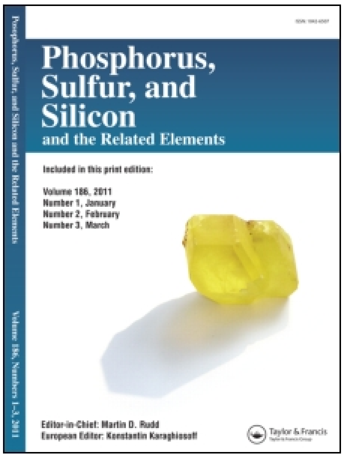

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

The Three-Center, Boron-Hydrogen-Metal, Coordinate Bond. Factors Influencing Bond Strength

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To cite this Article Parry, Robert W.(1994) 'The Three-Center, Boron-Hydrogen-Metal, Coordinate Bond. Factors Influencing Bond Strength', Phosphorus, Sulfur, and Silicon and the Related Elements, 87: 1, 177 — 191

To link to this Article: DOI: 10.1080/10426509408037452

URL: http://dx.doi.org/10.1080/10426509408037452

Phosphorus, Sulfur, and Silicon, 1994, Vol. 87, pp. 177–191

THE THREE-CENTER, BORON-HYDROGEN-METAL, COORDINATE BOND. FACTORS INFLUENCING BOND STRENGTH[1]

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The $\mathrm{B\underset{\smile}{-H-}\!\!\rightarrow M}$ bridge bond is responsible for the formation of stable molecular structures such as that seen in $Cl_2Zn\{B_2H_4 \cdot 2P(CH_3)_3\}$ and many related species. Factors involved in the stability of $\mathrm{B\underset{\smile}{-H-}\!\!\rightarrow M}$ linkages are examined using the premise that the bond is a perturbed (polarized) sigma bond. The analysis relates the existence of these coordination compounds to the "agostic hydrogens" of organic chemistry.

Key Words: Three-center boron-hydrogen-metal bridge bonds, coordination compounds, metal carbonyls, borane anions and fragments as ligands, agostic hydrogen.

BACKGROUND - THE EXISTENCE OF THE THREE CENTER $\mathrm{B\underset{\smile}{-H-}\!\!\rightarrow M}$ COORDINATE BOND

Anionic Borane Ligands

The borohydrides, MBH_4, were first identified[2] as distinct species by Schlesinger and Brown[3] and the chemistry of the borohydride anion was developed extensively by Schlesinger and his colleagues at the University of Chicago. As pointed out by Adams and Siedle[4] the borohydride anions were recognized at an early date as highly polarizable units. The bonding of BH_4^- to metal ions in metal borohydrides was classified as running from essentially ionic in KBH_4 to essentially a covalent $\mathrm{B\underset{\smile}{-H-}\!\!\rightarrow M}$ bridged structure in $Al(BH_4)_3$. Over the years a variety of metal borohydrides have been reported[4] including those of the alkali metals, the alkaline earth metals, Al^{+3}, Ga^{+3}, In^{+3}, Tl^{+}, Sn^{+2}, Th^{+4}, U^{+4}, Ti^{+3}, Zr^{+4}, Hf^{+4}, Cu^{+}, Ag^{+}, Zn^{+2}, Cd^{+2}, and NH_4^{+}. In all cases as the metal ion becomes more polarizing, distinct $\mathrm{B\underset{\smile}{-H-}\!\!\rightarrow M}$ bridges become clearer.

X-ray diffraction studies showed that the more ionic borohydrides had the sodium chloride structure while the more covalent compounds had distinctly visible bridge features [Figure 1(a-c)]. In solution, however, NMR shows that $Al(BH_4)_3$ is a fluctional molecule with all hydrogens becoming equivalent. The BH_4^- ion can

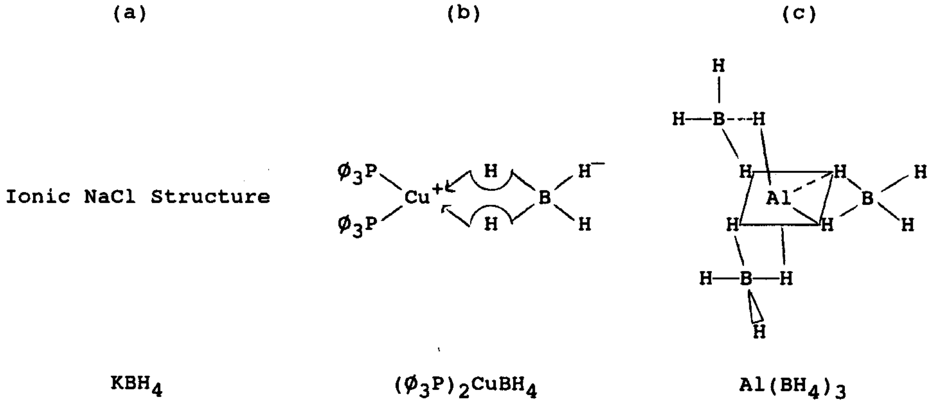


FIGURE 1 Representation of borohydride bridge features for structures of (a) KBH_4[4b]; (b) $(\text{ØP})_2CuBH_4$[5]; and (c) $Al(BH_4)_3$[6].

also coordinate as a monodentate anion, as can $H_3BCO(OC_2H_3)^-$. This fact was shown by Bommer and Morse.[7a-d] A detailed, definitive, collaborative study[7c] using neutron diffraction and x-ray diffraction established the structure of $(\text{Ø}_3P)_3CuBH_4$. It is shown in Figure 2.

