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PERSPECTIVE

# Exploring the interactions of d-block elements with boron. A case for electronically unsaturated metallaborane clusters

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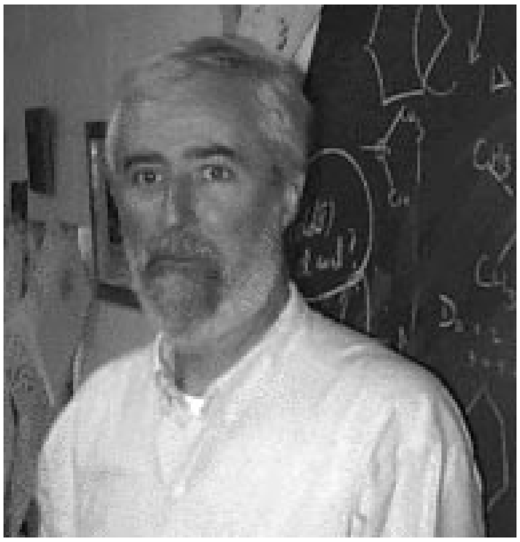
**The ability to synthesize metallaboranes of fixed cluster shape with varying numbers of metal atoms and metal identities highlights the unique ways in which the metals differ from their main-group counterparts in a cluster environment. Thus we have found that electronic unsaturation introduced by the use of early transition metals is expressed in an intriguing and novel manner in a metallaborane cluster.**

## 1 Introduction

Contemporary chemistry consists of a set of sub-disciplines each of which attracts scientists who identify with the particular section of nature subsumed. But it is one of the fascinating aspects of chemistry, as well as most scientific endeavors, that nature will not be constrained by a medieval approach to scientific farming that springs naturally from our limited intellectual capacities. Some of the most exciting developments arise from the recognition that an idea of one area fits very nicely with an idea or fact of another. This being the case, it is unfortunate that the most successful explanations of an aspect of chemistry often create barriers that hinder further development. These are sometimes so imposing that when they are broken by paradigm defying chemists the expression of surprise (or disbelief) is extraordinary, *e.g.*, Werner's six-co-ordinate octahedral metal complexes, Lipscomb's three-center two-electron bonds applied to 'electron deficient' boranes, Miller's and Paulson's syntheses of ferrocene and the analysis of its structure and bonding by Fischer, Wilkinson and Woodward, and Bartlett's synthesis of a compound of xenon. Forays into non-traditional areas force chemists to forge intellectual bridges and stimulate conceptual development.



*After graduating from Siena College in 1959, Thomas P. Fehlner obtained his Ph.D. in physical chemistry in 1963 at the Johns Hopkins University and was a research associate the following year at the same institution. He joined the Department of Chemistry at the University of Notre Dame in 1964 and presently holds the Grace-Rupley chair of chemistry. His research has ranged from the characterization of unstable species by mass and photoelectron spectroscopies to the syntheses of new cluster compounds and thin films. He has held DAAD, Guggenheim and Japan Society for the Promotion of Science Fellowships and received an award for Distinguished Achievements in Boron Science in 1990.*

## 2 The Chemistry of Clusters

Cluster chemistry is one such area. It is an area that overlays a substantial fraction of contemporary chemistry: organometallic, main-group inorganic, co-ordination chemistry, physical chemistry and solid-state chemistry. Cluster chemistry ranges from p-block to d-block element chemistry (boranes, polynuclear metal carbonyls), from early transition metals to beyond the late transition metals (zirconium clusters to gold clusters), from solution to solid-state chemistry (polynuclear Group 14 anions, Zintl phases), and from organometallic synthetic techniques to those of chemical physics or solid-state chemistry (chiral tetrahedral MM′M″C clusters by fragment substitution on $M_3C$ clusters, laser evaporated clusters, clusters excised from extended solid-state structures). It is a sign of the maturity of the area that many monographs[1–12] and review articles, too numerous to list here, address aspects of the topic. Another sign of maturity is the demonstrated success of the cluster electron counting rules initially presented in a usable form 25 years ago by Wade and Mingos.[13–21] Subsequent development and modification allow a simple electron counting connection between stoichiometry and structure. This provides the same practical guideline to the working cluster chemist that the 8, 18 electron rules continue to provide the main group and organometallic chemist.

The overlapping ideas of three (and four)-connect clusters, spherical and non-spherical clusters with intrinsic delocalized bonding, the isolobal principle, and the cluster fusion principle rationalize and interconnect the vast majority of main-group and transition metal clusters known and, at the same time, suggest the existence of an even larger number of possible clusters.[9] That is, these rules imply the existence of (a) sets of compounds of a given structure in which isolobal main-group and metal fragments are systematically varied, (b) a set of positional isomers for a given compound stoichiometry, (c) isomeric forms which are described by the capping principle as well as the fusion ideas of Mingos. In addition (d) the rules allow one to speculate on the possible formation of cluster types for which no exemplars exist at present.

