The relevance of boranes and metallaboranes to the structures of p-block element nanoparticles

Thomas P. Fehlner *

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, USA

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ABSTRACT

Recent d-block element metallaborane chemistry, in which metal identity is varied with constant ancillary ligand, demonstrates how the rising energy of the d orbitals as one moves to earlier metals gives rise to non spherical cluster shapes that permit low formal cluster electron counts. In essence, the separation of frontier orbitals from "nonbonding" orbitals required by the isolobal analogy breaks down and the resulting mixing generates additional high-lying empty orbitals concurrently with shape change. A very similar mechanism explains recent p-block cluster chemistry albeit with variation in extent of external cluster ligation as the variable and separation of external lone pair orbitals from cluster bonding as the problem. Sensible, novel explanations of the shape/electron count relationships can be discovered for large group 13 clusters by recognizing the perturbation in cluster orbital energies when stabilization by ligand interactions is removed. These observations are pertinent to an understanding of large p-block clusters with internal atoms often referred to as nanoparticles.

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1. Introduction

Electron counting has played an important role in chemistry for generations of chemists. The simplicity of the 8 and 18 electron rules as well as the concept of a two center-two electron (pair) bond not only introduces beginning chemists to systematic structural chemistry but also still serve as useful guides to the connection between composition and structure. Yet these are not universal rules. They presuppose high stability (large HOMO–LUMO gap in MO terms) and fail when applied outside the boundaries imposed by the set of assumptions that lie behind them. Interestingly it is these outliers that are often most useful, e.g., the role of 16 electron complexes in catalysis. We know from quantum mechanics that although localization of the heavy nuclei is valid, localization of the much lighter electron is not. Thus, any scheme in which electrons are partitioned, e.g., electron pair bonds, lone pairs or oxidation states, will have a limited range of validity. Still, even in the age of quantitative theoretical treatments, electron counting rules retain considerable value.

The early history of the boranes is illustrative of the futility of treating compounds with existing rules when they lie outside the range of validity, e.g., shoe horning diborane into the two center-two electron paradigm. It was the introduction of the three center-two electron bond, i.e., more delocalization of the electrons,

that permitted the observed composition and structure to be justified with a simple electronic model [1]. Four two center-two electron BH bonds and two three center-two electron bonds suffice to account for the composition which provides 14 valence orbitals and 12 valence electrons and the bridged structure. Although multicenter bond models could rationalize the more complex cage structures of the higher boranes (styx rules) this approach was not particularly useful in a predictive mode. As electron counting rarely gives much information on chemical and physical properties, their raison d'être outside of teaching must lie in their usefulness as a predictive tool. For the experimental chemist a counting rule that only rationalizes is like a model of a race car—fun to play with but useless to race with. In the early 1970s an electron counting rule capable of predicting stable cluster compositions was developed for boranes and an analogous one for metal clusters [2,3]. With the development of the idea of isolobal main group and transition metal fragments [4,5], these approaches could be applied to mixed metal/main group element clusters, e.g., metallaboranes. Here is where this story begins.

2. Cluster electron counting rules

In order to understand what follows it is necessary to recapitulate (a) the borane cluster electron counting rule and, most importantly, a key assumption that lies behind it, and (b) the isolobal concept and the assumptions that permit its application to metallaboranes.

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* Tel.: +1 574 631 7234; fax: +1 574 631 6652.
  E-mail address: fehlner.1@nd.edu

2.1. Boranes

Recognition by Williams of the possibility of deriving all the known structures of the boranes and carboranes from the 12 vertex deltahedron (icosahedron) [6] led directly to the rule derived by Wade for any deltahedron (a polyhedron with triangular faces only). By separating the external cluster bonding (most often BH two center-two electron bonds) from the internal cluster bonding, he showed that a deltahedron of order n can be usefully assigned $n + 1$ skeletal electron pairs (sep). If the number of BH fragments available is n, the cluster is known as *closo*-; if $n - 1$, *nido*-; and if $n - 2$, *arachno*-. Thus (Scheme 1), $[B_6H_6]^{2-}$ is a *closo*-octahedron, $[B_5H_5]^{4-}$ is *nido*-square pyramid (observed as B_5H_9 or $[B_5H_8]^-$), and $[B_4H_4]^{6-}$ is a *arachno*-"butterfly" (observed as B_4H_{10} or $[B_4H_9]^-$) but all have 7 sep and geometries derived from an octahedron.