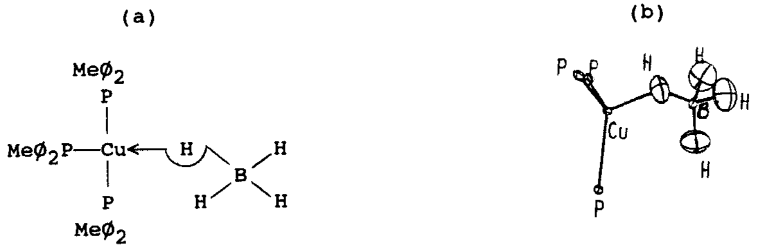


FIGURE 2 (a) Structure of $(\text{ø}_3P)_3CuBH_4$ and (b) x-ray diffraction picture. One hydrogen of BH_4^- is coordinated. *From* J Amer Chem Soc **103**, 5165 (1981), *with permission.*

A third type of borane coordination involving 3 of the hydrogens of a BH_4^- ion in B—H→M bonds has also been prepared by White, Deng, and Shore.[8] The structure has been established by x-ray diffraction [Figure 3]. Typical compounds are $(C_5H_5N)_4Yb(BH_4)_2 \cdot 2C_5H_5N$ and $(CH_3CN)_2Eu(BH_4)_2$. These compounds are of limited stability, decomposing to give the lanthanide borides with loss of both hydrogen and the organic ligand.

Other anions of boron such as $B_3H_8^-$ can serve as bidentate ligands to give relatively stable coordination compounds. The structures are well established. $(\text{Ø}_3P)_2CuB_3H_8$[9] has the structure shown schematically in Figure 4. The copper (I) ion shows distorted tetrahedral coordination.

Other less well characterized anions can also be recognized in coordination compounds. In 1965, Kaesz, Fellman, Wilkes and Dahl[10] described dark red needles of formula $Mn_3(B_2H_6)(CO)_{10}(\mu\text{-H})$ which were a by-product of the reaction between $Mn_2(CO)_{10}$ and an excess of $NaBH_4$. The structure as determined by Dahl and colleagues using x-ray diffraction is shown schematically in Figure 5. Using normal

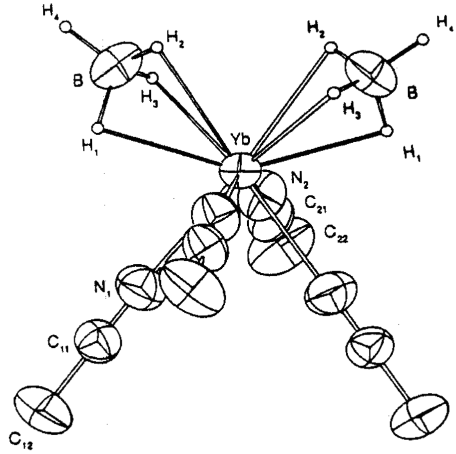


FIGURE 3 Representation of BH_4 compound prepared by White, Deng, and Shore,[9] $L_4Yb(BH_4)_2$. Three hydrogens of BH_4^- are coordinated. *From* Inorg Chem **30**, 2337 (1991), *with permission.*

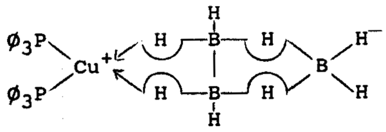


FIGURE 4 Structure of $(\emptyset_3P)_2CuB_3H_8$. Two hydrogens of $B_3H_8^-$ are coordinated.

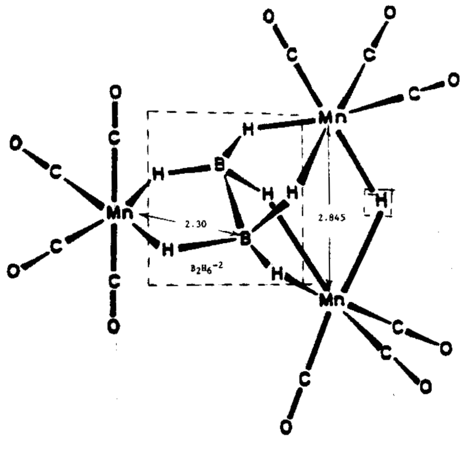


FIGURE 5 Structure of $Mn_3(B_2H_6)(CO)_{10}(\mu\text{-}H)$. Coordination of 6 hydrogens of $B_2H_6^{-2}$.

electron counting methods and considering that the bridging H^- unit has a charge of -1, each Mn would have a charge of +1 and the B_2H_6 unit would have a charge of -2. A number of significant points are seen in this structure[11]: (1) The anion $B_2H_6^{-2}$ forms bridge bonds to manganese atoms using all 6 hydrogens of the anion; (2) The Mn-Mn distance for the two Mn-Mn atoms, bound by four B—H→Mn bonds and one Mn—H→Mn bond, is significantly shorter (284.5 pm) than the single Mn-Mn bond in $Mn_2(CO)_{10}$ (292.3 pm). In summary, the $B_2H_6^{-2}$ ion can form 6 bridge bonds to metal atoms and the resulting structure is stable. Further, the $B_2H_6^{-2}$ structure in the complex shows a distinct B-B linkage (176 pm) which is roughly equivalent in length to the B-B distance in neutral B_2H_6 (177 pm) where the two boron atoms are held together by only two B—H→B bonds.

