NIDO-METALLOBORANES

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ABSTRACT
New developments in the area of *nido*-metalloboranes are reviewed with special emphasis on scope and structural aspects. New types of *nido*-metalloboranes described include those based on π-borallyl ($B_3H_7^{2-}$), π-$B_5H_5^{2-}$ and π-$B_9H_9^{2-}$ ligands and on the bidentate $B_9SH_{10}^-$, $B_{10}H_{12}^{2-}$ and $B_8H_{12}^{2-}$ ligands.
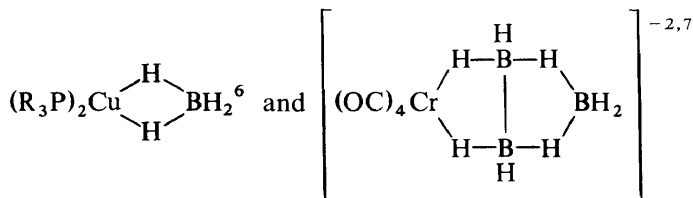
INTRODUCTION
The now-extensive class of metalloboranes[1] comprising complexes of metals and hydridoboron ligands may be differentiated by the structural character of the metal–borane interaction[2]. The structural subclasses are described as follows.

(1) *Closo*-metalloboranes
The metal nucleus in conjunction with a group of boron nuclei alone, or a group of boron and heteronuclei, describe the vertices of a polyhedron. Generally the polyhedron has all faces triangular[1]. Examples are the FeB_9C_2 icosahedron in π-$C_5H_5FeB_9C_2H_{11}$[3], the CoB_7C_2*sym*-bicapped square antiprism in $Co(B_7C_2H_9)_2^{-4}$ and the MnB_6C_2*sym*-tricapped trigonal prism in $Mn(B_6C_2H_8)(CO)_3^{-5}$.

(2) μ-H-*nido*-metalloboranes
This subclass comprises complexes of borohydride ions and metal nuclei with hydrogen bridge bonding between the metal and the boron nuclei. Examples are the complexes

$$(R_3P)_2Cu\overset{\displaystyle H}{\underset{\displaystyle H}{\diagdown\diagup}}BH_2^{\,6} \quad \text{and} \quad \left[(OC)_4Cr\begin{array}{c}H\\H{-}B{-}H\\\diagup \quad | \quad \diagdown\\ \quad | \quad BH_2\\\diagdown \quad | \quad \diagup\\H{-}B{-}H\\H\end{array}\right]^{-2,7}$$

The literature on this subclass has been reviewed recently[8]. This structural subclass extends to the limit represented by discrete ions as in $M^+BH_4^-$, $M^+B_9H_{12}S^-$, $M^+B_{10}H_{13}^-$, $M^+B_{11}H_{14}^-$, etc[2,9]. For example, for many

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metalloboranes, the M–H–B interaction is rather weak in solution as found for $(R_3P)_3CuB_9H_{14}$ and $(R_3P)_3CuB_9H_{12}S$ [9].

(3) *Nido*-metalloboranes

The metal–boron interaction is analogous to subclass (1) in that M—B bonding (two or multicentre in character) prevails. However, this subclass is distinguished by a collection of metal and boron nuclei that represent a *fragment* of a polyhedron. The 'parent' polyhedron is as defined in *closo*-metalloboranes. One or more nuclei, typically carbon or sulphur, may substitute for boron nuclei in the skeletal framework. There is, of course, the possibility of hybrid structures containing elements characteristic of classes (2) and (3). The last subclass, the *nido*-metalloboranes, is the subject of this discussion. Synthesis, structure, bonding and chemistry of established members of this subclass are reviewed[2, 9, 10–14]. The attempt to demonstrate the scope of chemistry will be explicit. Accordingly, structural and synthetic facets of new areas of *nido*-metalloboranes will be explored. Basic organization is on x-atom families where x represents the number of boron nuclei† in the polyhedral fragment.

