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Coordination compounds formed using three-center hydrogen bridge bonds: An extension of the Lewis donor–acceptor coordinate bond*

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CONTENTS

ABSTRACT

In 1959 it was suggested by Parry and Edwards that the concept of a coordinate covalent bond could be extended to include three-center bridge bonds. Although the $\mathrm{B}{-}\mathrm{H}{\rightarrow}\mathrm{M}$ bond was soon seen in metal borohydrides and salts of metals with other boron hydride anions, questions about ionic contributions to bonding in these structures rendered questionable the concept of valid coordination to a metal through a [boron–hydrogen–metal] three-center bond. Now complexes have been characterized with formulas of $ZnCl_2 \cdot L$, $(CuClL)_2$, $CuP\phi_3LCl$, $Ni(CO)_2L$, $Cr(CO)_4L$, $Mo(CO)_4L$, and $W(CO)_4L$ where L is the *bidentate, neutral, σ*-bonding ligand which can be compared in some sense to ethylenediamine:

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* Respectfully dedicated to the memory of John C. Bailar, Jr., one of the great inorganic chemists of the twentieth century, who patiently introduced the senior author to the field of coordination chemistry.

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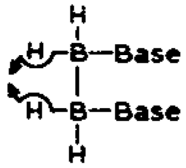
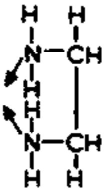


($B_2H_4 \cdot 2$ Base)



ethylene diamine

In these compounds, as in some of the boron hydrides such as B_2H_6, the $\mathrm{B}\overset{\mathrm{H}}{\longrightarrow}$ linkage is clearly and unequivocally the basis for compound stability.

Relatively unstable complexes of the formula $M(CO)_5[B_2H_4 \cdot 2P(CH_3)_3]$ have also been characterized where M is Cr and W, and where the $[B_2H_4 \cdot 2P(CH_3)_3]$ is a *monodentate* ligand. Even less stable monodentate complexes of formula $Cr(CO)_5(H_3B \cdot \text{Base})$ and $W(CO)_5(H_3B \cdot \text{Base})$ have been characterized where the bases fastened to BH_3 are $P(CH_3)_3$, $N(CH_3)$, and $P(C_6H_5)_3$. These borane ligands are excellent leaving groups.

1. THE CONCEPT OF THE COORDINATE COVALENT BOND

1.1 Werner's primary and secondary valences and the electronic pictures of G.N. Lewis

In his classical formulation of the coordination theory, Werner [1(b)] postulated two types of linkage which could join atoms together. He defined a primary valence for an atom which could account for the bond between a metal such as cobalt and a non-metal such as chlorine to give a stable species such as cobalt(II) chloride. This cobalt–chlorine linkage was the classical chemical bond of the day and was tied to the idea of definite bonding capacities (valences) of elements.

The existence of ammonia adducts with formulae such as $CoCl_2 \cdot 6NH_3$, $CoCl_2 \cdot 5NH_3$, $CoCl_2 \cdot 4NH_3$, etc., known since 1798 [2], required a perturbation of this classical valence concept, since varying numbers of NH_3 molecules could bind to a central cobalt atom. Without being specific about the nature of the linkage, Werner suggested that a molecule such as ammonia could bind to a metal such as cobalt through a secondary valence of cobalt; thus the cobalt atom displayed both primary and secondary valences which were defined only in an operational sense.

It remained for Lewis [3] to explain the ideas of primary and secondary valence in terms of the electronic structure of atoms and molecules. His classical and simple picture of the primary valence bond involved an electron pair with *each* bound *atom* providing one of the two electrons of the bonding pair. The secondary valence bond between two atoms was defined as a two-electron bond in which one of the two bound atoms contributed both electrons to form the linkage. The other atom accepted a share of the two electrons. Such a bond was called a coordinate–covalent or donor–acceptor bond. Coordination chemistry became an accepted and definable area of chemistry.

1.2 *A different approach to coordination. The* $\mathrm{B{-}H{\rightarrow}E}$ *three-center bridge bond*

In a paper considering the systematics of the boron hydrides in 1959, Parry and Edwards [4] proposed an operational extension of the coordinate covalent bond. They wrote: "The coordination analogy in boron hydrides may be carried somewhat farther with profit by an operational extension of the definition of a base. It is customary to consider borane fragments such as BH_3 or B_3H_7 as *Lewis acids* since they accept electrons easily from normal electron donors (classic Lewis bases). On the other hand the originally unexpected ability of these fragments to combine with other borane fragments (Lewis acids) suggests that the borane groups (i.e. BH_3) may be considered as operational 'electron deficient' *bases* as well as Lewis acids. In such interactions the formation of bridge bonds replaces the conventional donor–acceptor bond of classic coordination theory. In such a sense the borane groups are amphoteric. For example, diborane can be regarded as a coordination compound resulting from the combination of two BH_3 groups which serve as *both* an acid and a base ...".

"It is then convenient to consider diborane as just one member of a series of base borane coordination compounds*. If the premise is accepted, the BH_3 group itself can be placed in any series of Lewis bases which form coordination compounds with the Lewis acid BH_3. One could then write a series representing increasing strength of bases coordinating with BH_3 (the acid). Data now available suggest the following arrangement for a few selected bases: CO, PF_3, BH_3, H_2O, NH_3, etc., ...".