In the discussion following the presentation of this paper, Professor Sheldon Shore[12] reported that he and his coworkers have strong evidence for the compound $Rb_2B_2H_6$ in THF solution. Thus the anion is apparently a new member of the borane anion system. The $B_2H_6^{-2}$ anion is isoelectronic with ethane.

Another compound also appears to be a complex of the $B_2H_6^{-2}$ anion. Anderson and Fehlner[13] reported the compound $\{Fe(CO)_3\}_2B_2H_6$. While neither x-ray nor neutron diffraction techniques have been applied to the solid, techniques such as NMR, IR, and mass spectroscopy strongly support the structure shown (Figure 6)

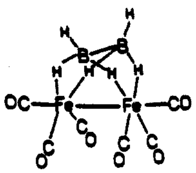


FIGURE 6 Proposed structure for $\{Fe(CO)_3\}_2B_2H_6$ compound.[13]
From J Amer Chem Soc **100**, 4606 (1978), *with permission.*

in which four of the 6 hydrogen atoms bind two $Fe(CO)_3^+$ groups to give the neutral compound. Again, the two parts of the molecule are held together by B—H→M linkages. No Fe—B—Fe or cage structures are indicated by available data.

The evidence for complexes of the anions BH_4^-, $B_3H_8^-$, and $B_2H_6^{-2}$ is overwhelming. Binding between the borons of the anion and the metal cations is achieved in each case by a B—H→M three-center bridge bond (or bonds). Available qualitative evidence indicates that the strength of the boron-hydrogen-metal bonds increases in the series BH_4^-, $B_3H_8^-$, and $B_2H_6^{-2}$. More precise quantitative data would be useful.

As is common in coordination chemistry, bidentate, monodentate, and tridentate linkages are established with certainty. The bidentate systems again appear to be the most stable. The "chelate effect" is real, but excessive distortion through coordination of 3H seems to correlate with easy loss of H_2 to give MB compounds.

Neutral Borane Ligands

In all of the foregoing compounds of borane anions the existence of a negative charge on the anion, a positive charge on the metal ion, and fluxional behavior in many of the systems studied raised questions about the importance of the

$\mathrm{B{-}\underset{\smile}{H}{\longrightarrow}M}$ linkage as opposed to plain old ionic interaction of admittedly polarized positive and negative ions. Additional evidence for coordination of NEUTRAL boranes and their derivatives to neutral metal species would help to further test the validity of the $\mathrm{B{-}\underset{\smile}{H}{\longrightarrow}M}$ link as an extension of Werner-Lewis coordination theory. A group of neutral borane ligands has been found and the characteristic metal complexes have been prepared and reported.[14]

The Derivatives of the B_2H_4 Neutral Borane Fragment

A series of compounds has been reported in which 2 molecules of a variety of bases have been coordinated to a B_2H_4 fragment to give stable molecules of the general form seen in Figure 7. A variety of bases can replace $(CH_3)_3P$. The bases used, the methods of synthesis, and the references are given in Table I. Certain members of this group [in particular those where L is H^- and L is $P(CH_3)_3$] have been shown to form coordination compounds with metals establishing unequivocally the $\mathrm{B{-}\underset{\smile}{H}{\longrightarrow}M}$ linkage as a valid coordinate bond without ionic components. The compounds illustrated in Figure 8 have been formed.

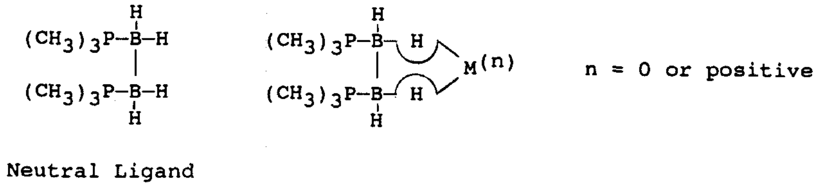


FIGURE 7 General form of stable molecules using B_2H_4 fragment.

More recently M. Shimoi and his co-workers in Japan have used photochemical activation of $M(CO)_6$ to generate a series of $\mathrm{B{-}\underset{\smile}{H}{\longrightarrow}M}$ carbonyl complexes from $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$. The following compounds[17] were prepared and in nearly all cases structures were determined by x-ray diffraction: $[Cr(CO)_4\{B_2H_4\cdot 2P(CH_3)_3\}]$, bidentate, and $[Cr(CO)_5\{B_2H_5\cdot 2P(CH_3)_3\}]$, monodentate. The monodentate complexes were significantly less stable than the chelated structures. The monodentate species appears to be an intermediate in the formation of the chelated compound. The tungsten analogues of both the monodentate and chelated Cr compounds were also prepared and structurally characterized.

