METALLOBORANES 1983

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Abstract - The various synthetic routes to metalloboranes are systematically classified and assessed. Numerous high-yield planned syntheses are available, but unsuspected side reactions leading to novel and unpredicted products still reward the adventurous experimenter. The known metalloborane cluster geometries are described: some of these parallel the familiar polyhedral shapes of the parent boranes and borane anions, but increasingly the flexibility introduced by the use of variable-valence metal centres having unusual (often high) connectivities permits the synthesis of stable metalloboranes which feature polyhedral cluster structures unknown amongst the parent boranes themselves. Some recently synthesized metallo-boranes and polymetalloboranes having unusual structures or chemical reactivity are described, and the importance of some hitherto unrecognized cluster rearrangements and isomerizations is emphasized.

INTRODUCTION

The rapidly expanding field of metalloborane compounds has been extensively documented during the past decade (refs. 1-8) and it is now appreciated that metals can confer on such clusters a flexibility of geometrical structure and chemical reactivity that far exceeds that of the parent boranes themselves. In addition to these more general reviews, several specific aspects have also received attention e.g.

(a) the stability conferred on clusters by the presence of metals (refs.5,7,8,9):

(b) structural characteristics of various types of metalloboranes (refs. 9-14);

(c) nuclear magnetic resonance properties (ref. 15);

(d) electrochemistry of metal-boron cluster compounds (ref. 16);

(e) oxidative cluster closures or fusions (refs. 5,17).

In presenting an overview of Metalloboranes 1983 it will be convenient first to summarize briefly the synthetic routes that are now available and which have been instrumental in opening up this exciting new field. Next, the various cluster geometries that have so far been established will be classified and listed in coded form. Finally, some of the recent and current work being done in the borane group at Leeds will be described with particular emphasis on the planned synthesis of polymetallo species and on the growing evidence for previously unsuspected cluster rearrangements which may occur during certain preparative reactions. The related phenomenon of metalloborane cluster isomerization which sometimes occurs under basic conditions will also be considered.

The review will be confined to those clusters that are composed solely of metal and boron atoms as vertices and which contain direct M-B connectivities. This excludes a large group of metalloboranes which are bonded only via M-H-B bonds, e.g. $[M(BH_4)_n]$, $[L_nM(BH_4)]$, $[L_nM(B_3H_8)]$ (ref. 11), $[(CO)_3Mn(B_8H_{13})]$, etc. (ref. 13), and the even larger class of metallacarbaboranes which feature clusters of general stoichiometry $M_xC_yB_z$ and which have themselves been the subject of numerous recent reviews. The reasons for this selectivity are partly pragmatic, since the total field is now so vast that any attempt to cover all aspects would be manifestly impossible in the space available. Moreover, by concentrating on "pure" metal-boron clusters that are bonded exclusively or at least predominantly by M_xB_y interactions, it becomes possible to isolate the various factors which influence the geometrical structure, thermal stability, and chemical reactivity of these compounds. For example, the concept of boron hydrides acting as ligands (ref. 18) can be considered in its strongest and most dramatic form, whereas the closely related (and somewhat earlier) concept of carbaboranes as ligands (ref. 19) though immensely fruitful in terms of synthetic strategies, owed much of its persuasive influence to the analogy of the C_2B_3 open face of the $C_2B_9H_{11}{}^{2-}$ anion with the cyclopentadienyl ligand in organometallic chemistry. Before the subsequent work on pure metal-boron clusters, the parent boron hydrides and their

anions were invariably classed as "electron-deficient compounds" which exhibited electron-acceptor properties but which were never considered as Lewis bases.

The perceptions arising from these various studies in several laboratories now indicate an essentially coherent and continuous gradation of cluster chemistry spanning the whole range from boron hydrides at one end, through metalloboranes, carbaboranes, metalla-carbaboranes and organometallic clusters, to polynuclear metal carbonyl cluster compounds and naked metal clusters at the other end.
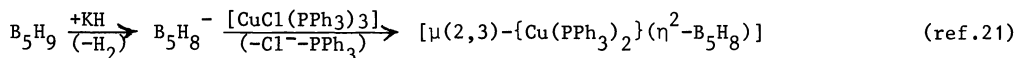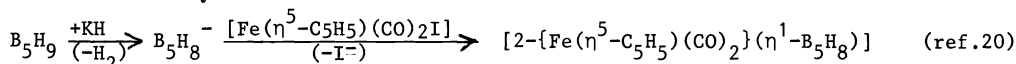
SYNTHESIS OF METALLOBORANES

No simple acceptable classification of the various routes to metalloborane clusters has yet been devised mainly because of the complexity of many of the actual syntheses reported in the literature: these often involve more than one type of reaction or are patently mechanistically complicated. In point of fact, mechanistic studies are almost entirely lacking, and most attempts at classification rely on a listing of the type of metal-containing reagent used, the type of borane substrate involved, or the observed overall result of the reaction, rather than on any detailed knowledge of the presumed mechanistic pathway followed. However, despite the embarassing lack of such theoretical underpinning and despite the acknowledged serendipidous nature of many of the most significant syntheses, a phenomenological base is now available to assist in planning the rational synthesis of many target clusters.

Undoubtedly the most general route so far devised involves *the reaction of a mononuclear metal coordination complex with a borane anion*. Simple metathesis may occur or a more complex series of reactions might ensue which may involve:
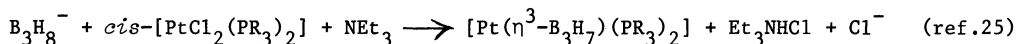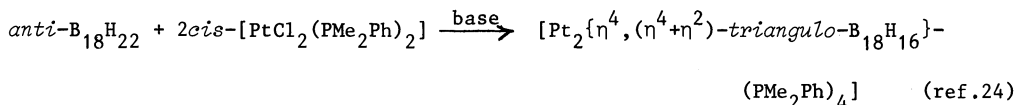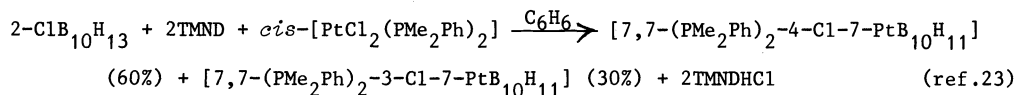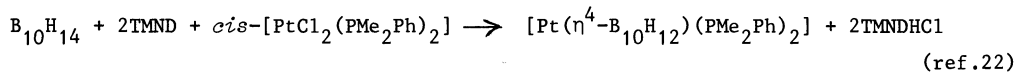
(a) polyhapto coordination of the metal centre by the borane anion with or without cluster rearrangement;

(b) oxidative insertion of the metal centre to give an expanded cluster;

(c) partial degradation of the borane anion itself, or of a metalloborane intermediate to give a product-metalloborane with fewer boron atoms in the cluster. An obvious extension is:

(d) deprotonation of a preformed metalloborane to give a metalloborane anion which can then be reacted with a further metal complex to give either a homo- or a hetero-polymetalloborane cluster.

Initial deprotonation of the borane can be effected by a metal hydride such as NaH or KH, by a metal alkyl such as LiMe, LiBu, or MEt_n, or more gently by use of N,N,N',N'-tetramethylnaphthalene-1,8-diamine (TMND, "proton sponge") which is an excellent Brønsted base (proton acceptor) but a very weak nucleophile (Lewis base) towards boron. Alternatively, the synthesis can start with a preformed borane anion such as $closo$-$B_{10}H_{10}^{2-}$, $nido$-$B_9H_{12}^-$, $arachno$-$B_9H_{14}^-$, etc. Many of these reactions occur rapidly in ethereal/CH_2Cl_2 solutions at room temperature or below, and conditions have been devised to make some of them virtually quantitative. Numerous examples are listed in the reviews cited above (especially refs. 7 and 10) and typical instances of each are given below.
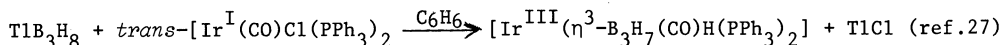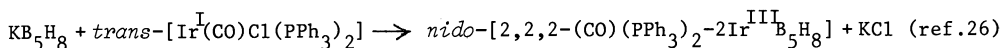
Reaction (i) Metathesis of a borane anion:

$$B_5H_9 \xrightarrow[(-H_2)]{+KH} B_5H_8^- \xrightarrow[(-I^-)]{[Fe(\eta^5-C_5H_5)(CO)_2I]} [2-\{Fe(\eta^5-C_5H_5)(CO)_2\}(\eta^1-B_5H_8)] \quad (ref.20)$$

$$B_5H_9 \xrightarrow[(-H_2)]{+KH} B_5H_8^- \xrightarrow[(-Cl^--PPh_3)]{[CuCl(PPh_3)_3]} [\mu(2,3)-\{Cu(PPh_3)_2\}(\eta^2-B_5H_8)] \quad (ref.21)$$

Reaction (ii) Polyhapto coordination with or without cluster rearrangement:

$$B_{10}H_{14} + 2TMND + cis\text{-}[PtCl_2(PMe_2Ph)_2] \longrightarrow [Pt(\eta^4-B_{10}H_{12})(PMe_2Ph)_2] + 2TMNDHCl$$
$$(ref.22)$$

$$2\text{-}ClB_{10}H_{13} + 2TMND + cis\text{-}[PtCl_2(PMe_2Ph)_2] \xrightarrow{C_6H_6} [7,7\text{-}(PMe_2Ph)_2\text{-}4\text{-}Cl\text{-}7\text{-}PtB_{10}H_{11}]$$
$$(60\%) + [7,7\text{-}(PMe_2Ph)_2\text{-}3\text{-}Cl\text{-}7\text{-}PtB_{10}H_{11}] \quad (30\%) + 2TMNDHCl \quad (ref.23)$$

$$anti\text{-}B_{18}H_{22} + 2cis\text{-}[PtCl_2(PMe_2Ph)_2] \xrightarrow{base} [Pt_2\{\eta^4,(\eta^4+\eta^2)\text{-}triangulo\text{-}B_{18}H_{16}\}\text{-}$$
$$(PMe_2Ph)_4] \quad (ref.24)$$

$$B_3H_8^- + cis\text{-}[PtCl_2(PR_3)_2] + NEt_3 \longrightarrow [Pt(\eta^3-B_3H_7)(PR_3)_2] + Et_3NHCl + Cl^- \quad (ref.25)$$