While the foregoing discussion was focussed on boron hydrides, compounds such as $Al(BH_4)_3$ and other metal borohydrides suggested that metal ions could serve as acceptor species in the three-center coordinate bond (i.e. $\mathrm{B{-}H{\rightarrow}M^{+n}}$). A number of metal borohydrides were known, and many more metal borohydride-type coordination compounds such as $(R_3P)_2CuBH_4$ and $(R_3P)_2CuB_3H_8$ were soon characterized, suggesting the reality of the $\mathrm{B{-}H{\rightarrow}M}$ linkage (Figs. 1 and 2). Still proton NMR data showed that all hydrogens of the borohydride were equivalent; thus the possibility remained that ionic interactions could well dominate the bonding while the three-center hydrogen bridge bond could be a secondary factor. In the intervening years since 1959, many metal borane and metal carborane compounds (the latter pioneered by Hawthorne [8]), have been prepared and characterized. An excellent review of this area was edited by Grimes [9] and published in 1982.† Although many types of boron–metal and boron–hydrogen–metal interactions were described, no cases were identified in which the $\mathrm{B{-}H{\rightarrow}M}$ linkage could be unequivocally identified as the bond between two species, each capable of independent exis-

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* The foregoing discussion was part of a presentation which also recognized $H_2B(NH_3)_2^+$ as a true coordination compound with H^- and NH_3 as ligands coordinated to a B(III) central moiety. Like Fe(II), Co(III), Cr(II), etc., B(III) forms coordination compounds. Its *incipient* metallic character cannot be denied.

† This work was dedicated to Professor Ralph Rudolph of Michigan, a brilliant and leading worker in the field who died very early in his career.

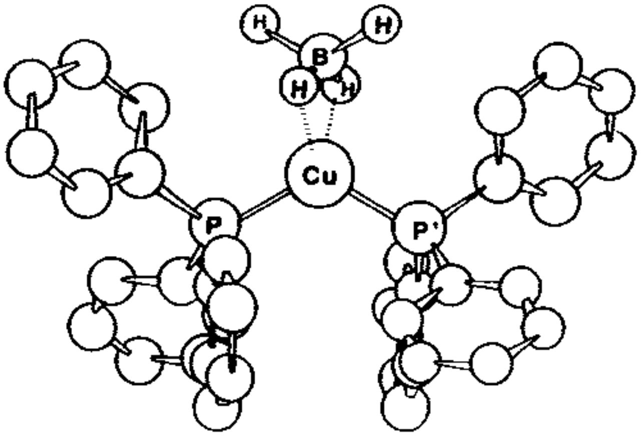


Fig. 1. Projection of borohydridobis(triphenylphosphine)copper(I) showing the molecular structure. Phenyl hydrogen atoms are not shown. (Modified from ref. 5).

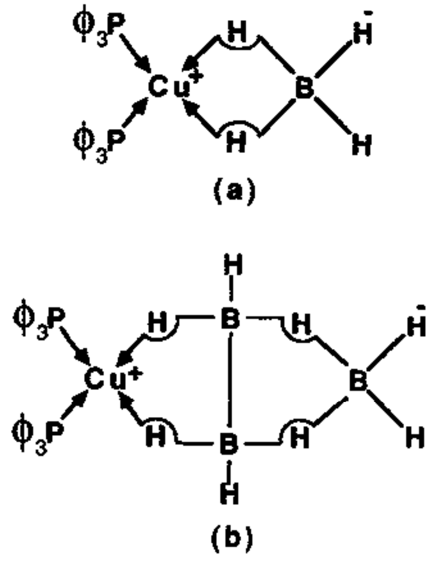


Fig. 2. (a) Diagram of structure of $Cu(P\phi_3)_2(BH_4)$ [6]. (b) Diagram of structure of $Cu(P\phi_3)_2(B_3H_8)$ [7].

tence. (Recall that the entire field of coordination chemistry began through attempts to explain the fact that nominally stable molecules, NH_3 and a metal chloride such as $CoCl_2$, combine to give stable adducts.) To test more effectively the concept of coordination through a $B-H\rightarrow M$ bond, a neutral ligand containing B–H linkages was needed.

2. A NEUTRAL LIGAND CAPABLE OF FORMING THREE-CENTER COORDINATE BONDS

2.1 Synthesis of the ligand

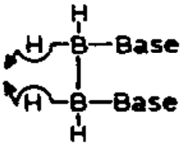
When tetraborane is treated with a base, a BH_3 unit is removed from the tetraborane and the products Base · BH_3 and Base · B_3H_7 result. The equation is:

$$B_4H_{10} + 2\ \text{Base} \rightarrow B_3H_7 \cdot \text{Base} + H_3B \cdot \text{Base} \qquad (1)$$

Additional base will split off another BH_3 to give $B_2H_4 \cdot$ 2Base and another molecule of $H_3B \cdot$ Base. The equation for the second process is:

$$B_3H_7 \cdot \text{Base} + 2\text{Base} \rightarrow B_2H_4 \cdot 2\text{Base} + H_3B \cdot \text{Base} \qquad (2)$$

