated to be −10.7 ± 0.3 Hz[10] as compared to −12.4 Hz in CH_4.[12]

Complexation of BH_4^- *via* covalent hydrogen bridge bonds to an electron-deficient species (**4**, **5**, **6**) may effect two important changes in the behavior of complexed BH_4^- as compared to free BH_4^-. First, the asymmetry associated with complexed BH_4^- will induce a nonzero angular dependence of the electric field gradient at boron (eq 1: $e^2qQ > 0$). This should induce more rapid ^{11}B and ^{10}B quadrupolar relaxation and effective decoupling of ^{11}B and ^{10}B from ^1H under appropriate conditions. This effect has been demonstrated using nmr spectroscopy repeatedly in a variety of BH_4^- complexes[3,7] and examples will be discussed below. Second, in a complex such as **5**, H_a and H_b are in different chemical or magnetic environments and would be expected to possess different ^1H nmr chemical shifts and boron-hydrogen spin-spin coupling constants. However, the chemical shifts of H_a



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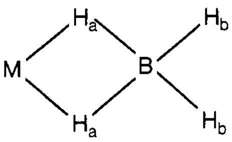

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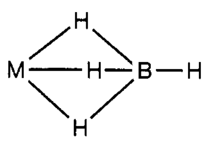

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M = Cu(I), Al(III), Hf(IV), Zr(IV), etc.

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(6) W. B. Moniz and H. S. Gutowsky, *J. Chem. Phys.*, **38**, 1155 (1963).

(7) T. J. Marks and L. A. Shimp, *J. Amer. Chem. Soc.*, **94**, 1542 (1972).

(8) G. Binsch, *Top. Stereochem.*, **3**, 97 (1968).

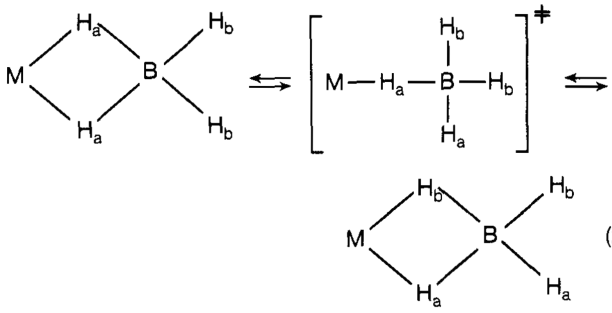
(9) (a) W. C. Price, *J. Chem. Phys.*, **17**, 1044 (1949); (b) A. M. Soldate, *J. Amer. Chem. Soc.*, **69**, 987 (1947); (c) R. A. Ogg, *J. Chem. Phys.*, **22**, 560 (1954); (d) J. N. Shoolery, *Discuss. Faraday Soc.*, **19**, 215 (1955); (e) S. G. Shore, C. W. Hickam, and D. Cowles, *J. Amer. Chem. Soc.*, **87**, 2755 (1965).

(10) R. E. Mesmer and W. L. Jolly, *J. Amer. Chem. Soc.*, **84**, 2039 (1962).

(11) (a) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959; (b) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic resonance Spectroscopy," Vol. 1-2, Pergamon Press, New York, N. Y., 1965.

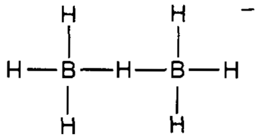
(12) M. Karplus, D. H. Anderson, T. C. Farrar, and H. S. Gutowsky, *J. Chem. Phys.*, **27**, 597 (1957).

and H_b and associated spin–spin coupling may be time-averaged to a single value *via* rapid intramolecular rearrangement (*e.g.*, eq 2). Slowing this exchange on the ^1H



(2)

nmr time scale should produce separate signals for H_a and H_b. The same rationale may be applied to **4** and **6**. There is evidence to support slow hydrogen scrambling on the dnmr time scale in the diborohydride ion (**7**)[13]



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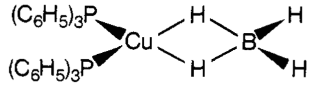
analogous to **4**. Efforts to observe slow intramolecular exchange using dnmr spectroscopy in a variety of metal–BH_4 complexes have not yet been successful, although clear evidence for terminal and bridging hydrogens obtained from infrared spectroscopy exists for such complexes. The inability of the dnmr method to detect slow BH_4^- rearrangement may be due to a very low classical (thermal) barrier to rearrangement or to quantum mechanical proton tunneling[14] of BH_4^- or to a combination of both effects. Indeed, lowering the temperature of a dnmr sample in an attempt to slow intramolecular exchange would be expected to increase the fraction of tunneling as compared to an exclusively thermally promoted rearrangement further complicating the situation.[15]

A recent X-ray crystallographic study of bis(triphenylphosphine)copper tetrahydroborate (**8**) indicates a tetra-



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hedral array about copper and boron[16a] and clear evidence for hydrogen bridge bonds between copper and boron. If hydrogen scrambling in the BH_4 moiety of **8** were slow on the ^1H nmr time scale, one would expect to observe different resonances for bridge and terminal protons. Examination of the ^1H dnmr spectrum (60 MHz) of **8** in 50% $CDCl_3$–50% CH_2Cl_2(v/v) at 20° revealed an almost undetectable signal for BH_4 indicating efficient boron quadrupolar relaxation even at this relatively high temperature (Figure 1).[3,16b] Upon lowering the temperature, the spectrum sharpens significantly (Figure 1) giving at −106° a broad singlet of essentially Lorentzian line shape. Boron–hydrogen spin–spin coupling is almost eliminated owing to quadrupolar relaxation. Significant ^1H–P coupling is not evident. These observations are consistent with the magnetic equivalence of all BH_4 protons in a static or dynamic form of **8**, or, more likely, with rapid intramolecular hydrogen scrambling time-averaging magnetically nonequivalent bridge and terminal protons in **8**. The development of superior solvent systems making possible dnmr experiments at much lower temperatures may shed light on the problem.

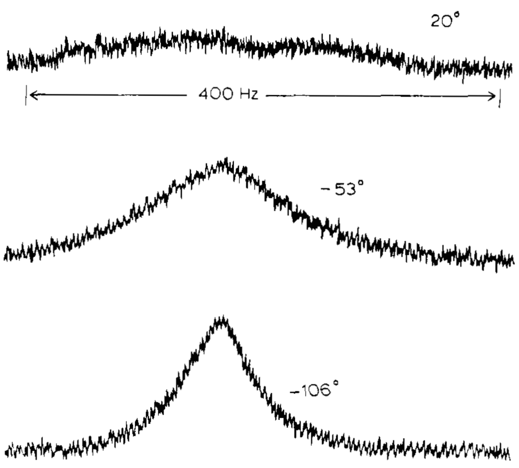

Figure 1. The ^1H dnmr spectrum (60 MHz) of the BH_4 hydrogens of $[(C_6H_5)_3P]_2CuBH_4$ in 50% $CDCl_3$/50% CH_2Cl_2 (v/v) (see ref 3).

The unusual covalent character of liquid aluminum borohydride, $Al(BH_4)_3$, has prompted dnmr studies directed toward structure elucidation. Evidence for two different processes has been obtained. First, examination of the room-temperature ^1H dnmr spectrum of freshly prepared $Al(BH_4)_3$ reveals a significantly broadened resonance having essentially no fine structure.[17] Irradiation at the ^{27}Al (I = $\frac{5}{2}$) resonant frequency sharpens the spectrum dramatically into a dominant 1:1:1:1 quartet (J (^{11}B,^1H) = 89 Hz)[17a] illustrating magnetically equivalent BH_4 protons. The demonstration of ^{27}Al–^1H coupling speaks for slow ligand dissociation on the dnmr time scale but with all BH_4 protons still at least magnetically equivalent. Heating a sample of neat $Al(BH_4)_3$[17a] or a benzene solution[17b] to higher temperatures (60 to 80°) produced a sharpening of the ^1H dnmr spectrum again into a dominant 1:1:1:1 quartet and an apparent loss of ^1H spin–spin coupling to ^{27}Al (Figure 2). This observation is consistent with a rate process involving rapid aluminum–hydrogen bond scission (*i.e.*, ligand exchange) leading to a loss of ^{27}Al–^1H coupling. However, prolonged heating (*ca.* 2 hr) of $Al(BH_4)_3$ at 80° in benzene produced an apparent irreversible structural modification[17b] of $Al(BH_4)_3$ which gives a sharp dominant 1:1:1:1 quartet (J (^{11}B,^1H) = 89 Hz) for the ^1H nmr spectrum even *at 35°*. Further cooling of this modified $Al(BH_4)_3$ produced a broad continuum for the ^1H dnmr spectrum at *ca.* −40° (Figure 3), and ^{27}Al irradiation at −80° restored the 1:1:1:1 quartet, indicating the existence of ^1H–^{27}Al spin–spin coupling, *i.e.*, apparently slow aluminum–hydrogen bond scission or ligand exchange, with all BH_4 protons again at least magnetically equivalent. These data provide some evidence for a ligand (BH_4) exchange process in the two undefined forms of $Al(BH_4)_3$, but the question of the equivalent BH_4 protons remains. It may be that another more rapid *intramolecu-*

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(13) D. F. Gaines, *Inorg. Chem.*, **2**, 523 (1963).

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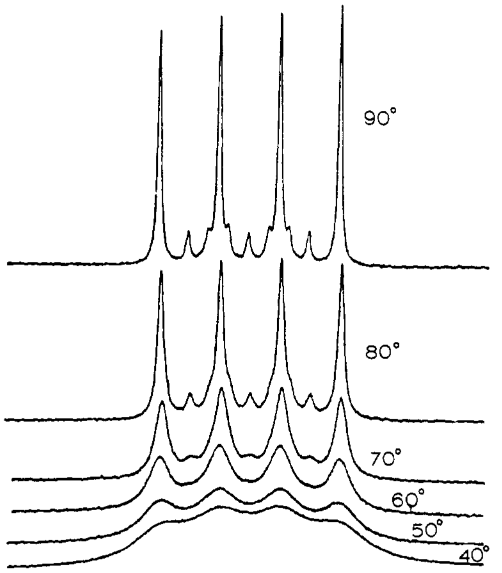


Figure 2. The ^1H dnmr spectrum (60 MHz) of freshly prepared $Al(BH_4)_3$ (J (^{11}B,H) = 89 Hz) (see ref 17b).

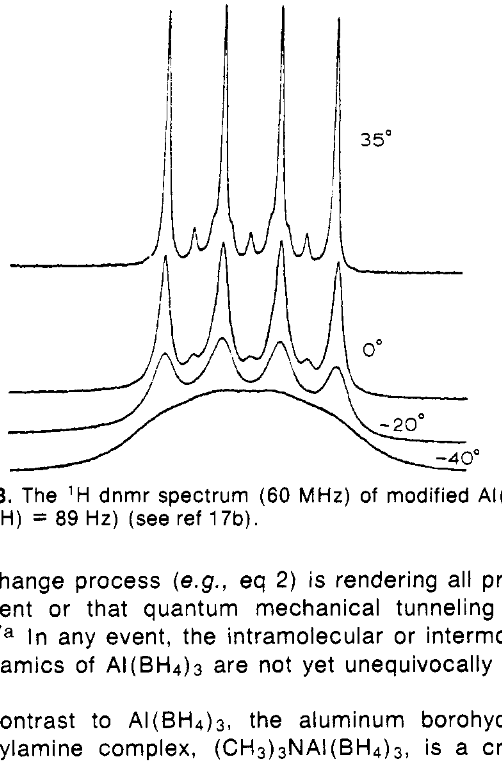


Figure 3. The ^1H dnmr spectrum (60 MHz) of modified $Al(BH_4)_3$ (J (^{11}B,H) = 89 Hz) (see ref 17b).

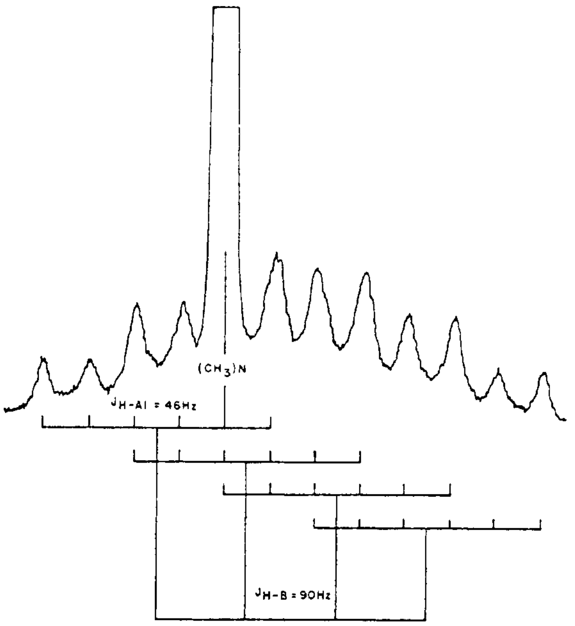
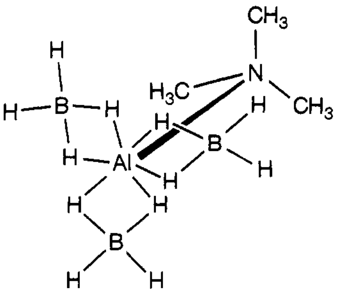


Figure 4. The ^1H nmr spectrum (60 MHz) of $(CH_3)_3NAl(BH_4)_3$ in benzene at room temperature (see ref 21).

lar exchange process (*e.g.*, eq 2) is rendering all protons equivalent or that quantum mechanical tunneling is at work.[17a] In any event, the intramolecular or intermolecular dynamics of $Al(BH_4)_3$ are not yet unequivocally delineated.

In contrast to $Al(BH_4)_3$, the aluminum borohydride-trimethylamine complex, $(CH_3)_3NAl(BH_4)_3$, is a crystalline material. A room-temperature X-ray crystallographic study of $(CH_3)_3NAl(BH_4)_3$ reveals an ethane-like arrangement of the carbon, nitrogen, aluminum, and boron atoms with each boron attached to aluminum *via* two hydrogen bridge bonds (**9**)[18] with nearly tetrahedral symmetry about aluminum and nitrogen. At −160°, the crystal structure of $(CH_3)_3NAl(BH_4)_3$ does not possess tetrahedral symmetry about aluminum.[18] It is noteworthy that the nitrogen-aluminum bond length (2.01 Å)[18] in $(CH_3)_3NAl(BH_4)_3$ is substantially shorter than the 2.19 Å in $(CH_3)_3NAlH_3$.[19] Cryoscopic measurement[20] and solution nmr studies[21] reveal monomeric behavior for $(CH_3)_3NAl(BH_4)_3$ as well as slow intermolecular trimethylamine exchange on the nmr time scale at room temperature. The ^1H nmr spectrum (Figure 4) of $(CH_3)_3NAl(BH_4)_3$ reveals again magnetically equivalent BH_4 protons spin-spin coupled to ^{11}B ($J_{B,H}$ = 87 Hz) as well as ^{27}Al ($J_{Al,H}$ = 46 Hz). Concomitant spin-spin coupling was observed in the ^{27}Al (J (Al,^{11}B) ~ 9 Hz) and ^{11}B spectra. Such observations are consistent with a slowly dissociating or exchanging complex, but the apparent magnetic equivalence of bridging and terminal BH_4 protons remains intriguing. Contrary to $Al(BH_4)_3$,[17a] the various nmr spectra of $(CH_3)_3NAl(BH_4)_3$ reveal clearly resolved coupling to ^{27}Al at room temperature consistent with a smaller electric field gradient at the ^{27}Al nucleus in $(CH_3)_3NAl(BH_4)_3$ and slower ^{27}Al quadrupolar relaxation.[21] In a recent report,[22] the coalescence of the spin-spin coupling in the ^1H nmr spectrum of $(CH_3)_3NAl(BH_4)_3$ at lower temperatures (−60°) was interpreted as being consistent with slowing the rate of exchange between terminal and bridging BH_4 protons. In light of recent reports[3,7] and from an examination of the observed line shapes, these spectral changes would seem to be rationalized better in terms of efficient quadrupole induced spin decoupling at low temperature.



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Although the structural information which can be derived from the ^1H and ^{11}B nmr spectra of $Al(BH_4)_3 \cdot 6NH_3$ in liquid ammonia is limited, the appearance in the ^{11}B spectrum of a 1:4:6:4:1 quintet at +38.4 ppm (from $BF_3 \cdot O(C_2H_5)_2$) and a 1:1:1:1 quar-

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[18] N. A. Bailey, P. H. Bird, and M. G. H. Wallbridge, *Inorg. Chem.*, **7**, 1575 (1968).