ONE-ATOM FAMILY (BORANE)

Borane, a modestly strong electron acceptor, interacts with transition metal complexes that have nucleophilic metal sites to yield $\diagdown M$—BH_3 derivatives[10]. Crystalline complexes have been obtained simply by diborane addition to ethereal solutions of metal carbonyl anions:

$$M^+Re(CO)_5^- + R_2OBH_3 \rightarrow M^+H_3BRe(CO)_5^- + R_2O$$
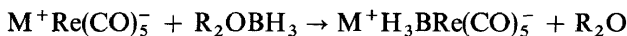
Reactivity of these simple acid–base adducts is modestly high. Hydrolysis in water is fast. In ether solutions, the coordinated BH_3 serves as a mild reducing moiety, e.g. reduction of quinones at $25°C$. This type of interaction, i.e. a single two-centre two-electron M—B bond, should be found in higher atom families, e.g. $L_2NiB_9H_{13}$ and $B_{10}H_{12}[Mn(CO)_5]_2$.
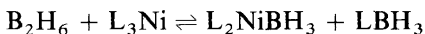
TWO-ATOM FAMILY

Diborane is formally analogous to ethylene in a structural and electronic sense although the $B\diagdown^{H}\diagup B$ unit is the literal distinguishing feature. Nevertheless, as pointed out by Hoffmann[15], the molecular orbitals of B_2H_6 resemble those of ethylene in symmetry and number of nodes; and accordingly there is the possibility of an 'ethylene' type π-complex between a transition metal and diborane provided the energy of the antibonding molecular orbital in diborane is not too high. Possibilities are

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† or of boron atoms plus heteroatoms.

$Ag(\pi\text{-}B_2H_6)^+PF_6^-$ and $[(RO)_3P]_2Ni(\pi\text{-}B_2H_6)$. The reported $(H_3B)_2Re(CO)_5^-$ complex[10] is perhaps the exemplary $\pi\text{-}B_2H_6$ complex, a structural possibility not originally considered[10]. We are examining these possibilities in collaboration with Professor F. Scholer at Cornell University. Anticipated equilibria are:

$$B_2H_6 + L_3Ni \rightleftharpoons L_2NiBH_3 + LBH_3$$

$$[BH]_3 + L_2NiBH_3 \rightleftharpoons L_2Ni(B_2H_6)$$

Hence elevated diborane pressures may be necessary for successful demonstration of this type of *nido*-metalloborane.

THREE-ATOM FAMILY

The $B_3H_8^-$ ion forms metalloboranes of subclass form (2). We have however succeeded in forming derivatives of the $B_3H_7^{2-}$ ion which is a special type of *nido*-metalloborane[13]. Reaction of bis-(trialkyl- or triaryl)phosphinoplatinum dichlorides with CsB_3H_8 in the presence of trialkylamines gives the bis-phosphinoplatinum derivatives of $B_3H_7^{2-}$:

$$(R_3P)_2PtCl_2 + CsB_3H_8 + NR_3 \rightarrow (R_3P)_2PtB_3H_7 + CsCl + R_3NHCl$$
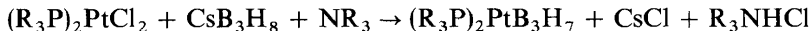
Because of the relatively unusual infra-red and n.m.r. spectral characteristics of the $B_3H_7^{2-}$ complexes and because of the isoelectronic relation between $B_3H_7^{2-}$ and $C_3H_5^-$, a π-allyl type of bonding and structure was proposed[13a] for this metalloborane (*Figure 1*).
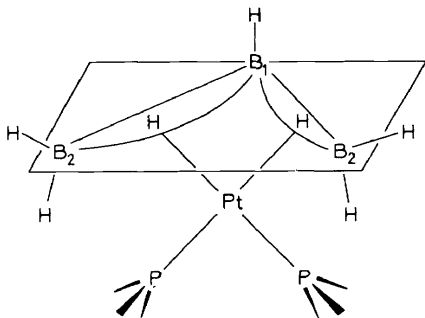