Reaction (iii) Oxidative insertion of a metal to give an expanded cluster:

$$KB_5H_8 + trans\text{-}[Ir^I(CO)Cl(PPh_3)_2] \longrightarrow nido\text{-}[2,2,2\text{-}(CO)(PPh_3)_2\text{-}2Ir^{III}B_5H_8] + KCl \text{ (ref.26)}$$

$$TlB_3H_8 + trans\text{-}[Ir^I(CO)Cl(PPh_3)_2 \xrightarrow{C_6H_6} [Ir^{III}(\eta^3\text{-}B_3H_7)(CO)H(PPh_3)_2] + TlCl \text{ (ref.27)}$$

Reaction (iv) Partial degradation of a borane anion or metalloborane intermediate:

$$B_9H_{14}^- + cis\text{-}[PtCl_2(PMe_2Ph)_2] \longrightarrow arachno\text{-}[7,7\text{-}(PMe_2Ph)_2\text{-}7\text{-}PtB_8H_{12}] \qquad \text{(ref.28)}$$

$$B_{10}H_{10}^{2-} + trans\text{-}[Ir(CO)Cl(PPh_3)_2] \xrightarrow{MeOH} \text{numerous metalloborane products}$$

containing 4-10 B atoms   (ref.29)

$$B_5H_8^- + CoCl_2 + C_5H_5^- \xrightarrow{thf} \text{numerous metalloborane products containing 3, 4, or}$$

9 B atoms   (ref.30)
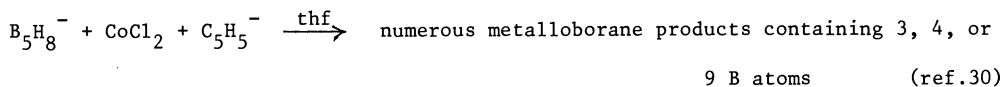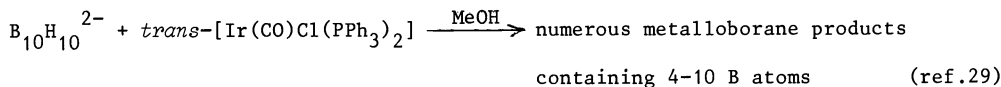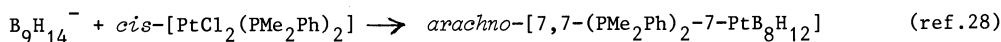
Reaction (v) Deprotonation of a metalloborane plus further metallation:

$$[Pt(\eta^3\text{-}B_8H_{12})(PMe_2Ph)_2] + cis\text{-}[PtCl_2(PMe_2Ph)_2] \xrightarrow{2KH} arachno\text{-}[6,6,9,9\text{-}(PMe_2Ph)_4\text{-}$$

$$6,9\text{-}Pt_2B_8H_{10}] \qquad \text{(ref.28)}$$

$$nido\text{-}[4,4,4\text{-}(PPh_3)_2(CO)\text{-}4\text{-}OsB_5H_9] + cis\text{-}[PtCl_2(PMe_2Ph)_2] \xrightarrow{2NaH} nido\text{-}[2,2,2\text{-}(PPh_3)_2$$

$$(CO)\text{-}7,7\text{-}(PMe_2Ph)Cl\text{-}\mu(2,7)\text{-}H\text{-}2,7\text{-}OsPtB_5H_7] \qquad \text{(refs.31,32)}$$
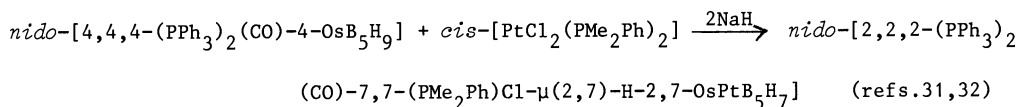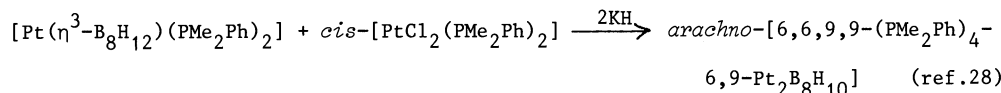
Another set of synthetic routes to metalloboranes involves *the direct reaction of a neutral borane with various reagents.* Though sometimes specific and of high yield, such reactions may also be complex and obscure, with several products often in low yield. The borane can act as (a) a simple ligand (i.e. electron-pair donor or Lewis base); (b) a proton donor (Brønsted acid); (c) an oxidizing agent; or (d) a source of borane cluster fragments. Thus,
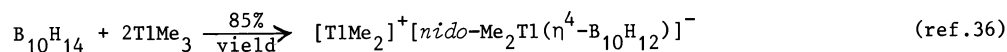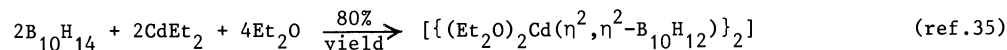
Reaction (vi) Borane acting as a simple 2-electron ligand:

$$B_6H_{10} + [Fe_2(CO)_9] \xrightarrow[77\%]{r.t.} [\mu(5,6)\text{-}\{Fe(CO)_4\}B_6H_{10}] + Fe(CO)_5 \qquad \text{(ref.33)}$$

$$B_6H_{10} + K[Pt(\eta^2\text{-}C_2H_4)Cl_3] \xrightarrow[54\%]{r.t.} trans\text{-}[Pt(\eta^2\text{-}B_6H_{10})_2Cl_2] + KCl + C_2H_4 \text{ (refs.33,34)}$$
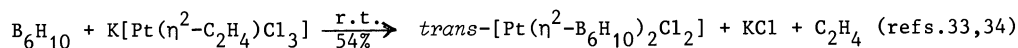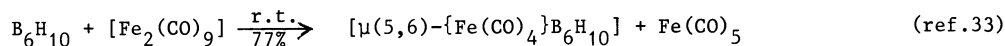
In these reactions $nido\text{-}B_6H_{10}$ displaces other ligands from their complexes by acting itself as a Lewis base via interaction with the basal B-B 2-electron bond (cf. $B_5H_8^-$ in reaction (i)).
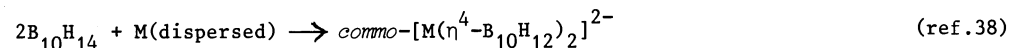
Reaction (vii) Borane as a Brønsted acid:

As Brønsted acids, boranes can be deprotonated by metal alkyls and other reagents to give a variety of metalloborane structure types, e.g.

$$2B_{10}H_{14} + 2CdEt_2 + 4Et_2O \xrightarrow[\text{yield}]{80\%} [\{(Et_2O)_2Cd(\eta^2,\eta^2\text{-}B_{10}H_{12})\}_2] \qquad \text{(ref.35)}$$

$$B_{10}H_{14} + 2TlMe_3 \xrightarrow[\text{yield}]{85\%} [TlMe_2]^+[nido\text{-}Me_2Tl(\eta^4\text{-}B_{10}H_{12})]^- \qquad \text{(ref.36)}$$

A closely related reaction in which the borane can be considered to act as an acid is the reaction of $B_{10}H_{14}$ with the electron-rich complex nickelocene, $[Ni(\eta^5\text{-}C_5H_5)_2]$, in monoglyme or benzene: if the reaction is stopped after 1 hour a 60% yield is obtained of $nido\text{-}[Ni(B_{10}H_{13})(\eta^5\text{-}C_5H_5)]$, whereas prolonged reaction yields $commo\text{-}[Ni(\eta^4\text{-}B_{10}H_{12})_2]^{2-}$ as the main metalloborane product (ref. 37).
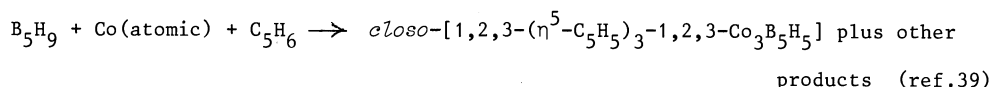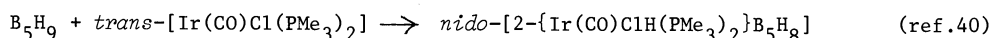
Reaction (viii) Borane plus dispersed metal:

Direct reaction of $B_{10}H_{14}$ with finely dispersed metals such as Zn, Co, or Ni can be regarded as involving decaborane either as an acid or as an oxidizing agent (cf. hydrogen chloride in the reaction $2HCl + Mg \longrightarrow MgCl_2 + H_2$). Thus

$$2B_{10}H_{14} + M(\text{dispersed}) \longrightarrow commo\text{-}[M(\eta^4\text{-}B_{10}H_{12})_2]^{2-} \qquad \text{(ref.38)}$$

Reaction (ix) Borane plus atomized metal:

Atomized metals, particularly in the presence of ligands, can be used to give a mixture of polymetalloboranes in rather low yield (cf. reaction (iv), e.g.

$$B_5H_9 + Co(atomic) + C_5H_6 \longrightarrow \text{closo-}[1,2,3-(\eta^5-C_5H_5)_3-1,2,3-Co_3B_5H_5] \text{ plus other}$$

products   (ref.39)

Reaction (x) Oxidative addition of B-H to Ir^I:

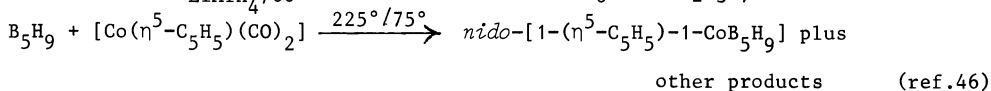$$B_5H_9 + \text{trans-}[Ir(CO)Cl(PMe_3)_2] \longrightarrow \text{nido-}[2-\{Ir(CO)ClH(PMe_3)_2\}B_5H_8] \qquad (ref.40)$$
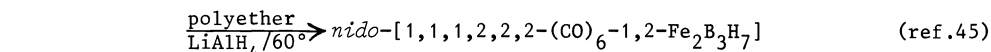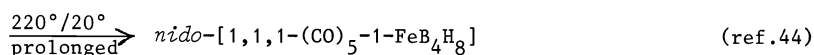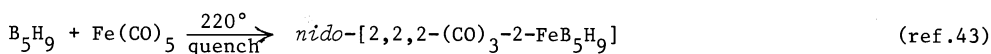
The reaction affords good yields of certain σ-bonded metalloboranes but appears not to be general. Of more pertinence is the elegant use of B_2H_6 to effect cluster expansion of a preformed metalloborane:

Reaction (xi) Cluster expansion by use of diborane:

$$\tfrac{1}{2}B_2H_6 + [\mu(5,6)-\{Fe(CO)_4\}B_6H_9]^- \longrightarrow [Fe(\eta^2-B_7H_{12})(CO)_4]^- \qquad (ref.41)$$
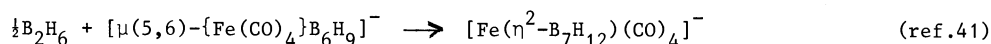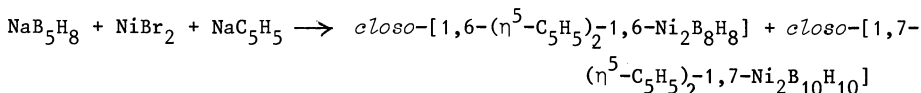
In this case the metalloborane anion, which is readily formed by deprotonation (using KH) of the product of reaction (vi), is clearly acting as an electron-pair donor to the acceptor $\{BH_3\}$ (cf. reaction type (v) above). Treatment of the product with anhydrous HCl at $-110°$ yields 1 mole of H_2 and the neutral metalloborane $[Fe(\eta^2-B_7H_{11})(CO)4]$. Occasionally the monoborane reagent $BH_3.thf$ can be used to generate a small metalloborane cluster *ab initio* from mononuclear units. Thus,

Reaction (xii) Synthesis of small clusters from mononuclear units:

$$3BH_3.thf + [Fe(CO)_4]^{2-} \xrightarrow[\text{yield}]{98\%} [\mu-\{Fe(CO)_4\}B_2H_5]^- + BH_4^- + 3thf \qquad (ref.42)$$
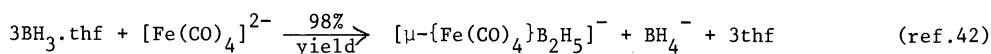
Reaction (xiii) Cothermolysis of a borane with a metal carbonyl:

Less specific syntheses have employed the cothermolysis of a borane with a metal carbonyl or related complex. The products, which are usually obtained in low yield (1-20%), can be varied by modifying the detailed reaction conditions e.g.

$$B_5H_9 + Fe(CO)_5 \xrightarrow[\text{quench}]{220°} \text{nido-}[2,2,2-(CO)_3-2-FeB_5H_9] \qquad (ref.43)$$

$$\xrightarrow[\text{prolonged}]{220°/20°} \text{nido-}[1,1,1-(CO)_5-1-FeB_4H_8] \qquad (ref.44)$$

$$\xrightarrow[\text{LiAlH}_4/60°]{\text{polyether}} \text{nido-}[1,1,1,2,2,2-(CO)_6-1,2-Fe_2B_3H_7] \qquad (ref.45)$$

$$B_5H_9 + [Co(\eta^5-C_5H_5)(CO)_2] \xrightarrow{225°/75°} \text{nido-}[1-(\eta^5-C_5H_5)-1-CoB_5H_9] \text{ plus}$$

other products   (ref.46)

So far in this classification of preparative routes to metalloboranes we have considered the various reactions of borane anions with metal complexes and a variety of reactions involving the parent boranes themselves. Some further reactions of borane anions and of halogen-substituted boranes can now be listed.

Reaction (xiv) Anodic dissolution of metals in the presence of a borane anion and appropriate ligands, e.g. (ref. 47):

$$Cu(anode) + B_3H_8^- + 2PPh_3 \xrightarrow{electrol.} [(PPh_3)_2CuB_3H_8]$$
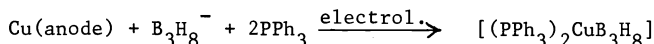
Reaction (xv) Cluster expansion during reaction of a borane anion with a metal halide in the presence of a ligand e.g. (ref.48):

$$NaB_5H_8 + NiBr_2 + NaC_5H_5 \longrightarrow \text{closo-}[1,6-(\eta^5-C_5H_5)_2-1,6-Ni_2B_8H_8] + \text{closo-}[1,7-$$
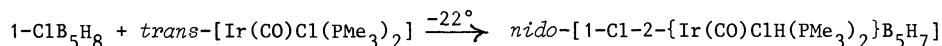$$(\eta^5-C_5H_5)_2-1,7-Ni_2B_{10}H_{10}]$$

Similarly NaB_5H_8 reacts with $[Ni(\eta^5-C_5H_5)_2]$ in thf in the presence of stoichiometric amounts of Na amalgam to give up to 17% of *closo-*$[1,2,7,8-(\eta^5-C_5H_5)_4-1,2,7,8-Ni_4B_4H_4]$ and 10% of *nido-*$[1,6,7,8-(\eta^5-C_5H_5)_4-1,6,7,8-Ni_4B_5H_5]$ (ref.48). The detailed course of these reactions is not clear.

Reaction (xvi) Metathesis of halogeno polyboranes with anionic metal complexes e.g. (ref.49):

$$2\text{-}ClB_5H_8 + Na[Mn(CO)_5] \longrightarrow nido\text{-}[2\text{-}\{Mn(CO)_5\}B_5H_8]$$
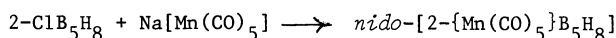
This reaction, which also works with the analogous anionic rhenium complex $[Re(CO)_5]^-$ is essentially the inverse of reaction (i). Curiously, the same basal-substituted product is obtained even if the apical halogenoboranes $1\text{-}ClB5H8$ or $1\text{-}BrB5H8$ are used in the reaction. So far only B5 derivatives have been exploited but the reaction could probably be extended to B6, B10 and other boranes for which halogeno- or polyhalogeno-derivatives are readily obtained.

Reaction (xvii) Oxidative addition of halogeno-boranes to Ir^I complexes (ref.40)(cf.reaction(x)):
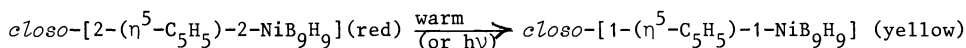
$$1\text{-}ClB_5H_8 + trans\text{-}[Ir(CO)Cl(PMe_3)_2] \xrightarrow{-22°} nido\text{-}[1\text{-}Cl\text{-}2\text{-}\{Ir(CO)ClH(PMe_3)_2\}B_5H_7]$$

This product rapidly isomerizes at room temperature by interchange of Cl (on B) with H (on Ir) to give the more stable $nido\text{-}[2\text{-}\{Ir(CO)Cl2(PMe3)2\}B5H8]$. Interestingly, both $1\text{-}BrB5H8$ and $2\text{-}BrB5H8$ when reacted with $trans\text{-}[Ir(CO)Cl(PMe3)2]$ give the basal substituted *dibromo* iridium complex $[2\text{-}\{IrBr_2(CO)(PMe_3)_2\}B_5H_8]$ in high yield - clearly both isomerization and trans-bromination occur as well as oxidative addition.

A further group of reactions uses preformed metalloboranes as starting materials to prepare new metalloboranes by means of (a) cluster isomerization, (b) ligand exchange reactions or (c) oxidative cluster reconstructions, all of which leave the number of metal and boron vertices in the product cluster unchanged. In addition, one can envisage (d) partial degradation of a cluster to one having fewer vertices, or (e) cluster aggregation reactions to give macropolyhedral metalloboranes. Examples follow (see also reactions (iv), (v), and (xi).
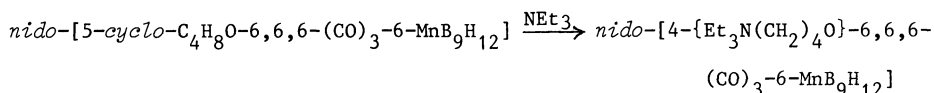
Reaction (xviii) Thermally or photolytically induced cluster isomerization of a preformed metalloborane cluster:

This affords a convenient route in certain very specific instances, of which the following is typical (refs. 37,50):

$$closo\text{-}[2\text{-}(\eta^5\text{-}C_5H_5)\text{-}2\text{-}NiB_9H_9](red) \xrightarrow[\text{(or h}\nu\text{)}]{\text{warm}} closo\text{-}[1\text{-}(\eta^5\text{-}C_5H_5)\text{-}1\text{-}NiB_9H_9] \text{ (yellow)}$$
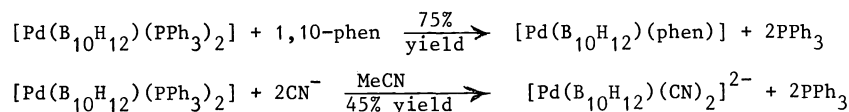
Reaction (xix) Basic-induced substituent rearrangement:

Treatment of the neutral thf adduct-derivative of $[Mn(B_9H_{13})(CO)_3]^-$ with NEt_3 induces C-O bond scission of thf and an apparent "migration" of the site of substitution as particularized by the equation (ref. 51):

$$nido\text{-}[5\text{-}cyclo\text{-}C_4H_8O\text{-}6,6,6\text{-}(CO)_3\text{-}6\text{-}MnB_9H_{12}] \xrightarrow{NEt_3} nido\text{-}[4\text{-}\{Et_3N(CH_2)_4O\}\text{-}6,6,6\text{-}$$
$$(CO)_3\text{-}6\text{-}MnB_9H_{12}]$$

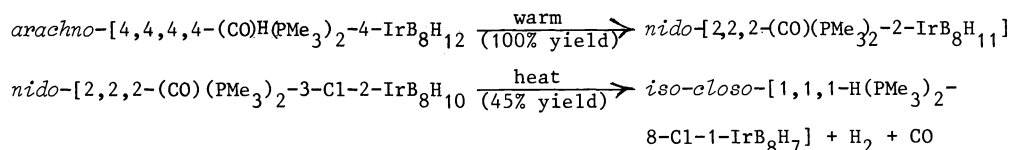Other base-induced cluster isomerizations are discussed more fully in a later Section.