Now the separation of the external BH bonding from the internal bonding is not an assumption justified by symmetry but rather one that depends on orbital energetics. In any given deltahdral *closo*-borane of order n, there will be a total of $5n$ MOs. A large HOMO–LUMO gap occurs between $2n + 1$ filled and $3n - 1$ empty orbitals (Scheme 2) [7]. The external BH bonding is strong; thus, there will be a set of n orbitals with large BH bonding character at low energy and one with large BH antibonding character at high energy. Hence, for the purpose of counting, we are justified in removing them from the filled and unfilled manifolds leading to $n + 1$ and $2n - 1$ filled and unfilled orbitals respectively. The low-lying $n + 1$ orbitals are assigned to cluster bonding. The assumption of separability restricts the $n + 1$ counting rule to systems for which it is valid. This point is crucial to what follows.
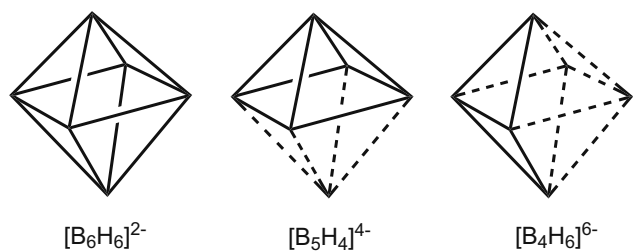
2.2. Metallaboranes

Move now to metallaboranes which can be viewed as borane clusters with one or more vertex replaced by a transition metal fragment. It is the isolobal principle that permits a large number
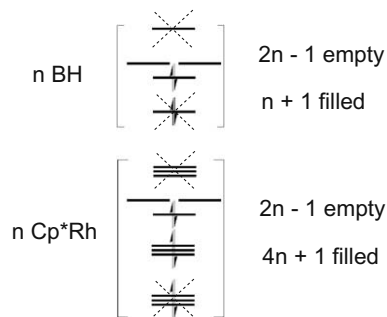
of these compounds to be considered analogous to boranes in terms of a relationship between structure and composition based on similar cluster electron count.

Consider first a *closo*-borane constructed from BH fragments (Scheme 3). Each BH fragment brings 5 MOs so a cluster of order n will have a total of $5n$ MOs as expected. If one ignores the high-lying BH antibonding orbital and the low-lying BH bonding orbital then the three remaining (frontier) orbitals generate $n + 1$ bonding and $2n - 1$ antibonding or nonbonding orbitals as before. The n BH fragments bring n electron pairs; hence, a *closo*-borane of order n requires a 2-charge. A metal fragment, e.g., Cp*Rh, where Cp is η^5-C_5Me_5, is a much more complex beast. The Cp* metal bonding can be considered to involve three metal orbitals yielding 3 bonding and 3 antibonding as the counterparts of the bonding and antibonding BH orbitals of the main group fragment. If these are similarly removed from the problem then a *closo*-metal cluster of order n will have a large HOMO–LUMO gap between $4n + 1$ filled orbitals and $2n - 1$ empty orbitals. The latter is identical to that for a borane—a point first observed by Mingos [8]. In terms of filled orbitals, the Cp*Rh fragment will behave like a BH fragment (same number of valence orbitals and electrons, i.e., 3 and 2, respectively) only if a set of three filled metal orbitals are cluster nonbonding (the "t_{2g}" set of Hoffmann) [5]. This is most likely for late transition metals with strong π-acceptor ligands like CO where the empty π^* orbitals of the CO interact strongly with the "t_{2g}" set thereby pushing these filled metal orbitals to lower energy. As a consequence, the assumption of three low-lying filled cluster nonbonding orbitals for each metal fragment in a metallaborane places an additional limitation on the systems for which it is valid. Of course, Hoffmann has relaxed this restriction ("into the t_{2g} set") but doing so introduces another variable and considerably reduces the predictive value of the concept.
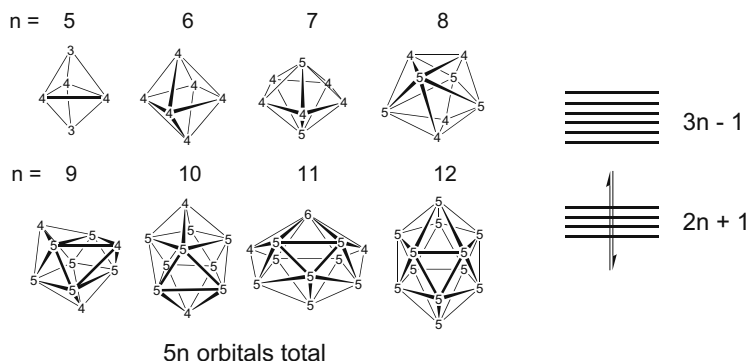
It is the observation of early transition metal systems that lie outside the region of validity of the isolobal/cluster electron count-

$[B_6H_6]^{2-}$ $[B_5H_4]^{4-}$ $[B_4H_6]^{6-}$

Scheme 1.

n BH   2n - 1 empty   n + 1 filled

n Cp*Rh   2n - 1 empty   4n + 1 filled

Scheme 3.

n = 5   6   7   8

n = 9   10   11   12

3n - 1

2n + 1

5n orbitals total

Scheme 2.

ing rule that led us subsequently to identify main group cluster systems that similarly lie outside the region of validity of Wade's rule. In the following the observations on selected metal systems are summarized (synthetic and structural work from our laboratory) and then the insights thus obtained are applied to p-block element clusters lacking external ligands (synthetic and structural work from other laboratories).