This process is represented structurally in Fig. 3. A family of $B_2H_4 \cdot$ 2Base compounds has been prepared in which the bases include: $P(C_6H_5)_3$ [10], PF_3 [11], CO [12,13], PF_2H [14,15], PF_2Cl [15], PF_2Br [15], $P(CH_3)_3$ [16,17], $N(CH_3)_3$ [18], mixed $P(CH_3)_3$–$N(CH_3)_3$ bases [19], and $P[N(CH_3)_2]F_2$ [14]. As will be described below, certain of these neutral $B_2H_4 \cdot$ 2Base compounds serve as effective bidentate ligands as suggested by the formula:



The formula also suggests quite clearly that the strength of the $B\!-\!H\!\rightarrow\!M$ bond from the ligand to the metal will be dependent on the electron-donating properties of the base attached to B_2H_4. The better the base is as an electron donor, the stronger the $B\!-\!H\!\rightarrow\!M$ linkage should be.

Since B_4H_{10} and $B_3H_7 \cdot$ Base compounds are not available commercially, Hertz et al. [16] suggested in 1978 that commercially available B_5H_9 would be a better starting material for preparing $B_2H_4 \cdot 2P(CH)_3$. They obtained a 70% yield based on the assumption of one $B_2H_4 \cdot 2P(CH_3)_3$ per B_5H_9. Lory and Ritter [14(b)] in 1976 had first used B_5H_9 as a boron source for preparing the compound $B_2H_6 \cdot 2PF_2N(CH_3)_2$, but with their ligand the process was not an effective synthetic procedure since a complex structure was obtained and product separation was difficult. In 1980, Kameda and Kodama [17] were able to obtain stoichiometric cleavage of B_5H_9 at −40°C in accordance with the equations:

$$B_5H_9 + 2P(CH_3)_3 \rightarrow B_5H_9 \cdot 2P(CH_3)_3 \qquad (3)$$

$$B_5H_9 \cdot 2P(CH_3)_3 + 3P(CH_3)_3 \rightarrow B_2H_4 \cdot 2P(CH_3)_3 + B_3H_5 \cdot 3P(CH_3)_3 \qquad (4)$$

Some of the $B_3H_5 \cdot 3P(CH_3)_3$ can be converted to $B_2H_4 \cdot 2P(CH_3)_3$ by a side

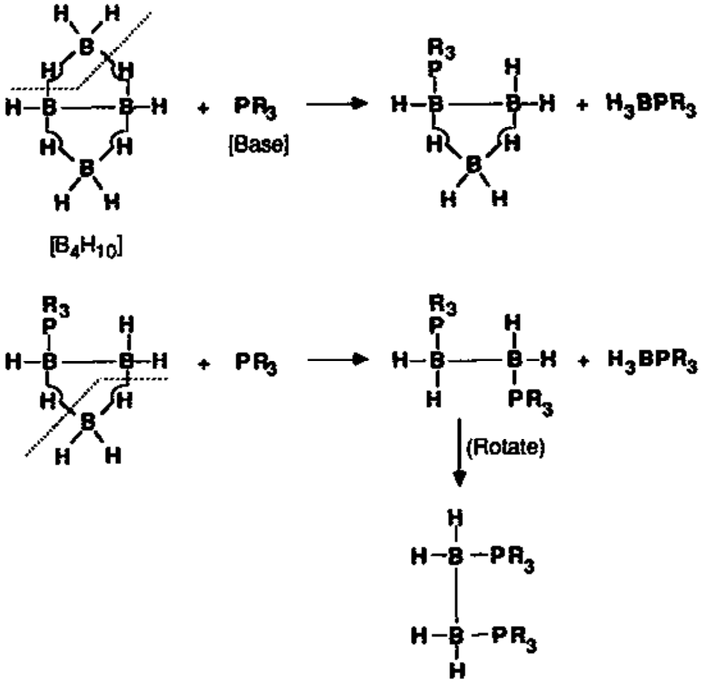
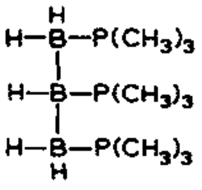


Fig. 3. Structural representation of the reaction of B_4H_{10} with a base such as $P(CH_3)_3$.

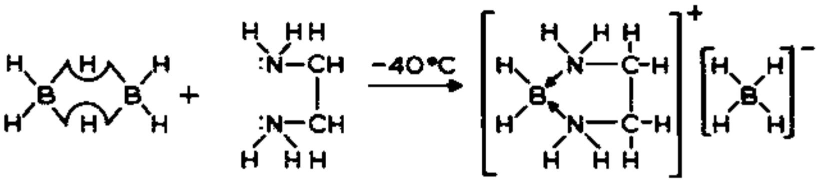
reaction. The product $B_3H_5 \cdot 3P(CH_3)_3$ was never isolated. Still very strong evidence for its existence was obtained. The compound $B_3H_5 \cdot 3P(CH_3)_3$ is also of interest as a ligand and preliminary data [20] suggest that it coordinates to Zn^{2+} in preference to $B_2H_4 \cdot 2P(CH_3)_3$:



2.2 Reactions of $B_2H_4 \cdot 2P(CH_3)_3$ as a ligand with boron hydrides

Very early work from this laboratory and others showed that certain bases such as NH_3, methylamine, etc. react with B_2H_6 and with B_4H_{10} through unsymmetrical cleavage of the double bridge bond to give ionic products. With B_2H_6, the product is $[H_2B(NH_3)_2]^+BH_4^-$. With B_4H_{10}, the product is