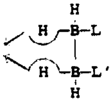
Some reactions carried out to extend the range of potentially reactive compounds were not successful. $(CH_3)_3PBH_3$ and $(CH_3)_3PB_3H_7$ would NOT react with $ZnCl_2$ under the conditions used to prepare $Cl_2Zn\{B_2H_4\cdot 2P(CH_3)_3\}$. On the other hand, using photoactivation techniques Shimoi, Katch, Uruichi, and Ogino[18] were able to prepare $W(CO)_5\{H_3BP(CH_3)_3\}$ and $W(CO)_5\{H_3BN(CH_3)_3\}$ as well as the Cr compounds. These monodentate systems were clearly less stable than their chelated analogues.

Cationic Boron Clusters

Up to the present time no cationic boron clusters have been identified as Ligands binding to metals through $\mathrm{B{-}\underset{\smile}{H}{\longrightarrow}M}$ linkages.

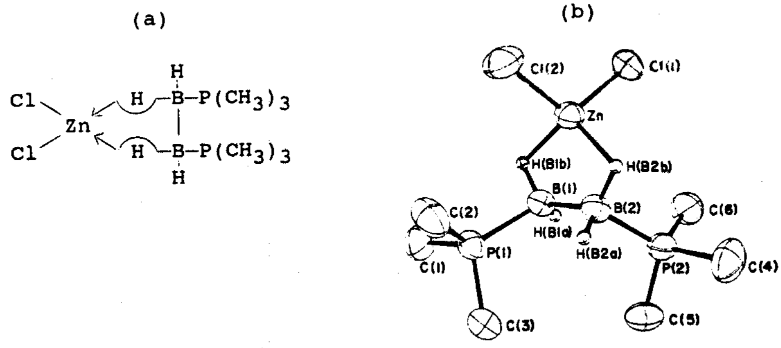
TABLE I

Compounds of the form

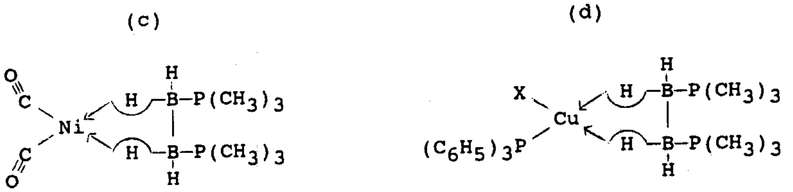


which are proven and potential ligands for coordination to metals through B— H →M three center bonds.

L	L′	Made From:	Reference
$(C_6H_5)_3P$	$(C_6H_5)_3P$	$(CH_3)_3NB_3H_7$ + $(C_6H_5)_3P_{(excess)}$ in benzene (50°)	B. M. Graybill and J. K. Ruff, *J. Am. Chem. Soc.*, 84, 1062 (1962).
F_3P	F_3P	$(CH_3)_2OB_3H_7$ + $PF_{3(excess)}$ (-16°)	W. R. Deever and D. M. Ritter, *J. Am. Chem. Soc.*, 89, 5073 (1962); W. R. Deever, E. R. Lory, and D. M. Ritter, *Inorg. Chem.*, 8, 1263 (1969).
F_2HP	F_2HP	$(CH_3)_2OB_3H_7$ + $F_2HP_{(excess)}$ also B_4H_{10} + $F_2HP_{(excess)}$	E. R. Lory and D. M. Ritter, *Inorg. Chem.*, 10, 937 (1971); E.R. Lory, *Ph.D. Thesis*, University of Washington, Seattle, WA.
R_2NF_2P	R_2NF_2P	B_4H_{10} + $R_2NF_2P_{(excess)}$ and B_5H_9 + $R_2NF_2P_{(excess)}$	E. R. Lory and D. M. Ritter, *Inorg. Chem.*, 10, 939 (1971); *Ibid.*, 9. 1847 (1970).
F_2ClP F_2BrP F_2IP	F_2ClP F_2BrP F_2IP	B_4H_{10} + $F_2PX_{(excess)}$ $(CH_3)_2OB_3H_7$ + $F_2PX_{(excess)}$	R. T. Paine and R. W. Parry, *Inorg. Chem.*, 14, 689 (1975); *Ibid.*, 11, 268 (1972).
CO	CO	OCB_3H_7 Structure $B_2H_4\cdot 2CO$ reported from x-ray	J. Rathke and R. Schaeffer, *Inorg. Chem.*, 13, 760 (1974).
$(CH_3)_3P$	$(CH_3)_3P$	B_5H_9 + $P(CH_3)_3$	R. K. Hertz, M. L. Denniston, and S. G. Shore, *Inorg. Chem.*, 17, 2673 (1978).
$P(CH_3)_3$	$P(CH_3)_3$	B_5H_9 + $P(CH_3)_3$	M. Kameda and G. Kodama, *Inorg. Chem.*, 19, 2288 (1980).
		Also formed $B_3H_5\cdot 3P(CH_3)_3$ ⟶	A New Ligand
$P(CH_3)_3$	$P(CH_3)_3$	$B_3H_7\cdot PCH_3$ + $2P(CH_3)_3$	G. Kodama and M. Kameda, *Inorg. Chem.*, 18, 3302 (1979).
		$B_5H_9\cdot 2P(CH_3)_3$ + $3P(CH_3)_3$	M. Kameda and G. Kodama, *Inorg. Chem.*, 19, 2288 (1980).
		$B_6H_{10}\cdot 2P(CH_3)_3$ + $4P(CH_3)_3$	M. Kameda and G. Kodama, *Polyhedron*, 2, 413 (1983).
		$B_4H_8\cdot 2P(CH_3)_3$ + $2P(CH_3)_3$	M. Kameda and G. Kodama, *Inorg. Chem.*, 29, 4837 (1990).
$N(CH_3)_3$	$N(CH_3)_3$	$THFB_3H_7$ + $N(CH_3)_{3(excess)}$	R. E. DePoy and G. Kodama, *Inorg. Chem.*, 24, 2871 (1985).
$N(CH_3)_3$	$P(CH_3)_3$	$(CH_3)_3PB_3H_7$ + $N(CH_3)_3$ CH_2Cl solution	R. E. DePoy and G. Kodama, *Inorg. Chem.*, 27, 1116 (1988).
$N(CH_3)_3$	$N(CH_3)_3$	$(CH_3)_2SB_3H_7$ + $3N(CH_3)_3$	M. Ishii and G. Kodama, *Inorg. Chem.*, 29, 2181 (1990).
$P(CH_3)_3$	$P(CH_3)_3$	$1\text{-}CH_3B_5H_8$ + $P(CH_3)_3$ Get $H_3CB_2H_3\cdot 2P(CH_3)_2$	M. Kameda, J. A. Driscoll, and G. Kodama, *Inorg. Chem.*, 29, 3791 (1990).
H^-	H^-	· · · · · · · · · · · · ·	S. G. Shore, to be published in 1994.