3. Early transition metal metallaboranes

We were far from the first in exploring metallaboranes and the early work of Greenwood [9], Kennedy [10], Hawthorne [11], Grimes [12], Shore [13], Gaines [14] and others revealed much of the considerable body of chemistry now known. However, most of these compounds contain late transition metals notably from groups 8 or 9 with π-acceptor ligands like CO or pseudo-multidentate ligands like Cp or Cp*. Generally these compounds were isolated from mixtures by chromatographic procedures not usually amenable to early metal properties. Further, yields were often low restricting derivative chemistry. Many, although not all, followed the Wade (or Mingos) electron counting rule combined with an application of the isolobal analogy—specifically three metal d orbitals were low-lying and filled and, as far a counting electrons was concerned, not involved in cluster bonding. Hence, this simple rule was very useful in preliminary identification of compounds from spectra as well as for defining reasonable synthetic targets. For example, all three cluster isomers for a dimetallapentaborane(9) are now known: 1,2-(Cp*Rh)$_2$B$_3$H$_7$ [15], 2,3-(Cp*Rh)$_2$B$_3$H$_7$ [16], and 2,4-(Cp*Co)$_2$B$_3$H$_7$ [17]. There can be no question but that the best description of these three borane–metal "complexes" is the cluster description.

After about 10 years of searching for a route to metallaboranes that was general in terms of transition metal, we discovered in the 1990s that the reaction of monoboranes ([BH$_4$]$^-$ and BH$_3$L) with protected metal chlorides gave good yields of metallaboranes from metals ranging from group 5 to group 9 [18–20]. For the first time this permitted the comparison of the structures and properties of metallaboranes of similar or identical molecular formulae but differing transition metals. The metal effect on structure could now be separated from that of the metal ancillary ligands as well, in some cases, from those of bridging hydrogens. Almost from the beginning we got surprises that pressed our understanding of the electronic structures even at the level of MO calculations. But as more and more compounds with differing metals were uncovered a sensible, rather general, explanation was revealed. As you will see, it has relevance outside of borane chemistry as well.

Three examples will be presented to make the point. Others will be found in our publications. The first example involves the comparison of structures of compounds containing the formula (Cp*M)$_2$B$_4$H$_8$—dimetallahexaboranes. These are known for M = Ir [21], Ru [16], Re [22], and Cr [23] and clearly the only variable is the metal identity. The iridaborane obeys Wade's rule plus simple application of the isolobal analogy; the ruthenaborane exhibits a capped structure permissible with transition metal clusters—it too obeys the rule. It is with the third and fourth that we observe the unexpected effect of the earlier metal.

The observed structures of (Cp*Re)$_2$B$_4$H$_8$ and (Cp*Cr)$_2$B$_4$H$_8$ are shown in Fig. 1 in schematic form. In terms of shape and connectivity they are the same despite the fact that the Cr compound has two fewer valence electrons. On closer examination one finds two striking differences in structure. The Re–Re distance is shorter than the Cr–Cr distance and the M–H–B hydrogens are displaced towards B in the Cr compound relative to the Re compound. The latter difference is striking in the proton NMR shifts. Clearly in moving from Re to Cr this cluster type distorts a measurable
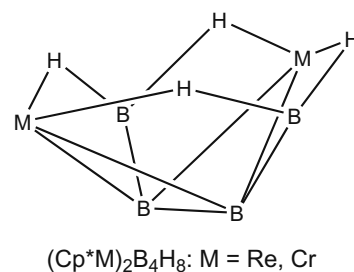

$(Cp^*M)_2B_4H_8$: M = Re, Cr

Fig. 1. The framework structure exhibited by both $(Cp^*Re)_2B_4H_8$ and $(Cp^*Cr)_2B_4H_8$. The terminal hydrogens on the framework boron atoms and the pentamethylcyclopentadienyl ligand on the metals are not shown for clarity.

amount. Probing the electronic structure with MO calculations shows that on rearrangement from the Re structure to the Cr structure one orbital, filled in the Re structure, rises in energy and is unfilled in the Cr structure [18]. Even though a few examples had been observed earlier in pure metal cluster systems, the structural distortion accompanying a shift from Re to Cr that permits a stable closed shell electronic structure for fewer electron pairs than prescribed by the electron counting rule and the isolobal analogy was not fully appreciated.