$[H_2B(NH_3)_2]^+(B_3H_8)^-$. The ion $[H_2B(NH_3)_2]^+$ can be considered as a valid coordination compound of boron(III) with H^- and NH_3 as ligands. When ethylenediamine is allowed to react with diborane, two types of product are obtained. One, reported by Kelly and co-workers [21] is $\overset{HHHH}{\underset{HHHH}{H_3BNCCNBH_3}}$. The other form is obtained from the reaction carried out at −40°C and below. At temperatures above −40°C, this ionic compound converts to the covalent form described by Kelly. The low stability of the ionic form is related to the BH_4^- anion. Ethylene diamine reacts with B_4H_{10} to give the ionic form with the $B_3H_8^-$ anion. This species is stable at room temperature [22]. The ligand $B_2H_4 \cdot 2P(CH_3)$ can be compared to ethylene diamine, i.e.



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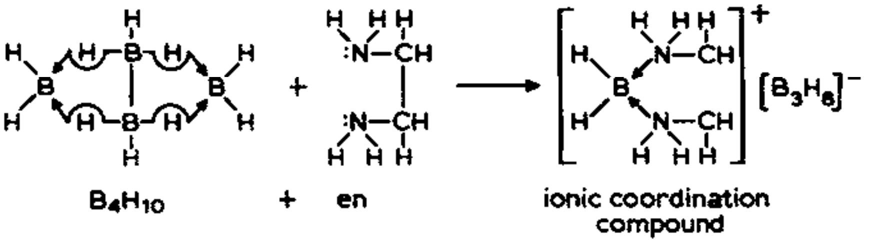

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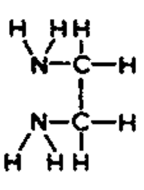
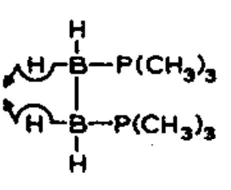




It reacts with B_4H_{10} in a strictly comparable fashion [23]. The structure of the cation as determined by Shimoi and Kodama [24] from X-ray diffraction data is seen in Fig. 4. The bis-*trimethylamine* B_2H_4 also reacts with tetraborane in a comparable fashion [18]. The data are quite clear; the neutral $B_2H_4 \cdot 2$Base adducts are reacting with borane in a manner comparable with the bidentate ethylenediamine.

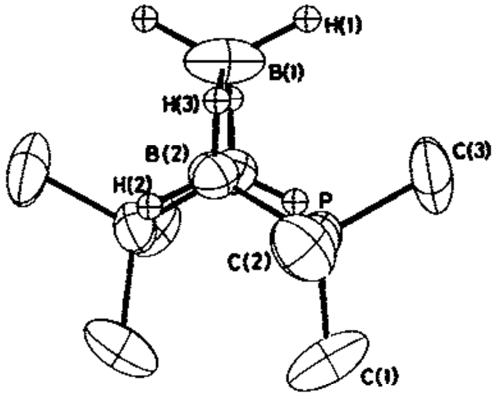
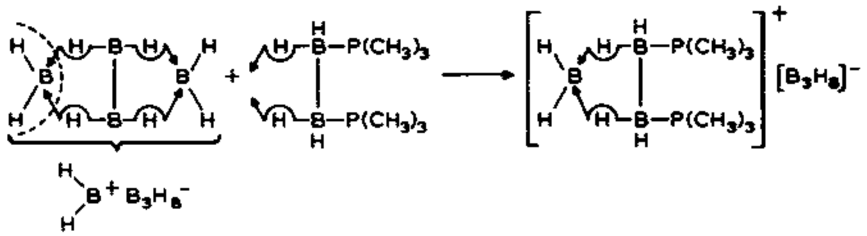


Fig. 4. The ORTEP plot of the structure of $[B_3H_6 \cdot 2P(CH_3)_3]^+$ cation (facing B–B axis) [24].



(7)

3. METAL COMPLEXES CONTAINING $B_2H_4 \cdot 2P(CH_3)_3$ AS A LIGAND

3.1 *Reactions of zinc(II) chloride with $B_2H_4 \cdot 2P(CH_3)_3$*

The suggested extension of the definition of a coordinate bond to include the three-center $\mathrm{B{\frown}H{\rightarrow}M}$ bond as an analogue of the two-center E→M coordinate bond suggests that neutral $B_2H_4 \cdot 2P(CH_3)_3$ should coordinate with metal salts. That expectation has been realized. Bis(trimethylphosphine)-diborane (eqn. (4)) quantitatively reacts at 25°C with zinc(II) chloride to give $ZnCl_2[B_2H_4 \cdot 2P(CH_3)_3]$ [25]. The structure of the complex shown in Fig. 5 shows clearly that Zn(II) has two coordinated chlorines and two $\mathrm{B\overset{H}{\frown}Zn}$ bonds. The new *neutral* ligand is bidentate as expected and may be compared with the *anionic* $B_3H_8^-$, which is known to bond in a bidentate manner to copper(I).