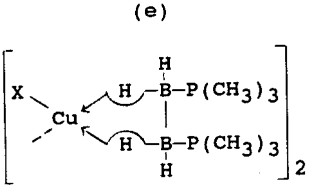


$ZnCl_2\{B_2H_4 \cdot 2P(CH_3)_3\}$



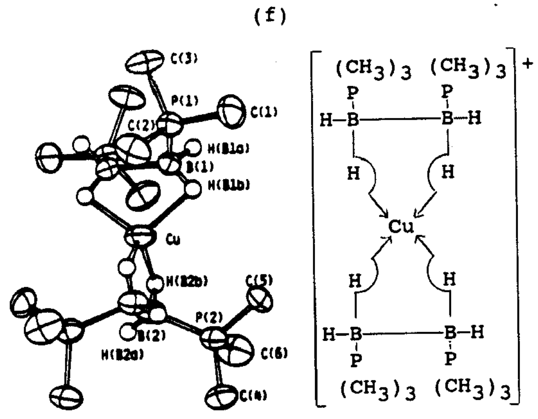
$(CO)_2Ni\{B_2H_4 \cdot 2P(CH_3)_3\}$

$CuX\{(C_6H_5)_3P\}\{B_2H_4 \cdot 2P(CH_3)_3\}$



$[CuX\{B_2H_4 \cdot 2P(CH_3)_3\}]_2$

X = Cl or I



$Cu\{B_2H_4 \cdot 2P(CH_3)_3\}_2^+$

FIGURE 8 Representation of coordinate three-center bonds in: (a,b) $ZnCl_2\{B_2H_4 \cdot 2P(CH_3)_3\}$ [15a]; (c) $(CO)_2Ni\{B_2H_4 \cdot 2P(CH_3)_3\}$ [15b]; (d) $(C_6H_5)_3PCuX\{B_2H_4 \cdot 2P(CH_3)_3\}$ [15b]; (e) $[CuX\{B_2H_4 \cdot 2P(CH_3)_3\}]_2$, X = Cl or I [16]; and (f) $[Cu\{B_2H_4 \cdot 2P(CH_3)_2\}_2]^+I^-$ [16]. *Section* **b** *from* Inorg Chem **23**, 511, (1984) *and section* **f**, *from* Inorg Chem **29**, 814, (1990), *with permission.*

FACTORS INFLUENCING THE STRENGTH OF THE THREE CENTER $B—\underset{\smile}{H}\longrightarrow M$ BOND

The Role of the Ligand Attached to the B_2H_4 Fragment in the Compounds of Formula $B_2H_4\cdot L\cdot L'$

While systematic, quantitative information on the factors determining the strength of the three-center $B—\underset{\smile}{H}\longrightarrow M$ bond is not yet available, a number of chemical observations provide clues to stability. Infrared arguments for $(OC)_2Ni\{B_2H_4\cdot 2P(CH_3)_3\}$ cited elsewhere[14a] offer strong support for the premise that the $B—\underset{\smile}{H}\longrightarrow M$ bond is a perturbed sigma bond in which the electron polarizability of the B-H linkage is important. Unless the B-H bond is quite polarizable (as favored by hydridic character of the H atom attached to boron). The three center bond to a metal will have little tendency to form. This argument suggests that those ligands attached to B_2H_4 which are the most effective in donating electrons to the borane fragment will give the strongest $B—\underset{\smile}{H}\longrightarrow M$ linkage. Thus two H^- ions attached to $B_2H_6^{-2}$ should give the most strongly binding $B—\underset{\smile}{H}\longrightarrow M$ structure. Data are consistent with $B_2H_6^{-2}$ forming 6 $B—\underset{\smile}{H}\longrightarrow M$ bonds to give stable structures. As a corollary, one notes that boron hydride anions were the first ligands to be recognized as forming $B— H \longrightarrow M$ linkages. The negative charge helps. Electron donating alkyl phosphines and amines form the most studied group of $B_2H_4\cdot 2L$ ligand compounds. As yet, data do not properly differentiate between the stabilities of the alkyl phosphine and the alkyl amine ligands. All coordinate rather weakly and the $B_2H_4\cdot 2L$ compounds are useful in synthesis as leaving groups. The compound $(OC)_2Ni(PH_3)_2$ could be made by displacing the $\{B_2H_4\cdot 2P(CH_3)_3\}$ from $(OC)_2Ni\{B_2H_4\cdot 2P(CH_3)_3\}$ using PH_3. No other synthesis of $(OC)_2Ni(PH_3)_2$ is known.