Points (a) and (d) concern us here. Given the connection between metal clusters and main-group clusters, another class of compounds, those containing varied mixes of both main-group and transition-metal fragments, should exist.[22] The electron counting rule for delocalized clusters (an *n* atom closed

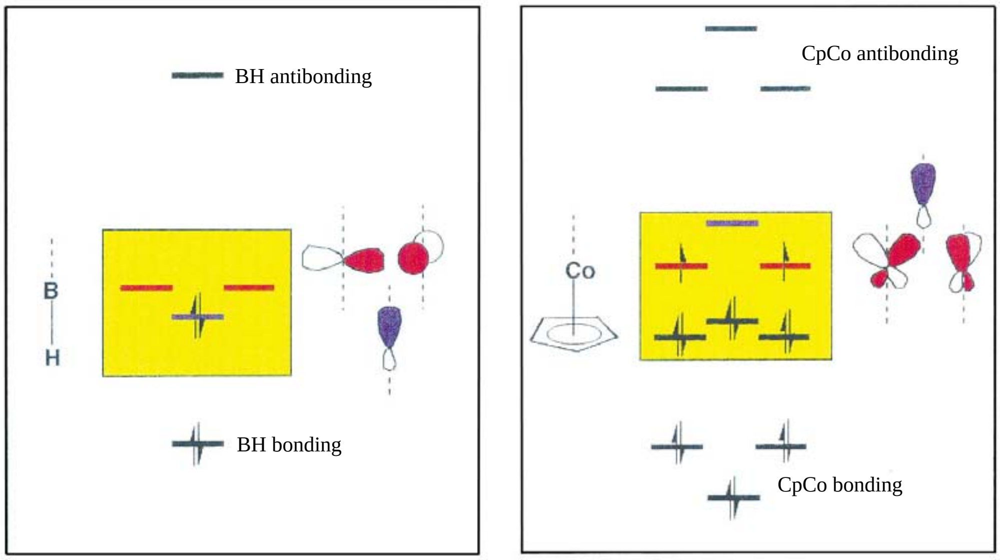


**Fig. 1** A comparison of the orbital properties of the BH and CpCo fragments. The yellow box contains the valence orbitals not used in atom–ancillary ligand bonding. The blue and red orbitals within each box represent the σ and π symmetry frontier orbitals, respectively

cluster will possess $2n + 2$ cluster bonding electrons) suggests that main group–transition-metal clusters will be most abundant for fragments that possess three frontier orbitals containing two electrons. Indeed, the BH fragment is a three orbital–two electron fragment (Fig. 1) and it was the structure determinations of polyborane clusters that gave us the three-center bond,[23] the perceptive analysis of geometry that gave us families of cluster shapes[24,25] and, ultimately, the electron counting rules mentioned above. The incorporation of metal fragments into a polyborane fragment generates metallaboranes and these species constitute a substantial class of compounds.[7,26–31] Although cluster charge and shape, number of bridging hydrogens, and metal ancillary ligands allow considerable flexibility in the metal identity, the number and types of metallaboranes containing Group 8 metals [$M(CO)_3$ fragments] and Group 9 metals [CpM fragments, $Cp = \eta^5\text{-}C_5H_5$] far exceed those for all other fragments. Although one cannot exclude bias from limited synthetic trials, the fact is that both of these fragments are three orbital–two electron fragments isolobal with BH (Fig. 1).

Although the frontier orbital properties of a main-group fragment are well defined, the five additional metal-based orbitals of a transition-metal fragment give it a flexible set of frontier orbitals with properties that vary depending on metal nuclear charge as well as ancillary ligand numbers, types and positions. Consequently, the bonding behavior exhibited by a given metal fragment type does not always correspond to that expected from a simple series of fragments. For example, it is well known that the fragment $CpFe(CO)_2$ mimics $CH_3$ (one orbital–one electron). From this one correctly concludes that $CpMn(CO)_2$ mimics $BH_3$ (one orbital–zero electron). However, in many instances $CpMn(CO)_2$ is better represented as $CH_2$ (two orbital–two electron).[32] The isoelectronic connection is there ($BH_3$ *vs.* $CH_2$) but the consequences for bonding are different. The set of three filled orbitals that are low-lying and non-bonding for the iron fragment (as with CpCo in Fig. 1) increasingly participate in bonding interactions in going to Mn.

It is this added variability relative to main-group fragments that makes metal clusters so fascinating albeit frustrating at times. For example, as shown in Fig. 2 for six-atom clusters, one can find examples of different cluster shapes for the same electron count as well as the same shape for different electron counts.[8] Understanding the possibilities for a given shape or electron count is one thing. Controlling the outcome of a synthesis is quite a different thing. But this is what the chemist requires in order to design syntheses of species with desired structure and properties.

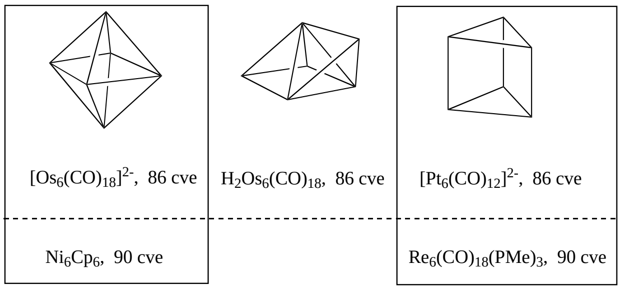


**Fig. 2** A comparison of six-atom clusters having (top row across) the same number of cluster valence electrons (cve) and different core shapes, and (first and third columns) the same core shape and different numbers of cluster valence electrons