The $ZnCl_2[B_2H_4 \cdot 2P(CH_3)_3]$ is a stable solid in an inert atmosphere up to temperatures over 150°C. The $[B_2H_4 \cdot 2P(CH_3)_3]$ can be displaced from the $ZnCl_2$ by excess $P(CH_3)_3$. When $ZnCl_2$ and $[B_2H_4 \cdot 2P(CH_3)_3]$ were mixed in diethyl ether at −40°C, the complex precipitated as a white solid. The solid could be purified by recrystallization from its CH_2Cl_2 solution. If the $ZnCl_2$ complex in CH_2Cl_2 was treated with anhydrous HCl, the B–B bond of the ligand was ruptured to give $(CH_3)_3PBH_3$ and $(CH_3)_3PBH_2Cl$. The complex was thus decomposed. It was noted

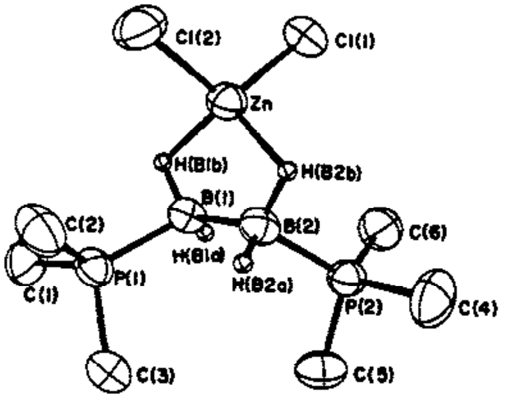
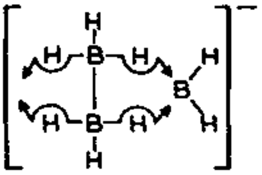


Fig. 5. The ORTEP plot of the molecular structure of $ZnCl_2 \cdot B_2H_4 \cdot 2P(CH_3)_3$ [25].



that neither $(CH_3)_3PBH_3$ *nor* $(CH_3)_3PBH_2Cl$ reacted with $ZnCl_2$ under the conditions used to prepare the $B_2H_4 \cdot 2P(CH_3)_2$ complex. NMR and IR data for the $ZnCl_2$ complex are given in ref. 25.

One interesting feature was observed in the NMR. In BH_4^- complexes such as those of Cu^+, the hydrogens were fluxional (bridging and non-bridging hydrogens of BH_4^- could not be distinguished by NMR). In contrast, the $ZnCl_2 \cdot B_2H_4 \cdot 2P(CH_3)$ proton NMR spectrum showed a doublet at 0.43 ppm ($^2J_{H-P} = 4.2$ Hz) assigned to the terminal B–H [H(B1a) and H(B2a)] and a broad singlet at $\delta = 0.33$ assigned to the bridging hydrogens [H(B1a) and H(B2a)]. The spectral pattern remained unchanged from −40 to +55°C.

3.2 Reactions of $B_2H_4 \cdot P(CH_3)_2$ with copper(I) salts

As noted earlier, boron hydride *anions* such as BH_4^- and $B_3H_8^-$ coordinate to Cu(I) to give complexes containing $B\frown H \rightarrow M$ linkages. It was thus of interest to see if *neutral* $B_2H_4 \cdot 2P(CH_3)_3$ would coordinate to the Cu(I) species. Mixing of CuX ($X = Cl^-$, Br^-, I^-) in a 1:1 ratio with $B_2H_4 \cdot 2P(CH_3)_3$ at 0°C using CH_2Cl_2 as a solvent gave evidence for the complexes $CuX[B_2H_4 \cdot 2P(CH_3)_3]$. Chloride, bromide, and iodide compounds were obtained. Evaporation of the solvent gave the chloride compound as a white powder which turned violet when the compound was allowed to stand at room temperature. A CH_2Cl_2 solution of the complex decomposed in 30 min at room temperature. $(CH_3)_3PBH_3$ was identified as one product. Based on analogy with other complexes of CuI, the compounds were assigned the dimeric structure seen in Fig. 6. Addition of one mole of $P(C_6H_5)_3$ per mole of $CuX \cdot B_2H_4 \cdot 2P(CH_3)_3$ gave a $P(C_6H_5)_3$ addition complex of formula $[CuX\{P(C_6H_5)_3\}\{B_2H_4 \cdot 2P(CH_3)_3\}]$. Characterization of all complexes was by analysis, NMR, and IR [20,25]. In CH_2Cl_2 solution in the presence of an excess of the ligand, rapid exchange between free and complexed ligand was observed through the use of NMR.

In 1990, Shimoi et al. [26] reported the synthesis of CuCl and CuI complexes containing *two* $B_2H_4 \cdot 2P(CH_3)_3$ ligands per CuX unit. The yield was very near to quantitative. The structure of the colorless crystalline CuI complex was established by X-ray diffraction. The structure is shown in Fig. 7. The crystal is composed of $[Cu\{B_2H_4 \cdot 2P(CH_3)_3\}_2]^+$ cations and I^- anions (Fig. 8). It is interesting that only hydrogens form the primary tetrahedral coordination sphere around Cu(I). These bridging H atoms deviate only slightly from planes defined by the two B atoms and

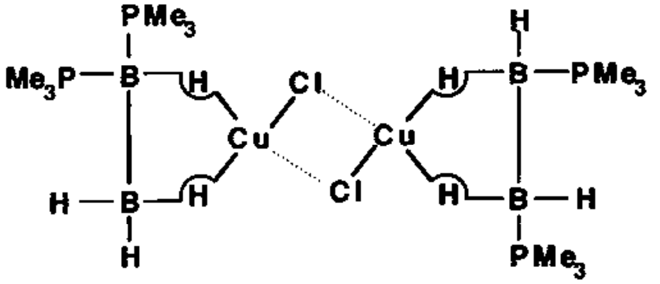


Fig. 6. The proposed solid state structure of $CuCl \cdot B_2H_4 \cdot 2P(CH_3)_3$ [20].