While data are not yet available on the metal coordinating ability of $B_2H_4\cdot 2PF_3$ and $B_2H_4\cdot 2CO$, the model used here indicates that both should be poor coordinating bidentate ligands, perhaps even weaker than the monodentate $H_3BP(CH_3)_3$ and $H_3BN(CH_3)_3$. The weakest ligands would be H_3BPF_3, H_3BCO, and all cationic borane fragments. These generalizations are summarized in Table II.

TABLE II

Borane ions and base adducts as ligands to bind to metals

Strength	Species	Argument
Best ↑	$B_2H_6^{-2}$ $B_3H_8^-$ BH_4^-	High electron density from H^-.
	$B_3H_5\cdot 3P(CH_3)_3$	Displaces $B_2H_4\cdot 2P(CH_3)_3$.
	$B_2H_4\cdot 3P(CH_3)_3$ $B_2H_4\cdot P(CH_3)_3N(CH_3)_3$ $B_2H_4\cdot 2N(CH_3)_3$	Current data do not yet permit differentiation of the $P(CH_3)_3$ ligands from the $N(CH_3)_3$.
Increasing strength as a ligand	$H_3BP(CH_3)_3$ $H_3BN(CH_3)_3$	Form unstable monodentate adducts with W, Mo, and Cr carbonyls. Significantly less stable than chelate ligands just above.
	$B_2H_4\cdot 2PF_3$ $B_2H_4\cdot 2CO$ $B_2H_4\cdot 2PF_2X$ (where X = Cl, Br, I)	No data available. Believe will not give stable complexes because ligands attached to B_2H_4 are electron attracting, not electron donating.
↓ Worst	H_3BPF_2X $H_3B\cdot P(C_6H_5)_3$ $H_3B\cdot PF_3$ $H_3B\cdot CO$ All Borane Cations	Should be poor; monodentate and poor electron donors.

Ring Size and The Chelate Effect

Data obtained so far provide no evidence for a $B_2H_4 \cdot 2L$ structure involving coordination of all four hydrogens of the B_2H_4 unit through 3-center bonds (Figure 9). Steric strain factors probably overcome the weak bonds. Rings such as the one seen in Figure 10 are characterized by x-ray and the structures are moderately stable but in a competition experiment (Figure 11) the lower 3-boron-unit took all of the $ZnCl_2$ indicating that the 6 membered ring (counting hydrogen atoms) is more stable than the five. This argument suggests that $B_3H_8^{-3}$ (if it could be made) or even the still unknown $\{B_3H_7 \cdot P(CH_3)_3\}^{-2}$ would be the strongest ligand of all considered.

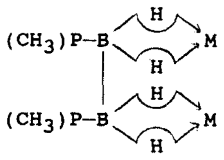


Figure 9 Structure of tetradentate $B_2H_4 \cdot 2P(CH_3)_3$ compound. Hypothetical but not known.

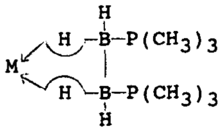


FIGURE 10 $M\{C_2H_4 \cdot 2P(CH_3)_3\}$ ring structure. Well known.

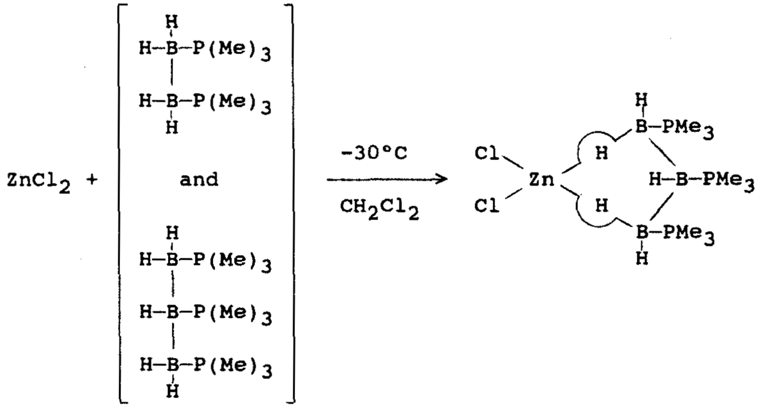


FIGURE 11 Competition experiment involving coordination to $ZnCl_2$.