## 3 Attractive Features of Metallaboranes

One motivation for our research originates in the idea that the synthesis of metallaboranes provides a significant simplification of the metal cluster problem. The step-wise incorporation of borane fragments in place of metal fragments in a metal cluster has several beneficial effects. First of all, the reaction chemistry is changed. As $E_{BB} > E_{MM}$, the potential energy surface associated with a metallaborane cluster core will have lower barriers than that of a polyborane cluster but higher barriers than that of a metal cluster {$C_2B_4H_6$ undergoes skeletal rearrangement only at high temperatures whereas $[Rh_2Fe_4(CO)_{16}B]^-$ rearranges at room temperature[33]}. This permits kinetic control to be achieved at convenient temperatures. It also suggests that longer sequences of reactions will be accessed so that intermediate products can be isolated. A set of compounds empirically connected by simple reactions is requisite for a basic understanding of the reaction chemistry.

Second, we reason that the incorporation of a number of boron fragments into a metal cluster bonding network limits the behavior of the metal fragment. In a sense, the less flexible bonding capabilities of the borane fragment relative to a metal fragment can act as a cluster enforcer. That is, the greater the number of boron atoms, the greater the tendency for 'normal' cluster behavior. Then, by decreasing boron content for a given cluster shape, the more flexible metal bonding capabilities are given scope and the unique characteristics imparted by a $(ML)_n$ fragment, $n = 1, 2, 3, \ldots$, if any, will be expressed.

Third, an additional interesting situation is created by varying the identity of the metal for a specified cluster size, structure and metal/boron ratio. The borane cluster orbitals for a given fragment are of fixed energy whereas the metal orbital energies vary depending on metal and ligands. As we scan the metal orbital energies through the boron frontier orbital energies different sets of metal orbitals will match up and it is not at all clear *a priori* how the block of available metal orbitals will be partitioned. In essence, the borane fragment fixes the cluster order and we can then examine the perturbation of structure and reactivity as the number and types of metal fragments are separately varied.

The last thought kindled an interest in the metals lying to the left of iron. Could we frustrate the cluster counting rules by blurring the orbital separation on the metal fragment implicit in the isolobal analogy and demanded by the borane fragment? In particular we wondered if a metal like Cr, which often tends to form paramagnetic 'electron deficient' organometallic compounds,[34] would likewise cause a breakdown in the cluster paradigm. Of course, other possible cluster responses to an insufficiency of electrons are possible. Clusters can reduce required electron counts by forming capped or fused clusters;[20] a structural response that can be restricted by working with small clusters. Metal species can respond to a reduced number of valence electrons by forming multiple bonds;[35] a structural response that would be evident in a two-metal cluster system if present.

The objective of this contribution is to compare a pair of related metal fragments in a single cluster environment. Selected metallaboranes from Groups 5 and 6, when compared to closely related metallaboranes from Group 9, reveal unexpected structural and bonding effects. We ascribe this unusual behavior to the presence of electronic unsaturation.

## 4 Synthesis

The ideas described above cannot be tested unless one has the ability of making specific compounds which are related in the desired fashion. Many metallaboranes exist and nicely illustrate the first two points discussed in the preceding section. However, as already noted, nearly all the metallaboranes with more than one metal fragment contain metals from either Group 8 or 9. Most of these compounds are less reactive than their isolobal pure borane counterparts and separation of complex mixtures is readily accomplished. This fact undoubtedly enhanced the number of compounds characterized. With some notable exceptions,[36] these compounds follow and nicely illustrate the consequences of the cluster electron counting rules combined with the isolobal principle.

After shifting research emphasis from more physical pursuits to synthesis in the mid-1970's, my group continually sought synthetic approaches that would be selective. We found that in instances where both borane and metal fragment source were comparably reactive, good yields of metallaboranes resulted. For this reason, monoboranes have been the boron reagents of choice in that the problems associated with activation of an intrinsically stable polyborane are avoided. Thus, we assemble our polyborane fragment on a metal fragment reminiscent of the manner that macrocyclic ligands are constructed.

The activation of the metal fragment has been the sticking point. Our slow progress in the synthesis of metallaboranes from monoborane and various organometallic species can be illustrated by three examples. Reactions of iron formyl anions gave highly complex mixtures of hydrocarbyl clusters and ferraboranes all in very low yields.[37] Reactions of cobalt phosphine complexes gave only cobaltaboranes but again mixtures and modest to low yields were encountered.[38] The use of 'lightly coordinated' iron carbonyl led to high yields of ferraboranes with selectivity largely controlled by initial stoichiometry.[39] All these examples reflect the difficulties we experienced in finding keys to unlock the metal fragment in the presence of monoboranes. As metallaboranes formed from the early transition metals probably would not be separable *via*, *e.g.* chromatographic techniques, selectivity became the most important issue in the chemistry which is the focus of this essay.