The second example was sufficiently dramatic to move the observation just described from the realm of bizarre observations to rational expectations. Thus, the reaction of (Cp*Re)$_2$B$_4$H$_8$ with borane or chloroborane permitted the isolation of dirhenaboranes containing 5 through 10 boron fragments [24,25]. The homologous closo-series shown in Fig. 2 has the general formula (Cp*Re)$_2$B$_n$H$_n$, n = 6–10 (for n = 6, a chloro-derivative was structurally characterized). All of the structures are deltahedra but, although they have the same total connectivities of the classic set of corresponding borane deltahedra, they are all distinctly oblate (flattened along the M–M axis) rather than closely spherical. The connectivities of the axial positions containing the Re atoms are 6 or 7—recall that only the problematical [B$_{11}$H$_{11}$]$^{2-}$ deltahedron has a connectivity 6 vertex all other borane deltahedra have vertices of 5 or lower. The boron atom positions in these rhenaboranes possess lower average connectivities than the corresponding borane deltahedra. Equal total connectivities between boranes and rhenaboranes of the same order implies that the rhenaborane structure can be reached from the corresponding classical borane deltahedron by diamond-square-diamond rearrangements.

With three filled cluster nonbonding d orbitals (see the discussion of isolobal above) the Cp*Re fragment is a three orbital, zero electron fragment relative to cluster bonding. Hence, each of the (Cp*Re)$_2$B$_n$H$_n$ clusters formally lack three cluster bonding pairs. Initially we interpreted the Re–Re cross cluster distances as indicative of metal–metal bonding; however, exhaustive DFT calculations disabused us of this idea [26]. Instead a careful analysis of the calculational results suggests that the structures presented by these very stable compounds arise via a beautifully intricate mutual perturbation of dimetal fragment and barrel-shaped borane cage. Bringing the two Cp*Re fragments together generates a set of frontier orbitals that can only interact with the frontier orbitals of a flattened, distinctly ring-like, borane fragment. Three orbitals on each of these complementary fragments, which normally would be filled in a late metal metallaborane in a spherical deltahedral shape, interact strongly to generate three low-lying filled orbitals and three high-lying unfilled orbitals. In the same way as in our first example involving Cr, a structural distortion permits orbital interactions within the filled frontier set to generate additional empty orbitals. In essence, the basis for the assumption of three filled cluster nonbonding d orbitals breaks down and a simple isolobal analysis is not possible. As this separation is no longer
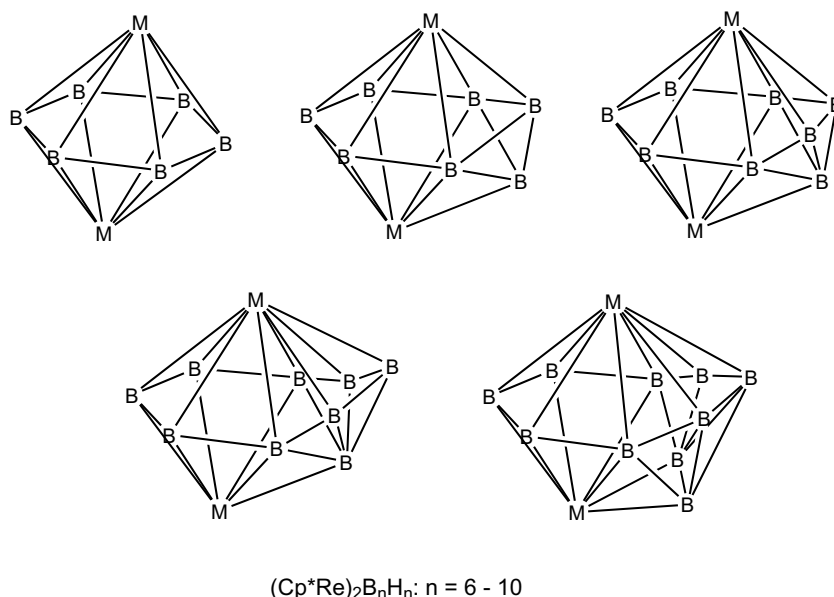
(Cp*Re)₂BₙHₙ: n = 6 - 10

Fig. 2. The framework structures of $(Cp^*Re)_2B_nH_n$; $n = 6–10$. The terminal hydrogens on the framework boron atoms and the pentamethylcyclopentadienyl ligand on the metals are not shown for clarity. The boron positions in bold type show how the original ring in $(Cp^*Re)_2B_6H_6$ is preserved up until $(Cp^*Re)_2B_{10}H_{10}$ as the BH fragments are added.

allowed it is not particularly useful to argue over the number of d electrons and orbitals utilized by the fragment in cluster bonding nor about the formal oxidation state of the metal in these highly covalent compounds.