Some Geometric Substitutions

As Figure 12 shows substitution in the $B_2H_6^{-2}$ ion will produce four different species two of which will coordinate to Zn^{+2} in $ZnCl_2$ and two of which will not. In the case of $B_3H_8^-$ the optimal chelation geometry and the negative charge make coordination possible. The neutral $(CH_3)_3PB_3H_7$ has the two coordinating hydrogens next to bridging hydrogens which are not optimal for transmitting electron density from $P(CH_3)$. In $B_2H_4 \cdot 2P(CH_3)_3$ optimal chelating geometry and direct boron $P(CH_3)_3$ contact make bidentate coordination possible. In $H_3BP(CH_3)_3$ the monodentate structure is marginally too unstable without a supporting negative charge.

The foregoing arguments are illustrated further in Figure 13.

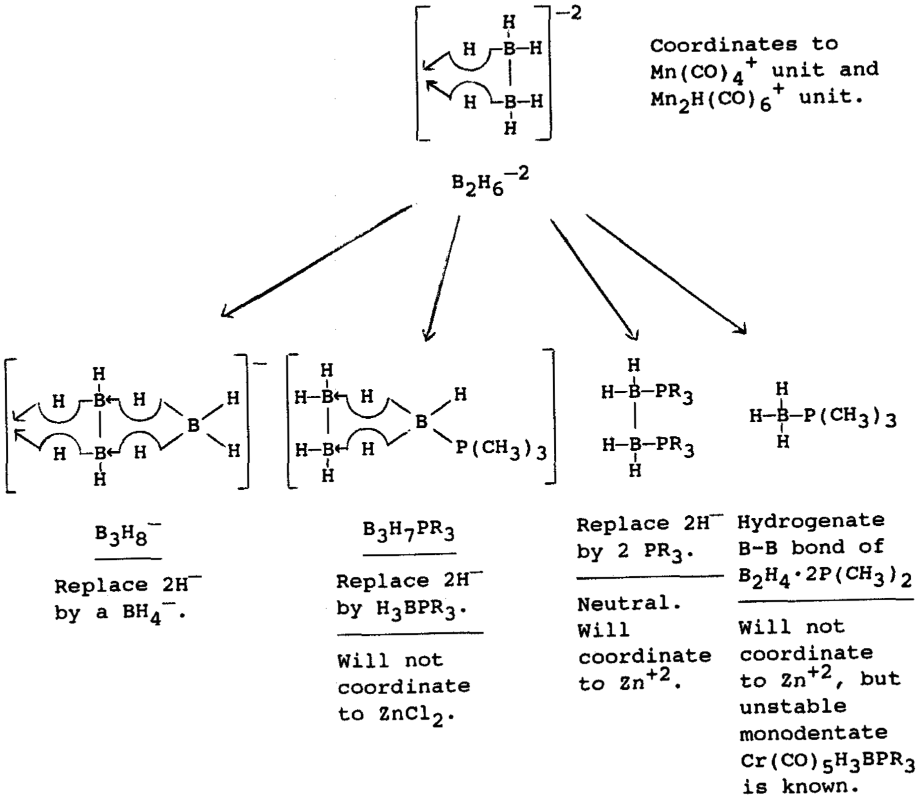
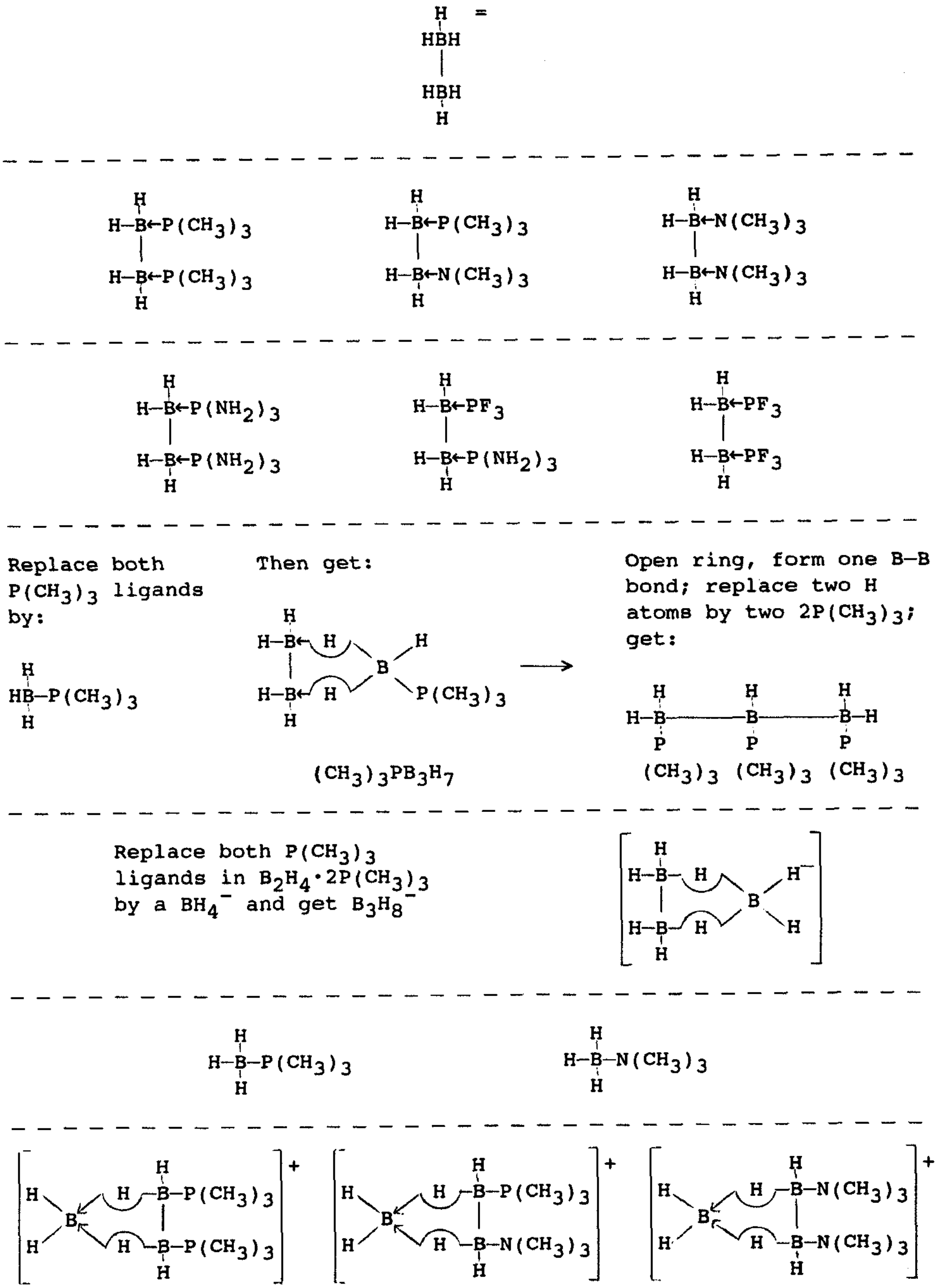