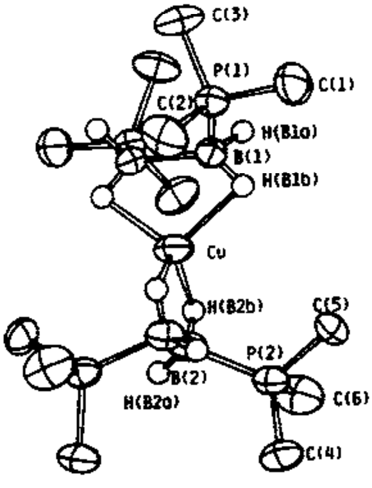


Fig. 7. ORTEP diagram of $[Cu\{B_2H_4 \cdot 2P(CH_3)_3\}_2]^+$ [26].

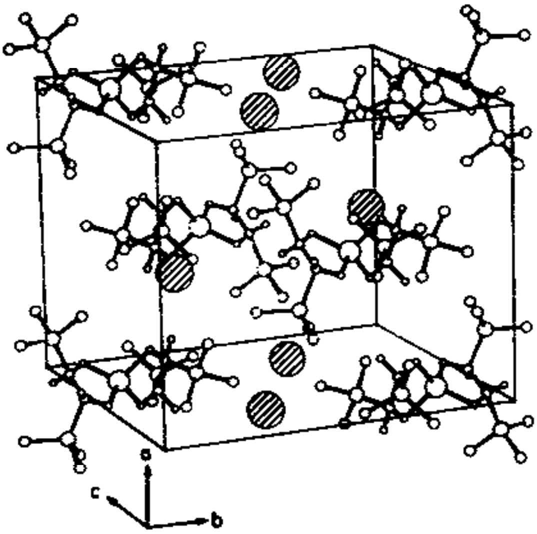


Fig. 8. Packing diagram for $[Cu\{B_2H_4 \cdot 2P(CH_3)_3\}_2]I$. Iodine atoms are hatched [26].

the Cu atom. On the basis of limited observations, the neutral borane ligand seems to give a somewhat less stable coordination compound than a related anionic ligand.

3.3 Reactions of $B_2H_4 \cdot 2P(CH_3)_3$ *with nickel carbonyl. The compound* $[(OC)_2Ni\{B_2H_4 \cdot 2P(CH_3)_2\}]$

A more severe test of the isolobal bonding concepts involving the ligand $B_2H_4 \cdot 2P(CH_3)_2$ would be its linkage to a metal (0) atom in a metal carbonyl. Such bonding does indeed occur [27]. The reaction of $Ni(CO)_4$ and $B_2H_4 \cdot 2P(CH_3)_3$ in dichloromethane at room temperature proceeds as shown by the equation:

$$Ni(CO)_4 + B_2H_4 \cdot 2P(CH_3)_3 \xrightleftharpoons[25°C]{CH_2Cl_2} [\{Ni(CO)_2\}_2\{B_2H_4 \cdot 2P(CH_3)_3\}] + 2CO \qquad (8)$$

Carbon monoxide had to be removed from the system as it was produced until the reaction was about 85% complete. The $[Ni(CO)_2\{B_2H_4 \cdot 2P(CH_3)_3\}]$ product could be isolated by adding pentane to the cold, concentrated toluene solution. It was a *green* solid. Attempts to displace all CO molecules around the Ni by pumping out CO to obtain $Ni[B_2H_4 \cdot 2P(CH_3)_3]_2$ were unsuccessful. Some metallic Ni was obtained. The compound was characterized by NMR, IR, and mass spectroscopy. The $B_2H_4 \cdot 2P(CH_3)_3$ ligand can be displaced from the complex by CO (completely at room temperature), PF_3 (complete at −80°C), rapidly by $P(C_6H_5)_3$ at −40°C, and very slowly by PH_3 at −20°C. HCl breaks the B—B bond. The infrared CO stretching frequencies (cm^{-1}) for $Ni(CO)_2(PF_3)_2$, $Ni(CO)_2[P(C_6H_5)_3]_2$, and $Ni(CO)_2(B_2H_4 \cdot 2PR_3)$ are tabulated here.