Figure 1. Idealized representation of the $\pi\text{-}B_3H_7Pt(R_3P)_2$ structure assuming a symmetrical interaction of the triborallyl ligand with the square planar platinum orbitals. x-Ray studies[13b] show that the interaction is not symmetrical. The B_3 system is skewed such that one of the platinum orbitals is pointed almost directly to one of the B_2 boron atoms and to the midpoint of the other B_2B_1 bond. The Pt—B_2 bond distance for the former interaction is 2.12 Å, while the nuclear separations between platinum and the other terminal (B_2) boron atom is 2.36 Å. The Pt—B_1 separation is 2.17 Å. The dihedral angle between the B_3 plane and the Pt—P_2 plane is about 115 degrees

Preliminary x-ray studies confirm this postulate[13b]. There is no bonding interaction between the B_2 nuclei (the $B_2B_1B_2$ angle is $\sim$116 degrees) as obtains in $B_3H_8^-$ and in metal complexes of $B_3H_8^-$. There is a skewing of the B_3 ligand, presumably due to the large B_1—B_2 distances ($\sim$1.8 Å versus

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~ 1.4 Å in π-C_3H_5 complexes). This skewing may yield a better bonding arrangement with a slightly larger σ Pt—B_2 overlap at one end and a slightly

larger π Pt—$\overset{\displaystyle B_1}{\underset{\displaystyle B_2}{|}}$ overlap at the other; this postulate is consistent with the two

Pt—B_2 distances of 2.12 and 2.36 Å [13b]. All hydrogens have not been located. We suspect that the two unique 'bridge' hydrogens project out of the B_3 plane *toward* the metal atom and these experience a paramagnetic shift in the n.m.r. experiment. This would account for the unusually high field†⋅ resonance for two BH hydrogen atoms[13]. The high stereochemical[13] rigidity of the $B_3H_7^{2-}$ complex—relative to $B_3H_8^-$ and its derivatives—is explicable for a π-allyl type of structure.

The π-borallyl ligand is displaced from these complexes by excess phosphine to give $(R_3P)_4Pt$ as is found for the analogous π-allylplatinum phosphine complexes[16]. Hydrolytic stability of the π-borallylplatinum complexes is markedly higher than for the $B_3H_8^-$ ion and its metal derivatives[13].

FOUR-ATOM FAMILY

No four-atom *nido*-metalloboranes have been reported. One possibility based on the $B_4H_8^{2-}$ ion is shown in *Figure 2*. This B_4 ligand would be

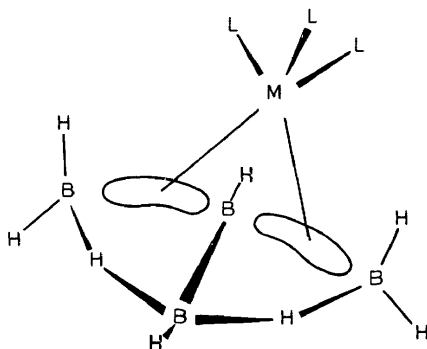*Figure 2*. Idealized representation of a possible metalloborane based on the $B_4H_8^{2-}$ ion. For the speculative metalloborane system the ML_3 fragment could represent $Fe[P(C_6H_5)_3]_3^{2+}$

analogous to the formally bidentate $B_{10}H_{12}^{2-}$, $B_9H_{10}S^-$ and $B_8H_{12}^{2-}$ ligands in metalloborane chemistry. The latter sets are described in following sections.

A possible synthetic route to a $B_4H_8^{2-}$ derivative would be from pentaborane(11):

$$B_5H_{11} + HClFeL_4 + L \rightarrow H_2BL_2^+ + Cl^- + H_2 + B_4H_8FeL_3$$

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† $+4.9$ ppm as compared with -1.1 to -0.11 ppm for terminal BH hydrogen atoms (tetramethylsilane reference)[13].