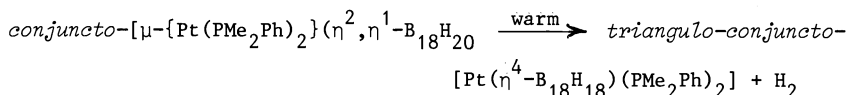*Reaction (xx) Ligand exchange reactions at the metal centre of a preformed metalloborane:*

This affords an almost trivially obvious way of producing new complexes of an unmodified substrate e.g. (ref. 52):

$$[Pd(B_{10}H_{12})(PPh_3)_2] + 1,10\text{-}phen \xrightarrow[\text{yield}]{75\%} [Pd(B_{10}H_{12})(phen)] + 2PPh_3$$

$$[Pd(B_{10}H_{12})(PPh_3)_2] + 2CN^- \xrightarrow[45\% \text{ yield}]{MeCN} [Pd(B_{10}H_{12})(CN)_2]^{2-} + 2PPh_3$$

Reaction (xxi) Thermally induced oxidative cluster closure:

Known examples include *arachno* → *nido* or *nido* → *closo* cluster modification via loss of H_2 (ref. 53) and the reconstruction of an edge-fused *conjuncto*-metalloborane cluster into a *triangulo* face-fused cluster (ref. 54):

$$arachno\text{-}[4,4,4,4\text{-}(CO)H(PMe_3)_2\text{-}4\text{-}IrB_8H_{12} \xrightarrow[\text{(100\% yield)}]{\text{warm}} nido\text{-}[2,2,2\text{-}(CO)(PMe_3)_2\text{-}2\text{-}IrB_8H_{11}]$$

$$nido\text{-}[2,2,2\text{-}(CO)(PMe_3)_2\text{-}3\text{-}Cl\text{-}2\text{-}IrB_8H_{10} \xrightarrow[\text{(45\% yield)}]{\text{heat}} iso\text{-}closo\text{-}[1,1,1\text{-}H(PMe_3)_2\text{-}$$
$$8\text{-}Cl\text{-}1\text{-}IrB_8H_7] + H_2 + CO$$

$$conjuncto\text{-}[\mu\text{-}\{Pt(PMe_2Ph)_2\}(\eta^2,\eta^1\text{-}B_{18}H_{20} \xrightarrow{\text{warm}} triangulo\text{-}conjuncto\text{-}$$
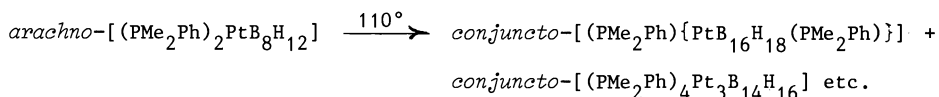
$$[Pt(\eta^4\text{-}B_{18}H_{18})(PMe_2Ph)_2] + H_2$$

Reaction (xxii) Partial degradation (monodeboronation of a preformed metalloborane):

This can sometimes be smoothly effected, e.g. (ref. 55):

$$arachno\text{-}[6,6\text{-}(PEt_3)_2\text{-}9\text{-}L\text{-}6PtB_9H_{11}] + 3EtOH \longrightarrow arachno\text{-}[7,7\text{-}(PEt_3)_2\text{-}$$

$$7\text{-}PtB_8H_{12}] + B(OEt)_3 + H_2 + L$$
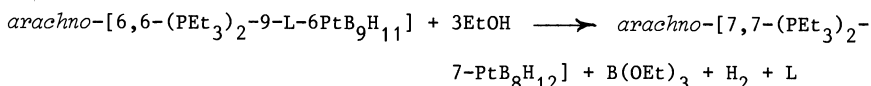
Reaction (xxiii) Thermally induced metal-assisted cluster aggregation to give a macro-polyhedral metalloborane species:

This can be illustrated by the thermolysis in boiling toluene of $arachno\text{-}[7,7\text{-}(PMe_2Ph)_2\text{-}7\text{-}PtB_8H_{12}]$ to give several products in small yield e.g. (ref. 56):

$$arachno\text{-}[(PMe_2Ph)_2PtB_8H_{12}] \xrightarrow{110°} conjuncto\text{-}[(PMe_2Ph)\{PtB_{16}H_{18}(PMe_2Ph)\}] +$$

$$conjuncto\text{-}[(PMe_2Ph)_4Pt_3B_{14}H_{16}] \text{ etc.}$$

Both the products mentioned have been fully characterized by single-crystal X-ray diffraction analysis.

There remain a few miscellaneous reactions which cannot readily be fitted into the preceding broad categories and which give a variety of products in rather modest or low yields. Despite their obscure nature such reactions have yielded a rich harvest of previously unsuspected metalloborane structure types. Two examples must suffice.
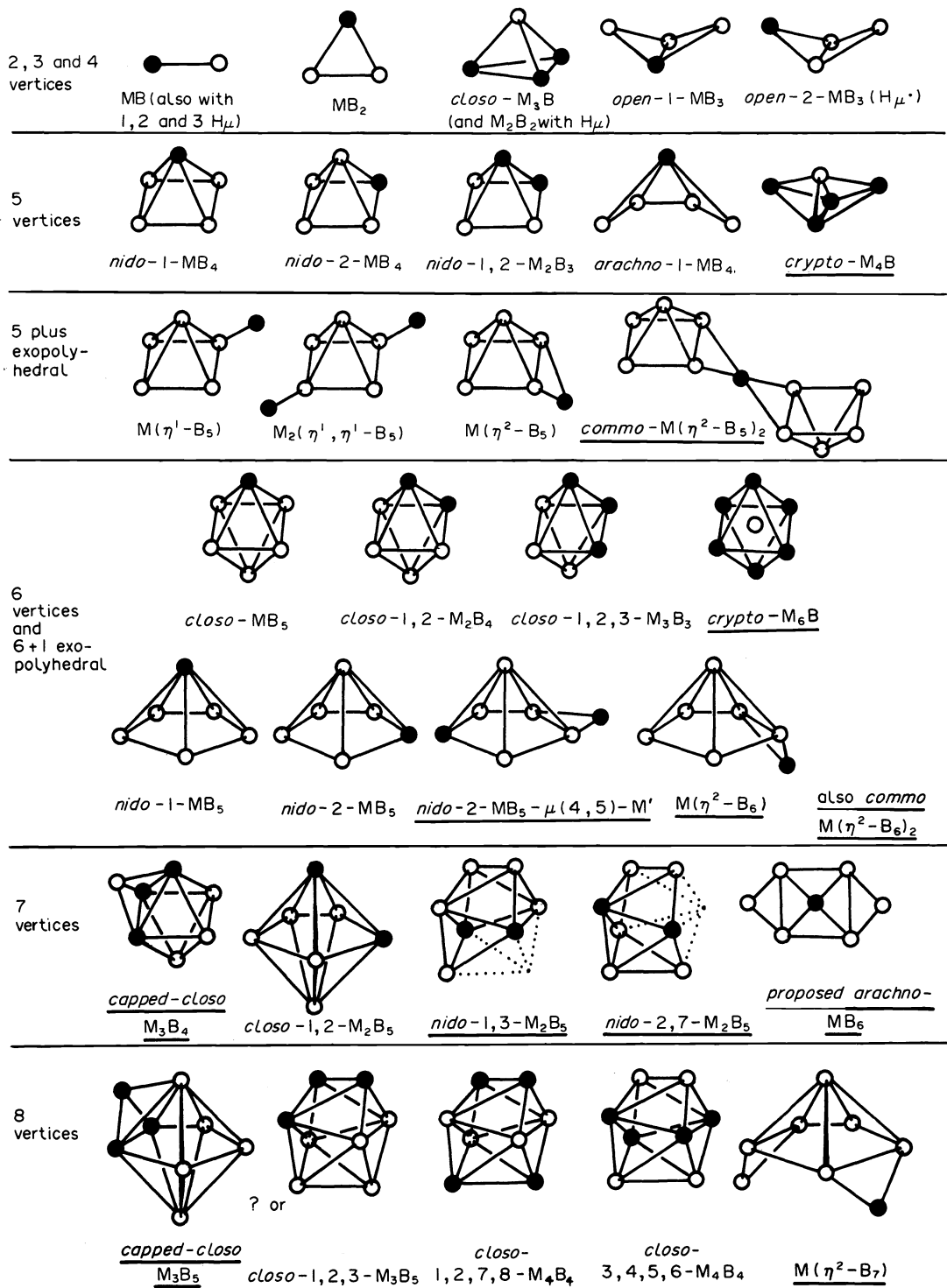
Reaction (xxiv): Treatment of bisdecaboranyl oxide, $[6,6'\text{-}(B_{10}H_{13})_2O]$ with $cis\text{-}[PtCl_2(PMe2Ph)_2]$ in neutral dipolar solvents at room temperature affords several metalloboranes including $arachno\text{-}[Pt(\eta^3\text{-}B_8H_{12})(PMe_2Ph)_2]$, $nido\text{-}[Pt(\eta^4\text{-}B_{10}H_{12})(PMe_2Ph)_2]$ and the novel $conjuncto\text{-}[\{Pt(\eta^3\text{-}B_6H_9)(PMe_2Ph)\}_2]$ which features an unprecedented central linear P-Pt-Pt-P unit to which are attached the $nido\text{-}\{\eta^3\text{-}B_6H_9\}$ fragments in transoid configuration (ref. 57).

Reaction (xxv): Cluster degradation and reconstruction also attends the reaction of $arachno\text{-}[4\text{-}(Me_2S)\text{-}7\text{-}(MeO)B_9H_{12}]$ with $cis\text{-}[PtCl2(PMe2Ph)_2]$ in the presence of base (ref. 58). In addition to the expected $arachno\text{-}[(PMe_2Ph)_2PtB_8H_{11}OMe]$ which was obtained in 50% yield, other products included 8% of the known $[(PMe_2Ph)_2PtB_3H_7]$ (see reaction (ii)), 35% of the dimer $[\{Pt(\eta^3\text{-}B_6H_9)(PMe_2Ph)\}_2]$ just mentioned in reaction (xxiv) and about 3% of the novel $conjuncto\text{-}[(PMe_2Ph)_2Pt_2(B_2H_5)(B_6H_9)]$ which also features a central linear P-Pt-Pt-P group.

CLUSTER GEOMETRY OF METALLOBORANES

The rich variety of cluster shapes that have been formed amongst the metalloboranes is exemplified by the 70 coded structures shown on the next three pages. In these diagrams the metal and boron atoms are represented by full and open circles respectively and all other atoms (including H-atoms and ligands) have been omitted, whether or not they contribute to the formal skeletal electron count. As already mentioned in the Introduction, the examples are restricted to those clusters which have only M and B as cluster vertices, with no other heteroatoms, and also to those clusters which have at least some direct M-B connectivities. Of course, many of the compounds listed, in addition to having these direct M-B links, also feature B-H-B, M-H-B, and/or M-H-M bonds, but metalloboranes bonded only by M-H-B bonds have been omitted. [Some exceptions are included in the first row of structures where for completeness some H_μ-bonded derivatives of BH_4^- $B_2H_6^{2-}$ and 2-subrogated B_4H_{10} are additionally noted (refs. 10,11,13).]