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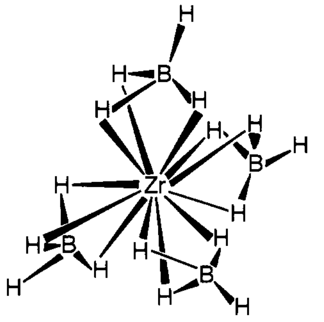
[22] N. A. Bailey, P. H. Bird, N. Davies, and M. G. H. Wallbridge, *J. Inorg. Nucl. Chem.*, **32**, 3116 (1970).

tet in the ^{1}H spectrum ($J_{\mathrm{B,H}}$ = 82 Hz) with no apparent ^{27}Al–^{1}H coupling is consistent with a "free" or rapidly exchanging BH_4^- group.[23] This behavior is in contrast to $(CH_3)_3NAl(BH_4)_3$ discussed above.

Examination of the ^{11}B nmr spectrum of $HAl[N(CH_3)_2]_2{\cdot}2BH_2N(CH_3)_2$ at 25 and −55° revealed no changes in the 1:2:1 triplet pattern consistent with boron coupling to three equivalent protons and no apparent coupling to Al–H–B or B–H–B brdiging hydrogens.[24] This observation is consistent with rapid dissociation of three complexed moieties in $HAl[N(CH_3)_3]_2{\cdot}2BH_2N(CH_3)_2$ or with no complexation at all.

In the case of $Zr(BH_4)_4$, infrared spectra,[7,25] X-ray diffraction data[26] at −160°, and electron diffraction data on the vapor[27] indicate clearly the presence of hydrogen bridges and the possibility of magnetic nonequivalence among the BH_4 protons. The interesting implication derived from the X-ray data[26] at −160° and the electron diffraction studies[27] is the involvement of three hydrogens of a given BH_4 moiety in bridging to zirconium (**10**).



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Although the experimental data regarding the structure of $Hf(BH_4)_4$ are limited,[7] it is apparent that it has a structure very similar to $Zr(BH_4)_4$. A dnmr investigation of $Zr(BH_4)_4$ and $Hf(BH_4)_4$ revealed changes in the ^{1}H dnmr spectrum at low temperatures consistent only with quadrupole-induced spin decoupling (Figure 5)[7] and verified by total nmr line-shape techniques. It is apparent from these studies[7] that intramolecular scrambling of the BH_4 groups is still rapid on the nmr time scale at −80°. Rapid intramolecular scrambling in $Zr(BH_4)_4$ and $Hf(BH_4)_4$ at −80° is not surprising in light of the apparently rapid exchange in $[(C_6H_5)_3P]_2CuBH_4$ at −110°.[16] Analogous to the above compounds, $(\pi\text{-}C_5H_5)_2Zr(BH_4)_3$ possesses an infrared spectrum indicating bridging and terminal B–H groups, although the ^{1}H and ^{11}B nmr spectra again reveal all hydrogens to be equivalent, *i.e.*, apparently rapid BH_4 scrambling.[28]

The infrared spectra of the apparently square-planar trans complexes $(R_3P)_2MH(BH_4)$, in which R = cyclohexyl or isopropyl and M = Pd or Ni, suggest double hydrogen bridges for BH_4. However, the lone hydrogen bonded to the metal shows equivalent spin–spin coupling to all four BH_4 protons[29] consistent with all BH_4 hydrogens being equivalent and rearranging rapidly.

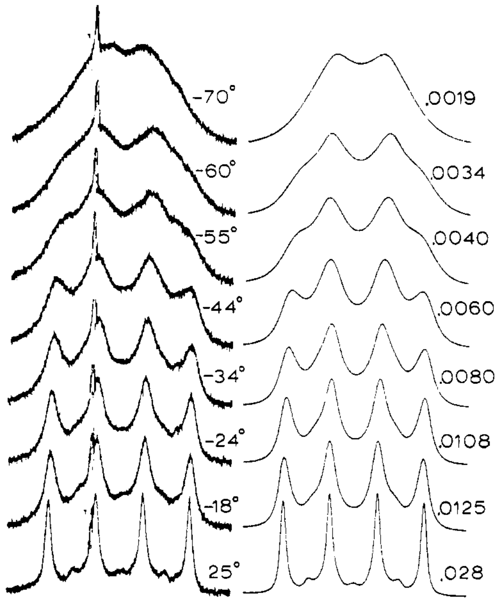
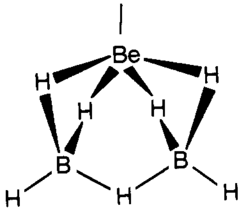


Figure 5. The experimental ^{1}H dnmr spectrum (90 MHz) of $Zr(BH_4)_4$ in toluene-d_8 and computed spectra as a function the ^{11}B spin–lattice relaxation time (T_1) (see ref 7).

Electric deflection,[30] dipole moment,[31] and infrared spectroscopic studies[32] of gaseous $Be(BH_4)_2$ seem to support a structure similar to **11**. A recent X-ray crystallographic study of $Be(BH_4)_2$ reveals a structure which consists of a helical polymer of BH_4Be and BH_4 units (**12**).[33]



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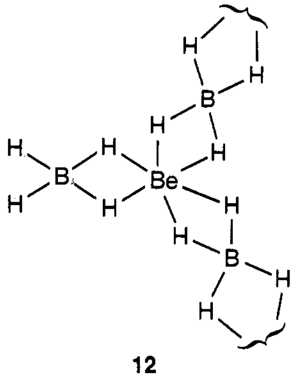

12

Although the above data indicate clearly the presence of different types of hydrogens in $Be(BH_4)_2$, little dnmr data[34] have been forthcoming relating to the static or dynamic structure of $Be(BH_4)_2$. The ^{1}H nmr spectrum of CH_3BeBH_4 dimer (**13**) in benzene-toluene at room tem-

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(29) M. L. H. Green, H. Munakata, and T. Saito, *J. Chem. Soc. A*, 469 (1971).

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(34) T. H. Cook and G. L. Morgan, *J. Amer. Chem. Soc.*, **92**, 6487 (1970).

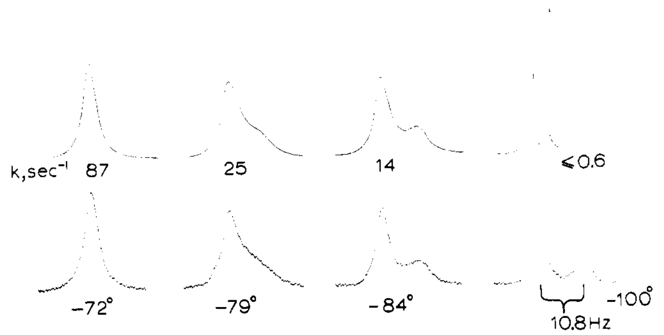
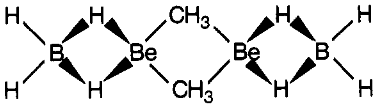


Figure 6. The ^{1}H dnmr spectrum (60 MHz) of the *tert*-butyl resonance of $(t\text{-}C_4H_9)(CH_3)_2NBH_3$ in CH_2CHCl (see ref 37).

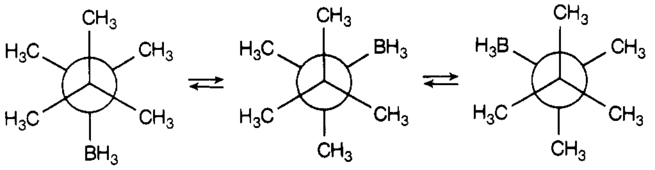


13

perature[34] consists of a sharp singlet resonance (τ 10.11, CH_3) and a 1:1:1:1 quartet (τ 9.20, $J_{B,H}$ = 86.0 Hz, BH_4) with respective relative intensities of 3:4. The 1:1:1:1 quartet observed for the BH_4 proton resonance is again consistent with all BH_4 hydrogens being equivalent owing to rapid intramolecular exchange or consistent with the unlikely happening of equivalent spin-spin coupling of bridge and terminal protons to boron in a static or dynamic system.

III. Amine-Boranes and Aminoboranes

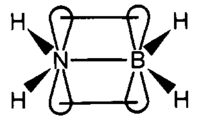
Although recent theoretical calculations concerning the barrier to rotation in $H_3N\text{-}BH_3$ ($\Delta H^* = 3$ kcal/mol)[35] suggest conformational dynamics similar to ethane (ΔH^* = 3 kcal/mol),[36] there exists a dearth of data regarding rotation about nitrogen-boron bonds in amine-boranes or phosphorus-boron bonds in phosphine-boranes. Recent reports indicate that borane complexation of a trialkylamine can affect markedly the conformational dynamics of the central carbon-nitrogen bond as compared to the free amine. For example, examination of the ^{1}H dnmr spectra of $(t\text{-}C_4H_9)(CH_3)_2NBH_3$ and $(t\text{-}C_4H_9)(CH_3)_2NBD_3$ in vinyl chloride revealed changes in the spectrum (Figure 6) consistent with slowing *tert*-butyl rotation (eq 3).[37]



(3)

A total dnmr line-shape analysis of this spectral behavior (Figure 6) gave activation parameters for *tert*-butyl rotation in $(t\text{-}C_4H_9)(CH_3)_2NBH_3$ ($\Delta H^* = 11.2 \pm 0.3$ kcal/mol, $\Delta S^* = 6 \pm 2$ eu, $\Delta G^* = 10.0 \pm 0.1$ kcal/mol at −79°) and also in $(t\text{-}C_4H_9)(CH_3)_2NBD_3$ ($\Delta H^* = 11.1 \pm 0.3$ kcal/mol, $\Delta S^* = 5 \pm 2$ eu, $\Delta G^* = 10.1 \pm 0.1$ kcal/mol at −77°) indicating little effect of deuterium on the rate of *tert*-butyl rotation. However, increased vicinal repulsions in the two amine-boranes lead to a significantly higher barrier to *tert*-butyl rotation than those observed in a number of uncomplexed *tert*-butyldialkylamines (ΔH^* = 6-7 kcal/mol).[38]

Optimized orientation of the empty 2p atomic orbital of boron with respect to the lone-pair atomic orbital of nitrogen in aminoborane ($H_2N\text{-}BH_2$) leads to π-bonding between nitrogen and boron (**14**). The net result of this π-



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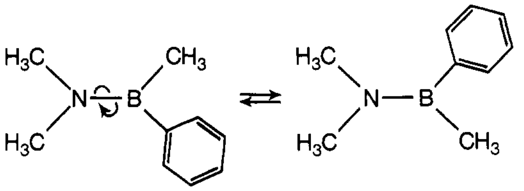
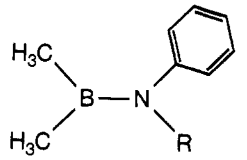
bonding is a reduced pyramidality at nitrogen (as compared to the free amine) similar to that observed in simple amides such as formamide[39] and a situation isoelectronic as well as isosteric with ethylene. Depending on the extent of π-bonding in aminoboranes, there exists a measurable barrier to B-N bond rotation.[40] In sufficiently asymmetric compounds, cis and trans isomers are observed.[41] In the case of (dimethylamino)phenylmethylborane, the barrier to B-N bond rotation was observed to be 26.6 kcal/mol (eq 4).[42] For the series **15** and **16**, the



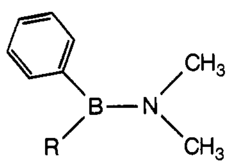
(4)

barriers to B-N bond rotation ranged from 10 to 19 kcal/mol.[42,43] Actually, the bulk of the barriers in **15** and **16**



15

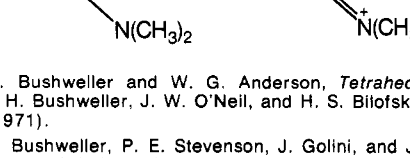
R = Me, Et, *i*-Pr, *i*-Bu,
t-Bu



16

R = Me, Et, *i*-Pr, *i*-Bu,
t-Bu, Cl

were in the range 14-19 kcal/mol with compounds such as **16** (R = *t*-Bu) at 10 kcal/mol, indicating a destabilization, *i.e.*, twisting, of the approximately planar ground state because of increased steric repulsions involving *tert*-butyl. In bis(dimethylamino)boranes and in tris(dimethylamino)borane, simple molecular orbital considerations would predict reduced B-N bond orders owing to "competitive" π-bonding[39] among multiple $B\text{-}N(CH_3)_2$ moieties (below) and a concomitant lowering of the B-N



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(40) G. E. Ryschkewitsch, W. S. Brey, Jr., and A. Saji, *J. Amer. Chem. Soc.*, **83**, 1010 (1961); W. S. Brey, Jr., M. E. Fuller, II, G. E. Ryschkewitsch, and A. S. Marshall, *Advan. Chem. Ser.*, **No. 42** (1964).

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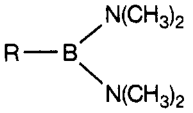
(42) H. Watanabe, T. Totani, K. Tori, and T. Nakogawa in "Proceedings of the XIIIth Colloque Ampere," L. Van Garven, Ed., North Holland Publishing Co., Amsterdam, 1965.

(43) P. A. Barfield, M. F. Lappert, and J. Lee, *Proc. Chem. Soc.*, 421 (1961); K. Niedenzu, J. W. Dawson, G. A. Neece, W. Sarodny, D. R. Squire, and W. W. Weber, *Inorg. Chem.*, **5**, 2161 (1966).

rotational barrier. Dnmr studies reveal an apparent lowering of the B-N rotational barrier in **17a** ($\Delta H^* = 11.1$ kcal/mol) and **17b** ($\Delta H^* = 13.7$ kcal/mol)[44] as compared to the less hindered members of the series **15** and **16.** Consistent with the molecular symmetry, tris(dimethylamino)borane exhibited no changes in the dnmr spectrum to −145°, although the barrier to B-N rotation must be similar to that in **17b.** Interestingly, the B-N rotational barrier in **18** ($\Delta H^* = 12.7$ kcal/mol) is significantly lower than the C-N barrier in the isoelectronic octamethyloxamidinium bromide (**19**, $\Delta H^* = 25$ kcal/mol),[44] indicating a substantial difference in π-bonding characteristics between **18** and **19.**



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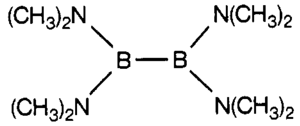
17a, R = C_6H_5
b, R = $N(CH_3)C_6H_5$



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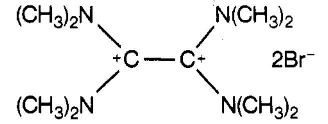
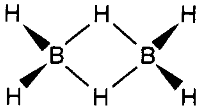


19

IV. Diboranes and Diborohydrides

The dynamical properties of diborane (**20**) are reasonably well defined. Examination of the ^{11}B dnmr spectrum of gaseous diborane reveals a triplet of triplets ($J_{\mathrm{B,H\,bridge}} = 46$ Hz; $J_{\mathrm{B,H\,terminal}} = 135$ Hz) which is invariable over a range of temperature and pressure;[45] *i.e.*, bridge and terminal hydrogens are exchanging slowly. ^{1}H nmr data for diborane are entirely consistent with the ^{11}B spectra.[45b] However, the ^{11}B dnmr spectrum of diborane in diethyl ether solution at 30° is a broad, non-Lorentzian singlet exhibiting no fine structure (Figure 7)[13] consistent with a rate process which is rapid on the nmr time scale. Indeed, lowering the temperature to about −36° restored the identical triplet of triplet spectrum observed for neat nonexchanging diborane. Warming the diethyl ether solution to about 84° produced a seven-line multiplet consistent with ^{11}B coupled to six equivalent hydrogens and rapid hydrogen scrambling. The seven-line multiplet observed in diethyl ether at 84° (Figure 7) is present at room temperature in an ethylene glycol dimethyl ether solution. All of these spectral data in ether solution are consistent with more rapid hydrogen scrambling as compared to neat diborane. It is apparent that ethers catalyze the intramolecular scrambling in diborane (*e.g.*, eq 5). The observation of the seven-line multiplet in ethylene glycol dimethyl ether at room temperature as compared to 84° in diethyl ether suggests that the more basic the ether the more effective the catalysis. The ^{11}B nmr spectra of several neat methyldiboranes also indicate static structures on the nmr time scale at room temperature.[46]



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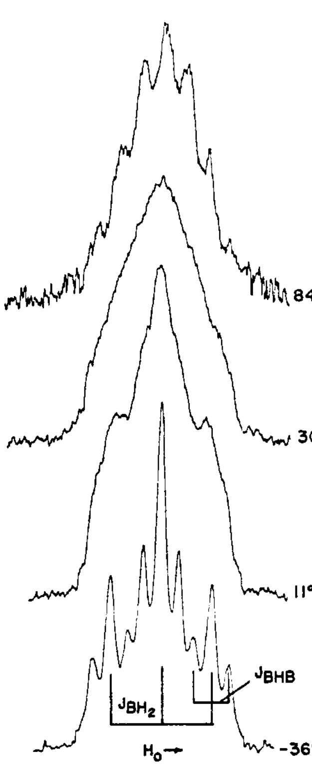
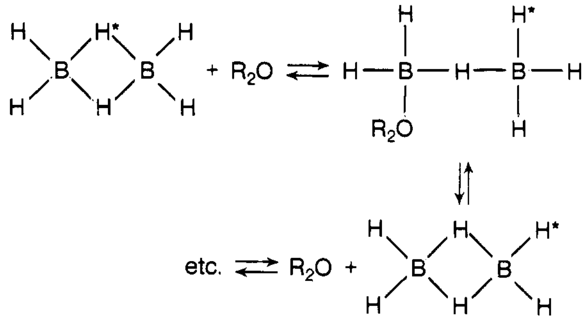


Figure 7. The ^{11}B dnmr spectrum of B_2H_6 in diethyl ether (see ref 13).