FIVE-ATOM FAMILY

The $B_5H_8^-$ ion has been obtained from pentaborane(9) and alkyllithium reagents[17, 18]. Spectral and chemical data establish a pentaborane(9) type skeleton for the ion with three bridging hydrogen atoms about three of the four basal edges[19]. Stereochemical nonrigidity is evident; basal boron atom equivalence on the n.m.r. time-scale suggests rapid bridge–terminal hydrogen positional exchange in the basal part of the framework (*Figure 3*)[17–19]:
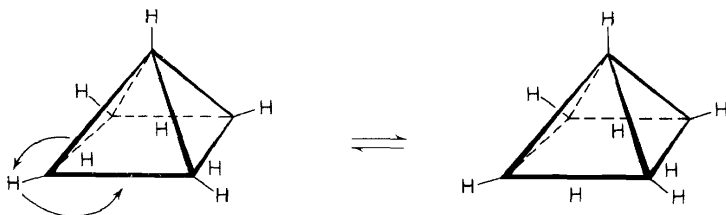

*Figure 3.* Presumed mechanism for hydrogen atom positional exchange in the $B_5H_8^-$ ion

Metal and metal-bonded derivatives of $B_5H_8^-$ have been prepared; these are of the type μ-$R_3MB_5H_8$ with M = Si, Ge, Sn and Pb[20, 21]. These

$M{\overset{\diagup B}{\underset{\diagdown B}{|}}}$ isomers rearrange with a base catalyst to 2-$R_3MB_5H_8$, the isomer

with M terminally bonded to a basal boron atom[22].

A long-term objective of our work in the five-atom family is to prepare a metal derivative of the C_{4v} $B_5H_5^{2-}$ ion. Electronically, this dianion is analogous to cyclobutadiene. Degeneracy will be removed in a *closo*-metalloborane with the square face π-bonded to a metal nucleus. We have obtained complexes analytically and spectrally consistent with a π-bonded $B_5H_5^{2-}$ ion but the reactions have been complex and variable in character as in the reaction:

$$LiB_5H_8 + HMn(CO)_5 \overset{\Delta}{\rightarrow} 2H_2 + 2CO + Li^+(B_5H_5)Mn(CO)_3^- \quad \text{(low yield)}$$

An alternative synthetic approach now being explored is 'BH addition' analogous to the polyhedral borane synthesis[1b], e.g.

$$(R_3P)_2PtB_3H_7 + B_2H_6 \rightarrow (R_3P)_2PtB_5H_5 + 4H_2$$
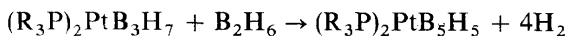
SIX-ATOM FAMILY

The $B_6H_9^-$ ion may react with metal dihalide complexes in the presence of a trialkyl amine to give bidentate complexes. Preliminary studies indicate that this approach may be successful. Extensions to reactions of $B_6H_{11}^-$ are also being examined.

SEVEN-ATOM FAMILY

No examples of *nido*-MB$_7$ skeleton are known but degradation of larger metalloborane skeletons, e.g. of $L_2PtB_8H_{12}$, or BH addition[1b] to smaller

skeletons may provide entry to $L_xMB_7B_{11}$ complexes which would be close analogues of octaborane(12).