Metallo derivatives of $nido\text{-}B_5H_9$ have been known for nearly a decade and the growing number of geometrical and structural variants (η^1, η^2, η^3, η^4, $commo\text{-}$ and dimetallo) have been fully discussed in several recent reviews (e.g. refs. 7,10). Of more recent vintage is $arachno\text{-}[1,1,1\text{-}(CO)(PMe_3)_2\text{-}1\text{-}IrB_4H_9]$ (ref. 59) and its $bis\text{-}(PMe_2Ph)$ analogue (ref. 60). Comparison of this $arachno$ cluster with the now classical $nido\text{-}[1,1,1\text{-}(CO)_3\text{-}1\text{-}FeB_4H_8]$ (ref.44) is instructive: Ir is in the next periodic group to Fe and so can contribute one extra electron to this cluster; this together with the electron from the additional H atom confers two extra electrons on the skeletal electron count, consistent with the change from a $nido\text{-}$ to an $arachno$ structure. The recently synthesized $crypto\text{-}M_4B$ cluster $[H\{Fe(CO)_3\}_4BH_2]$ is also of considerable theoretical interest (ref. 61). The structure consists of an Fe_4 butterfly fragment bridged across the wing tips by an H-B-H group, and with a further H_μ bridging the two "hinge" Fe atoms.

2, 3 and 4 vertices

MB (also with 1, 2 and 3 H_μ)   MB₂   *closo* - M₃B (and M₂B₂ with H_μ)   *open* - 1 - MB₃   *open* - 2 - MB₃ (H_μ·)

5 vertices

nido - 1 - MB₄   *nido* - 2 - MB₄   *nido* - 1, 2 - M₂B₃   *arachno* - 1 - MB₄,   *crypto* - M₄B

5 plus exopoly-hedral

M(η^1 - B₅)   M₂(η^1, η^1 - B₅)   M(η^2 - B₅)   *commo* - M(η^2 - B₅)₂

6 vertices and 6 + 1 exo-polyhedral

closo - MB₅   *closo* - 1, 2 - M₂B₄   *closo* - 1, 2, 3 - M₃B₃   *crypto* - M₆B

nido - 1 - MB₅   *nido* - 2 - MB₅   *nido* - 2 - MB₅ - μ(4, 5) - M′   M(η^2 - B₆)   also *commo* M(η^2 - B₆)₂

7 vertices

capped - closo M₃B₄   *closo* - 1, 2 - M₂B₅   *nido* - 1, 3 - M₂B₅   *nido* - 2, 7 - M₂B₅   *proposed arachno-* MB₆

8 vertices

capped - closo M₃B₅   ? or   *closo* - 1, 2, 3 - M₃B₅   *closo* - 1, 2, 7, 8 - M₄B₄   *closo* - 3, 4, 5, 6 - M₄B₄   M(η^2 - B₇)

The geometrical details of the structure, coupled with the unusual ^{11}B nmr chemical shift (δ = 106), suggest that the cluster is not a *closo*-trigonal bipyramid but an *arachno*-4 atom cluster with an interstitial B atom: this would require 14 skeletal electrons – 2 from each of the 4 $\{Fe(CO)_3\}$ groups one from each of the 3 H_μ, and all 3 valence electrons from the interstitial B atom. The ruthenium analogue $[H\{Ru(CO)_3\}_4BH_2]$ is also known (ref. 62) but there is no borane counterpart.

Another *crypto* (interstitial boride) cluster which has no analogue amongst the parent boranes or borane anions is the octahedral cobalt carbonyl derivative $[\{Co(CO)_3\}_6B]$ (ref. 63). This can be made by heating a benzene solution of $[Co_2(CO)_8]$ with B_2H_6 at 8 – 10 atm or with BBr_3 at 60°C, and, although no definitive X-ray structure is available, spectroscopic studies suggest that it may be isostructural with the so called "86-electron" octahedral interstitial carbides $[Ru_6(CO)_{17}C]$ and $[Fe_6(CO)_{16}C]^{2-}$.

Metallo derivatives of *nido*-B_6H_{10} are now well established, with the metal subrogating either the apical or a basal B atom, or being attached exopolyhedrally to the borane acting as a ligand. Preparative routes and references have already been noted above: see reaction types (xiii) (refs. 43,46), (iii) (ref. 26), (xi) (ref. 64), and (vi) (refs. 33,34) respectively.

Of perhaps even greater interest are the various 7-vertex metalloboranes, since no 7-vertex boranes or borane anions are known. By contrast, for the metalloboranes *capped-closo*, *closo*, *nido*, and *arachno* clusters have been identified. The *capped-closo*, $2n$-skeletal electron cluster type is represented by $[1,2,3-\{Co(\eta^5-C_5H_5)\}_3B_4H_4]$ (reaction (iv) refs. 30,64). The *closo* pentagonal bipyramidal ($2n$ + 2)-electron species is exemplified by *closo*-$[1,2-(\eta^5-C_5Me_5)_2-1,2-CoB_5H_7]$, prepared in very low yields by reaction-type (iv) using $C_5Me_5^-$ instead of $C_5H_5^-$ (ref. 65). The *nido* 7-vertex structure can be envisaged as being related to the 8-vertex D_{2d} dodecahedron by removal of either a 4-connected vertex or a 5-connected vertex. Such structures might be expected for 18-skeletal electron clusters (i.e. $2n$ + 4). The compound *nido*-$[1,3-(C_5Me_5)-1,3-CoB_5H_9]$, formed in very low yield by reaction-type (iv) (ref. 65), is an example of the first structure, whereas the second is exemplified by the compound *nido*-$[2,2,2-(PPh_3)_2(CO)-7,7-(PMe_2Ph)Cl-\mu(2,7)-H-2,7-OsPtB_5H_7]$ formed in high-yield by the planned synthesis shown in reaction (v) (ref. 32). Finally, a 7-vertex *arachno* structure has been proposed for the reactive compound $[AlB_6H_{13}]$, which can be considered as an analogue of the unknown *arachno*-$[B_7H_{13}]$ (ref. 66); the structure has not yet been established with certainty, however.
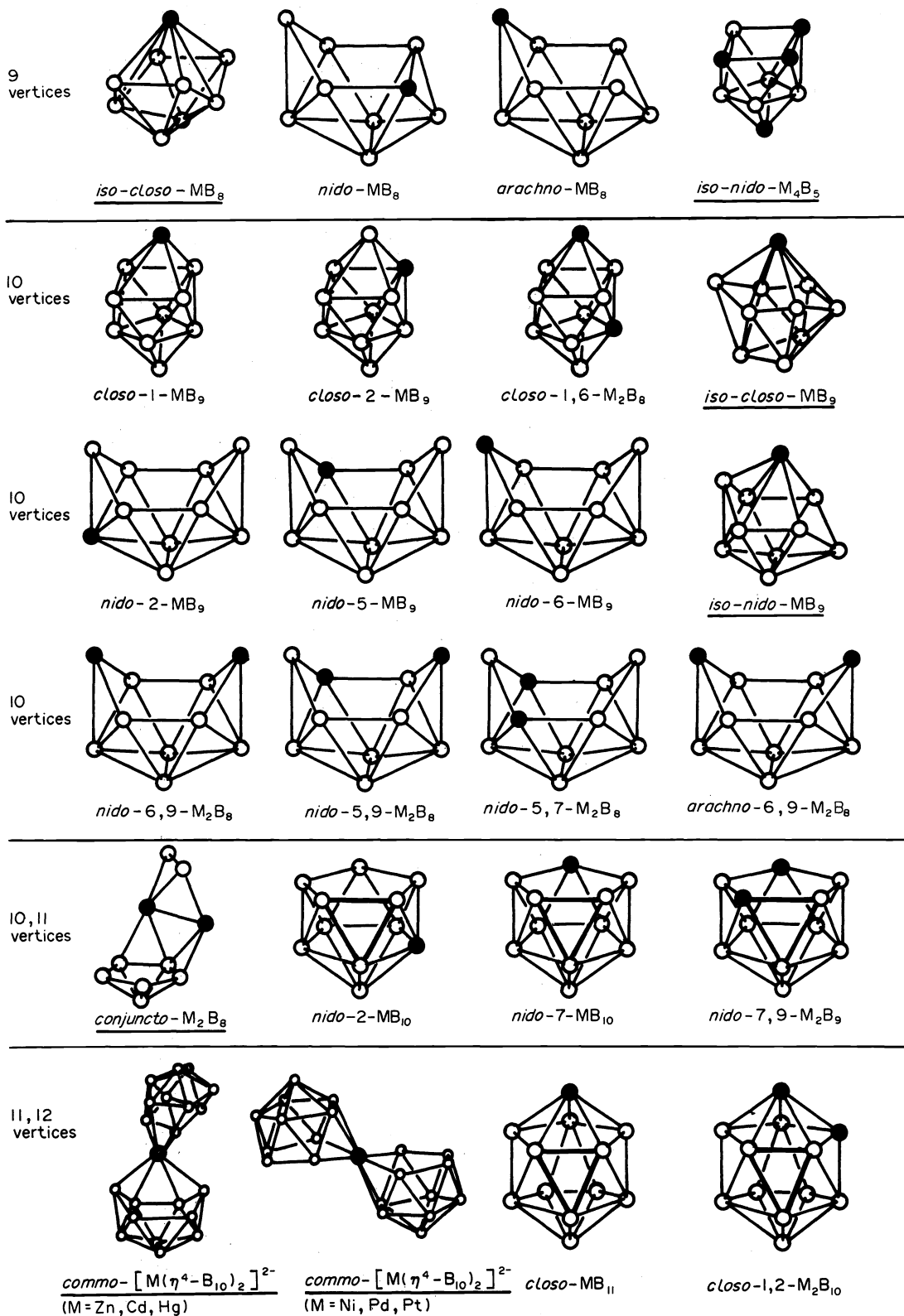
The dodecahedron is generally accepted as the archetype of 8-vertex deltahedral clusters and this structure (or the *capped-closo*-pentagonal bipyramidal) has been proposed for the $2n$ cluster $[1,2,3-\{Co(\eta^5-C_5H_5)\}_3B_5H_5]$, one of the products of reaction (ix) (ref.39). The interesting pair of *closo*-D_{2d} compounds $[1,2,7,8-\{Ni(\eta^5-C_5H_5)\}_4B_4H_4]$ (reaction (xv) ref. 48) and $[3,4,5,6-\{Co(\eta^5-C_5H_5)\}_4B_4H_4]$ (reaction (iv) ref. 30) have been the subject of much theoretical interest (refs. 48,67-70) since the 20-electron Ni compound has 2 more skeletal electrons and the 16-electron Co compound has 2 less skeletal electrons than the 18 ($2n$ + 2) required for the *closo* structure. It will be noted that Ni occupies the 4-connected vertices and features a very short Ni-Ni distance of only 235 pm, whereas Co occupies the 5-connected vertices in the central belt.