(5)

The ^{11}B dnmr spectrum of μ-dimethylaminodiborane was observed early to be temperature dependent, consistent with a dynamic structure for the molecule.[47] However, this early dnmr study[47] was not conducted over the whole range of spectral changes. A later report involved a complete study of the ^{11}B dnmr spectrum of μ-dimethylaminodiborane in ethylene glycol dimethyl ether (Figure 8).[48] At −39°, the ^{11}B spectrum is a triplet of doublets consistent with strong coupling of boron to two terminal hydrogens ($J = 130$ Hz) and weak coupling to one bridging hydrogen ($J = 30$ Hz). At 83°, the spectrum has changed into a sextet possessing intensities consistent with coupling of boron to five equivalent hydrogens, *i.e.*, rapid hydrogen tautomerism (eq 6). As in the case of diborane,[13] the rate of exchange seems to be a function of the basicity of ethereal solvents. An activation energy for hydrogen exchange in μ-dimethylaminodiborane of 3.7 kcal/mol in ethylene glycol dimethyl ether was calculat-

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(44) M. J. S. Dewar and P. Rona, *J. Amer. Chem. Soc.*, **91**, 2259 (1969).

(45) (a) D. F. Gaines, R. Schaeffer, and F. Tebbe, *J. Phys. Chem.*, **67**, 1937 (1963); (b) R. A. Ogg, Jr., *J. Chem. Phys.*, **22**, 1933 (1954); J. N. Shoolery, *Discuss. Faraday Soc.*, **19**, 215 (1955); W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **81**, 4496 (1959); T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).

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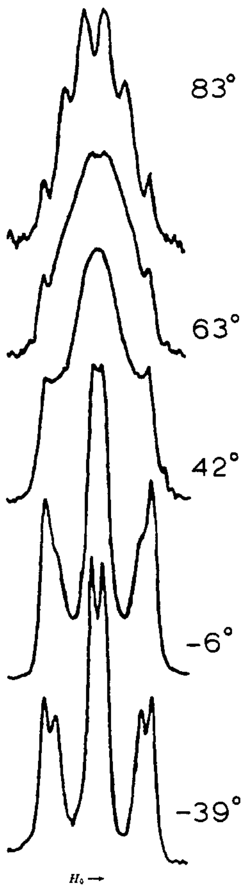
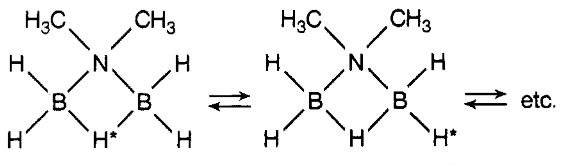


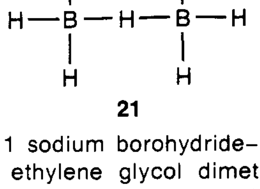
Figure 8. The ^{11}B dnmr spectrum of μ-dimethylaminodiborane in ethylene glycol dimethyl ether (see ref 48).



(6)

ed from the nmr line-shape changes using an approximate method. This compares with 4.8 kcal/mol for diborane in diethyl ether using essentially the same approximate nmr line-shape method.[45a] However, these activation energies must be viewed with discretion owing to their approximate nature and the possibility of significant systematic errors in the analysis.[8]

As predicted from topological theory,[49] the diborohydride ion should have the structure **21**. The ^{11}B nmr



$$\left[\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H- & B & -H- & B & -H \\ & | & & | & \\ & H & & H & \end{array}\right]^-$$

21

spectrum of a 1:1 sodium borohydride–sodium diborohydride mixture in ethylene glycol dimethyl ether at 30° shows the BH_4^- quintet and a broad 1:3:3:1 quartet for B_2H_7- (Figure 9).[13,50] The broadened 1:3:3:1 quartet observed for $B_2H_7^-$ is consistent with coupling of boron to *three* equivalent terminal hydrogens (J = 102 Hz) and weak, unresolved coupling to the bridge hydrogen (**21**); *i.e.*, hydrogen tautomerism is slow on the nmr time scale in $B_2H_7^-$ under these conditions. If one thinks of $B_2H_7^-$ as a complex between BH_3 and BH_4^-, the static behavior of $B_2H_7^-$ is in marked contrast to a host of other metal tetrahydroborate complexes discussed above. Upon warming the 1:1 sodium borohydride:sodium diborohydride solution, the BH_4^- and $B_2H_7^-$ ^{11}B resonances coalesced consistent with an increasing rate of *intermolecular* scrambling between BH_4^- and $B_2H_7^-$ (Figure 9). In contrast, the intermolecular exchange between $B_2H_7^-$ and B_2H_6 is apparently rapid even at room temperature.[13] Recently, $CH_3P(C_6H_5)_3B_2H_7$ was prepared.[51] The ^1H nmr spectrum of the B_2H_7 protons in $CH_3P(C_6H_5)_3B_2H_7$ at 33° consists of a 1:1:1:1 quartet ($J_{H,B}$ = 106 Hz; τ 8.9) and a broad unresolved resonance at τ 14.5 of relative intensities 6:1. ^1H-^1H spin-spin coupling between terminal and bridging hydrogens (J = 5.6 Hz) is also observed. The ^{11}B nmr spectrum at 33° reveals a broadened 1:3:3:1 quartet (J (^{11}B,H) = 106 Hz). All of these observations are consistent again with a static, single hydrogen-bridged $B_2H_7^-$.

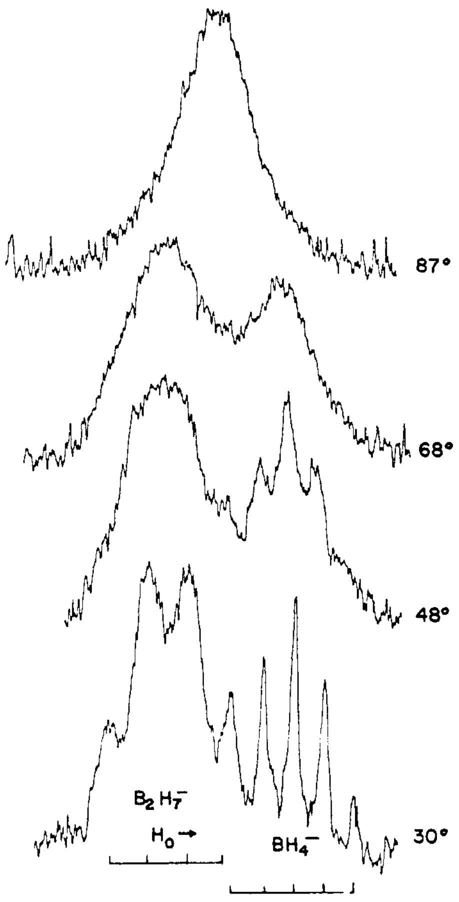


Figure 9. The ^{11}B dnmr spectrum of 1:1 sodium borohydride–sodium diborohydride in ethylene glycol dimethyl ether (see ref 13).

V. Triborane (B_3H_7)

The X-ray crystallographic structure of $H_3NB_3H_7$ reveals an interesting asymmetric molecular geometry (**22**).[52] However, the solution nmr spectra of a number of appropriate static B_3H_7 adducts are more consistent with a structure of greater symmetry (**23**) or with a very rapid torsional motion of the BH_2L moiety (eq 7) on the nmr time scale. It is also conceivable that the BH_2L group is rotat-

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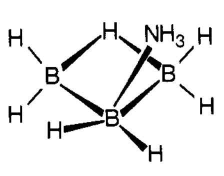
(49) R. E. Dickerson and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 212 (1957).

(50) B. J. Duke, O. W. Howarth, and J. G. Kenworthy, *Nature (London)*, **202**, 81 (1964).

(51) R. K. Hertz, H. D. Johnson, II, and S. G. Shore, Abstracts, 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 27–Sept 1, 1972, No. INOR-142.

(52) C. E. Nordman and C. Riemann, *J. Amer. Chem. Soc.*, **81**, 3538 (1959).



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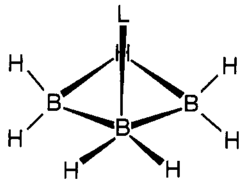

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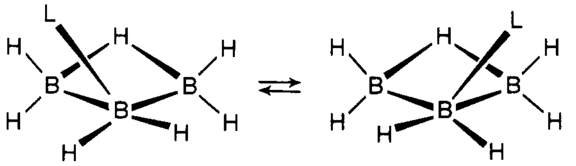
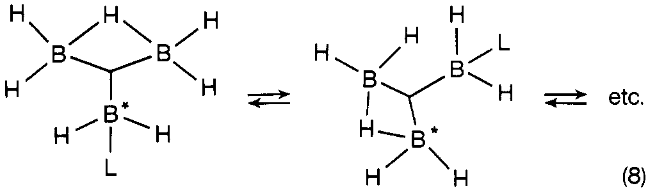
ing completely and rapidly about an axis passing through the boron bonded to L and the bridging hydrogen. Since this kind of rotation has sixfold character, the barrier would be expected to be very low.



(7)

The rate of intramolecular hydrogen tautomerism as well as the rate of ligand dissociation in Lewis base B_3H_7 adducts (**23**) is a significant function of the Lewis basicity of L (**23**). The ^{11}B nmr spectrum of $(C_2H_5)_2O{\cdot}B_3H_7$ consists of one diffuse symmetrical octet ($J_{B,H} \sim 30$ Hz) with relative peak intensities consistent with coupling to seven effectively equivalent hydrogens; *i.e.*, rapid hydrogen exchange *and* ligand dissociation are occurring (*e.g.*, eq 8).[47,53] Similar observations are made for the THF·B_3H_7 adduct.[54] In contrast to ether·B_3H_7 adducts, the ^{11}B nmr spectrum of $(CH_3)_3N{\cdot}B_3H_7$ consists of two closely spaced octets with the relative intensities of the low- to high-field octet being 2:1.[53] The observation of two ^{11}B signals supports a model in which ligand exchange is slow on the nmr time scale consistent with $(CH_3)_3N$ being a stronger Lewis base than $(C_2H_5)_2O$. However, the fact that both ^{11}B resonances are octets (*i.e.*, boron is coupled to seven magnetically equivalent hydrogens) speaks for rapid B_3H_7 hydrogen tautomerism in $(CH_3)_3N{\cdot}B_3H_7$. These data suggest that Lewis base exchange and B_3H_7 hydrogen scrambling are not necessarily coupled rate processes and that one process may occur at a substantially different rate than the other. Very few attempts have been made to observe slow B_3H_7 scrambling using the dnmr method. In one report concerning the ^1H dnmr spectrum of $(C_6H_5CH_2)_2CH_3N{\cdot}B_3H_7$ in vinyl chloride,[55] the broad unresolved B_3H_7 protons singlet sharpened dramatically at low temperatures (Figure 10) into a relatively sharp singlet due to efficient quadrupole induced spin decoupling. The singlet observed at −80° (Figure 10) for the B_3H_7 protons is consistent with rapid hydrogen scrambling at this temperature. However, at lower temperatures, the B_3H_7 resonance undergoes significant differential broadening as compared to the $N{-}CH_3$ resonance and gives a flat-topped peak at −150° (Figure 10). This spectral behavior is rationalized on the basis of slowing B_3H_7 proton exchange and represents a low barrier to hydrogen tautomerism of approximately 6 kcal/mol.



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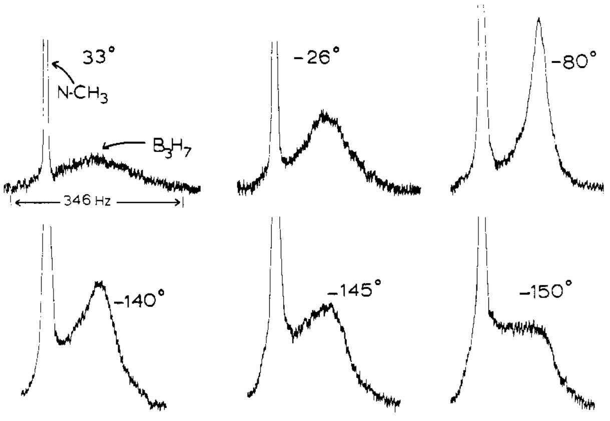
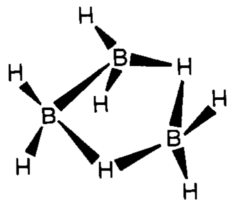


Figure 10. The ^1H dnmr spectrum of the CH_3 and B_3H_7 protons of $(C_6H_5CH_2)_2CH_3NB_3H_7$ in CH_2CHCl (see ref 55).

Examination of the ^{11}B nmr spectra from −40 to 30° of the series $F_2XP{\cdot}B_3H_7$ (X = H, F, Cl, Br, $N(CH_3)_2$) as well as OCB_3H_7 revealed static B_3H_7 systems.[56] In general, the ^{11}B nmr spectra of $F_2XP{\cdot}B_3H_7$ gave a broad low-field triplet of relative intensity 2, assigned to the H_2BHBH_2 portion of the complex and a four-line multiplet at higher field of relative intensity 1 due to $H_2B{-}PXF_2$ displaying coupling of boron to phosphorus and the two terminal hydrogens. The ^{11}B spectrum of $OC{\cdot}B_3H_7$ gives an expected low-field triplet and higher field triplet of relative intensities 2:1, again consistent with a static system. There have been no reports of attempts to measure the rate of B_3H_7 hydrogen scrambling in $F_2PX{\cdot}B_3H_7$ or OCB_3H_7 using the dnmr method *above* room temperature. It is evident from the above static B_3H_7 systems that the symmetry in solution is either that associated with **23** or that rapid torsional motion (eq 7) or essentially free rotation of BH_2L is occurring.

VI. Triborohydride Ion ($B_3H_8^-$)

Early ^{11}B and ^1H solution nmr strudies of noncomplexed $B_3H_8^-$ salts, *e.g.*, NaB_3H_8, revealed single ^{11}B or ^1H resonances exhibiting coupling consistent with all borons and hydrogens being equivalent, *i.e.*, rapid intramolecular exchange.[47,57] The observation of boron-hydrogen spin-spin coupling for NaB_3H_8 under conditions of rapid hydrogen tautomerism led to the postulation of an intramolecular dynamical model in which electron pair bonding remains essentially invariant and internal rearrangement occurs.[53b] An X-ray crystallographic study of $[(H_3N)_2BH_2]^+B_3H_8^-$ revealed the "free" $B_3H_8^-$ ion to have the geometry **24** with the B-B bond distance 1.80



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(53) (a) R. E. Williams, *J. Inorg. Nucl. Chem.*, **20**, 198 (1961); (b) W. N. Lipscomb, *Advan. Inorg. Chem. Radiochem.*, **1**, 132 (1959); (c) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963.

(54) M. A. Ring, E. F. Witucki, and R. C. Greenough, *Inorg. Chem.*, **6**, 395 (1967).

(55) W. J. Dewkett, H. Beall, and C. H. Bushweller, *Inorg. Nucl. Chem. Lett.*, **7**, 633 (1971).

(56) R. T. Paine and R. W. Parry, *Inorg. Chem.*, **11**, 268 (1972); E. R. Lory and D. M. Ritter, *ibid.*, **10**, 939 (1971).

(57) (a) A. D. Norman and R. Schaeffer, *J. Phys. Chem.*, **70**, 1662 (1966); (b) B. M. Graybill, A. R. Pitochelli, and M. F. Hawthorne, *Inorg. Chem.*, **1**, 626 (1962); W. V. Hough, L. J. Edwards, and A. D. McElroy, *J. Amer. Chem. Soc.*, **78**, 689 (1956).