EIGHT-ATOM FAMILY

One representative of this family is $(R_3P)_2PtB_8H_{12}$ obtained by alcohol degradation of $(R_3P)_2PtB_9H_{11}$(ligand) (see below)[11]. Structural details are not as yet uniquely defined but the probable structure is illustrated in *Figure 4*[11]. This formulation is derived from that of $(R_3P)_2PtB_9H_{11}$(ligand),
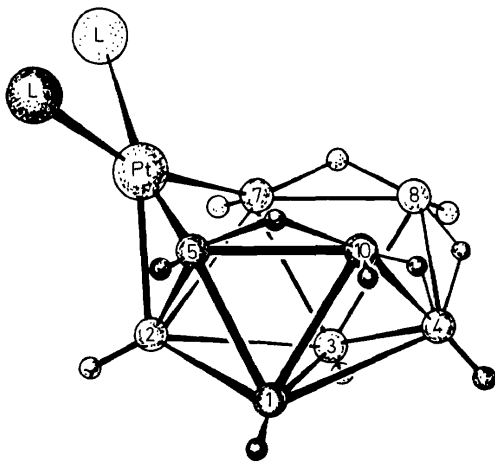
Figure 4. Proposed structure for the metalloborane, $(R_3P)_2PtB_8H_{12}$. This structural formulation is related to that illustrated in *Figure 6* by substitution of protons at the bridging positions 4,10 and 4,8 for the unit BH(ligand)$^{2+}$

see *Figure 6* below, by elision of BH(ligand)$^{2+}$ and addition of $2H^+$ at edge bridging positions. The metal atom is within bonding distance of three boron nuclei but we prefer to visualize the $B_8H_{12}^{2-}$ ligand as being bidentate. This may be visualized by lines from Pt to the midpoints of the 2,5 and 2,7 BB edges for the platinum–B_8H_{11} interaction (*Figure 4*)[11].

NINE-ATOM FAMILY

Closo-nonahydridononaborate (2 −), $B_9H_9^{2-}$, is a wholly characterized polyhedral anion[23, 24]. As shown in *Table 1*, symmetry arguments qualitatively identify the D_{3h} sym-tricapped trigonal prism as a closed shell structure. These molecular orbital calculations also show $B_9H_9^{2-}$ in C_{4v} monocapped square antiprismatic form to be doubly degenerate with the last two electrons going into an e level. This degeneracy, analogous to cyclobutadiene, should be removed in a complex formation with a transition metal moiety such as $(R_3P)_2Pt^{2+}$, $(R_3P)_2Ni^{2+}$, $(OC)_3Fe$ and $(R_3P)_2Co^+$ (see *Figure 5*). Attempts to prepare such *closo*-metalloborane complexes directly from the polyhedral $B_9H_9^{2-}$ ion have been unsuccessful. At present, u.v. activation of $B_9H_9^{2-}$,

Table 1. One electron energies for D_{3h} and C_{4v} models of $B_9H_9^{2-}$

C_{4v}		D_{3h}	
Level	Energy/eV	Level	Energy/eV
b_2	57.945	e''	59.488
b_1	57.944	a_1'	50.835
a_1	45.394	a_2''	49.717
e	42.787	e'	41.672
a_1	38.267	e'	31.490
e	35.178	e''	25.558
b_1	23.398	a_1'	23.598
b_2	23.396	e'	20.268
a_1	21.987	e'	15.088
e	21.612	a_1'	7.925
a_1	12.558	a_2'	7.444
a_1	11.278	e''	4.996
e	8.522	a_2''	4.504
a_2	7.243	a_1''	0.492
e	5.969	e''	-0.958
b_2	-0.057	e'	-2.914
b_1	-0.058	a_2''	-6.553
a_2	-0.390	a_2'	-9.355
e	-2.630	e'	-9.724
e	-8.682	e''	-10.545
e	-10.386	a_1'	-11.224
b_2	-10.920	a_2''	-12.059
b_1	-10.920	e'	-12.450
a_1	-11.136	a_1'	-13.928
e	-12.058	e''	-15.680
a_1	-12.437	a_1'	-15.843
a_1	-14.063	e'	-16.385
a_1	-15.913	a_2''	-18.327
b_2	-15.956	e'	-19.721
b_1	-15.957	a_1'	-22.987
e	-16.298		
e	-19.271		
a_1	-19.475		
a_1	-22.904		