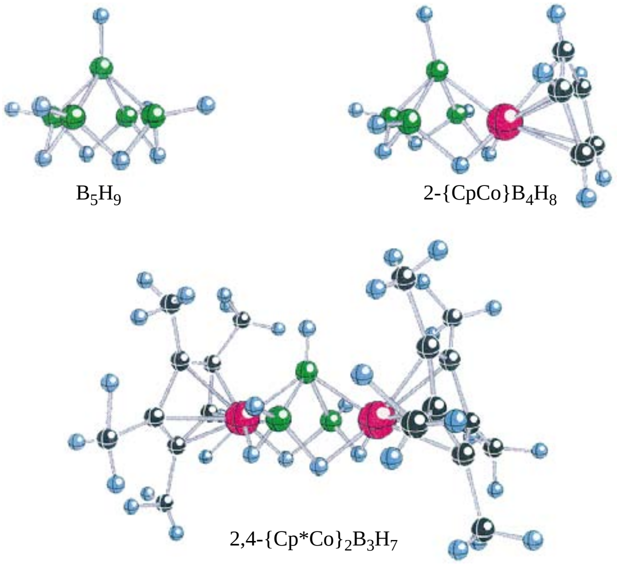


**Fig. 3** The molecular structures of *nido*-$B_5H_9$, *nido*-2-$\{CpCo\}B_4H_8$, and *nido*-2,4-$\{Cp^*Co\}_2B_3H_7$

The report by Ting and Messerle of the preparation of $[\{Cp^*Ta\}B_2H_6]_2$ from $[\{Cp^*Ta\}Cl_2]_2$ and $[BH_4]^-$, ($Cp^* = \eta^5$-$C_5Me_5$)[40] reinforced by the results of Leach and co-workers on the apparently complex reaction of Mo and W monocyclopentadienyl hydrides and halides with tetrahydroborate,[41] led us to initiate a more general investigation of the reactions of monocyclopentadienylmetal halide oligomers with monoboranes. Thus far, this approach has yielded new metallaboranes of Co,[42] Rh,[43] Cr,[44] Mo,[45] W[46] and Ta[47] and the generally high yields and clean chemistry have provided opportunities to study the reaction chemistry of these compounds. Both borane and tetrahydroborate yield new compounds and the similarities and differences between the two reagents reflect their differing reduction and co-ordination properties as well as the properties of the Cp*M fragments.

A key feature of the chemistry associated with neutral borane, *e.g.*, $BH_3 \cdot THF$, is its facile reaction with the metal halide to produce metallaboranes accompanied by the release, in all except one case of $BH_2Cl$ [equation (1)].[42] Reaction conditions are mild and in most cases a single metallaborane product is formed in very good yield. The structure of 2,4-$\{Cp^*Co\}_2B_3H_7$ is shown in Fig. 3. Note that borane serves a dual role: it removes the Cl, thereby activating the metal fragment, and provides the borane units for the $B_3H_7$ fragment. Occasionally it serves a third role in the prereduction of a monocyclopentadienylmetal halide to the lower oxidation state that yields the metallaborane. The last is not a necessary feature of the chemistry but is a synthetic convenience when the desired monocyclopentadienylmetal halide is only obtainable from a precursor in a higher oxidation state.

$$[Cp^*CoCl]_2 + 5\,BH_3 \cdot THF \longrightarrow 2,4\text{-}\{Cp^*Co\}_2B_3H_7 + 2\,BH_2Cl \quad (1)$$

Tetrahydroborate first acts as a pseudo-halide displacing the halide from the metal. The first formed metal tetrahydroborate (isolated in the case of Cr[44]) then converts into metallaboranes by loss of $H_2$ and the formation of B–B bonds,[40] *e.g.*, equation (2),[48] or by more complex processes.

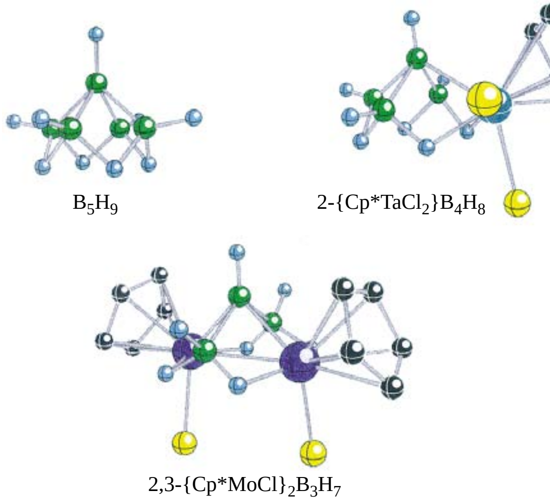


**Fig. 4** The molecular structures of *nido*-$B_5H_9$, *nido*-2-{Cp*$TaCl_2$}-$B_4H_8$, and *closo*-2,3-{Cp*MoCl}$_2B_3H_7$. The methyl groups have been removed to improve the view of the core geometries