Our third and last example is that of group 8 metallaboranes in which manifestation of a similar cluster bonding effect is more subtle. In fact, structural deviations of the type to be described have been known for many years due largely to the work of Kennedy in which he shows that such systems can also be classified in a set of deltahedra analogous to those of the *closo*-boranes [27]. Called *isocloso*-deletahedra they can be related by a diamond-square-diamond rearrangement to the classical structures. Still we include one of our examples to show that the structural deviation accompanying a low formal cluster electron count cannot be attributed to metal ancillary ligand type nor to substitution at boron, i.e., in our example the metal contains a Cp* ligand, the borons terminal hydrogens, and there are no main group heteroatoms such as carbon in the framework.

With the Cp* ancillary ligand, a diruthenaborane analogue *nido*-$B_{10}H_{14}$ might be expected to exhibit the formula $(Cp^*Ru)_2B_8H_{14}$ (Cp^*Ru is a three orbital-one electron donor to cluster bonding based on the isolobal analogy and in decaborane-14 there are 12 sep). Indeed a compound with that composition was isolated and characterized; however, the structure adopted is that of a metallaborane analogue of a dimetallapentalene complex (Fig. 3) [28]. Alternatively it can be viewed as an edge-fused pair of *nido*-ruthenahexaboranes. This does not mean that a single cage species cannot be made (negative evidence proves little) and we did isolate a diruthenaborane in a decaborane-like single cage geometry. But it has the formula $(Cp^*Ru)_2B_8H_{12}$ with two fewer hydrogens. Its structure may be seen in Fig. 3. The only difference between its structure and that of *nido*-$B_{10}H_{14}$ is a single diamond–square–diamond rearrangement that increases the connectivity at the two metal centers by one each and decreases it at two boron centers by one each. In Kennedy's nomenclature this would be an *isonido*-diruthenaborane but its relationship to our first two examples should be clear. Although this particular system has not yet been examined thoroughly via calculations, it would be fair to predict the source of the "electron deficiency" will be found in the same
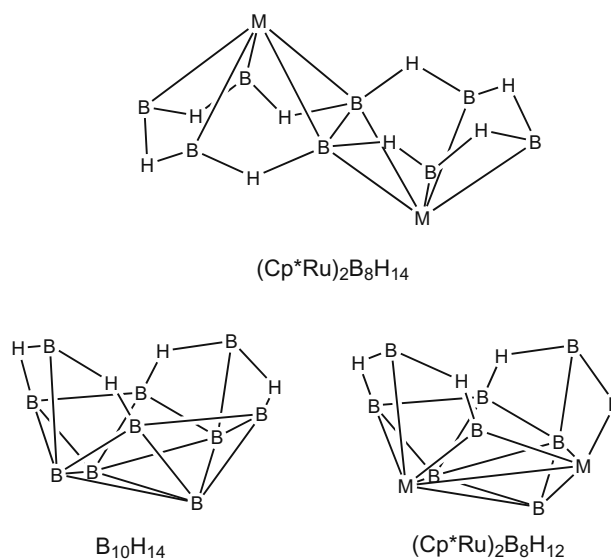

(Cp*Ru)₂B₈H₁₄

B₁₀H₁₄   (Cp*Ru)₂B₈H₁₂

Fig. 3. The framework structures of $(Cp^*Ru)_2B_8H_{14}$ and $(Cp^*Ru)_2B_8H_{12}$. The terminal hydrogens on the framework boron atoms and the pentamethylcyclopentadienyl ligand on the metals are not shown for clarity. To the left of the metallaborane structure the framework of $B_{10}H_{14}$ is shown for comparison.

kind of connection between the less spherical geometry observed and the emptying of an orbital which is filled in the most spherical geometry of the boranes.

We can generalize our observations as follows. As shown in Scheme 4, with late transition metals possessing strong π-acceptor ligands, the scenario shown at the left obtains and the isolobal analogy/cluster electron counting rule suffice to predict/rationalize the cluster geometry. However, on moving to earlier metals or π-donor ancillary ligands there is no longer any significant energy difference between the filled d orbitals. A less spherical geometry becomes more favorable with concomitant orbital mixing and stabilization/destabilization. If one or more orbitals are sufficiently destabilized they will create a new HOMO–LUMO gap and a lower

late metal   early metal

metal cluster orbitals

t_{2g}

spherical geometry   less spherical geometry
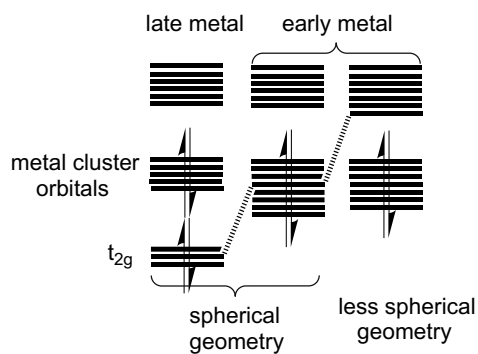
Scheme 4.

electron count. This generalization, which has been established for metallaboranes, also can be applied in a modified form to partially ligated or ligand free (bare) main group clusters of the p-block elements. Let us see how.