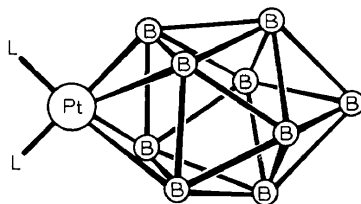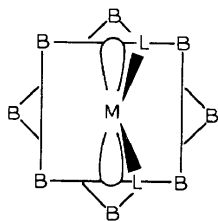Figure 5. Probable structure for a closo-metalloborane based on the C_{4v} $B_9H_9^{2-}$ ion. On the right side is a side view, structural representation, for an L_2Pt^{2+} derivative. The overall skeletal geometry approximates to that of a symmetrically bicapped square antiprism. The terminal hydrogen atoms attached to the boron nuclei are not depicted. On the left side is an alternative view of the structure proposed for this type of metalloborane.

BH addition (diborane reaction) to species like $(R_3P)_2PtB_3H_7$, and thermolysis of $(R_3P)_2PtB_9H_{11}$(ligand) are being examined as alternative synthetic routes.

Nine-atom *nido*-metalloboranes are represented by the set of $(R_3P)_2PtB_9H_{11}$(ligand) complexes which are structural analogues of the $B_{10}H_{12} \cdot 2$(ligand) complex whereby a metal atom is substituted for a 6(9) BH(ligand)$^{2+}$ unit[11]. A proposed structure, representative of this set, is
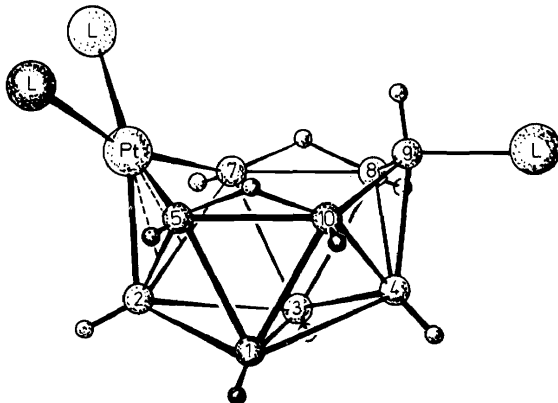

Figure 6. The proposed structure for the metalloborane $(R_3P)_2PtB_9H_{11}$(ligand). This metalloborane is presumed to be isostructural with $B_{10}H_{14}^{2-}$.

depicted in *Figure 6* and the $B_9H_{11}L^{2-}$ ligand is formally considered to be bidentate. These $B_9H_{11}L^{2-}$ complexes have been prepared in high yield from the $B_9H_{12}^-$ ion in donor solvents (L):

$$(R_3P)_2PtHCl + CsB_9H_{12} + L \rightarrow (R_3P)_2PtB_9H_{11}L + CsCl + H_2$$

$$L = R_3N, RCN, R_3P \text{ and } R_2S$$
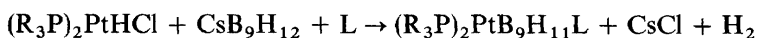
In alcohol, the nine-atom complexes degrade to the eight-atom species, $(R_3P)_2PtB_8H_{12}$, described above.

TEN-ATOM FAMILY

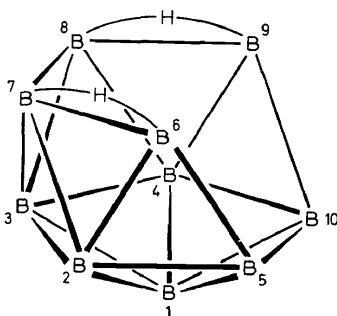*Figure 7.* A possible structure for the $B_{10}H_{12}^{2-}$ ion. The terminal hydrogen atoms are not depicted