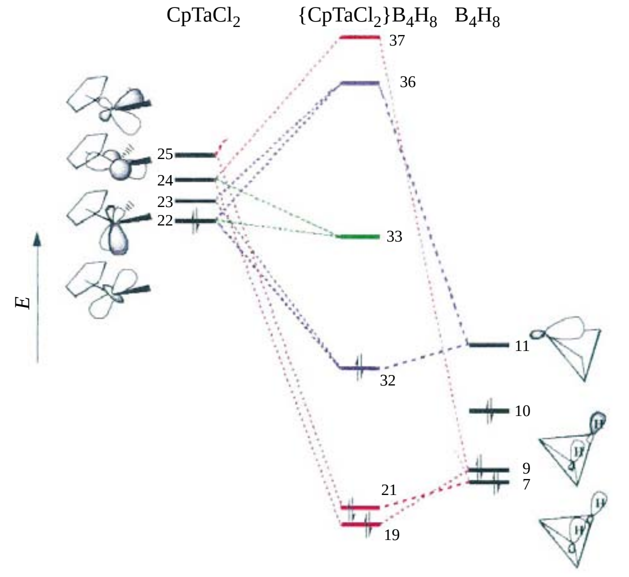


**Fig. 5** A MO correlation diagram for *nido*-2-{$CpTaCl_2$}$B_4H_8$ showing the interactions of the valence orbitals of the $CpTaCl_2$ fragment with those of the $B_4H_8$ fragment

$$[\text{Cp*MoCl}_2]_2 + 2[\text{BH}_4]^- \longrightarrow \{\text{Cp*MoCl}\}_2(\text{B}_2\text{H}_6) + \text{H}_2 + 2\ \text{Cl}^- \quad (2)$$

Most of the metallaboranes isolated to date by this approach obey the cluster electron counting rules. These compounds constitute interesting new examples of metallaboranes but the focus of this essay is on a small set of compounds that stretch the cluster electron counting rules. Thus, the following sections feature selected compounds formally derived from five- or six-atom borane frameworks by subrogation of one or two BH fragments by metal fragments.

## 5 Unsaturated Clusters

### 2-{CpCo}$B_4H_8$ *vs.* 2-{Cp*$TaCl_2$}$B_4H_8$

The cobaltaborane, 2-{CpCo}$B_4H_8$ (Fig. 3), one of many precedent-setting metallaboranes from Grimes' laboratory,[49] has a structure that conforms to expectations based on the isolobal analogy between BH and CpCo fragments.[50] As illustrated in Fig. 1, of the six valence energy metal orbitals containing eight electrons which remain after forming the metal–ligand bonds, three containing two electrons serve in cluster bonding and three containing six electrons are cluster non-bonding. The similarity of the geometry of the $B_4H_8$ fragment relative to the same fragment within $B_5H_9$ itself (Fig. 3), as well as the positioning of the bridging hydrogens, provides structural corroboration of the isolobal analogy.

In a geometric sense the tantalaborane, 2-{Cp*$TaCl_2$}$B_4H_8$ (Fig. 4) is the partner of the cobaltaborane.[47] That is, if one simply replaces the 14-electron CpCo fragment with the 12-electron Cp*$TaCl_2$ fragment the structure of the observed compound is generated. The borane fragments are very similar. This creates a problem. That is, the valence energy metal-based orbitals of $CpMnL_2$ (four orbitals containing six electrons; see above) give a Cp*$TaCl_2$ fragment a set of three empty and one filled valence orbitals. If one presumes that the three highest energy empty orbitals will be used in cluster bonding 2-{Cp*$TaCl_2$}$B_4H_8$ ends up two cluster bonding electrons short to accommodate the geometric structure displayed. The question is why?

As this question involves the partitioning of the metal-based valence electrons, geometry, with or without formal electron counting, cannot provide an answer. One needs to dissect the cluster bonding in a systematic fashion. Approximate molecular orbital (MO) methods[51] provide the knife for this dissection using cobaltaborane, a molecule we consider well understood in terms of cluster bonding, as a control. As schematically illustrated in Fig. 5, this MO analysis suggests the tantalum fragment effectively provides two electrons to the $B_4H_8$ fragment as does CpCo in 2-{CpCo}$B_4H_8$. Contrary to initial expectations the fourth and lowest energy metal orbital of the $CpML_2$ fragment, which is the only one filled for Cp*$TaCl_2$, is involved in cluster bonding.

But how does the Cp*$TaCl_2$ act as a surrogate BH fragment? Based on overlap populations, all four of the metal-based valence orbitals of the Cp*$TaCl_2$ fragment are substantially involved in binding the $B_4H_8$ fragment. However, two orbitals of Cp*$TaCl_2$ are partitioned between a bonding interaction with the $B_4H_8$ valence orbitals and a metal-localized non-bonding orbital which is empty. Upon tracking down the corresponding MO of the latter in the cobaltaborane, we find it to be the HOMO which is of δ symmetry relative to the principal symmetry axis of the CpCo fragment. Thus, the MO which is the LUMO in the case of the tantalaborane is the HOMO of the cobaltaborane. The two 'missing electrons' of {Cp*$TaCl_2$}$B_4H_8$ effectively come from the 'lone pairs' of the metal atom rather than from the cluster bonding network. This MO of the tantalaborane lies at higher energy and is unfilled because of the lower effective nuclear charge of the earlier transition-metal atom and the perturbation of the metal orbitals by the Cl ligands.