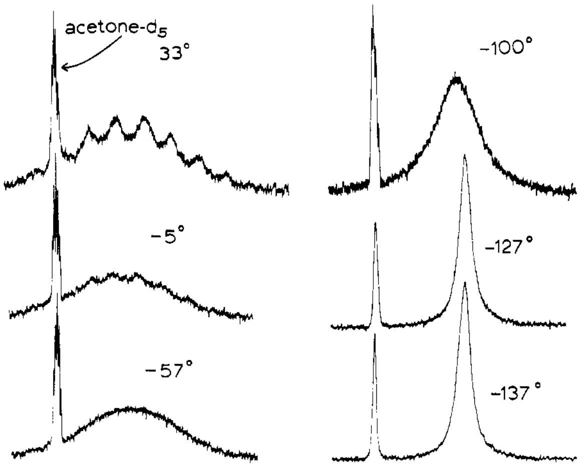
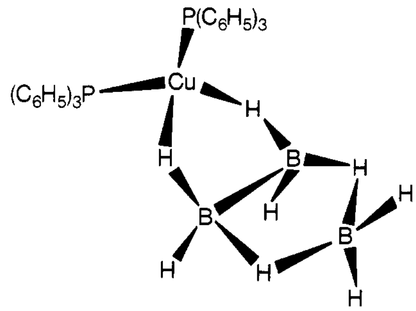


Figure 11. The ^{1}H dnmr spectrum (60 MHz) of TlB_3H_8 in 50% CD_3OD-50% CD_3COCD_3 (v/v) ($J(^{11}B,^1H)$ = 33 Hz) (see ref 3).

Å, an apex boron-hydrogen bridge bond of 1.5 Å, and base boron-bridge hydrogen bond of 1.2 Å and overall C_{2v} symmetry.[58] A more recent X-ray crystallographic study of $[(C_6H_5)_3P]_2CuB_3H_8$ gave the structure **25** for the case of a complexed $B_3H_8^-$ ion.[59] A recent nonempirical molecular orbital (NEMO) calculation suggests that a somewhat less symmetric structure is preferred for the free $B_3H_8^-$ ion.[60]



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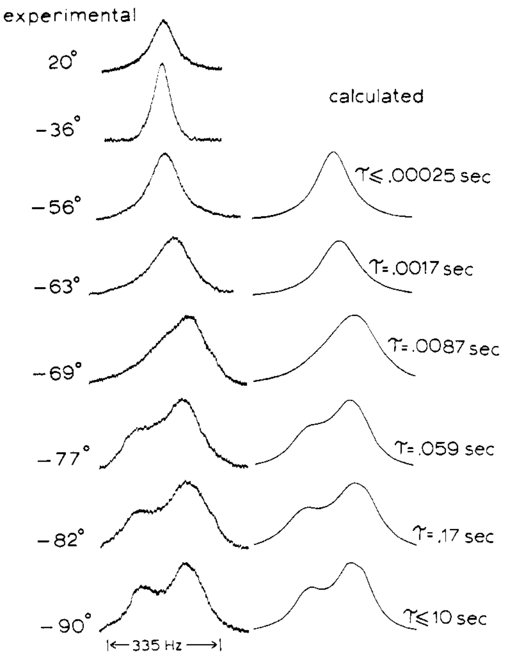
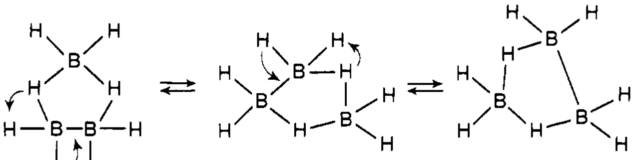


Figure 12. Experimental and theoretical ^{1}H dnmr spectrum of $[(C_6H_5)_3P]_2CuB_3H_8$. τ = lifetime of a proton at any site in B_3H_8 moiety (see ref 3).

Several recent dnmr studies of various $B_3H_8^-$ salts have revealed changes in the ^{1}H dnmr spectrum at low temperatures consistent with both quadrupole-induced spin decoupling and variable rates of $B_3H_8^-$ internal exchange depending on structure. The ^{1}H dnmr spectrum of TlB_3H_8 in 50% CD_3OD-50% CD_3COCD_3 (v/v) at 33° consists of a ten-line multiplet (two outer peaks lost in noise) revealing coupling to three equivalent ^{11}B nuclei (I = $^3/_2$; $J_{\mathrm{H,B}}$ = 33 Hz)[61] with smaller ^{10}B coupling in the background and consistent with rapid scrambling of B_3H_8 hydrogens (Figure 11). Upon lowering the temperature, the spin-spin coupling pattern coalesced and the B_3H_8 spectrum sharpened into a singlet resonance at about $-127°$. Essentially identical behavior is observed for $(CH_3)_4NB_3H_8$.[61,62] The loss of ^{10,11}B-^{1}H spin-spin coupling in TlB_3H_8 and $(CH_3)_4NB_3H_8$ at lower temperatures is completely consistent with more efficient boron quadrupole relaxation effectively decoupling boron from hydrogen. In addition, the observation of a singlet B_3H_8 resonance at $-137°$ (Figure 11) is best rationalized on the basis of fast B_3H_8 scrambling or "pseudorotation" (eq 9)[53b] at this very low temperature. It is interesting to note also that the quintet due to CD_2HCOCD_3 in the TlB_3H_8 dnmr sample (Figure 11) collapses to a singlet at low temperatures, consistent with more efficient deuteron (I = 1) quadrupole relaxation.



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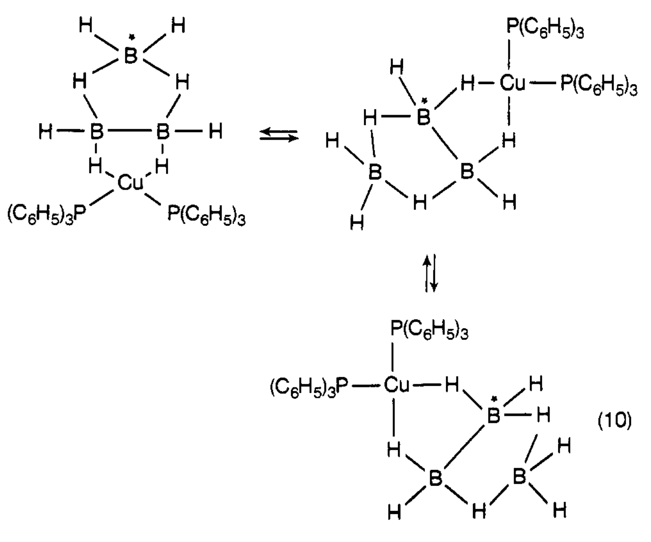
In contrast to TlB_3H_8 and $(CH_3)_4NB_3H_8$, the ^{1}H dnmr spectrum of $[(C_6H_5)_3P]_2CuB_3H_8$ (**25**) in 50% $CDCl_3$-50% CD_2Cl_2 at 20° is a broad singlet with no fine structure (Figure 12).[61] Upon lowering the temperature, the B_3H_8 resonance sharpens to some extent (quadrupole-induced decoupling), then broadens in an asymmetric fashion and separates into several resonances at $-90°$ (Figure 12). This behavior is best rationalized in terms of slowing B_3H_8 pseudorotation at low temperatures (eq 10) and a static B_3H_8 system at $-97°$. A ^{31}P dnmr study of [(p-



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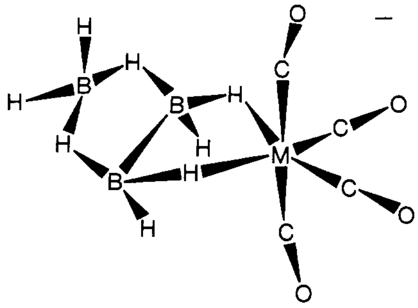
[59] S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, **8**, 2755 (1969).

[60] P. E. Stevenson, *J. Amer. Chem. Soc.*, **95**, 54 (1973).

[61] C. H. Bushweller, H. Beall, M. Grace, W. J. Dewkett, and H. S. Bilofsky, *J. Amer. Chem. Soc.*, **93**, 2145 (1971); H. Beall, C. H. Bushweller, W. J. Dewkett, and M. Grace, *ibid.*, **92**, 3484 (1970).

[62] D. Marynick and T. Onak, *J. Chem. Soc. A*, 1160 (1970).

$CH_3C_6H_5)_3P]_2CuB_3H_8$ in CH_2Cl_2 revealed a transition of the spectrum from a singlet resonance at *ca.* −80° to an AB spectrum ($\Delta\nu_{AB}$ = 2.0 ppm; $J_{P,P}$ = 91 Hz) at −120°, consistent with slowing an exchange process which equilibrates phosphine environments,[63] *i.e.*, exchange between axial and equatorial triphenylphosphines in **25**. Below −20°, addition of excess tri-*p*-tolylphosphine to the sample of $[(p\text{-}CH_3C_6H_5)_3P]_2CuB_3H_8$ resulted in the observation of two separate ^{31}P signals due to free and complexed ligand supporting the unimolecularity of the rate process slowed below −80°. However, above −20°, the ^{31}P resonances of free and complexed ligands coalesce to a single signal providing evidence for an additional *intermolecular* exchange. Analogous behavior was observed in the ^1H dnmr spectrum of $[(C_6H_5O)_3P]_2CuB_3H_8$ (Figure 13), although the spectral transitions consistent with slowing B_3H_8 pseudorotation occur at higher temperatures than for $[(C_6H_5)_3P]_2CuB_3H_8$, indicating a somewhat slower rate of scrambling in $[(C_6H_5O)_3P]_2CuB_3H_8$.[64] Changes in the ^1H dnmr spectrum of the aromatic protons of $[(C_6H_5O)_3P]_2CuB_3H_8$ also occur consistent with exchange of the triphenyl phosphite ligands between axial and equatorial sites.[64] The ^{11}B nmr spectra of $(OC)_4MB_3H_8^-$ ion (**26**, M = Cr, Mo, W) in CH_3CN at room temperature consist of two broadened signals at 23.0 and 61.3 ppm (relative to $B(OCH_3)_3$) of relative intensity 1:2.[65] These spectra are clearly consistent with slow B_3H_8 pseudorotation on the nmr time scale at room temperature and represent a more static B_3H_8 system than in the (triarylphosphine)$_2CuB_3H_8$, TlB_3H_8, or $(CH_3)_4NB_3H_8$. However, it is clear that complexation of $B_3H_8^-$ by a metal *via* hydrogen bridge bonds slows the rate of B_3H_8 pseudorotation as compared with free $B_3H_8^-$; *i.e.*, the complexed metal acts as a "lock" on the pseudorotatory process. The apparently slower rate of B_3H_8 pseudorotation in $[(C_6H_5O)_3P]_2CuB_3H_8$ and $(OC)_4MB_3H_8$ as compared to $[(C_6H_5)_3P]_2CuB_3H_8$ attests to the different electronic characters of $(C_6H_5O)_3P$ and $(C_6H_5)_3P$ as well as the different bonding characteristics of various metals.



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Although there are data concerning the rate of B_3H_8 pseudorotation as a function of different ligands and metals, an extensive, systematic experimental and theoretical study is still in order to provide an incisive depiction of the important factors in the dynamics of the B_3H_8 system.

VII. Tetraborane Derivatives

A. B_4H_8·(*N,N,N′,N′*-Tetramethylethylenediamine)

When the 1:1 addition product of B_5H_9 and *N,N,N′,N′*-tetramethylethylenediamine (TMED) is allowed to react with methanol, hydrogen gas is evolved, and a new compound which was definitively characterized to be B_4H_8·TMED is formed (eq 11).[66] Of the various structural possibilities that were considered, structure **27** was favored.[66]

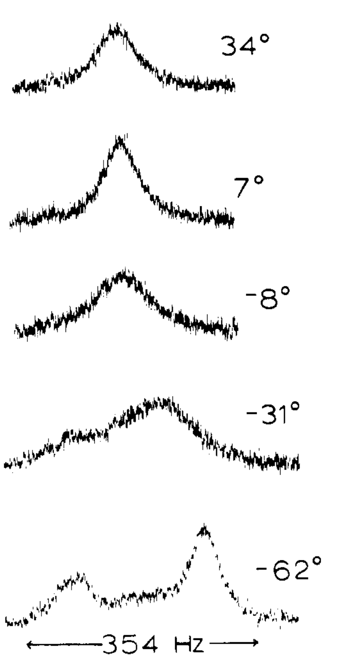
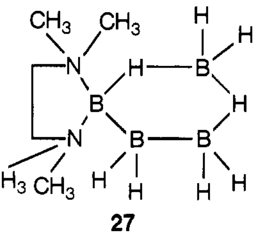


Figure 13. The ^1H dnmr spectrum of the B_3H_8 protons of $[(C_6H_5O)_3P]_2CuB_3H_8$ in 50% $CDCl_3$–50% CD_2Cl_2 (v/v) (see ref 64).

$$B_5H_9\cdot TMED + 3CH_3OH \longrightarrow B_4H_8\cdot TMED + B(OCH_3)_3 + 2H_2 \quad (11)$$



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The ^{11}B nmr spectrum of B_4H_8·TMED showed two broad resonances of relative intensities 1:3. Since there are no equivalent boron atoms in the proposed structure (**27**), accidental peak overlap or boron atom equilibration must be assumed. The ^1H nmr spectrum at room temperature of the B_4H_8 portion of the molecule is comprised of a very broad resonance which collapsed to a single sharp peak upon irradiation at the ^{11}B frequency. Proton tautomerism is almost assured in this molecule, no matter what the structure. An X-ray study of B_4H_8·TMED would be illuminating.

B. Nonahydrotetraborate (1−) Ion ($B_4H_9^-$)

The anion $B_4H_9^-$ has been prepared in the unsymmetrical cleavage of B_5H_{11} by ammonia (eq 12)[67] and by

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(63) E. L. Muetterties, W. G. Peet, P. A. Wegner, and C. W. Alegranti, *Inorg. Chem.*, **9**, 2447 (1970).

(64) H. Beall, C. H. Bushweller, and M. Grace, *Inorg. Nucl. Chem. Lett.*, 7, 641 (1971).

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(67) (a) G. Kodama, *J. Amer. Chem. Soc.*, **92**, 3482 (1970); (b) G. Kodama, J. E. Dunning, and R. W. Parry, *J. Amer. Chem. Soc.*, **93**, 3372 (1971).

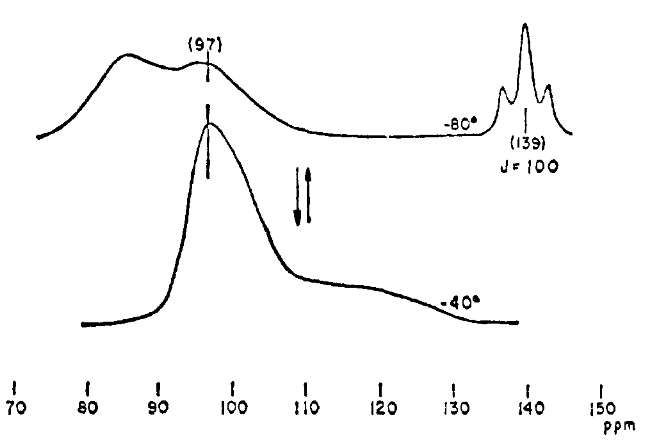
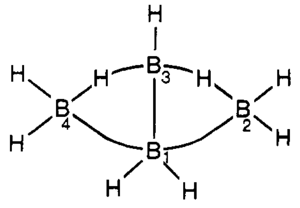


Figure 14. The ^{11}B nmr spectrum of the system $[BH_2(NH_3)_2]^+[B_4H_9^-]$ taken at two temperatures at 32.1 MHz. The change between −40 and −80° is reversible. The solvent is diethyl ether and the standard for chemical shift is $B(CH_3)_3$ (see ref 67b).

$$B_5H_{11} + 2NH_3 \longrightarrow [H_2B(NH_3)_2]^+[B_4H_9]^- \qquad (12)$$

the deprotonation of B_4H_{10} by ammonia[68] and methyllithium.[69] Structural data for this ion agree with Lipscomb's prediction[53b,c] (**28**). The ^{11}B nmr spectrum of the $B_4H_9^-$ ion has been found to be strongly temperature dependent.[67b-69] At −45°, the ^{11}B nmr spectrum of KB_4H_9 in ether[68] consists of a triplet of relative intensity 1.0 (53.2 ppm relative to $BF_3{\cdot}O(C_2H_5)_2$, J = 96 Hz) and two broad resonances at 9.7 and 0.4 ppm with a combined relative intensity of 2.8. The triplet may be assigned to B(1), the resonance at 9.7 ppm to B(2,4) and that at 0.4 ppm to B(3). When the nmr sample is warmed to 0°, the triplet (53.2 ppm) broadens and disappears with a concomitant broadening and disappearance of the resonance at 0.4 ppm. The resonance at 9.7 ppm becomes sharper as the temperature increases. Above 0°, a new resonance appears which sharpens to a doublet (26.5 ppm, J = 105 Hz) at room temperature. This doublet has an intensity equal to the resonance at 9.7 ppm and a weighted average chemical shift of the low-temperature resonances at 53.2 and 0.4 ppm. Thus, the doublet at 26.5 ppm can be attributed to B(1) and B(3) which have become equivalent on the dnmr time scale due to rapid proton exchange (eq 13). The doublet multiplicity of the room-temperature time-averaged B(1) and B(3) resonances at 26.5 ppm (J = 105 Hz) is also consistent with one *nonexchanging* hydrogen on each boron. The magnitude of the coupling constant suggests strongly that the static hydrogens are terminal in nature.