FIGURE 12 Coordination through $\mathrm{M}\overset{\mathrm{H}}{\swarrow\quad\searrow}\mathrm{B{-}X}$ role of substitution and of geometric factors.



Replace both $P(CH_3)_3$ ligands by:

Then get:

$(CH_3)_3PB_3H_7$

Open ring, form one B–B bond; replace two H atoms by two $2P(CH_3)_3$; get:

Replace both $P(CH_3)_3$ ligands in $B_2H_4 \cdot 2P(CH_3)_3$ by a BH_4^- and get $B_3H_8^-$

FIGURE 13 Substitutions of $B_2H_6^{-2}$ to get new structures.

E-H DONORS WHERE E IS AN ELEMENT OTHER THAN BORON

Elements of Lesser Electronegativity Than Boron [i.e. Al, Ga, etc.]

With elements of lower electronegativity than boron, for example Al and Ga, the easiest path to decomposition seems to be to transfer the hydrogen completely leaving the free Al or Ga for further change. No systematic attempt to make complexes of $H_3AlN(CH_3)_3$ has been reported yet but such complexes would probably be stable at low temperatures. Geometric factors may permit chelation and the hydridic hydrogen on the Al would polarize easily. At higher temperatures hydrogen loss would be expected.

Elements of Greater Electronegativity Than Boron [i.e. Carbon]

Because of the fact that the carbon nucleus contains one more proton than does the boron nucleus, bonds of the $\mathrm{C{-}\underset{\smile}{H}{\rightarrow}}$ type are less polarizable than those involving the $\mathrm{B{-}\underset{\smile}{H}{\rightarrow}}$ structure. Thus interactions of the "agostic hydrogen" type may well be involved in C-H activation but the interactions are not strong enough to support separate compound formation of the type described here.[19]

ACKNOWLEDGEMENT

The author thanks his colleagues in both the U.S. and Japan for making data available and for their discussions. He also thanks The University of Utah for financial assistance in paper preparation.

REFERENCES

1. This paper is respectfully dedicated to Professor Alan L. Cowley on the occasion of his 60th birthday. Alan is a long-term friend and colleague who has contributed much to inorganic chemistry. It is a pleasure to be a part of this symposium which recognizes his contributions to science in all of its many ramifications.
2. Sodium borohydride was prepared in two ways by Stock, although he did not identify the compound in either case. "Sodium hypoborate," prepared by Stock from B_2H_6 and aqueous NaOH was shown years later by Davis and Gottbraith to be a mixture of $NaBH_4$ and $Na\{B(OH)_4\}$. Similarly, "sodium diborane" reported by Stock was shown by Kaspar and by Hough and Edwards to be a mixture containing a large fraction of the boron as $NaBH_4$. [This historical note was described by R. M. Adams and A. R. Siedle in *Boron, Metalloboron Compounds, and Boranes*, Chapter 6, edited by R. M. Adams, ed., Interscience Publishers, New York, NY, 1964, p. 374.]
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11. This review focuses on those systems in which bonding between boron and metal occurs exclusively through a $\mathrm{B{-}\underset{\smile}{H}{\longrightarrow}M}$ bond. It does not treat those compounds such as $Fe_2(B_3H_7)(CO)_6$ in which the metal atom is included as part of the boron cage and in which three center $\genfrac{}{}{0pt}{}{\mathrm{B}}{\mathrm{B}}{>}\mathrm{M}$ bonds are involved.
12. In a discussion of this paper Professor Sheldon Shore of Ohio State University in Columbus, Ohio commented that they have strong NMR evidence for $Rb_2B_2H_6$ in THF solution which properly puts the $B_2H_6^{-2}$ ion in the same group as BH_4^- and $B_3H_8^-$. Professor Shore will publish this work soon. They also have evidence for BH_3^{-2} in solution.
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