The final 8-vertex structure type $[M(\eta^2-B_7)]$ at the foot of the first page of coded structures is particularly significant, as the isolation at low temperatures of the compound $[Fe(\eta^2-B_7H_{11})(CO)_4]$ (reaction (xi) (ref. 41)) implies the stabilization of the unknown *nido*-borane B_7H_{11} by donation of an electron pair to the acceptor group $\{Fe(CO)_4\}$.

At the top of the second page of structures are listed the four 9-vertex clusters so far characterized. The first three form an important series since the *arachno*-iridium(III) compound $[4,4,4,4-(CO)H(PMe_3)_2-4-IrB_8H_{12}]$ can be quantitatively dehydrogenated to the *nido*-iridium(III) compound $[2,2,2-(CO)(PMe_3)_2-2-IrB_8H_{11}]$ by mild thermolysis of 50-100°C, and further heating at 135°C results in loss of a further H_2 + CO to give a small yield of the *iso-closo*-iridium(V) compound $[1,1,1-H(PMe_3)_2-1-IrB_8H_8]$ (ref. 53). The monochloro substituted derivative acts similarly:

$$\textit{arachno} \xrightarrow[100\%]{-H_2} \textit{nido} \xrightarrow[45\%]{-H_2-CO} \textit{iso-closo}$$
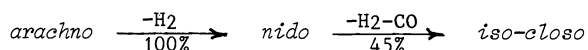
This was the first time this sequence had been realized experimentally. The *iso-closo* structure is also of interest since the close approach of Ir to 6 B in the inverted-boat configuration prevents *trans*-cluster bonding between B(2)$\cdots$B(4) and B(5)$\cdots$B(7) such as is observed in the more usual *closo* 9-vertex tricapped trigonal prismatic geometry. The *iso-nido*-M_4B_5 structure (formed by notional removal of a 4-connected vertex from *closo*-$B_{10}H_{10}^{2-}$ rather than the more common notional removal of a 5-connected vertex) is represented by $[1,6,7,8-(\eta^5-C_5H_5)_4-1,6,7,8-Ni_4B_5H_5]$ (reaction xv, ref. 48).

9 vertices

iso-closo–MB_8 nido–MB_8 arachno–MB_8 iso-nido–M_4B_5

10 vertices

closo-1–MB_9 closo-2–MB_9 closo-1,6–M_2B_8 iso-closo–MB_9

10 vertices

nido-2–MB_9 nido-5–MB_9 nido-6–MB_9 iso-nido–MB_9

10 vertices

nido-6,9–M_2B_8 nido-5,9–M_2B_8 nido-5,7–M_2B_8 arachno-6,9–M_2B_8

10,11 vertices

conjuncto–M_2B_8 nido-2–MB_{10} nido-7–MB_{10} nido-7,9–M_2B_9

11,12 vertices

commo–$[M(\eta^4-B_{10})_2]^{2-}$ (M=Zn,Cd,Hg)   commo–$[M(\eta^4-B_{10})_2]^{2-}$ (M=Ni,Pd,Pt)   closo–MB_{11} closo-1,2–M_2B_{10}

Many 10-vertex metalloborane compounds have been characterized and examples of *mono*- and di-metallo *closo*, *nido*, and *arachno* clusters have been synthesized with various sites subrogated by the metal centre e.g. *closo*-[1- and 2-{Ni(η^5-C$_5$H$_5$)}B$_9$H$_9$] (refs. 37,50), *closo*-[1,6-{Ni(η^5-C$_5$H$_5$)}$_2$B$_8$H$_8$] (ref. 48), and similarly for *nido*-x-MB9 and *nido*-x,y-M$_2$B$_8$ (refs. 7,10,65). The dimetallo-*arachno*-M$_2$B$_8$ species such as *arachno*-[6,9-{Pt(PMe$_2$Ph)$_2$}$_2$B$_8$H$_{10}$] and its PdPt and IrPt analogues (refs. 10, 28) differ from the dimetallo-*nido*-M$_2$B$_8$ compounds such as *nido*-[6,9-{Co(η^5-C$_5$Me$_5$)}$_2$(B$_8$H$_{12}$)] (ref. 65) in having only two H$_\mu$ bridging B(5,10) and B(7,8) rather than four H$_\mu$ bridging B(5,6), B(6,7), B(8,9) and B(9,10).

A structure type not found among the parent boranes or their anions is the *iso-closo*-MB9 cluster which has idealized C_{3v} symmetry (MB3B3B3) rather than the normal 4-fold symmetry of B$_{10}$H$_{10}^{2-}$ (e.g. MB4B4B). Thus, facile thermal dehydrogenation of *nido*-[6,6,6-H(PMe$_3$)$_2$-6-IrB$_9$H$_{13}$] yields *iso-closo*-[1,1,1-H(PMe$_3$)$_2$-1-IrB$_9$H$_9$] (ref. 71). Likewise, thermolysis of the PPh3 analogue at 100°C effected quantitative loss of 3H$_2$ to give the the orthocycloboronated product *iso-closo*-[1,1,1-H(PPh$_3$)(PPh$_2$-*ortho*-C$_6$H$_4$)-1-IrB$_9$H$_8$-2$^-$] (ref. 72). Another structure type not found among the parent boranes is that of *iso-nido*-[7,7,9-(PPh$_3$)$_3$-7-IrB$_9$H$_{10}$] (refs. 10,71); like the normal *nido* 10-vertex structure this is based on the 11-vertex *closo*-B$_{11}$H$_{11}^{2-}$ structure but is formed by notional removal of a 4-connected vertex rather than the more usual unique 6-connected (apical) vertex. Accordingly, as seen in the diagram, the compound features a 4-membered open face rather than the familiar 6-membered boat-shaped open face of *nido*-B$_{10}$H$_{14}$ and its derivatives.

An entirely different structure-motif is found in the *conjuncto* ten-vertex cluster [μ-{Pt(PMe$_2$Ph)}$_2$(B$_2$H$_5$)(B$_6$H$_9$)] (reaction xxv, ref. 58); the structure features a central linear P-Pt-Pt-P spine which supports an {η^3-B$_2$H$_5$} and an {η^3-B$_6$H$_9$} sub-cluster. It is thus quite different from the more conventional *arachno* cluster [6,9-{Pt(PMe$_2$Ph)$_2$}$_2$B$_8$H$_{10}$] considered in a preceding paragraph, with which it is isoelectronic (the 4 extra H atoms of the *conjuncto* compound supplying the 4 electrons equivalent to those donated by the two extra phosphine ligands in the *arachno* species).

The 11-vertex *nido*-7-MB$_{10}$ cluster and the related *commo*-[M(η^4-B$_{10}$)$_2$]$^{2-}$ clusters were among the very first metalloboranes to be prepared and characterized (refs. 1,10) and need not be discussed further. The isomeric *nido*-2-MB$_{10}$ cluster has been made by reaction-type xv using Fe^{2+}, B$_5$H$_8^-$ and C$_5$H$_5^-$ in thf at -78°; one of the products was the yellow compound *nido*-[2-{Fe(η^5-C$_5$H$_5$)}B$_{10}$H$_{15}$] which as 5H$_\mu$ in the 5-membered open face (ref. 73). By contrast the very recently synthesized *nido*-7,9-M$_2$B9 compound *nido*-[7,7-(PMe$_3$)$_2$-9,9,9-H(PPh$_3$)(PPh$_2$C$_6$H$_4$)-7,9-PtIrB$_9$H$_{10}$(-4$^-$)] (ref. 71, see also later Section) has the two metal atoms in the 5-membered open face and only two bridging hydrogen atoms - between B(10)B(11) and Ir(9)B(8) respectively.

The two *closo* icosahedral clusters at the foot of the second page of structures are exemplified by the bright yellow anion *closo*-[Ni(η^5-B$_{11}$H$_{11}$)(η^5-C$_5$H$_5$)]$^-$ (ref. 74) and the golden-brown neutral compound *closo*-[1,7-{Ni(η^5-C$_5$H$_5$)}$_2$B$_{10}$H$_{10}$] (ref. 48) and introduce no new principles.

The third page of structure types lists known examples of *conjuncto*-macropolyhedral metalloboranes having 14-22 vertices. The first two are very reminiscent of *conjuncto*-[μ-{Pt(PMe$_2$Ph)}$_2$(B$_2$H$_5$)(B$_6$H$_9$)] described above and were, indeed, the first two such compounds to be prepared (reaction xxiv, refs. 10,57). Thus the extraordinarily stable *conjuncto*-[μ-{Pt(PMe$_2$Ph)}$_2$(η^3-B$_6$H$_9$)$_2$] can now be prepared by a variety of routes and, when deprotonated with KH and treated with *cis*-[PtCl$_2$(PMe$_2$Ph)$_2$] as in reaction (i), yields the trimetallo-borane complex *conjuncto*-[μ-{Pt(PMe$_2$Ph)}$_2$(B$_6$H$_9$){B$_6$H$_8$-μ-*cis*-PtH(PMe$_2$Ph)$_2$}] (ref. 10). The next two macropolyhedral structures are 17-vertex species formed by the reconstructive thermolysis reaction (xxiii) (ref. 56). *Conjuncto*-[7,9'-(PMe$_2$Ph)$_2$-7-PtB$_{16}$H$_{18}$] can be regarded as an η^6-complex of the as yet unknown hexadecaborane derivative B$_{16}$H$_{22}$L which can itself be regarded as being derived from the familiar *arachno*-B$_{10}$H$_{12}$L$_2$ structure by replacing one L by the Lewis base B$_6$H$_{10}$ (cf. reaction (vi)). *Conjuncto*-[{Pt(PMe$_2$Ph)}$_2${Pt(PMe$_2$Ph)$_2$}B$_{14}$H$_{16}$] has an even more complex structure (ref. 75): two B$_6$ pentagonal pyramids with their bases parallel are conjoined by an unprecedented Pt$_2$B$_2$Pt central belt.

The five metallo- and bimetallo-derivatives of B$_{18}$ clusters have already been previously reviewed (refs. 8,10,24). Their interest lies in the elegant structural isomerism that is possible with metalloboranes derived from *syn* and *anti*-B$_{18}$H$_{22}$ and in the importance of metal-assisted cluster reconstructions which generate *triangulo* face-fused sub-clusters from originally edge-fused *conjuncto* species.