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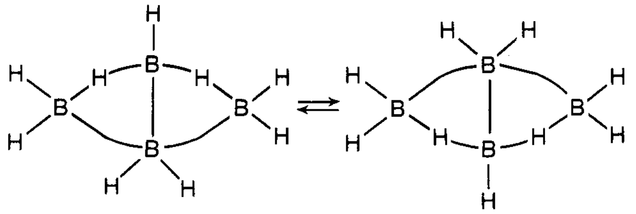


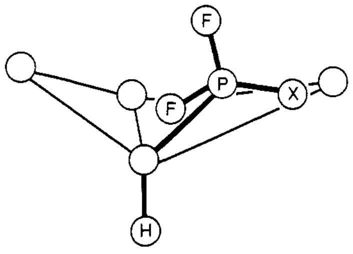
(13)

At −80°, the ^{11}B nmr spectrum of $[H_2B(NH_3)_2]^+[B_4H_9]^-$ (Figure 14) consists of two broad overlapping resonances at 86 and 97 ppm in addition to a well-defined triplet at 139 ppm (J (^{11}B,^1H) = 100 Hz). The triplet is most reasonably assigned to B(1) of $B_4H_9^-$ (**28**) which is bonded to two terminal and no bridge hydrogen atoms. The resonance due to the $[H_2B(NH_3)_2]^+$ cation is expected at about 102 ppm[70] and is concealed under the peak at 97 ppm. The two broad resonances can be attributed to B(2,4) and B(3) of $B_4H_9^-$ (**28**).

When the sample is warmed to −40°, the triplet at 139 ppm and the peak at 86 ppm disappear while the peak at 97 ppm becomes sharper and a very broad band centered at 110–120 ppm develops. In light of the previous dnmr spectral data on KB_4H_9,[68] the behavior in $[H_2B(NH_3)_2]^+[B_4H_9]^-$ may be again attributed to a rapid tautomerism which equilibrates B(1) and B(3) on the nmr time scale (eq 13). Thus, in the −40° spectrum the very broad band most likely represents the spectroscopically equivalent B(1) and B(3), and the peak at 97 ppm represents B(2,4) of $B_4H_9^-$.

C. $F_2XP{\cdot}B_4H_8$

The ^{19}F dnmr spectrum of $F_2XP{\cdot}B_4H_8$ is temperature dependent for those cases where X is $(CH_3)_2N$, F, Cl, Br, or I, but not when X is H.[71] An X-ray crystal study of $(CH_3)_2NF_2P{\cdot}B_4H_8$[72] has shown its structure to be that of isomer **29**. The temperature dependence of the ^{19}F dnmr spectrum of $F_2XP{\cdot}B_4H_8$ has been explained[71a] in terms of the existence in solution of two distinct isomers at low temperature which interconvert rapidly when the temperature is raised. Isomers **29** and **30** have been suggested[71a] as those involved in this interconversion. The compound $F_2HP{\cdot}B_4H_8$ shows evidence for only one isomer in the ^{19}F nmr and no temperature dependence. Concerning the **29** $\rightleftarrows$ **31** equilibration, it is apparent that rota-



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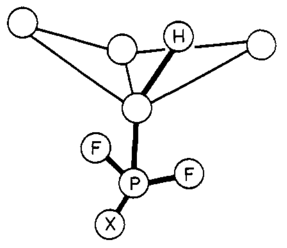

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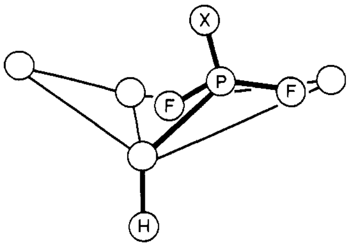

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(69) A. C. Bond and M. L. Pinsky, *J. Amer. Chem. Soc.*, **92**, 7585 (1970).

(70) (a) T. P. Onak and I. Shapiro, *J. Chem. Phys.*, **32**, 952 (1960); (b) C. W. Heitsch, *Inorg. Chem.*, **4**, 1019 (1965).

(71) (a) R. T. Paine and R. W. Parry, *Inorg. Chem.*, **11**, 1237 (1972); (b) L. F. Centofanti, G. Kodama, and R. W. Parry, *Inorg. Chem.*, **8**, 2072 (1969).

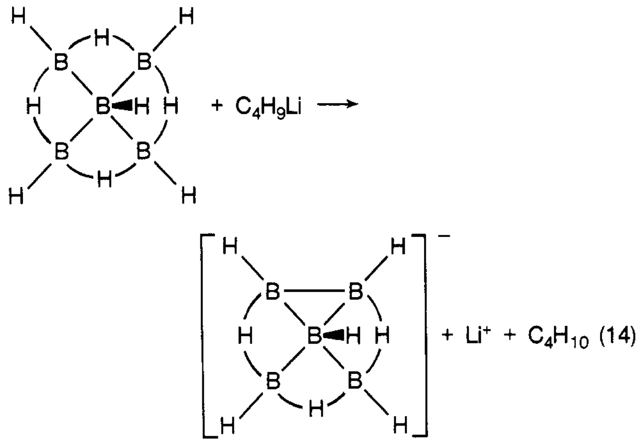
(72) M. D. LaPrade and C. E. Nordman, *Inorg. Chem.*, **8**, 1669 (1969).

tion about the B-P bond at the temperatures observed (−40 to +40°) is either very slow or very fast on the nmr time scale. Consideration of steric effects would make the latter seem more likely.

VIII. Pentaborane Derivatives

A. Octahydropentaborate (1−) Ion ($B_5H_8^-$)

A proton can be removed from B_5H_9 by the action of a strong base,[73] and experimental evidence[73a] verifies that the proton removed comes from a bridge position as predicted by Lipscomb[53c,74] (eq 14).



(14)

The ^{11}B dnmr spectrum of LiB_5H_8 shows a strong temperature dependence (Figure 15).[75a] At ambient temperature, this spectrum consists of two doublets, the smaller of which is upfield and can be assigned to the apical boron atom and the larger to the four basal borons. Since all four basal boron atoms are not equivalent in the presumed structure (eq 14) of this ion, it is likely that proton exchange is occurring. When the solution is cooled, the larger downfield doublet collapses to a significantly broadened singlet resonance and the smaller upfield doublet becomes sharper. The behavior of the downfield resonance can be attributed to decrease in the ^{11}B quadrupole relaxation time or to slowing of the proton exchange. The reason for the sharpening of the upfield doublet is not known with certainty. It has been postulated[75b] that this sharpening is the result of decoupling of the basal borons from the apex as a result of spin relaxation induced by the basal boron quadrupoles.

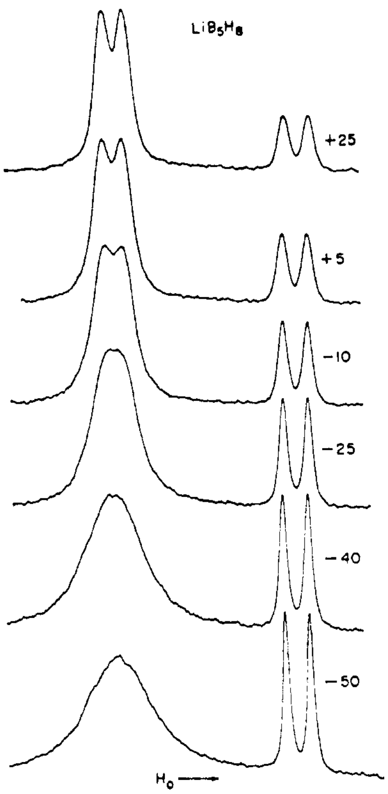
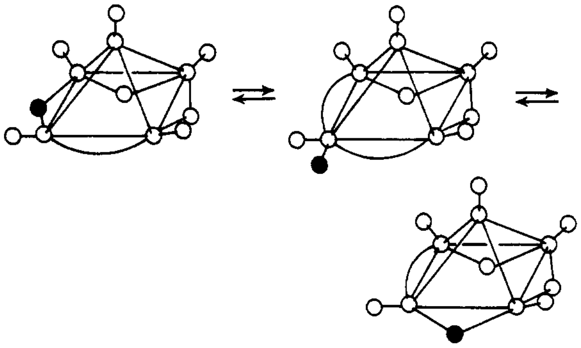


Figure 15. The 32.1-MHz ^{11}B nmr spectra of LiB_5H_8 in $(C_2H_5)_2O$, 1.5 *M*, at several temperatures (see ref 75).

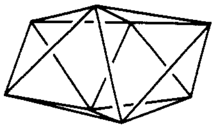
A mechanism for tautomerism in $B_5H_8^-$ in which only bridge hydrogen atoms migrate and terminal and bridge hydrogen atoms do not exchange has been favored.[75a] This mechanistic preference is based on the observed doublet in the ^{11}B nmr spectrum for the basal borons indicating coupling to only one terminal proton. If terminal and bridge hydrogen atoms were exchanging, coupling of the basal borons to all basal protons would be expected. However, coupling to bridge protons may be relatively small and not resolved. In the $B_3H_8^-$ case discussed previously, terminal and bridge protons are postulated to exchange,[53b,c,61] and, in fact, time-averaged coupling between ^{11}B and all eight protons is observed.[61,62] A mechanism for such exchange in B_6H_{10} (to be discussed) has been proposed[53b,c] which is applicable also to $B_5H_8^-$ and $B_6H_9^-$. Applying this mechanism to $B_5H_8^-$, a proton shifts from a bridge position to a position in a BH_2 group (eq 15). In such a mechanism, bridge and terminal protons need not exchange.[75]



(15)

B. $C_3B_5H_7$

The structure is not known with certainty for the unusual three-carbon carborane $C_3B_5H_7$,[76] but by analogy with the known structures of the isolectronic $B_8H_8^{2-}$ [77] and $C_2B_6H_8$[78] it is reasonable that the carbon and boron atoms in $C_3B_5H_7$ should be located at the apices of a dodecahedron of approximately D_{2d} symmetry (**32**). In



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(73) (a) D. F. Gaines and T. V. Iorns, *J. Amer. Chem. Soc.*, **89**, 3375 (1967); (b) T. Onak, G. B. Dunks, I. W. Searcy, and J. Spielman, *Inorg. Chem.*, **6**, 1465 (1967); (c) R. A. Geanangel, and S. G. Shore, *J. Amer. Chem. Soc.*, **89**, 6771 (1967).

(74) W. N. Lipscomb, *J. Phys. Chem.*, **62**, 381 (1958).

(75) (a) H. D. Johnson, II, R. A. Geanangel, and S. G. Shore, *Inorg. Chem.*, **9**, 908 (1970); (b) J. B. Leach and T. Onak, *J. Magn. Resonance*, **4**, 30 (1971).

(76) M. L. Thompson and R. N. Grimes, *J. Amer. Chem. Soc.*, **93**, 6677 (1971).

(77) F. Klanberg, D. R. Eaton, L. J. Guggenberger, and E. L. Muetterties, *Inorg. Chem.*, **6**, 1271 (1967).

(78) H. Hart and W. N. Lipscomb, *Inorg. Chem.*, **7**, 1070 (1968).

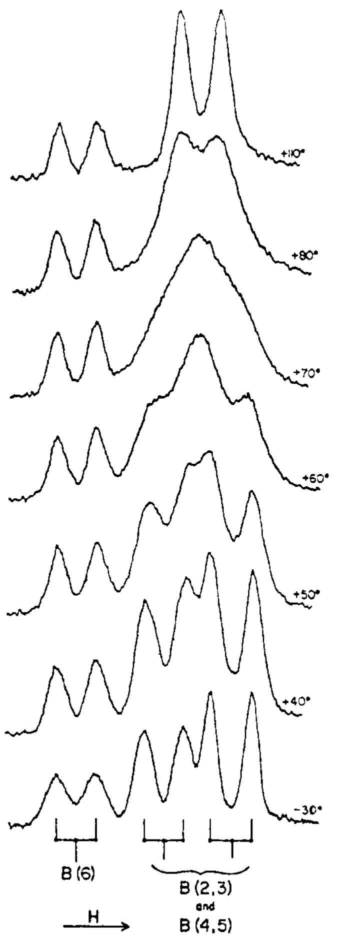
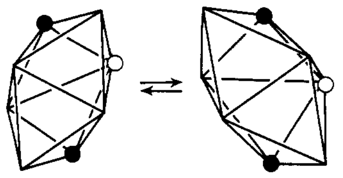


Figure 16. Temperature-dependent boron-11 nmr spectra of CB_5H_7 (see ref 81).

possible structures employing this framework geometry, there would be B-H groups at five apices, C-H groups at two apices, and a carbon atom without a terminal hydrogen atom at one apex.

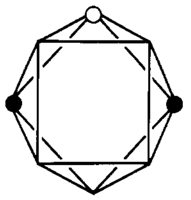
Both the ^1H and ^{11}B nmr spectra of $C_3B_5H_7$ have been reported.[76] The ^{11}B nmr spectrum contains three doublets in the ratio 2:2:1, indicating only three spectroscopically distinguishable BH groups. This result is in agreement with the ^1H nmr spectrum which in addition to a single C-H group resonance contains three quartets, indicating coupling of ^{11}B to three magnetically distinct groups of protons. There is no way to reconcile these nmr results (*i.e.*, only one CH environment and only three BH environments) with a rigid structure based on a D_{2d} dodecahedron unless considerable accidental overlap of peaks is assumed. However, a model employing a rapid tautomerism between two dodecahedral structures (eq 16) is also consistent with the observed nmr spectra.[76]



(16)

· = BH
● = CH
○ = C(no terminal H)

The time-averaged geometry in this case will be that of a D_{4d} square antiprism (**33**).



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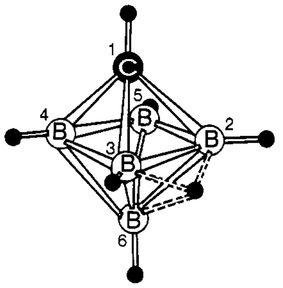
$C_3B_5H_7$ is an example of a possible tautomerism involving the movement of cage atoms (C and B) rather than migration of hydrogen atoms. Other possible examples will be discussed.

C. CB_5H_7

Pyrolysis[79] or electric discharge[80] of 1-methylpentaborane yields the carborane CB_5H_7 (**34**)[79] for which spectral data support the structure of a distorted octahedron. This structure is unusual in having a closed cage geometry but bearing a bridging hydrogen atom. The ^{11}B dnmr spectra of CB_5H_7 (Figure 16) and also of $1\text{-}CH_3CB_5H_6$ have been found to be temperature dependent.[81] At lower temperatures the ^{11}B nmr spectrum of CB_5H_7 (Figure 16) shows three doublets consistent with the structure **34.** As the temperature is raised, two of these doublets coalesce into a single doublet and the spectrum at 100° is consistent with a structure in which the bridge hydrogen atom is moving rapidly around the octahedron so as to render the equatorial boron atoms B(2,3,4,5) spectroscopically equivalent. Temperature independence of the ^1H nmr spectrum of the bridge region at the ^{11}B nmr spectrum coalescence temperature has been offered as evidence against intermolecular exchange.[81]



34 (see ref 81)

A mechanism for intramolecular exchange has been suggested[81] in which the exchanging bridge proton between B(2) and B(3) occupies a bridging position between B(3) and B(6) in an unstable intermediate or transition state in moving to the analogous position between B(3) and B(4). In this mechanism bridging and terminal protons would not exchange. It has been further pointed out[81] that this kind of mechanism would be served by a static structure in which the bridging proton occupies a location reasonably close to B(6) and more in the octahedral face formed by B(2,3,6) than in the equatorial plane determined by B(2,3,4,5). This postulated structure which is indicated in **34** has the bridging proton bonded to three boron atoms by a four-center bond in a manner which may be similar to that of the "anomalous" hydrogen of B_5H_{11}.[53c]

An alternative mechanism for tautomerism in CB_5H_7 involves a bridge proton–terminal proton exchange (eq

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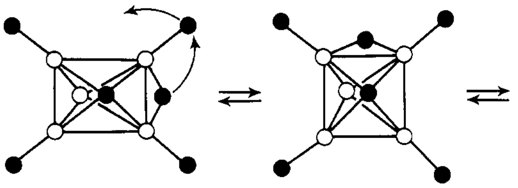
(79) T. Onak, P. Mattshei and E. Groszek, *J. Chem. Soc. A*, 1990 (1969).