An alternative view of these $MB_4$ compounds adds understanding. Almost all monometal metallaboranes can be viewed equally well as metal complexes with a ligand set that includes a borane. Thus, $\eta^4$-$C_4H_4$ is viewed as a four-electron donor to a CpCo fragment as is the isoelectronic $\eta^4$-$B_4H_8$ ligand [Fig. 6(a) and 6(b)]. As the latter compound is simply 1-{CpCo}$B_4H_8$ in cluster notation, the $B_4H_8$ fragment in 2-{CpCo}$B_4H_8$ [Fig. 6(c)] must be a four-electron donor to the CpCo fragment even though no organometallic analog exists for comparison. In effect, the tantalaborane contains a 16-electron metal center and can be considered an analog of a compound like $Cp_2TiCl_2$. It behaves as one might expect if one had viewed it as a mimic of an early-transition-metal organometallic complex rather than an isolobal analog of a borane cluster. But, will the same be true of a dimetal cluster of the same shape?

### 2,4-{Cp*Co}$_2B_3H_7$ *vs.* 1,5-{CpMoCl}$_2B_3H_7$

The synthetic chemistry provides us with a cobalt complex, *nido*-2,4-{Cp*Co}$_2B_3H_7$ (Fig. 3),[52] which can be compared with a molybdenum complex, *closo*-2,3-{Cp*MoCl}$_2B_3H_7$ (Fig. 4).[45]

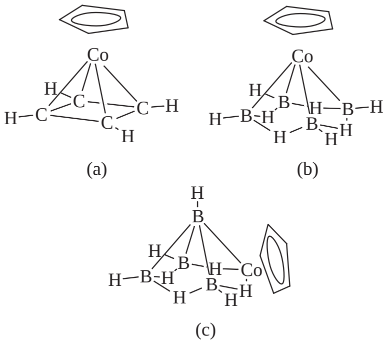


**Fig. 6** Schematic drawings of the structures of CpCo($\eta^4$-$C_4H_4$) (a), CpCo($\eta^4$-$B_4H_8$) ≡ *nido*-1-{CpCo}$B_4H_8$ (b), and *nido*-2-{CpCo}$B_4H_8$

Again the geometry of the cobalt complex corresponds to that of the isolobal pentaborane(9) cluster, *e.g.*, the $B_3H_7$ fragments are very similar and the CpCo fragment is isolobal with BH.

Consider now the molybdenum cluster which also looks very similar to the cobalt cluster. A CpML fragment has five valence energy metal-based orbitals. Let us be more flexible now. We can see that the CpMoCl fragment can serve as a three-orbital–zero-, two- or four-electron fragment. Ah, it is simple you say, CpMoCl acts as a two-electron fragment like $CpTaCl_2$ thereby meeting the requirements of a *nido* five-atom cluster. However, life becomes more complicated if we pay attention to the distinctive geometric differences between the two metallaboranes.

A comparison of the structural parameters of the Co and Mo clusters defines the problem. The Co–Co distance in 2,3-$\{Cp^*Co\}_2B_3H_7$ (3.36 Å) confirms the lack of a direct M–M bonding interaction as required by its formulation as a *nido* cluster. The Mo–Mo distance in $\{Cp^*MoCl\}_2B_3H_7$ (3.096 Å) is long but still suggests a bonding interaction. Further, the $B_3$ fragment in the molybdenum compound is significantly more open than that of the cobaltaborane (118 *vs.* 101°). Both observations are consistent with the geometrical expectations of a trigonal bipyramid, *i.e.*, $\{CpMoCl\}_2B_3H_7$ is a *closo* cluster.

So the dilemma is the following. If each Mo fragment contributes three orbitals and two electrons to cluster bonding then the geometry should be analogous to that of the cobalt compound. However, it is not. If each Mo fragment contributes three orbitals and zero electrons then the cluster lacks two electrons relative to the number expected for the observed trigonal-bipyramidal structure. Both Cp*MoCl fragments are in equivalent environments and it is not reasonable to consider one a two-electron donor and the other a zero-electron donor. Thus, a simple selection of the three orbitals to be used by the metal fragment from the five available provides no solution to the problem.

Again, a molecular orbital analysis is helpful. In comparing the MO behaviors of the Co and Mo compounds (Fig. 7) we see two things. First, the structural distortion that brings the two Mo atoms closer together and opens the boron fragment causes a large splitting of a pair of orbitals which are Mo–Mo bonding and Mo–Mo antibonding, respectively. In the Mo complex, the latter ends up at high energy and empty. The pair of orbitals represent a net Mo–Mo bonding interaction. Both of the corresponding orbitals are at lower energy and filled in the case of the cobaltaborane. Second, just as in the case of the tantalaborane, one of the filled, metal-based cluster non-bonding orbitals of the Co compound is found at higher energy and empty in the Mo compound.

Thus, the higher metal d orbital energies of the Mo compound *vs.* the Co compound play the same role they did in the tantalaborane but, in addition, a structural distortion creating a M–M bond leads to the destabilization of a second orbital. As one is hard put to assign a specific isolobal character to the Cp*MoCl fragment, we consider the molybdaborane an unsaturated metallaborane cluster with some similarities to a 16-electron transition-metal complex but with a closer connection to an unsaturated compound such as $H_2Os_2(CO)_{10}$.[8] However, in the molybdaborane there is no Mo–Mo double bond and the unsaturation is thought to be substantially spread over the cluster network. Clearly it is spread over the two metal centers but there is evidence that it is spread over the entire cluster framework as well. That is, saturated molybdaboranes, *e.g.* $\{Cp^*Mo\}_2B_5H_9$[41] (see below) have shorter M–M distances and longer M–B distances relative to $\{Cp^*MoCl\}_2B_3H_7$. This is consistent with the M–M δ bonding and M–B antibonding nature of the MO which is filled in the former and empty in the latter.