An early example of structural versatility among metalloboranes was the macro-polyhedral dimer *conjuncto*-[μ-{Cd(OEt$_2$)$_2$}$_2$(η^2,η^2-B$_{10}$H$_{12}$)$_2$] (reaction (vii), ref. 35). The final set of four structures are based on B$_{20}$H$_{26}$ isomers, i.e. x,y'-(B$_{10}$H$_{13}$)$_2$. They resemble the 11-vertex *nido*-7-MB$_{10}$ clusters already mentioned, the only new features being (a) the possibility of geometric and optical isomerism resulting from the position (x,y') of the B-B *conjuncto* link, (b) the choice of which B$_{10}$ unit is metallated when these are
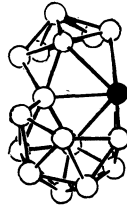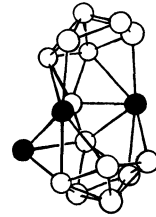
14,15,17 vertices
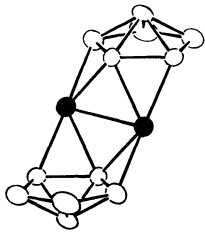
conjuncto-M(η^3-B$_6$)$_2$
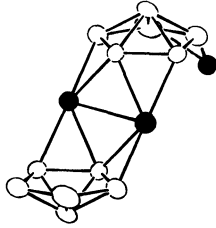
conjuncto-M$_2$(η^3-B$_6$)$_2$ (μ-M)

conjuncto-M(η^6-B$_{16}$)

conjuncto-M$_3$B$_{14}$

19 vertices
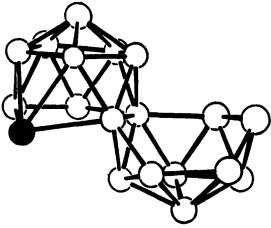
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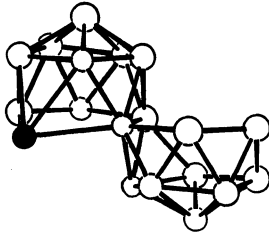
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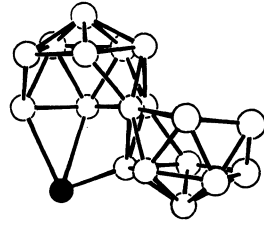
conjuncto-μ-M(η^1,η^2-*anti*-B$_{18}$)

19,20,22 vertices
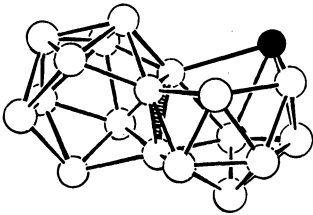
triangulo-MB$_{18}$
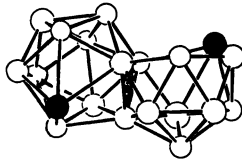
triangulo-M$_2$B$_{18}$
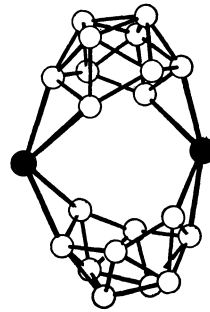
conjuncto-(μ-M)$_2$(η^2,η^2-B$_{10}$)$_2$

21,22 vertices
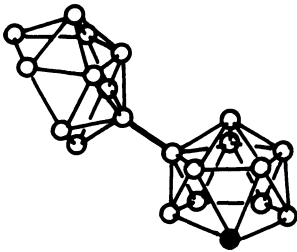
conjuncto-(4,2')-7-M(η^4-B$_{20}$)
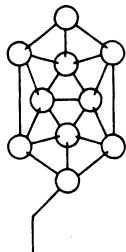
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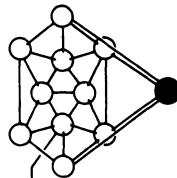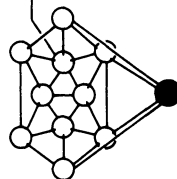
cisoid

transoid

conjuncto-(4,6')-7,7'-M$_2$(B$_{10}$)$_2$
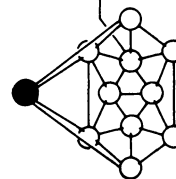
conjuncto-(4,4')-7,7'-M$_2$(B$_{10}$)$_2$

different, and (c) the possibility of *cisoid* and *transoid* bimetallation even when the two B_{10} units are the same as shown schematically in the final structures (ref. 22).

The preceding discussion indicates the wide variety of structural types already encountered among the metalloboranes and it is quite certain that many new and unsuspected cluster geometries remain to be synthesized in the future. In addition to positional isomerism of the site(s) of subrogation on classical borane clusters, modified *(iso-)* cluster geometires have been found in numerous cases, as well as structures entirely absent from the parent boranes and their anions. These structural variants reflect the flexibility introduced by the variable size, connectivity, number of bonding orbitals, and number of electrons contributed by the metal centre to the cluster bonding. Detailed analysis of the significance of many of these factors in specific instances are included in the references cited.

CLUSTER REARRANGEMENTS AND DESIGNED SYNTHESES

A series of recent experiments has revealed that 10- and 11- atom *nido* clusters are far less rigid than had previously been supposed and that frequently they can be induced to undergo facile cluster rearrangements or isomerizations which interchange various vertices under extremely mild conditions. Thus, deprotonation of *nido*-$[2-\text{ClB}_{10}\text{H}_{13}]$ with "proton sponge" (i.e. N,N,N',N'- tetramethylnaphthalene-1,8-diamine) in benzene solution followed by treatment with *cis*-$[\text{PtCl}_2\text{L}_2]$ in CH_2Cl_2 at room temperature (reaction (ii)), results in a 60-70% yield of the expected *nido*-$[4-\text{Cl}-7-(\text{L}_2\text{Pt})\text{B}_{10}\text{H}_{11}]$, but also a 30% yield of the 3-Cl isomer:

$[2-\text{ClB}_{10}\text{H}_{13}]$ $[4-\text{Cl}-7-(\text{L}_2\text{Pt})\text{B}_{10}\text{H}_{11}]$ $[3-\text{Cl}-7-(\text{L}_2\text{Pt})\text{B}_{10}\text{H}_{11}]$
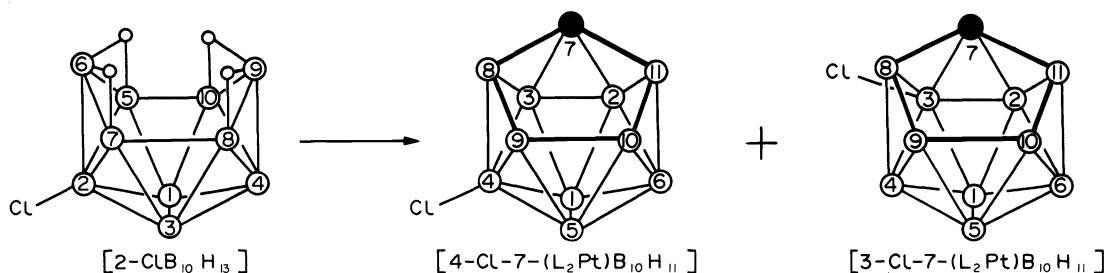
Similarly *nido*-$[2,4-\text{Cl}_2\text{B}_{10}\text{H}_{12}]$ yields the expected *nido*--$[4,6-\text{Cl}_2-7-(\text{L}_2\text{Pt})\text{B}_{10}\text{H}_{10}]$ and the rearranged *nido*-$[3,9-\text{Cl}_2-7-(\text{L}_2\text{Pt})\text{B}_{10}\text{H}_{10}]$ in an approximate 2:1 mole ratio. The preservation of the "diamond" Cl_2B_4 configuration throughout the reaction and the virtual absence of other products is particularly notable. There is no evidence of independent
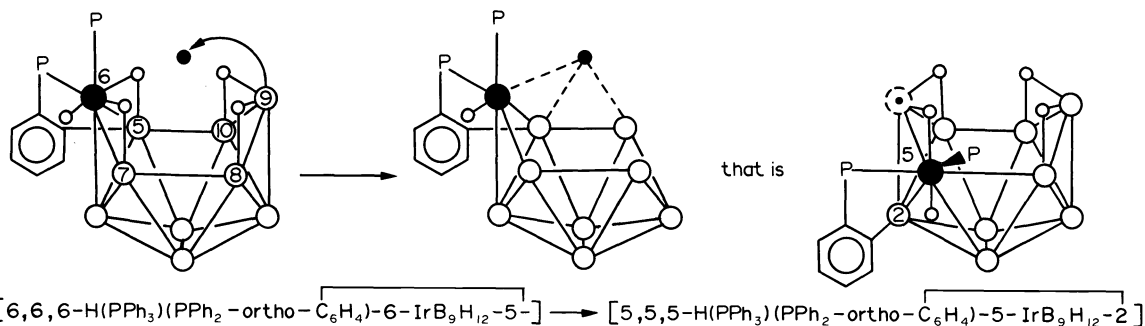

$[2,4-\text{Cl}_2\text{B}_{10}\text{H}_{12}]$ $[4,6-\text{Cl}_2-7-(\text{L}_2\text{Pt})\text{B}_{10}\text{H}_{10}]$ $[3,9-\text{Cl}_2-7-(\text{L}_2\text{Pt})\text{B}_{10}\text{H}_{10}]$
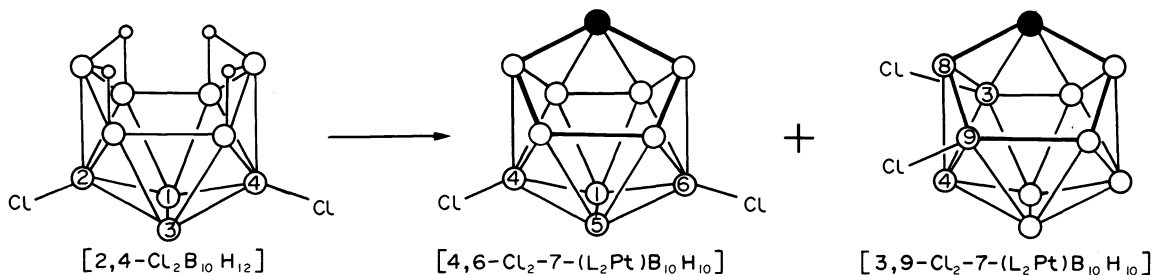
chlorine migration around the cluster. In each case the "expected" product is presumably formed by deprotonation of $H_\mu(9,10)$ followed by attachment of the Pt centre and subsequent elimination of HCl by removal of $H_\mu(5,6)$. The rearranged product might be formed by initial attack of the Pt complex at the electron rich B(2)-B(6) bond with consequent rearrangement during cluster expansion, or by a "vertex swing" of the type invoked to explain the obscure but fascinating rearrangement which attends the cleavage of coordinated thf by Et_3N and which thereby converts *nido*-$[6-\{\text{Mn(CO)}_3\}\text{B}_9\text{H}_{12}-2-\text{cyclo}-(\text{C}_4\text{H}_8\text{O})]$ into the isomerized acyclic derivative *nido*-$[6-\{\text{Mn(CO)}_3\}\text{B}_9\text{H}_{12}-8-\{\text{O(CH}_2)_4\text{NEt}_3\}]$ (ref. 51). It should be noted that such rearrangements do not always occur during metallation; for example, whereas $2-\text{ClB}_{10}\text{H}_{13}$ gives both the 4-Cl- and 3-Cl- substituted products as indicated above, $2-\text{BrB}_{10}\text{H}_{13}$ and $2-\text{IB}_{10}\text{H}_{13}$ only give the non-rearranged 4-substituted product. Likewise, $6-\text{ClB}_{10}\text{H}_{13}$ and $6-\text{PhOB}_{10}\text{H}_{13}$ give only the non-rearranged 8-substituted product (ref. 23).