(80) T. Onak, R. Drake, and G. B. Dunks, *J. Amer. Chem. Soc.*, **87**, 2505 (1965).

(81) E. Groszek, J. B. Leach, G. T. F. Wong, C. Ungerman, and T. Onak, *Inorg Chem.*, **10**, 2770 (1971).

17) similar to that proposed for $B_3H_8^-$.[53b,c] For this



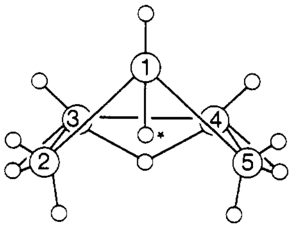
etc. (17)

mechanism a static structure in which the bridge proton is near the equatorial plane (**34**) is more probable since this will minimize the movement required of the hydrogen atoms. However, under conditions of rapid exchange, time-averaged coupling between the equatorial boron atoms B(2,3,4,5) and all five equatorial protons would lead to a sextet for the ^{11}B(2,3,4,5) resonance. Since a doublet is observed, this mechanism does not seem likely.

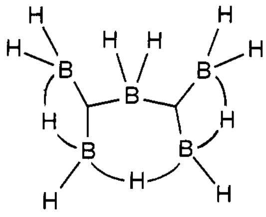
The coalescence temperature of the ^{11}B nmr spectrum (Figure 16) of CB_5H_7 is 70 ± 10° and that of the 1-methyl derivative $CH_3CB_5H_6$ is about 50° lower. Estimated values of ΔG^* for these compounds are 14 ± 0.5 kcal and 12 ± 1 kcal, respectively. The lowering of the barrier to exchange in the methyl derivative has been postulated[81] as being the result of increased electron density at B(6) transmitted through the cage from the methyl group. This would allow a greater degree of bonding of the bridging proton to B(6) and allow a less obstructed pathway about the octahedron in terms of the first mechanism given above. Further work on the structure and means of tautomerism of CB_5H_7 and its derivatives is warranted.

D. Pentaborane(11) (B_5H_{11})

The crystal structure[82] of B_5H_{11} (**35**) almost certainly establishes the molecular symmetry as C_s, and the bonding can be topologically[53c] represented by one of the two following diagrams (**36**, **37**). Of these, **36** is favored by recent SCF calculations.[83] In the solid-state structure, B(1) is bonded to two terminal protons, although one of these protons (the "anomalous" proton) is close enough to B(2) and B(5) (1.77 ± 0.19 and 1.68 ± 0.19 Å) for some interaction. The ^{11}B nmr spectrum[84] shows the resonance of B(1) split only into a doublet. It is conceivable that this apparent coupling of B(1) could be the result of a slight change in structure and equilibration when in solution (eq 18). However, it is more likely that the bonding of the "anomalous" proton is of sufficient bridge nature that its coupling to B(1) is not observed. SCF calculations[85a] and ^{1}H nmr spectral studies[85b] both show that the properties of the "anomalous" proton are intermediate between those of bridge and terminal protons.



35 • = anomalous proton



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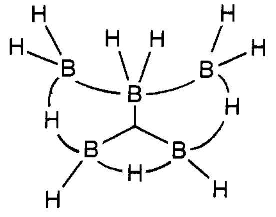

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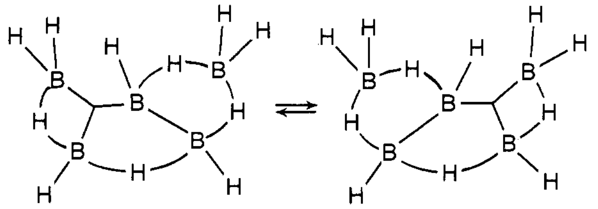


(18)

E. Dodecahydropentaborate (1−) Ion ($B_5H_{12}^-$)

Treatment of KB_4H_9 with diborane leads to the preparation of KB_5H_{12}.[86] The ^{11}B nmr spectrum of this ion[86] consists of two apparent singlets in the area ratio of 3.9:1.0, suggesting a square-pyramidal arrangement of boron atoms and a C_4 axis of symmetry. There is no obvious way that this degree of symmetry can be achieved without rapid equilibration in solution.

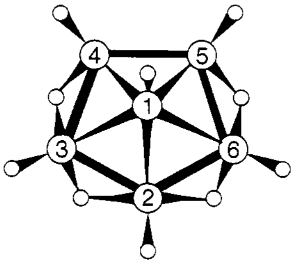
F. Pentaborane(9) (B_5H_9)

Quadrupole-induced spin relaxation has recently been observed for the basal boron atoms of B_5H_9[87] and for some B_5H_9 derivatives.[75b,88]

IX. Hexaborane Derivatives

A. Hexaborane(10) (B_6H_{10})

At room temperature, the ^{11}B nmr spectrum[89] of B_6H_{10} shows only two doublets of relative areas 5:1. Since the crystal structure (**38**)[90] has boron atoms in four different environments, rapid exchange of bridge protons around the base of the pentagonal pyramid rendering all five basal boron atom equivalent on the nmr time scale is



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(82) L. Lavine and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 614 (1954).

(83) E. Switkes, W. N. Lipscomb, and M. D. Newton, *J. Amer. Chem. Soc.*, **92**, 3847 (1970).

(84) R. Schaeffer, J. N. Shoolery, and R. Jones, *J. Amer. Chem. Soc.*, **79**, 4606 (1957).

(85) (a) E. Switkes, I. R. Epstein, J. A. Tossell, R. M. Stevens, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **92**, 3837 (1970); (b) T. Onak and J. B. Leach, *J. Amer. Chem. Soc.*, **92**, 3513 (1970).

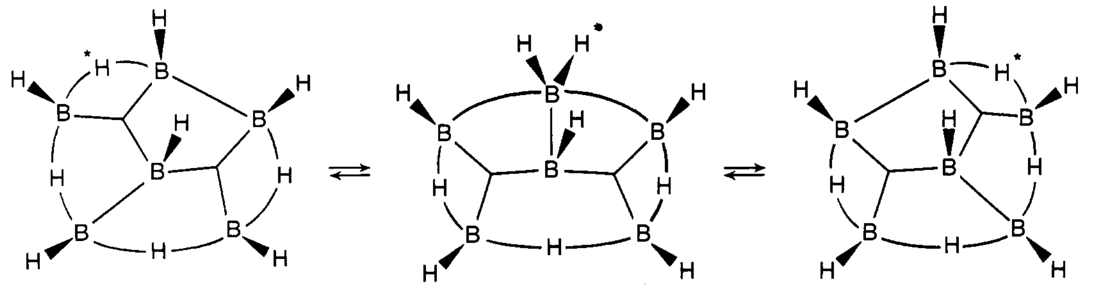
(86) H. D. Johnson and S. G. Shore, *J. Amer. Chem. Soc.*, **93**, 3798 (1971).

(87) D. W. Lowman, P. D. Ellis, and J. D. Odom, *J. Mag. Resonance*, **8**, 289 (1972).

(88) (a) T. C. Geisler and A. D. Norman, *Inorg. Chem.*, **11**, 2549 (1972); (b) T. C. Geisler and A. D. Norman, *ibid.*, **9**, 2167 (1970).

(89) R. E. Williams, S. G. Gibbins, and I. Shapiro, *J. Chem. Phys.*, **30**, 320 (1959).

(90) (a) R. E. Dickerson, P. J. Wheatley, P. A. Howell, and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 200 (1957); (b) K. Eriks, W. N. Lipscomb, and R. Schaeffer, *ibid.*, **22**, 754 (1954); (c) F. L. Hirshfeld, K. Eriks, R. E. Dickerson, E. L. Lippert, Jr., and W. N. Lipscomb, *ibid.*, **28**, 56 (1958).


(19)

likely. Variable-temperature ^{1}H and ^{11}B nmr experiments[91a] have shown that the exchange can be slowed at about −110°. Recent published studies[91b] have extended and modified this earlier work and give a limiting ^{1}H nmr spectrum (^{11}B decoupled) which consists of resonances for three types of basal terminal hydrogen atoms, two types of bridge hydrogen atoms, and the apical terminal hydrogen atom. These results are in full agreement with the crystal structure (**38**). The ^{11}B nmr spectrum at about −110° is made up of a broad resonance of area 4, a doublet of area 1 which is assignable to the unique basal boron atom B(2), and the upfield doublet of area 1 which can be assigned to the apex boron atom B(1).

In an earlier variable-temperature ^{11}B nmr study[92] in which the minimum reported temperature was −70°, coalescence of the downfield doublet of the basal boron atoms was observed, whereas the upfield doublet was temperature independent. This situation is similar to that observed for the $B_5H_8^-$ ion and can be attributed to quadrupole-induced spin relaxation or slowing of the proton exchange.

There is much evidence which shows unquestionably that proton exchange in B_6H_{10} does not involve scrambling of bridge and terminal hydrogen atoms. As with $B_5H_8^-$ discussed previously, if all basal boron atoms were exchanging, coupling would be expected between all basal boron atoms and all basal hydrogen atoms. Instead the ^{11}B nmr spectrum shows only a doublet indicative of coupling to one terminal proton only. The 100-MHz ^{1}H nmr spectrum[92] of B_6H_{10} consists of a downfield quartet arising from the basal terminal protons and an upfield quartet from the apical proton superimposed over the bridge resonance. Separate bridge and terminal resonances would not be observed if these protons were exchanging rapidly on the nmr time scale. Furthermore, it has been shown by nmr[93] that when B_2D_6 is allowed to react with B_6H_{10} only the basal terminal hydrogen atoms of the B_6H_{10} exchange for deuterium.

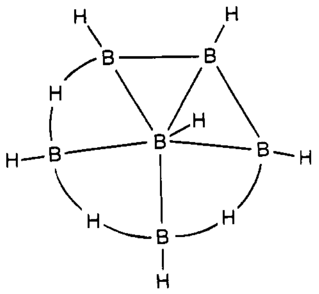
Thus, it appears certain that the mechanism for tautomerism in B_6H_{10} is that originally predicted[53c] in which the process passes a stage containing a BH_2 group (eq 19) and in which terminal and bridge protons are always segregated. The mechanistic details are the same as those proposed for $B_5H_8^-$ (eq 15).

B. Nonahydrohexaborate(1−) Ion ($B_6H_9^-$)

Reaction of B_6H_{10} with $LiCH_3$, NaH, or KH at low temperature leads to the preparation of the ion $B_6H_9^-$ (eq 20).[94] It has been shown[94] that the proton removed

$$B_6H_{10} + MB \longrightarrow MB_6H_9 + HB \qquad (20)$$
$$MB = LiCH_3,\ NaH,\ KH$$

comes from a bridge position. Early predictions[53c] of the structure of a possible $B_6H_9^-$ ion included one or two BH_2 groups, but these are not supported by the ^{11}B nmr spectrum of the ion which is qualitatively identical[94] with that of B_6H_{10}. It is likely that the structure of $B_6H_9^-$ is simply that resulting from the removal of a bridge proton from B_6H_{10} without further rearrangement (**39** or **40**).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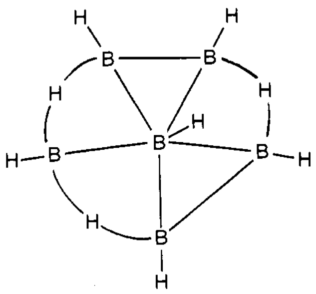
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Since either of these and any other reasonable $B_6H_9^-$ structure has boron atoms in more than two environments, proton exchange is likely. Again, as in $B_5H_8^-$ and B_6H_{10}, the observations of a doublet for the basal boron atoms in the ^{11}B nmr spectrum mitigate against exchange between bridge and terminal protons.

The ^{11}B dnmr spectral behavior of $B_6H_9^-$ is remarkably similar[75] to that of $B_5H_8^-$ and B_6H_{10} with coalescence of the larger downfield doublet at low temperature (Figure 17).

The uncertainty of the structure of $B_6H_9^-$ renders extensive discussion of the mechanism of likely proton exchange unwarranted. However, it seems possible that an intermediate structure containing a BH_2 group occurs in a situation similar to those postulated for $B_5H_8^-$ (eq 15) and B_6H_{10} (eq 19).

C. Undecahydrohexaborate(1−) Ion ($B_6H_{11}^-$)

Reaction of $B_5H_8^-$ with B_2H_6 results in addition of BH_3 to $B_5H_8^-$ and formation of the new anion $B_6H_{11}^-$ (eq 21).[86] A structure (**41**) for $B_6H_{11}^-$ has been proposed,[86]

$$LiB_5H_8 + {}^1\!/_2B_2H_6 \xrightarrow[(CH_3)_2O]{-78^\circ} LiB_6H_{11} \qquad (21)$$

in which the BH_3 group has entered the vacant bridge site in the base of the $B_5H_8^-$ unit. The ^{11}B nmr spectrum of LiB_6H_{11} (Figure 18)[86] is interpretable as consisting of

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(91) (a) J. C. Carter and N. L. H. Mock, personal communication; (b) V. T. Brice, H. D. Johnson, II, and S. G. Shore, *J. Chem. Soc., Chem. Commun.*, 1128 (1972).

(92) J. D. Odom and R. Schaeffer, *Inorg. Chem.*, **9**, 2157 (1970).

(93) J. C. Carter and N. L. H. Mock, *J. Amer. Chem. Soc.*, **91**, 5891 (1969).

(94) H. D. Johnson, II, S. G. Shore, N. L. Mock, and J. C. Carter, *J. Amer. Chem. Soc.*, **91**, 2131 (1969).

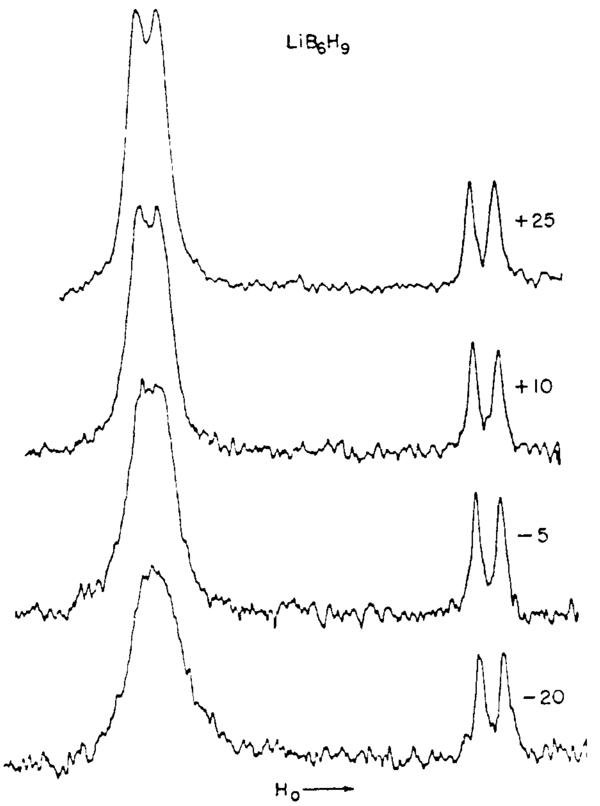


Figure 17. The 32.1-MHz ^{11}B nmr spectra of LiB_6H_9 in $(C_2H_5)_2O$, 0.7 *M*, at several temperatures (see ref 75).

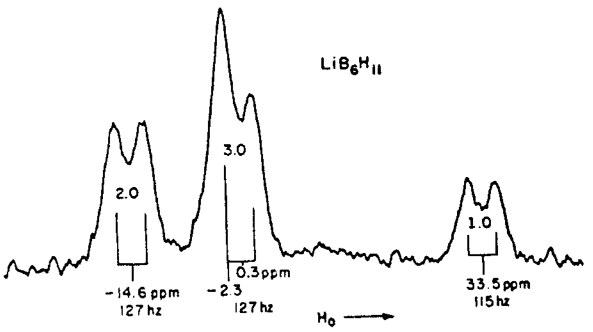
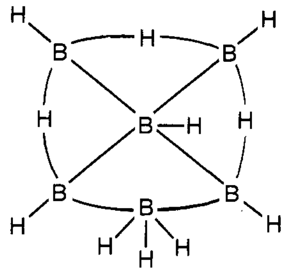


Figure 18. Boron-11 nmr spectrum (32.1 MHz) of LiB_6H_{11} at −20°. Chemical shifts are relative to $BF_3{\cdot}O(C_2H_5)_2$ (see ref 86).