Frequency	$(CO)_2Ni(PF_3)_2$	$(CO)_2Ni[P(C_6H_5)_3]_2$	$(CO)_2Ni[B_2H_4 \cdot 2P(CH_3)_3]$
A_1	2094	2005	1993
B_2	2052	1950	1909

Commonly used arguments [28] indicate that a ligand which is a poor electron donor (i.e. a π acceptor such as PF_3 bound to a metal) should reduce the ability of the *metal* to donate electrons to the antibonding CO orbital of the coordinated CO, thus the antibonding orbital is less populated and the CO frequency should approach that of free CO. On the other hand, a sigma donor ligand such as the ligand $B_2H_4 \cdot 2P(CH_3)_3$ (i.e. through $\mathrm{B}\!-\!\underset{\smile}{\mathrm{H}}\!\rightarrow\!\mathrm{M}$ linkage) should increase electron density on the metal. Thus, it should increase the electron population available for π bonding from metal d orbitals into the antibonding orbitals of the CO. As a consequence, the CO frequency should fall. The observations shown above are consistent with that argument. In fact π-bonding to the H-bridge bond would seem to be quite unrealistic. Weak σ-bonding would be expected, and the conventional infrared arguments for the compounds are consistent with that postulate.

4. PHOTOCHEMICAL SYNTHESIS OF COMPOUNDS CONTAINING THE $\mathrm{B}\!-\!\underset{\smile}{\mathrm{H}}\!\rightarrow\!\mathrm{M}$ BOND

In a very recent series of excellent papers, Shimoi and his co-workers in Japan have described the use of photochemical techniques to synthesize complexes of bidentate $B_2H_4 \cdot 2P(CH_3)_3$ and even monodentate $H_3BP(CH_3)$ from hexacarbonyls of chromium, molybdenum, and tungsten. Of particular interest in this work is the fact that the non-chelating ligands $H_3BP(CH_3)_3$ and $H_3BN(CH_3)_3$ displaced CO to give complexes. These molecules did *not* coordinate in earlier studies with Zn(II) and Cu(I) compounds.

4.1 Photochemical reactions of [$B_2H_4 \cdot 2P(CH_3)_3$] with metal hexacarbonyls of Cr, Mo, and W

Shimoi et al. [29] used a mercury vapor UV lamp to irradiate a 1:1 mole mixture of $B_2H_4 \cdot 2P(CH_3)_3$ and $M(CO)_6$ where M was Cr, Mo, or W. Toluene was the solvent. After 90 min of irradiation, work-up of the mixture containing $Cr(CO)_6$ yielded yellow crystals of $Cr(CO)_5[B_2H_4 \cdot 2P(CH_3)_3]$ (yield 24%) and yellow crystals of $Cr(CO)_4[B_2H_4 \cdot 2P(CH_3)_3]$ (yield 64%). The structure of $Cr(CO)_5[B_2H_4 \cdot 2P(CH_3)_3]$ is shown in Fig. 9; that of $Cr(CO)_4[B_2H_4 \cdot 2P(CH_3)_3]$ is shown in Fig. 10. The former contains monodentate $B_2H_4 \cdot 2P(CH_3)_3$. The molybdenum complex $Mo(CO)_5[B_2H_4 \cdot 2P(CH_3)_3]$ could not be isolated, but its transient existence in the system was confirmed by ^1H NMR spectroscopy. Tungsten hexacarbonyl, like $Cr(CO)_6$, gave both the monodentate and bidentate addition compounds. Structures of both were determined by X-ray diffraction. The chelated structures, $M(CO)_4[B_2H_4 \cdot 2P(CH_3)_3]$, are stable to air *in the solid state*, but solutions oxidize

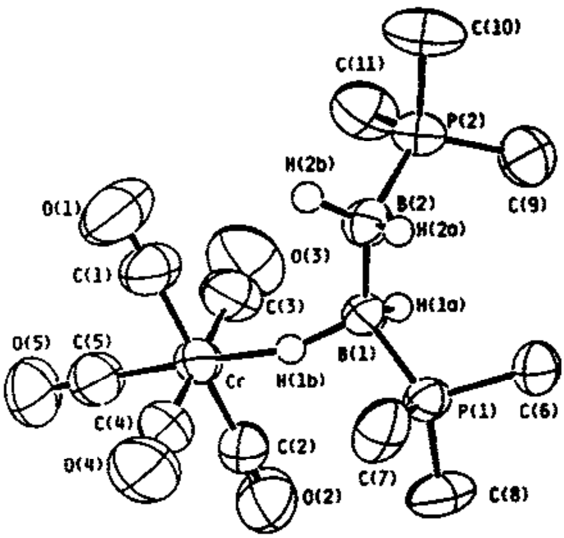


Fig. 9. ORTEP diagram of [Cr(CO)$_5${B$_2$H$_4$·2P(CH$_3$)$_3$}] [29(b)].

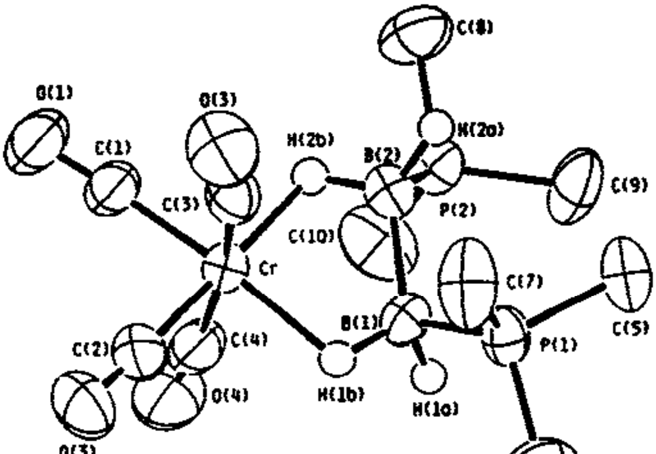


Fig. 10. ORTEP diagram of [Cr(CO)$_4${B$_2$H$_4$·2P(CH$_3$)$_3$}]. [29(b)].