4. Partially ligated p-block clusters

A deltahedral n atom ligand free group 14 cluster is isoelectronic with a B_nH_n cluster and might be expected to obey the same electron counting rule, i.e., like B_6H_6 an octahedral Ge_6 cluster should be stable as a dianion. Yet, as pointed out above, the external hydrogen atoms on the borane are important in permitting the separation between external and internal bonding that lies behind the $n + 1$ bonding rule. In Scheme 5 the effect on two isoelectronic cluster compositions of removing external ligands is examined schematically. The cluster at the left, e.g., E = group 13 element, is conceptually converted to the one at the right, e.g., E = group 14 element, by moving the ligand proton into the nucleus. As a result, one orbital is removed from the system for each H atom. Thus, in effect, one BH antibonding and one BH bonding orbital collapse into a single orbital near the HOMO–LUMO gap for each external ligand removed. In the example shown, this generates a set of 6 orbitals in the former HOMO–LUMO gap that would be filled if the structure is unchanged. They are, in effect, lone pair orbitals. However, just as in the case of the early transition metal metallaboranes, there may exist a structural rearrangement that will raise one (or more) of these new frontier orbitals to an energy sufficient to empty it thereby increasing the HOMO–LUMO gap. This molecule would have a different shape and a lower electron count than expected from Wade's rule. So there are two scenarios possible for a partially ligated cluster: a Wade count and structure (with lone
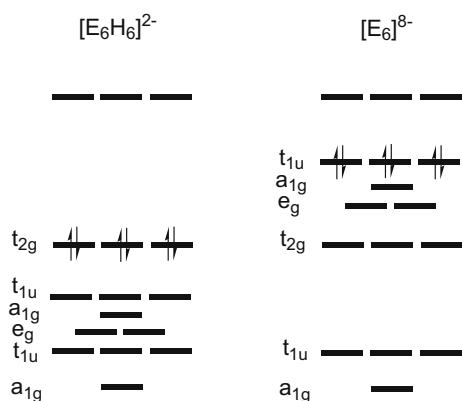
pairs) or a lower count and distorted structure. Clearly in the second case the cluster electron counting rule based on the behaviour of boranes will not be a useful predictor.

A number of bare and partially ligated p-block clusters have been characterized in recent years and some small germanium ones are shown in Fig. 4 [29]. All of these clusters obey the electron counting rule and exhibit geometries analogous to those of the boranes. So where is the problem? Before considering examples of larger clusters that are problematic, a very simple cluster system that illustrates the essential point will be described.

Many prismatic cluster shapes have been characterized for group 14 ligated element clusters. For these, a simple two center-two electron bond treatment is adequate as each group 14 element exhibits only four bonding interactions, e.g., the cubane Ge_8R_8 possesses 40 valence electrons and 40 valence orbitals just sufficient to make 12 Ge–Ge bonds and 8 Ge–R bonds. But what does one do with Sn_8R_4 [30]? The cluster structure is shown in Fig. 5 where it is seen to be a distorted cube—the cross face distances between the bare tin atoms are only 0.1 Å longer than the bonded edges. There are, unfortunately only 36 valence electrons and 36 valence orbitals yet evidence of more bonding interactions than found in Ge_8R_8!

Rather than seek a solution using delocalized MOs it is more instructive to use Lipscomp's approach and place localized bonds where one can justify them and use less localized bonds for the remainder keeping in mind that nature requires all valence electrons AND all valence orbitals to be utilized. Taking this approach we first construct the principal framework bonding and ligand bonding with 12 Sn–Sn and 4 Sn–R two center-two electron bonds thereby using 32 electrons and 32 orbitals. We are left then with one Sn p orbital on each unligated Sn atom and 4 valence electrons (left hand side of Scheme 6). These four orbitals, lying in the plane of the rectangle of Sn atoms, can be combined into a four-center bond system as shown on the right hand side of Scheme 6. Two net bonding orbitals are generated just perfect for accommodating the four available valence electrons. Note if the four atoms formed a square the HOMO and LUMO would be degenerate; however, in rectangular form the HOMO has more Sn–Sn bonding character and the LUMO more Sn–Sn antibonding character.