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(from low to high field) a doublet of weight 2, a singlet of weight 1 superimposed on a doublet of weight 2, and a doublet of weight 1. The upfield doublet is most reasonably assigned to the apex B–H unit and the singlet to the added BH_3 group. The lack of resolvable spin coupling in this singlet resonance has been attributed to either a rapid tautomerism which scrambles the terminal hydrogen atoms in the BH_3 group, presumably, with the bridge hydrogen atoms, or to thermal decoupling.[86]

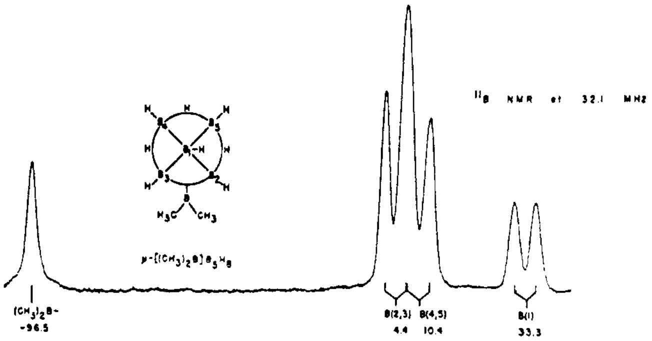

Figure 19. The ^{11}B nmr spectrum (32.1 MHz) of μ-$[(CH_3)_2B]B_5H_8$. Chemical shifts (ppm) are relative to $BF_3{\cdot}O(C_2H_5)_2$ ± 0.5. Observed coupling constants (Hz ± 10) are B(2,3)–H, 170; B(4,5)–H, 202; B(1)–H, 181 (see ref 95).

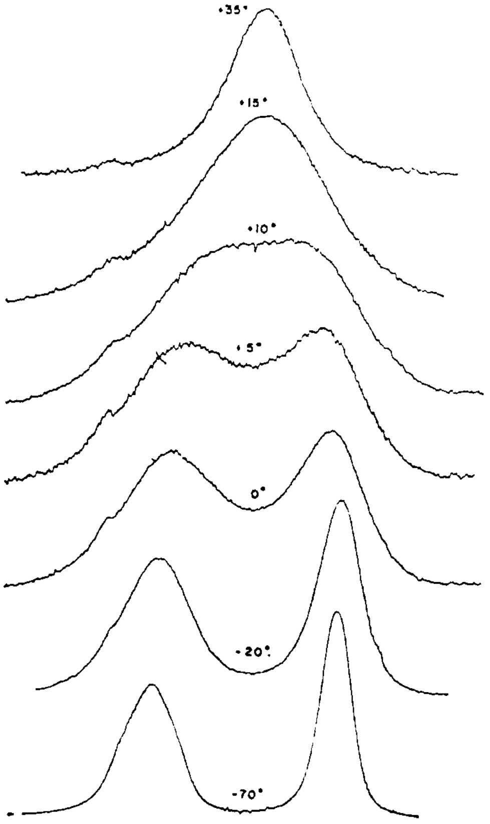

Figure 20. The temperature dependence of the 100-MHz ^1H nmr spectrum of μ-dimethylborylpentaborane(9). The peak separation at −70° is 19.3 Hz (see ref 95).

D. μ-$[(CH_3)_2B]B_5H_8$

The anion $B_5H_8^-$ reacts readily with dimethylboron chloride to form a bridge-substituted pentaborane(9) derivative (eq 22).[95] The ^{11}B nmr spectrum (Figure 19) of

$$LiB_5H_8 + (CH_3)_2BCl \longrightarrow \mu\text{-}[(CH_3)_2B]B_5H_8 + LiCl \qquad (22)$$

μ-$[(CH_3)_2B]B_5H_8$ is consistent with the proposed structure (Figure 19). The singlet must be attributed to the bridging $(CH_3)_2B$ group, and its position at very low field is rationalized on the basis that this boron atom is essentially sp^2 hybridized.[95]

Of particular interest with regard to this compound is the temperature dependence of the ^1H nmr spectrum of the methyl protons (Figure 20).[95] The single resonance which is observed above room temperature broadens and

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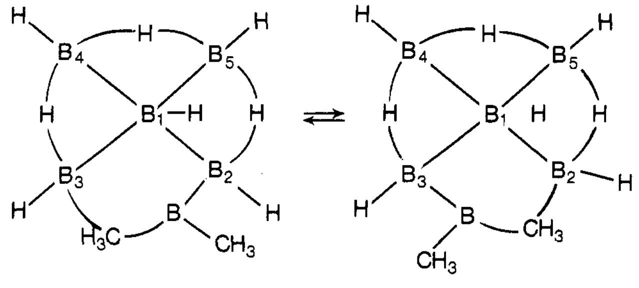
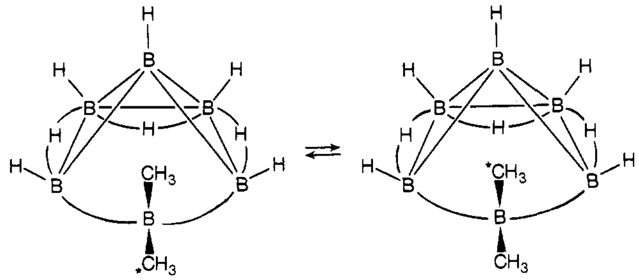
(95) D. F. Gaines and T. V. Iorns, *J. Amer. Chem. Soc.*, **92**, 4571 (1970).

then separates into two peaks when the temperature is lowered. These two peaks have the same area but quite different widths at half-height. Two different interpretations of the nature of this dynamic process can be envisioned. One involves static structures in which one of the methyl groups occupies a bridging position and the other a terminal position (eq 23). Static structures of this kind, however, would result in nonequivalence of B(2) and B(3) and of B(4) and B(5) which should be observed in a variable-temperature ^{11}B nmr experiment.



(23)

A much more attractive explanation of the dynamic process in μ-[$(CH_3)_2B$]B_5H_8 involves rotation of the entire $(CH_3)_2B$ group about the axis of the sp^2-hybridized orbital which bonds it to the pentaborane(9) framework. In this process (eq 24) the static structure will possess a plane of symmetry. The difference in widths at half-height of the two methyl groups at low temperature has been interpreted[95] as being the result in a difference in quadrupolar environment and different degrees of quadrupole-induced spin decoupling.



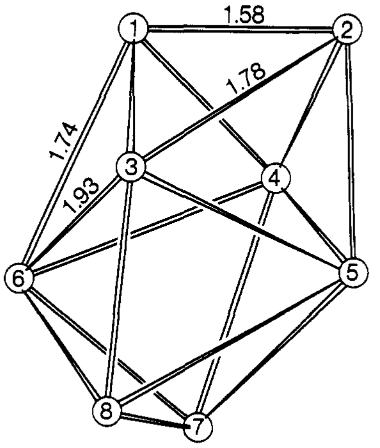
(24)

A structurally analogous situation results when phosphine derivatives of the type R_2PCl are allowed to react with LiB_5H_8.[96] By this type of reaction μ-[$(CH_3)_2P$]B_5H_8 can be formed in which the expected structure is that given in eq 24 with substitution of the bridging B by P. However, rapid equilibration of the $(CH_3)_2P$ group does not occur at room temperature, and resonances for CH_3 groups in two different environments were observed by ^1H nmr.[96] The similar CH_3CF_3PCl reaction led to formation of two isomers as would be reasonably expected.[96]

X. Octaborane Derivatives

A. Octahydrooctaborate(2−) Ion ($B_8H_8^{2-}$)

A single-crystal X-ray structure determination of the tetraammine zinc(II) salt of $B_8H_8^{2-}$ has shown that the configuration of the eight boron atoms is essentially that of a dodecahedron, point symmetry D_{2d} (**42**).[97] In this structure there are two groups of equivalent boron atoms, B(1,2,7,8) and B(3,4,5,6). However, in solution the ^{11}B nmr spectrum of the $B_8H_8^{2-}$ ion consists of a single doublet (J (^{11}B,H) = 128 Hz).[97] This result can be explained in terms of accidental peak overlap or difference of structure in solution because of solvation effects. Rapid tautomerism in solution is an attractive possibility and may involve the same geometric pathway as that proposed for the isoelectronic $C_3B_5H_7$ (eq 16) having the D_{4d} square antiprism (**33**) as the time-averaged geometry.



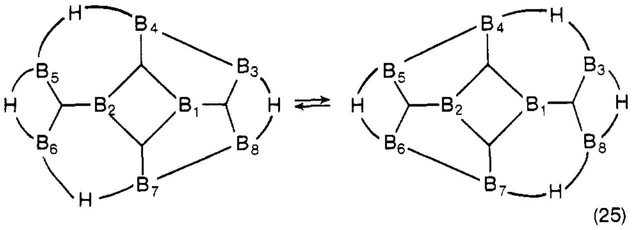
42 (see ref 97)

B. Octahydrooctaborate(1−) Ion ($B_8H_8^-$)

An intermediate in the preparation of $B_8H_8^{2-}$ is the radical anion $B_8H_8^-$.[97] The esr spectrum of this anion has been recorded and found to be very complex with more than 300 lines. A theoretical esr spectrum in agreement with the observed spectrum was calculated assuming that all boron atoms and all hydrogen atoms are equivalent and that the single unpaired electron is equally shared by all eight BH groups. If the structure of $B_8H_8^-$ is that of a D_{2d} dodecahedron, the esr spectrum is explainable in terms of rapid tautomerism on the esr time scale or in terms of very similar hyperfine coupling constants for boron and hydrogen atoms in different environments in the dodecahedron.

C. Octaborane(12) (B_8H_{12})

The X-ray crystal structure[98] (see structure in Figure 21) of B_8H_{12} includes boron atoms in five different environments B(3,8), B(1), B(2), B(4,7), and B(5,6). The 70.6-MHz ^{11}B nmr spectrum of B_8H_{12} (Figure 22)[99] gives evidence of boron atoms in only three different environments and this result may be explained in terms of extensive accidental overlap of resonances or tautomerism in solution (eq 25). If this tautomerism is rapid on the nmr time scale, the number of spectroscopically distinguishable groups of boron atoms will be reduced to three, B(1,2), B(4,7), and B(3,5,6,8). In an earlier low-field ^{11}B



(25)

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(96) A. B. Burg and H. Heinen, *Inorg. Chem.*, **7**, 1021 (1968).

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(99) R. R. Rietz, R. Schaeffer, and L. G. Sneddon, *Inorg. Chem.*, **11**, 1242 (1972).

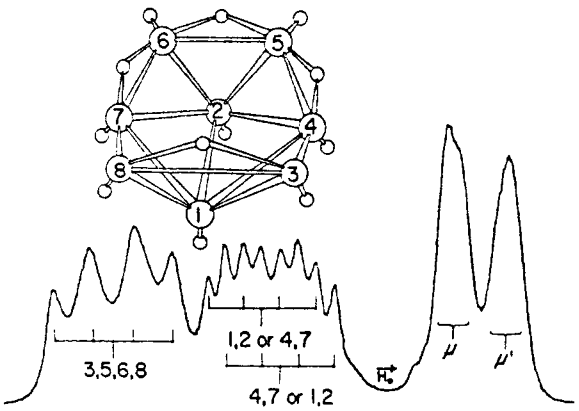


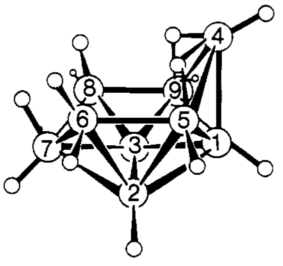
Figure 21. Structure and 220-MHz proton nmr spectrum of octaborane(12) at −20° (see ref 99).

nmr spectrum,[100] the doublets assigned to B(1,2) and B(4,7) overlapped to form a single doublet, and this was interpreted[101] in terms of an averaged structure of C_{4v} symmetry resulting from eight tautomers. However, the 220-MHz ^1H nmr spectrum (Figure 21)[99] shows two different bridge proton environments, giving the two upfield resonances in Figure 21, whereas the C_{4v} averaged structure would show only one. Temperature independence of the ^1H nmr spectrum of B_8H_{12}[99] at temperatures down to −31° is evidence for a dynamic process occurring rapidly on the nmr time scale at this temperature.

XI. Nonaborane Derivatives

A. $B_9H_{14}^-$

An X-ray crystal study of CsB_9H_{14} gives the structure in **43** for the anion $B_9H_{14}^-$.[102] The most highly resolved



43 (see ref 102)

^{11}B nmr spectrum (Figure 23) consists of three doublets of equal weight of which two overlap.[102] This spectrum would be consistent with a structure having a threefold rotation axis and only one terminal hydrogen atom bonded to each boron atom. A system which is equilibrating rapidly on the nmr time scale could have a static structure as shown in **43** with rapid exchange between the two bridge protons and the upward pointing terminal protons. There would then be boron atoms in only three environments: B(1,2,3), B(4,6,8), and B(5,7,9). Indeed, the ^1H nmr spectrum of CsB_9H_{14} consists of a broad upfield singlet of relative intensity five indicating five magnetically equivalent or rapidly exchanging bridging protons and three overlapping 1:1:1:1 quartets which can be attributed to the nine nonexchanging terminal protons. Isotope studies[103] have shown that five protons will rapidly exchange for deuterium in weak base and that the broad upfield singlet is not present in the ^1H nmr spectrum of the exchanged sample.

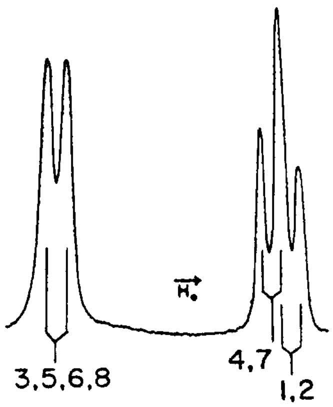


Figure 22. The 70.6-MHz boron-11 nmr spectrum of octaborane(12) at −23° (see ref 99).

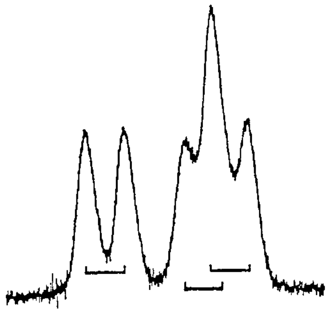
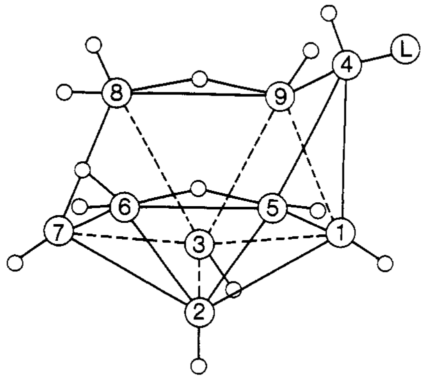


Figure 23. The 28.87-MHz ^{11}B nmr spectrum of CsB_9H_{14} (in Me_2SO) (see ref 102).

B. $B_9H_{13}L$ Compounds

Although the B_9H_{13}-Lewis base compounds have a boron cage which is isoelectronic with $B_9H_{14}^-$, the single-crystal X-ray study of $B_9H_{13}{\cdot}NCCH_3$[104] showed that this compound (**44**) was not isostructural with $B_9H_{14}^-$ owing to differing placement of bridge protons. Of the various ^{11}B nmr spectra of $B_9H_{13}L$ compounds that have been reported,[104-106] there has not been evidence of spectroscopic threefold symmetry as exists in $B_9H_{14}^-$, indicating that intermolecular exchange of L is slow on the nmr time scale. However, peak assignments in the



44 (see ref 105)

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(100) J. Dobson and R. Schaeffer, *Inorg. Chem.*, **7**, 402 (1968).

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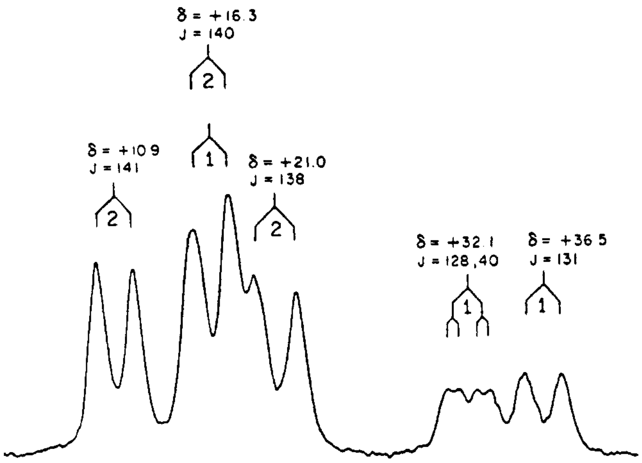


Figure 24. The 60-MHz ^{11}B nmr spectrum of $(CH_3)_3NH$-(3)-1,2-$B_9C_2H_{12}$ in acetone (see ref 109).