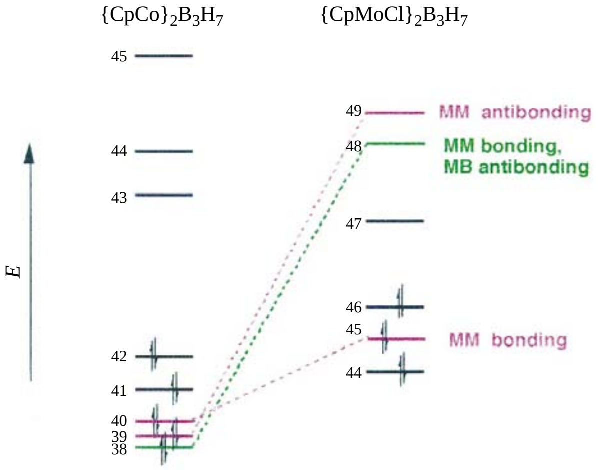


**Fig. 7** A MO correlation diagram for *nido*-2,4-$\{CpCo\}_2B_3H_7$ and *closo*-2,3-$\{CpMoCl\}_2B_3H_7$, showing the origins of the four-electron difference between the two cluster structures

In our tight focus on the *nido*-$M_nB_{5-n}$ system, the existence of closely related 'normal' metallaboranes as controls is very important. A low formal electron count for a single compound is not unambiguous evidence of electronic unsaturation as even in main-group clusters geometric distortions can lead to non-standard counts.[20] These have been discussed before in various contexts, *e.g.*, predicted distortions leading to a stabilization of $Si_n$ *vs.* $[Si_n]^{2-}$ clusters.[53] However, in the comparison of closely related $M_nB_{5-n}$ clusters one can distinguish the unusual unsaturated systems from the normal ones.

## 6 Reaction Chemistry

The real proof, and usefulness, of delocalized cluster unsaturation must be found in the reaction chemistry of these molecules. Thus far, only the reaction chemistry of the first example of an unsaturated metallaborane, $\{Cp^*Cr\}_2B_4H_8$, has been investigated.[44,54–56] The analysis of the bonding in this species is analogous to that of the Mo compound;[57] it lacks two of the prescribed electrons required by its geometry. However, in this case we have no 'normal' transition metal analog with which to compare it and the interpretation of the molecular orbital calculations is not as firmly based.

The chromaborane reacts selectively with a variety of substrates all of which are formal Lewis bases. The reactions established to date are shown in the reaction wheel in Fig. 8. Except for one, the products have at least the prescribed number of electrons for the cluster geometry displayed, *i.e.*, the cluster bonding is saturated. Clearly this is one driving force for the reactions although there must be others because $\{Cp^*Cr\}_2B_4H_8$ has a rather selective reactivity. For example, the reaction of $\{Cp^*Cr\}_2B_4H_8$ with $CS_2$ results in clean hydroboration of both C–S bonds and binding of the resulting $H_2CS_2$ fragment to the cluster.[54] On the other hand, alkynes and alkenes fail to react. An interesting reaction is the one in which an electron is added to form the radical anion. Rapid electron exchange is observed