readily in air at 25°C. Solutions in THF or CH_3CN were stable in the absence of air. The monodentate complexes, M(CO)$_5$[B$_2$H$_4$·2P(CH$_3$)$_3$], are, as expected, much less stable than the chelated molecules. For example, the *solid* monodentate species oxidizes slowly in air. In both THF and CH_3CH solutions, the molecule [B$_2$H$_4$·2P(CH$_3$)$_3$] is displaced by the solvent. These weakly bound sigma bonding ligands are excellent leaving groups for metal (0) species.

4.2 Reaction of non-chelating $H_3BP(CH_3)_3$ and $H_3BN(CH_3)_3$ with metal hexacarbonyls

Recall that, when $ZnCl_2$ was treated with $B_2H_4 \cdot 2P(CH_3)_3$, a chelated $ZnCl_2$ complex was produced. On the other hand, when $ZnCl_2$ was treated with $H_3BP(CH_3)_3$ under comparable conditions, no complex was detected. The extra stability conferred by chelation was important.

When $M(CO)_6$ molecules were irradiated with $B_2H_4 \cdot 2P(CH_3)_3$, fairly stable chelated and relatively unstable non-chelated substituted carbonyls were obtained. The fact that relatively unstable monodentate carbonyl of $B_2H_4 \cdot 2PR_3$ could be isolated, raised again the question that H_3BPR_3 might serve as a ligand to generate a relatively unstable complex. Shimoi et al. [30] irradiated a mixture of $M(CO)_6$, where M = Cr or W, and H_3BPR_3 in toluene for 120 min using a UV lamp. Processing the reaction mixture *at −20°C* gave a yield of crude $[M(CO)_5H_3BP(CH_3)_3]$, M = Cr or W. Recrystallization from pentane at low temperature gave the pure product (work-up at 25°C gave an intractable mess). The corresponding Mo complex could not be isolated but evidence for its formation in solution was reported. The structure of $[W(CO)_5H_3BP(CH_3)_3]$ is shown in Fig. 11*.

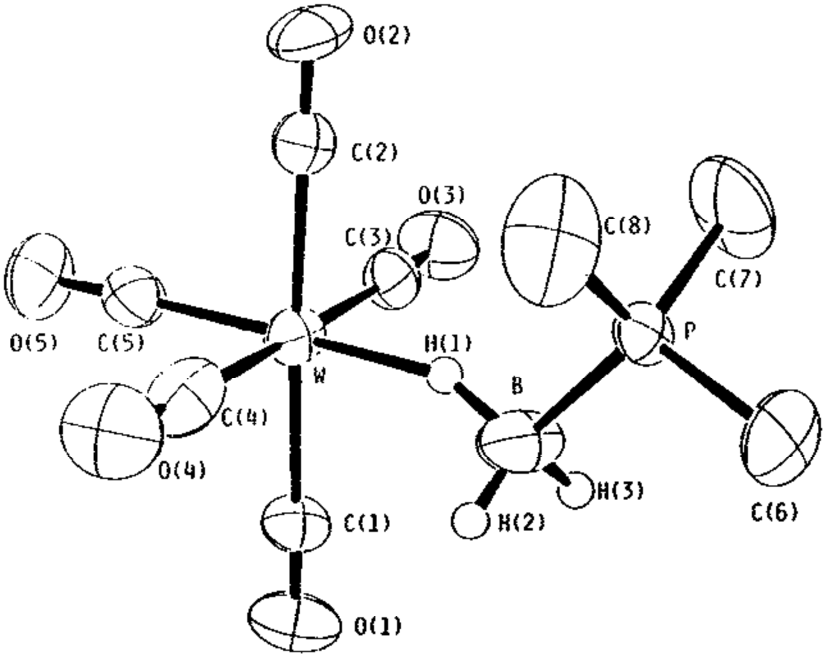


Fig. 11. ORTEP diagram of $[W(CO)_5\{BH_3 \cdot P(CH_3)_3\}]$ [30].

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* The coordination of H_3BPR_3 as a unidentate ligand using an $M-\underset{\smile}{M}\rightarrow B$ linkage is formally analogous in some respects to the unidentate-σ-coordination of an ethane molecule. Such sigma complexes of alkanes have been suggested as intermediates in C–H activation processes.

The coordination of $H_3BP(CH_3)_3$ is clearly unidentate. As expected, these complexes are clearly less stable than their chelate analogue formed from $B_2H_4 \cdot 2P(CH_3)_3$. All attempts to replace two CO molecules in $M(CO)_6$ with two $H_3BP(CH_3)_3$ molecules were unsuccessful.

The authors [30] noted in passing that $M(CO)_5H_3B \cdot P(C_6H_5)_3$ and $M(CO)_5H_3BN(CH_3)_3$ were also obtained using their procedures, but detailed information on the compounds was not provided. Basic arguments suggest that these compounds should be less stable than those of $H_3BP(CH_3)_3$.

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