80.2-MHz ^{11}B nmr spectrum of $B_9H_{13}[S(C_2H_5)_2]$ attributes an apparent doublet to the B(6,8) group.[105] This is analogous to the doublets that are observed in the ^{11}B nmr spectrum of $B_9H_{14}^-$ for B(6,7,8) which are bonded to two terminal protons in the solid-state structure.[102] Therefore, rapid exchange of the bridge hydrogen atoms and the upward pointing terminal hydrogen atoms of B(6,8) in $B_9H_{13}[S(C_2H_5)_2]$ seems likely.

C. Metal Complexes of $B_9H_{14}^-$ and $B_9H_{12}S^-$

Derivatives of the general type $L_nMB_9H_{14}$ and $L_nMB_9H_{12}S$ have been prepared where L is a triarylphosphine or -arsine, n = 2, 3, or 4, and M is copper, silver, or gold.[63,107] Only L_4Cu^+ salts of $B_9H_{14}^-$ and $B_9H_{12}S^-$ salts could be isolated, but the ^{31}P nmr spectra of these salts below −100° showed resonances for the L_4Cu-borane and L_3Cu-borane species.[63] The equilibrium between these species at low temperature could be shifted essentially completely to the L_4Cu-borane by addition of excess L. Above −95°, L exchange between L_4Cu-borane and L_3Cu-borane is sufficiently fast on the nmr time scale to give only a single ^{31}P nmr resonance.[63]

Compounds of the type L_4Ag-borane showed coupling between ^{31}P and ^{107}Ag as well as ^{109}Ag below about −50°. This coupling disappears at higher temperatures indicating rapid intermolecular exchange of L on the nmr time scale.[63]

The ^{31}P nmr spectra of $L_4AuB_9H_{14}$ complexes gave evidence for rapid intermolecular exchange of L.[63]

D. $B_9C_2H_{12}^-$ Ions

Base degradation of the icosahedral carboranes 1,2-$B_{10}C_2H_{12}$ (*o*-carborane) and 1,7-$B_{10}C_2H_{12}$ (*m*-carborane) yields two monoanions, (3)-1,2-$B_9C_2H_{12}^-$ and (3)-1,7-$B_9C_2H_{12}^-$, respectively.[108] It is generally assumed that in each of these ions the boron-carbon skeleton is as shown in **45**. In each case B(3) has been removed from the parent carborane and each remaining boron and carbon atom is bonded to one terminal proton. The carbon atoms occupy positions 1 and 2 in (3)-1,2-$B_9C_2H_{12}^-$ and 1 and 7 in (3)-1,7-$B_9C_2H_{12}^-$. In both ions the 12th proton is presumed to be situated somewhere in the open face of the heavy atom skeleton and the relative simplicity of the ^{11}B nmr spectra[108b,109] (Figures 24 and 25) of these ions indicates that this proton is located on the molecular mirror plane at least on the nmr time scale. In both cases, studies have shown[109] that replacement of the 12th proton by deuterium causes collapse of fine structure in the ^{11}B resonances centered at δ +32.1 for (3)-1,2-$B_9C_2H_{12}^-$ (Figure 24) and δ 22.4 for (3)-1,7-$B_9C_2H_{12}^-$ (Figure 25). This fine structure results from a $^{11}B,^{1}H$ coupling constant of about 40 Hz, indicative of bridge bonding for the 12th hydrogen atom. These results argue for a static structure for (3)-1,7-$B_9C_2H_{12}^-$ in which the 12th hydrogen atom bridges between B(4) and B(8). For (3)-1,2-$B_9C_2H_{12}^-$, two reasonable possibilities exist: (1) a static structure in which the 12th proton is bridge bonded to three boron atoms B(4,8,7) or (2) the more likely case where this proton is rapidly exchanging between the B(4,8) bridge position and the B(7,8) bridge position. A variable-temperature study would be very useful in this case.

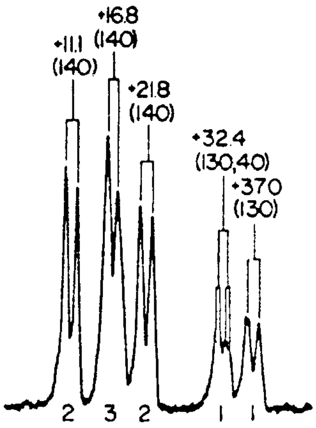
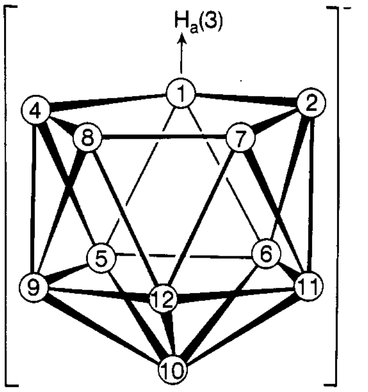


Figure 25. The 80.5-MHz ^{11}B nmr spectrum of $(CH_3)_3NH$-(3)-1,7-$B_9C_2H_{12}$ in CH_3CN (see ref 109).



45 (see ref 109)

E. Alkylaluminum and Alkylgallium Derivatives of (3)-1,2-$B_9C_2H_{13}$

Triethylaluminum, trimethylaluminum, and triethylgallium all react with (3)-1,2-$B_9C_2H_{13}$ to liberate 1 mol of ethane or methane and yield compounds of the type $B_9C_2H_{12}MR_2$.[110] An X-ray diffraction study[110] of $B_9C_2H_{12}Al(CH_3)_2$ gave the structure **46** but did not locate the 12 hydrogen atoms. Geometric considerations indicated that two of these hydrogen atoms occupy bridging positions between B(7) and Al and between B(8) and Al.

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(107) F. Klanberg, E. L. Muetterties, and L. J. Guggenberger, *Inorg. Chem.*, **7**, 2272 (1968).

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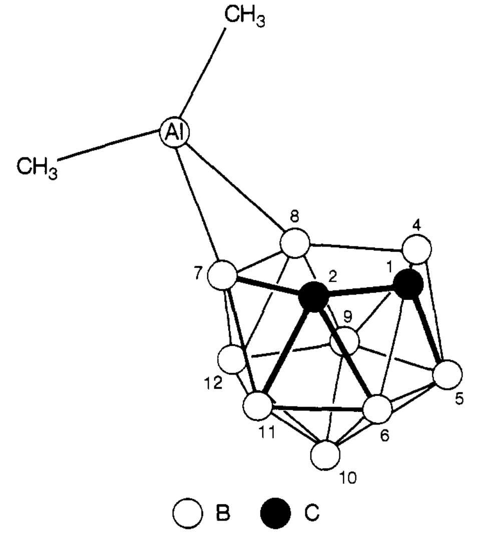
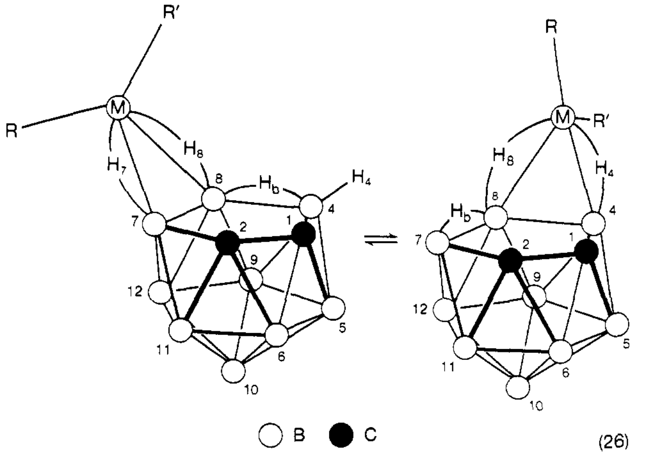


46 (see ref 111)

A broad band of weight one in the 250-MHz ^1H nmr spectrum gave evidence for one bridging hydrogen atom located in the general vicinity of the open face of boron-carbon cage. The other nine hydrogen atoms would be expected to have normal terminal bonding to B(4,5,6,9,10,11,12) and C(1,2).

All of these $B_9C_2H_{12}MR_2$ compounds had ^{11}B nmr spectra which showed temperature dependence (Figure 26) which was attributed to tautomerism in solution (*e.g.*, eq 26).[111] The higher temperature spectrum of $B_9C_2H_{12}Al(CH_3)_2$ is consistent with a time-averaged structure having C_{2v} symmetry. In particular, the resonance at 28.6 ppm having a small observed coupling constant (58 Hz) can be assigned to B(8), the one boron atom in the structure bonded at all times to a bridge proton. A value for $\Delta G^* = 10.6 \pm 0.5$ kcal/mol was calculated for the tautomerism based on the observed ^{11}B chemical shifts and the observed coalescence temperature of $-22 \pm 5°$.[111]



(26)

(see ref 111)

The tautomerism process proposed for these molecules also exchanges the alkyl groups on the aluminum or gallium atoms, and evidence for the slowing of this exchange was observed in the variable-temperature ^1H nmr. Thus when $B_9C_2H_{12}Al(CH_3)_2$ was cooled to $-84°$ the methyl resonance split into two separate signals at τ 10.20 and 10.26. This corresponds to $\Delta G^* = 10.0 \pm 0.5$ kcal/mol for methyl exchange which is in excellent agreement with the ^{11}B nmr result.

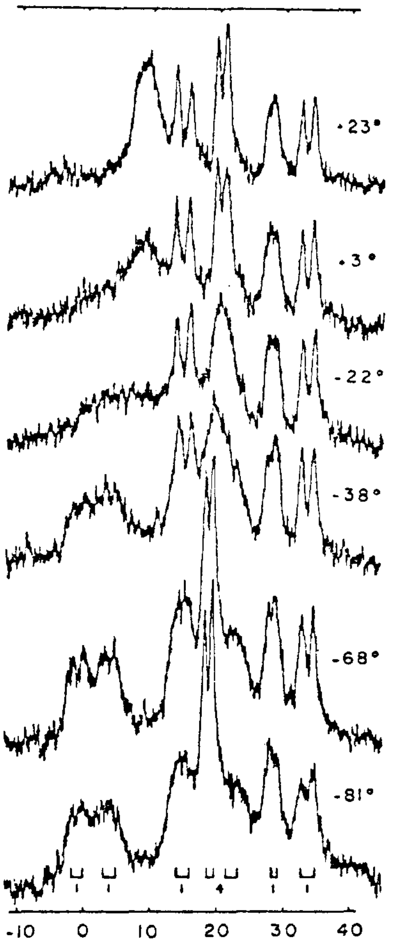


Figure 26. ^{11}B nmr spectra (80 MHz) of $B_9C_2H_{12}Al(CH_3)_2$ solution; temperatures and chemical shifts in part per million from $BF_3 \cdot O(C_2H_5)_2$ are indicated (see ref 111).

XII. Decaborane Derivatives

A. $B_{10}H_{12}(NCCH_3)_2$

It has been stated[112] that when $B_{10}H_{12}(NCCH_3)_2$ is dissolved in dimethylformamide, the ^{11}B nmr spectrum is quite different from the "normal" ^{11}B nmr spectrum with acetonitrile as solvent.[112] Tautomerism in solution has been suggested[53a] as an explanation for this behavior, but experimental details are lacking.

B. $B_{10}H_{15}^-$ Ion

The ^{11}B nmr spectra of $B_{10}H_{15}^-$ [113] and acidified $B_{10}H_{14}^{2-}$ (presumably the same species)[113] are remarkably simple and consist of only three peaks. Fast proton exchange may explain the simplicity of these spectra.

C. Metal Complexes of $B_{10}H_{13}^-$

Below about $-90°$, the ^{31}P nmr spectrum of $L_2CuB_{10}H_{13}$ (L = triarylphosphine) showed an AB pattern indicative of two different phosphorus environments.[63] This behavior is similar to that of the analogous B_3H_8 compound discussed previously, but is not structurally definitive owing to the much greater complexity of the $B_{10}H_{13}^-$ ion. Above $-90°$, this AB pattern merged into a single peak, indicating rapid ligand exchange on the nmr

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(111) D. A. T. Young, R. J. Wiersema, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **93**, 5687 (1971).

(112) R. J. Pace, J. Williams, and R. L. Williams, *J. Chem. Soc.*, 2196 (1961).

(113) (a) J. A. Dupont and M. F. Hawthorne, *Chem. Ind. (London)*, 405 (1962); R. Schaeffer and F. Tebbe, *Inorg. Chem.*, **3**, 1638 (1964); (c) J. Q. Chambers, A. D. Norman, M. R. Bickell, and S. H. Cadle, *J. Amer. Chem. Soc.*, **90**, 6056 (1968); (d) E. L. Muetterties, *Inorg. Chem.*, **2**, 647 (1963).

time scale.[63] Above −80°, rapid exchange between $L_2CuB_{10}H_{13}$ and free L was shown to occur by the appearance of only one phosphorus resonance when equimolar amounts of $L_2CuB_{10}H_{13}$ and L were mixed.

When solutions of $L_4AgB_{10}H_{13}$ were warmed above about −40°, coupling between ^{107}Ag or ^{109}Ag and ^{31}P disappeared, showing that rapid intermolecular exchange of L was occurring.[63]

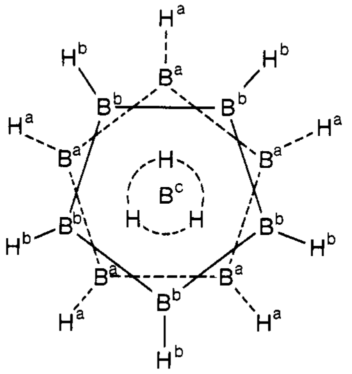
D. Icosahedral Carboranes

Quadrupole-induced spin relaxation has been shown to occur in 1,2-$B_{10}C_2H_{12}$ (*o*-carborane) and 1,7-$B_{10}C_2H_{12}$ (*m*-carborane)[61] and in the halogenated derivatives of these compounds.[114] In all cases observed, all of the protons on a specific compound have approximately the same chemical shift.

XIII. Undecaborane Derivatives

A. $B_{11}H_{14}^-$ Ion

The $B_{11}H_{14}^-$ ion has been predicted[115] to have a boron skeleton which is an icosahedron with one vertex removed, one terminal hydrogen atom per boron atom, and an H_3 group at the open face of the icosahedron perpendicular to the axis of the molecule (**47**). Both the ^1H and ^{11}B nmr spectra of $B_{11}H_{14}^-$ have been described.[116] The ^{11}B spectrum is simply a symmetrical doublet (J = 130 Hz) which collapses to a singlet on ^1H irradiation. This indicates a minimum of one boron environment with coupling of each boron atom to a single terminal proton. The ^{11}B-decoupled ^1H nmr spectrum, however, shows two overlapping resonances which total to a weight of 11 (probably, five plus six) and an upfield resonance of weight three which is, most likely, the H_3 group at the open face of the boron cage. These data support time-averaged symmetric structure probably containing a C_5 axis. This situation would require rapid rotation of the H_3 group (**47**). Consistent with the above suggestion, it has been shown[117] that all of the protons in $B_{11}H_{14}^-$ will exchange for deuterium in D_2O and that the H_3 group will do so most rapidly.



47 (see ref 116)

B. $B_{11}H_{13}^{2-}$ Ion

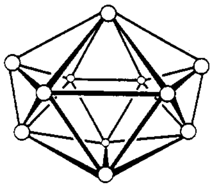
Reaction of $B_{11}H_{14}^-$ with strong base has been shown to yield the ion $B_{11}H_{13}^{2-}$.[116] The ^{11}B nmr spectrum of the ion consists of two doublets of relative weight 10:1.[118] Rapid proton exchange may account for this simple spectrum.

C. Metal Complexes of $B_{11}H_{14}^-$

Metal complexes of the type $L_4MB_{11}H_{14}^-$ have been prepared, where L is a triarylphosphine and M is copper, silver, or gold.[63] These have been shown to undergo exchange phenomena which are the same as those for the analogous $B_9H_{14}^-$ derivatives.[63]

D. Undecahydroundecaborate (2−) Ion ($B_{11}H_{11}^{2-}$)

The ^{11}B nmr spectrum of $B_{11}H_{11}^{2-}$ was originally reported to consist of two doublets in the ratio of 10:1,[117] but more recent work has determined that the smaller of these is, probably, the result of $B_{10}H_{10}^{2-}$ contamination.[118] The proposed structure[119] of the isoelectronic $B_9C_2H_{11}$ is that of a octadecahedron (**48**), and $B_{11}H_{11}^{2-}$ would reasonably be expected to be isostructural. In the octadecahedron structure, a decaborane(14) framework is capped by an 11th vertex, and such a geometry would be expected to give rise to more than just the one ^{11}B resonance observed. Accidental overlap of chemical shifts or rapid polyhedral rearrangement would account for the observed spectrum.



48 (see ref 117)

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