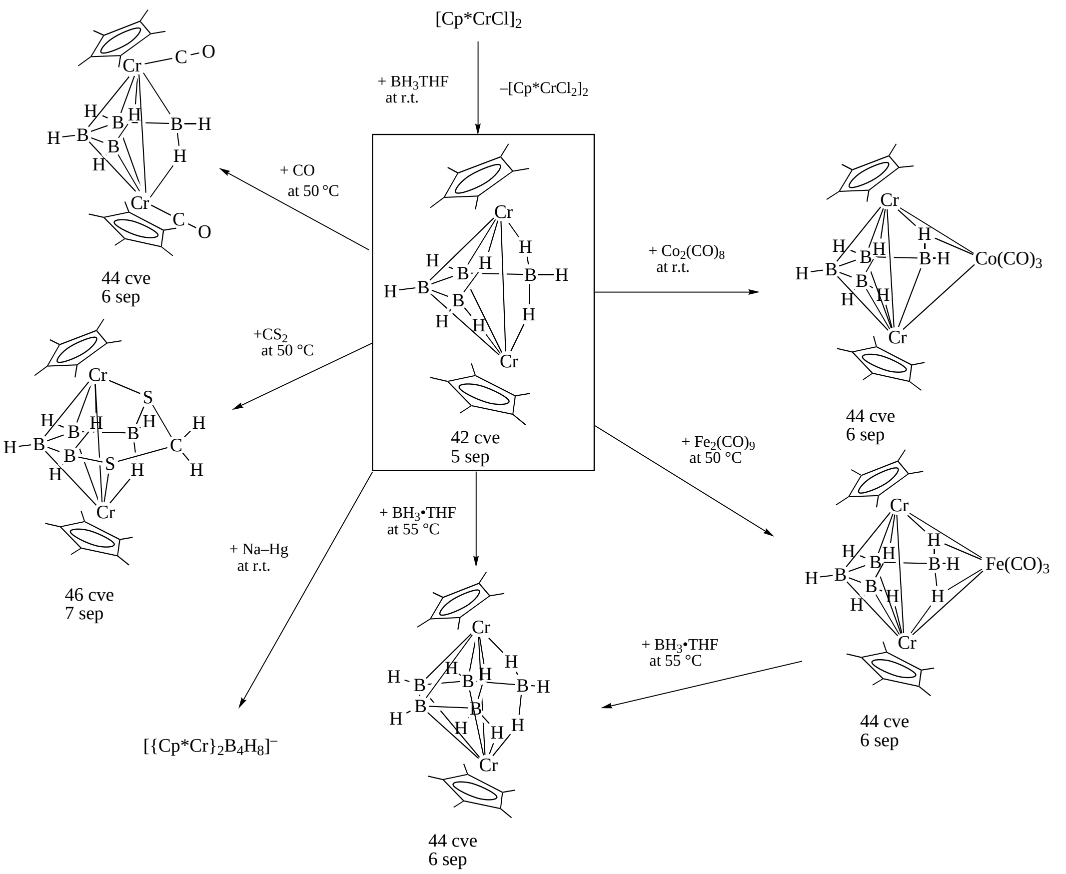


**Fig. 8** Schematic diagram of the preparation of $\{Cp^*Cr\}_2B_4H_8$ and its reactions with main-group and transition-metal moieties

between the anion and the neutral precursor establishing the basic similarity of the two cluster structures.[58]

A particularly revealing set of reactions is the addition of isolobal BH and $Fe(CO)_3$ fragments to unsaturated $\{Cp^*Cr\}_2B_4H_8$ when compared to the addition of the same fragments to saturated $\{Cp^*Mo\}_2B_5H_9$.[59] The BH fragment inserts into $\{Cp^*Cr\}_2B_4H_8$ to form $\{Cp^*Cr\}_2B_5H_9$ with a structure analogous to that of $\{Cp^*Mo\}_2B_5H_9$. The isolobal $Fe(CO)_3$ fragment, on the other hand, simply co-ordinates to $\{Cp^*Cr\}_2B_4H_8$ with only minor changes in the cluster geometry of the latter.[55] In co-ordinating the chromaborane, the iron fragment contributes two electrons to the $\{Cp^*Cr\}_2B_4H_8$ cluster bonding system making it saturated and, at the same time, receives four electrons thereby satisfying the 18-electron rule. The $Fe(CO)_3$ fragment is only loosely connected to the bridging hydrogens as it swings back and forth between the two equivalent sites on the NMR time-scale. Addition of $BH_3$ removes the iron fragment and produces $\{Cp^*Cr\}_2B_5H_9$. The analog $\{Cp^*Mo\}_2B_5H_9$ also adds $Fe(CO)_3$ but the two electrons the iron fragment contributes to the saturated $\{Cp^*Mo\}_2B_5H_9$ cluster results in formation of a bicapped octahedron with the iron fragment fully incorporated into the octahedral core. This is perfectly in accord with expectations based on the electron counting rules. Addition of a two-electron metal fragment to the unsaturated compound produces no major cluster structure modification whereas similar addition to the saturated cluster results in the expected core structural change.

## 7 Final Remarks

It is a curious fact that neither $\{Cp^*MoCl\}_2B_3H_7$ nor $\{Cp^*Cr\}_2B_4H_8$ adopt localized M–M multiple bonding to make up for the low electron counts. Metal–metal multiple bonding is a common response for dinuclear organometallic species and is found in one organometallic relative of $\{Cp^*Cr\}_2B_4H_8$ which has a Cr–Cr triple bond (Fig. 9).[60] However, although metallaborane chemistry is clearly related to organometallic chemistry, we do not expect it to be identical. In fact, it is the differences that one finds meaningful.

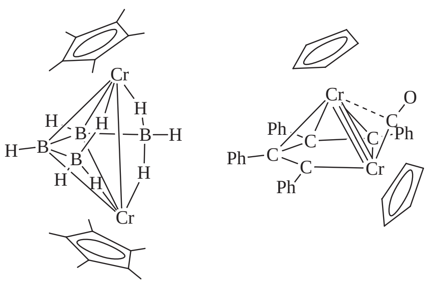


**Fig. 9** A comparison of schematic drawings of the structures of $\{Cp^*Cr\}_2B_4H_8$ (42 cve) and $\{CpCr\}_2(CO)(C_4Ph_4)$ (44 cve). The latter can also be compared with $\{Cp^*Cr(CO)\}_2B_4H_6$ (44 cve) which is shown in Fig. 8

It is also true that the large majority of the known metallaboranes as well as those of the earlier transition metals obey the electron counting rules. It is only in the comparison with the geometric and electronic behavior of these 'normal' metallaboranes that the unusual properties of electronically unsaturated metallaboranes are revealed.

This is work in progress and much remains to be accomplished. We must, of course, go on to systems containing three metal atoms but first many more metals remain to be explored in the $MB_n$ and $M_2B_n$ cluster networks. We fully expect more surprises on the way to gaining a better understanding of transition metal–main group cluster systems. After all, the full scope of organometallic chemistry was only revealed when compounds containing metal–carbon bonds for all metals became accessible.

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