An extensive series of *nido*-metalloboranes exists in which ten boron atoms and one metal atom yield an eleven-atom icosahedral fragment[25]. In these the $B_{10}H_{12}^{2-}$ ion effectively functions as a bidentate ligand (*Figure 7*) as illustrated for tetrahedral and square planar metal complexes in *Figures 8*
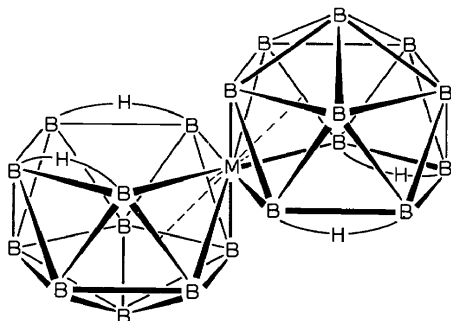
Figure 8. The heavy atom structure proposed for the square planar transition metal complex, $M(B_{10}H_{12})_2^{2-}$. The dotted lines directed from the metal nucleus to the edge midpoints of the two B_{10} frameworks are used to illustrate the presumed, formally square planar interaction
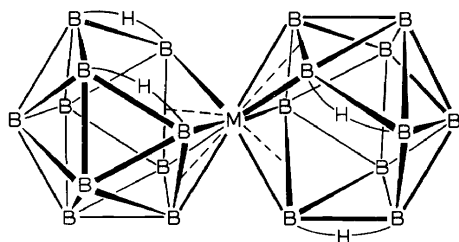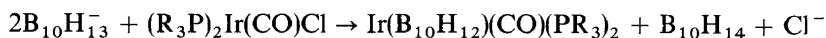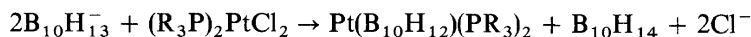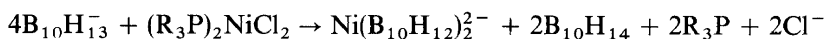
Figure 9. The heavy atom structure proposed for the tetrahedral transition metal complex, $M(B_{10}H_{12})_2^{2-}$. The dotted lines from the central metal atom to the edge midpoints of the two boron polyhedra illustrate the presumed tetrahedral interaction

and 9[25]. The structural details for the nickel and zinc complexes are explicable only if the $B_{10}H_{12}^{2-}$ ligand is formally considered to be bidentate (see *Figures 7–10*). The structure of the square planar nickel complex, $Ni(B_{10}H_{12})_2^{2-}$, has been established by x-ray analysis[26] (*Figure 10*).

Syntheses of the $B_{10}H_{12}^{2-}$ complexes are partially outlined in the equations below[25]:

$$4B_{10}H_{13}^- + (R_3P)_2NiCl_2 \rightarrow Ni(B_{10}H_{12})_2^{2-} + 2B_{10}H_{14} + 2R_3P + 2Cl^-$$

$$2B_{10}H_{13}^- + (R_3P)_2PtCl_2 \rightarrow Pt(B_{10}H_{12})(PR_3)_2 + B_{10}H_{14} + 2Cl^-$$

$$2B_{10}H_{13}^- + (R_3P)_2Ir(CO)Cl \rightarrow Ir(B_{10}H_{12})(CO)(PR_3)_2 + B_{10}H_{14} + Cl^-$$

$$4B_{10}H_{13}^- + Pt(diene)Cl_2 \rightarrow Pt(B_{10}H_{12})_2^{2-} + 2B_{10}H_{14} + diene + 2Cl^-$$