Now the analogy with the metallaboranes becomes clear. Just as in the case of the early metal metallaboranes where the distinction between frontier orbitals and the three "t_{2g}" type metal d functions is lost, so too here the distinction between "lone pairs" on the bare Sn atoms and the rest of the valence electrons is lost. There are no "lone pairs" in Sn_8R_4. A structural distortion accompanies the generation of two high-lying, unfilled orbitals thereby permitting the reduced electron count observed. There is an interesting connection between Sn_8R_4 and C_{60}. In neither do the bare atoms have lone pairs; rather there is an external delocalized net bonding system between the unligated atoms that adds additional stability to the primary bonding network which can be adequately described with localized bonding models.

Consider now 64 valence electron $[Ga_{19}R_6]^-$ with structure shown in Fig. 6 [31]. It is a compound that does not follow the borane structural motif or electron count. This type of cluster, a capped prismane, has been examined earlier for molecules "synthesized" and characterized by powerful calculational methods. For 20 examples of capped prismanes formed of CH and BH fragments a new cluster counting rule was developed. It is based on considerations of the electronic requirements for aromaticity in three-membered rings and capped four- and five-membered rings. The result is: cluster electron count = $6m + 2n$, where m is the number of capped rectangles or pentagons and n is the number of triangles [32]. Based on our discussions immediately preceding, in order to apply this rule to partially ligated clusters we must include the external electrons as well. So for our purposes the rule
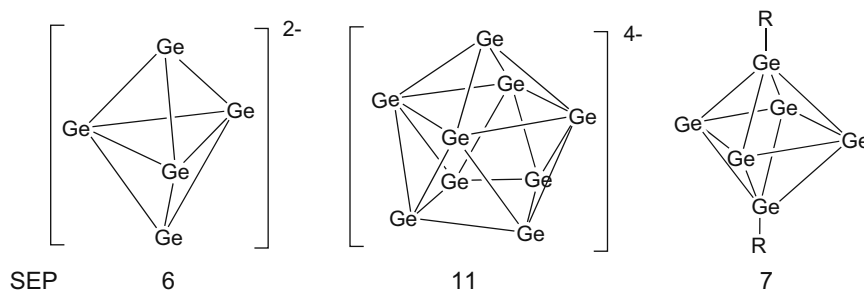
$[E_6H_6]^{2-}$ $[E_6]^{8-}$

t_{1u}
a_{1g}
e_g

t_{2g} t_{2g}

t_{1u}
a_{1g}
e_g
t_{1u} t_{1u}

a_{1g} a_{1g}

Scheme 5.

Fig. 4. The structures and skeletal electron counts for $[Ge_5]^{2-}$, $[Ge_9]^{4-}$ and Ge_6R_2.
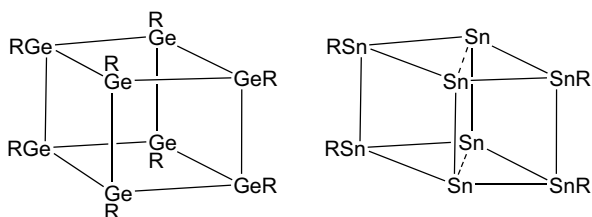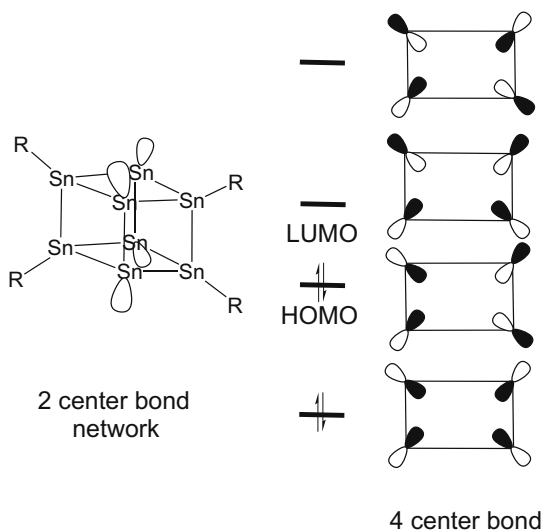

Fig. 5. A comparison of the frameworks of the cubane clusters Ge_8R_8 and Sn_8R_4. The dashed line in the latter indicate the Sn–Sn cross cube distances that are about 0.1 Å longer than the average of the cube edge distances.
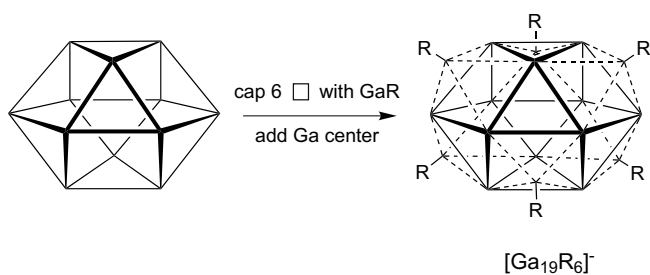

Scheme 6.