Isomerization of a preformed substituted metalloborane can also be readily effected under extremely mild conditions. Thus, in CH_2Cl_2 solution at room temperature, "proton sponge" (TMND) effects the following isomerizations:

$[4\text{-}X\text{-}7\text{-}(L_2Pt)B_{10}H_{11}]$ $\xrightarrow{\text{1 hr}}$ $[3\text{-}X\text{-}7(L_2Pt)B_{10}H_{11}]$ (X=Cl,Br,I) >80% conversion

$[8\text{-}Cl\text{-}7(L_2Pt)B_{10}H_{11}]$ $\xrightarrow{\frac{1}{2}\text{ hr}}$ 60% [3-Cl-] + 15% [4-Cl-]

$[8\text{-}(PhO)\text{-}7\text{-}(L_2Pt)B_{10}H_{11}]$ $\xrightarrow{\text{8 hr}}$ 40% [3-(PhO)-] + 16% [9-(PhO)-]
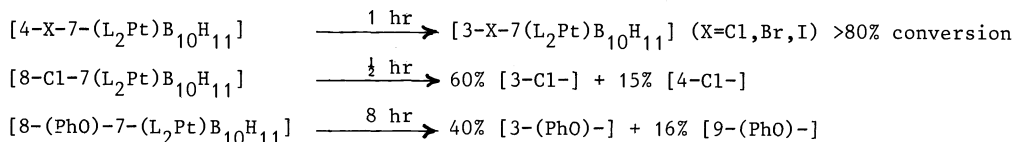
By contrast, under the same conditions, $[3\text{-}Cl\text{-}7\text{-}(L_2Pt)B_{10}H_{11}]$ only reconverted to the 4-Cl derivative to the extent of 1-2% even after 8 hr. Further work to elucidate the detailed course of these isomerizations is in progress.

A related isomerization accompanies (at least to some extent) the formation of nido-$[H(PPh_3)(PPh_2C_6H_4)IrB_9H_{12}]$ by the reaction of nido-$B_9H_{12}^-$ with $[IrCl(PPh_3)_3]$ in 50/50 CH_2Cl_2/pentane at room temperature: addition of the iridium centre occurs predominantly (80-85%) so as to give 6-subrogated derivatives as expected (ref. 72). However, up to 20% of 5-subrogated derivatives were also isolated. As illustrated below this can be reasonably interpreted in terms of a simple vertex swing of a BH group from B(9) to a position where it triangulates B(6), B(5), and B(10) (ref.71). In this case the possible vertex movements are

$[6,6,6\text{-}H(PPh_3)(PPh_2\text{-}ortho\text{-}C_6H_4)\text{-}6\text{-}IrB_9H_{12}\text{-}5^-]$ $\longrightarrow$ $[5,5,5\text{-}H(PPh_3)(PPh_2\text{-}ortho\text{-}C_6H_4)\text{-}5\text{-}IrB_9H_{12}\text{-}2^-]$

both constrained by and can be monitored by the presence of the orthocycloboronated link. Of the 5-subrogated products the main one is the 5-Ir, 2-orthophenylene isomer as shown. However, because the 6-Ir, 5-orthophenylene cluster is chiral, the alternative (clockwise) vertex swing of B(9) so as to triangulate B(6), B(7), and B(8) results in the formation of 5-Ir, 10-orthophenylene as a minor product. Numerous other examples of such isomerizations are now coming to light in the area of metalloborane chemistry (refs. 23, 71).

That these vertex swings are of even more general occurrence and significance is indicated by the very recent report (ref. 76) of the intriguing optical resolution of the chiral dicarbaborane nido-$[5,6\text{-}C_2B_8H_{12}]$: the racemic (±), mixture when treated with the chiral base (+)-N-methylcamphidine in n-hexane, undergoes an 85% total conversion to the laevorotatory enantiomer (-)-$[5,6\text{-}C_2B_8H_{12}]$. The fact that more than 50% of the racemic mixture was recovered as the (-)-enantiomer indicates that, in the presence of the base, some of the (+)-enantiomer was converted into the (-)-isomer. A possible mechanism for this unusual interconversion would be deprotonation of $H_\mu(9,10)$ followed by a vertex swing of C(6) to triangulate C(5), B(10), and B(9) (nido-$B_{10}H_{14}$ numbering scheme).

A final area of current work to which attention should be drawn is the planned high-yield synthesis of polymetalloboranes using various monometalloboranes as the starting point. This use of monometallated borane clusters (B-frames) as substrates for the synthesis of polymetallated species has become possible because of the development of high-yield syntheses of several very stable metalloboranes, and this, in turn, enables the construction of both homo- and hetero-bimetalloboranes in which the metal atoms are either contiguous, or separated by one or by two B atoms. In this connection the deprotonation of the 9-vertex cluster $[Pt(\eta^3\text{-}B_8H_{12})(PMe_2Ph)_2]$ with KH, followed by reaction with a second mole of cis-$[PtCl_2(PMe_2Ph)_2]$ to give the bimetallo 10-vertex species arachno-$[6,6,9,9\text{-}(PMe_2Ph)_4\text{-}6,9\text{-}Pt_2B_8H_{10}]$ has already been mentioned (reaction (v), ref. 28). Here the two Pt atoms in the open face are spearated by two B atoms in the sequence PtBBPtBB. Likewise, the high-yield preparation of the unrearranged 10-vertex cluster nido-$[6,6,6\text{-}H(PPh_3)(PPh_2\text{-}ortho\text{-}C_6H_4\text{-}6\text{-}IrB_9H_{12}\text{-}5^-]$ described above, permits the synthesis of the rearranged 11-vertex cluster nido-$[7,7\text{-}(PMe_3)_2\text{-}9,9,9\text{-}H(PPh_3)(PPh_2\text{-}ortho\text{-}C_6H_4)\text{-}7,9\text{-}PtIrB_9H_{10}\text{-}4^-]$ in >50% yield, as indicated the the top of the next page. It is clear that the Pt and Ir atoms are separated by a single {BH} group and the detailed molecular structure has been defined by single-crystal X-ray diffraction (ref. 77).
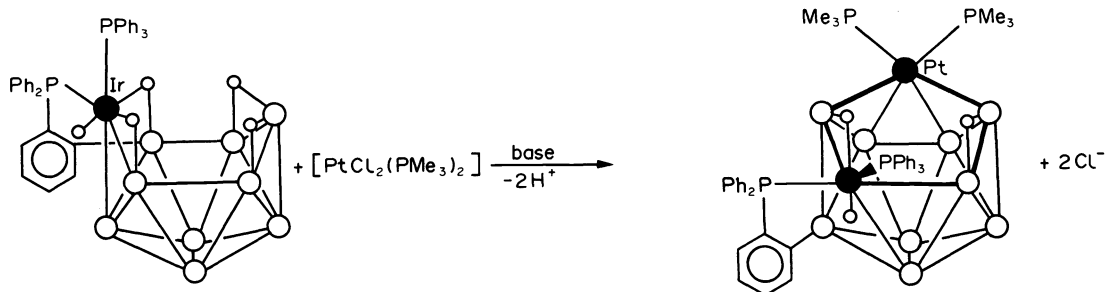
As an example of a heterobimetallic B-frame compound with contiguous metal atoms we can refer to the 7-vertex *nido*-OsPtB$_5$ cluster prepared in good yield by reaction (v) (refs. 31,32) and already mentioned in connection with the description of the coded structures based on the *closo*-B$_8$ dodecahedron by removal of a 5-connected vertex. The detailed molecular geometry can be seen in the attached diagram:

ORTEP drawing of the molecular structure of [2-{(PPh$_3$)$_2$(CO)Os}-7-{(PMe$_2$Ph)ClPt}H($\mu_{2,7}$)B$_5$H$_7$] with all except the *P*-carbon atoms omitted from the organic groups of the phosphine ligands for clarity. The rather long Os(2)-Pt(7) distance of 295.9 pm is notable; other inter-atomic distances all fall within normal ranges.
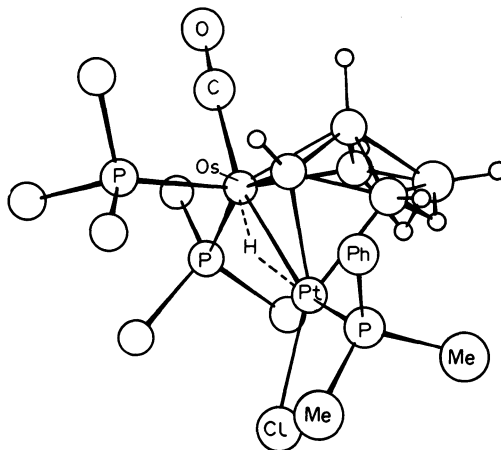
All atoms were located except for the Os-H-Pt bridging H atom (hatched lines) of which the position *trans* to CO and P(Pt) and *cis* to the two P atoms attached to Os was established by n.m.r. spectroscopy [δ(^{1}H)-10.61 ppm, ^1J(^{195}Pt-^{1}H) 555 Hz, ^2J(^{31}P-^{1}H) 98, 19, and 5 Hz. The compound has considerable significance not only for synthetic and structural reasons but also for its implications for electron counting rules and bonding consideration, as amplified in a forthcoming publication (ref. 32).

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