Chemical reactivity of these metalloboranes is sensitive to the nature of the metal nucleus and its ancillary ligands, if any[26]. The nickel complex is stable
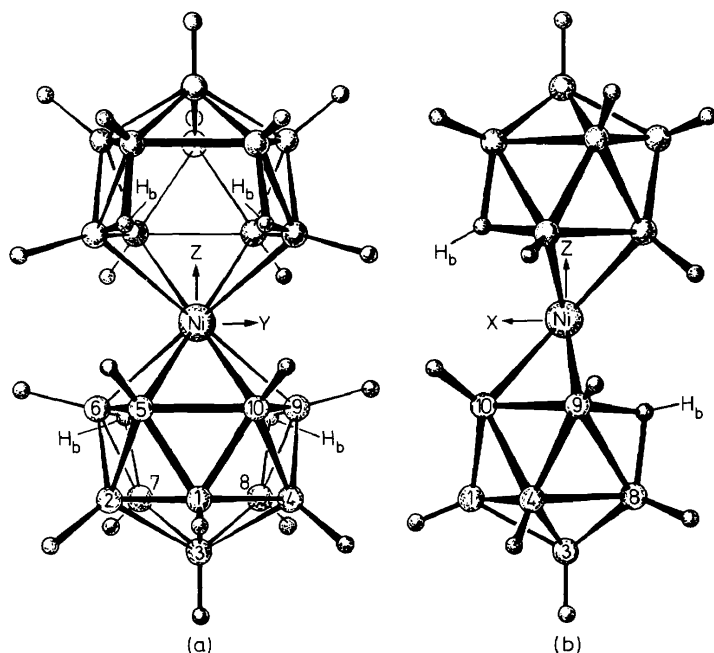
(a)   (b)

Figure 10. The front and side view of the $Ni(B_{10}H_{12})_2^{2-}$ structure established from the crystal structure determination of the tetramethylammonium salt[26]

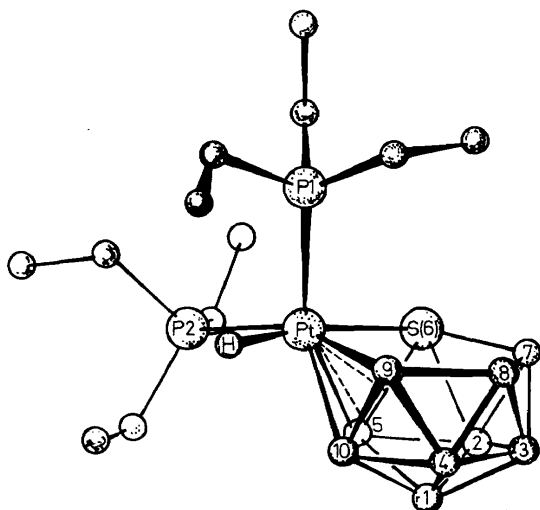*Figure 11.* The established structure for the metalloborane, $[(C_2H_5)_3P]_2Pt(H)B_9H_{10}S$. Each of the nine boron atoms in this metalloborane has a terminal ·hydrogen atom which is not depicted. The extra boron-hydrogen also not shown is probably associated with one or more atoms in the open face of the icosahedral fragment. The carbon–hydrogen atoms associated with the ·phosphine ligands are not shown in the drawing

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in air and water but is degraded by aqueous base. All other $B_{10}H_{12}^{2-}$ metallo-boranes prepared to date appear less stable than the nickel complex.

There should be many analogues of the $B_{10}H_{12}^{2-}$ metalloboranes. One analogue, based on a B_9S–metal framework, is $(R_3P)_2PtB_9H_{10}S(H)$. The $B_9SH_{10}^-$ ion is isoelectronic with $B_{10}H_{12}^{2-}$ and this formalism is borne out by the x-ray structural study. The platinum atom is bonded to two phosphorus atoms (from the phosphine ligands) and to a hydrogen atom. The remainder of the platinum coordination sphere is completed by close approach of three boron atoms and one sulphur atom of the $B_9SH_{10}^-$ ligand (*Figure 8*). By analogy, $B_9SH_{10}^-$ is considered as a bidentate ligand as shown schematically in *Figure 11*.

COINAGE METAL METALLOBORANES

The interactions of phosphino–copper, –silver and –gold(I) cations (L_xM^+) with the borane anions $B_3H_8^-$, $B_9H_{14}^-$, $B_9H_{12}S^-$, $B_{10}H_{13}^-$, $B_{10}H_{15}^-$ and $B_{11}H_{14}^-$ traverse the forms of M—H—B, M—B and M—B_x interactions to $M^+B_xH_y^-$ tight ion pairs. This area of metalloboranes has been comprehensively surveyed in an earlier paper[9].

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