Fig. 6. The structure of $[Ga_{19}R_6]^-$ as constructed by centering and capping the six rectangular faces of a 12 vertex polyhedron with all vertices of connectivity 4.

will be modified as: total electron count $= 6m + 2n + 2p$, where p is the number of external ligand bonds. If, as shown in Fig. 6, we cap the 6 rectangles of the basic prismane framework with R groups and add a centering Ga atom, we get a total predicted electron count of $= 6 \times 6 + 2 \times 8 + 2 \times 6 = 64$ in perfect agreement with the experimental composition. One should not consider lone pairs in these systems.

An insightful paper appeared in 1991 that showed that, as the radius of curvature (related directly to cluster nuclearity) increases, the occupation of lone pair orbitals becomes less likely [33]. Empty orbitals are not implied by this statement but rather the external orbitals mix with other cluster orbitals to enhance the overall bonding. This then brings us to a consideration of very large clusters of p-block elements also known as nanoparticles.

5. Nanoparticles

Nanoparticles are species of intense interest simply because they lie somewhere between discrete molecules and extended solids. Hence, they are expected to and do exhibit properties that differ from both. In a recently published textbook [34], my coauthors and I have used these systems as a vehicle for a broad consideration of the electronic structure of clusters. It includes the small clusters discussed above, where nearly every atom is a surface atom, as well as solid state systems where the surface atoms are typically neglected. In doing so, we introduce internal atoms to the former and surfaces to the latter. The meeting point is nanoparticles. The icon for this book is the very large group 13 clusters of Schnöckel particularly $[Al_{77}R_{20}]^{2-}$ a cluster that, in contrast to most nanoparticles, has been characterized by X-ray crystallography [35]. Onion-like, it is made up of a centered 12 atom core which is surrounded by a 44 atom shell which in turn is capped with 20 AlR fragments. It is, then, a cluster that is partially ligated in the manner of the ones discussed above but one that also contains a large number of internal atoms. It also differs in that it has 253 valence electrons and is an open shell system.

What can electron counting tell us about these large systems? First one must adapt the counting rules for large metal clusters developed by Mingos and Wales to main group atoms. Their limiting models based on extent of radial and tangential bonding yield counts of 228 and 268 bracketing the observed count but not coming very close [34]. Further, DFT calculations of the density of states of Al bulk metal, the Al_{77} core of $[Al_{77}R_{20}]^{2-}$ and an octahedral Al_6 molecule shows that the HOMO–LUMO gap of the Al_{77} cluster is only millivolts. This suggests that one fundamental criterion for an electron counting rule, a large HOMO–LUMO gap is violated. "Suggest" is used as you will recall from above that the introduction of the 20 external ligands may well open up a larger gap.

At first sight, these results, as well as the odd electron count, do not look promising for an electron counting procedure to have any relevance. But this need not be the case. Consider the situation of cubane metal clusters such as $(CO)_8Ni_8(PPh_3)_6$ [36]. It has 8 NiCO

fragments in a cubic array with 6 face bridging phosphines and a total of 120 valence electrons. Thus, it obeys the cluster electron counting rules for metal clusters. However, there are dozens of clusters of the same structure type known with electron counts running from 99 to 120. It is the high connectivity of the atoms in the cluster core that hinders cluster distortion and permits variation in observable count. How does this help with $[Al_{77}R_{20}]^{2-}$? The odd electron count metal clusters were something of a problem for cluster chemists and often discussed as different species. It was only after many examples were uncovered and considerable theoretical effort that the connection was understood. These Al clusters are isolated under stringent conditions, one might say unique, and are highly reactive. It is quite possible that the electron count observed is less than the maximum possible for its shape. Again, the high connectivity present in the cubane transition metal clusters is also present in the Al cluster—$[Al_{69}R_{18}]^{3-}$ has a similar, but not identical, core. Thus, the final answer to the question posed at the beginning of this section must await the development of more structural and theoretical information.

One final comment: the existence of more than a single electron count for a given structure type is a complication but may also be a property of value in designing electron transfer systems [37,38]. To be a good mediator for electron transfer, the structural change on addition or subtraction of an electron should be very small. One needs to understand the very stable systems in order to develop the rubrics of the electronic structure. Once done, it is the less stable, more reactive systems that are most interesting because it is from them that new chemistry will flow.

6. Summary

The relevance of the observations of "violations" of the isolobal/electron counting rule in transition metal clusters to partially ligated clusters and, in turn, to nanoparticles has been presented. All chemistry is connected and many times in ways unexpected. Hence, even the study of a niche area like metallaborane chemistry can provide the key to understanding in other, potentially more technologically relevant, areas.

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