

A molecular orbital analysis of four chromaboranes On the curious behavior of ($\eta^5\text{-C}_5\text{R}_5$)Cr fragments in a borane cluster environment¹

Thomas P. Fehlner

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

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Abstract

Fenske–Hall molecular orbital calculations have been carried out on $\text{Cp}_2\text{Cr}_2\text{B}_4\text{H}_8$ (**1'**), $\text{Cp}_2\text{Cr}_2(\text{CO})_2\text{B}_4\text{H}_6$ (**2'**), $\text{Cp}_2\text{Cr}_2\text{B}_4\text{H}_8\text{Fe}(\text{CO})_3$ (**3'**), and $\text{Cp}_2\text{Cr}_2\text{B}_4\text{H}_6(\text{S}_2\text{CH}_2)$ (**4'**) ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) with structures based on the known compounds with $\eta^5\text{-C}_5\text{Me}_5$ ligands. It is demonstrated that the dinuclear Cp_2Cr_2 fragment is capable of providing an additional low energy (filled) or high energy (unfilled) orbital to the cluster bonding network with only small distortions of the Cr_2B_4 cluster core geometry. By this mechanism, the cluster core geometry changes required by Wade's rules are decoupled from cluster electron count. Thus, both electron poor and electron rich clusters, as defined by the Wade prescription, are stable and exhibit the same qualitative cluster geometry. The electronic origin of this behavior resides in the close energy match of the metal fragment ' t_{2g} ' orbitals with those of the borane fragment combined with the perturbation of differing ligands associated with the cluster. © 1998 Elsevier Science S.A.

Keywords: Cluster; Metallaborane; Chromium; Boron

1. Introduction

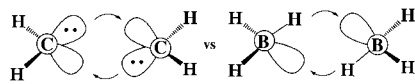
The expressions of the eight and 18 electron rules in compound stoichiometries provide the fundamental rationale for electron counting in elementary main group and organometallic chemistry utilizing electron pair bonds. These rules are operative even in the absence of the necessary numbers ligands and/or electrons required to provide sufficient two-center electron pair bonds. Thus, loss of ligands in dinuclear compounds leads to the formation of multiple bonds such that each center still obeys the eight or 18 electron rule: e.g. $\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4$ or $[\text{Cp}_2\text{Fe}_2(\text{CO})_4] \rightarrow [\text{Cp}_2\text{Fe}_2(\text{CO})_3]$ [1], both of which are considered to have double bonds and said to be unsaturated. More than an intellectual fit to the rules, the multiple bond has experimentally accessible structural parameters and constitutes a characteristic and useful site of reactivity in both main group and organometallic species.

The dimerization of BH_3 , a species with only six

valence electrons, by the formation of two three-center two-electron bonds also can be considered an expression of the eight electron rule. Each boron atom is associated with four electron pairs, two from terminal BH and two from three-center two-electron BHB bridge bonds. Thus, although often referred to as 'electron deficient' it is only such if the bonding is artificially restricted to the two-center type. In the same manner $[(\text{CO})_5\text{CrHCr}(\text{CO})_5]^-$ [2] obeys the 18 electron rule at both Cr centers if the CrHCr structural feature is considered a three-center two-electron bond.

C_2H_4 (unsaturated) and B_2H_6 (electron deficient) are isoelectronic, and a revealing way of comparing the two is to consider their respective hypothetical formation from singlet methylene and borane fragments in a dual acid–base reaction (Scheme 1). The BH bond has some Lewis basic character as shown by the ability of neutral boranes to coordinate to metals via BH bonds [3]. It is, of course, a much weaker donor than the lone pair of electrons on the CH_2 fragment. From this perspective, multiple bonds and multicenter bonding can both be thought of as responses to forces expressed by these counting rules. Indeed the bridge bonds in

¹ Dedicated to Professor Kenneth Wade on the occasion of his 65th birthday.



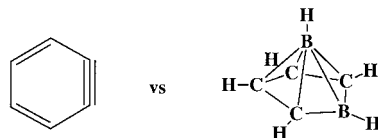
Scheme 1.

B_2H_6 have been considered as protonated lobes of a double bond.

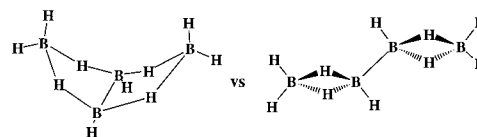
Despite this, unsaturation and multicenter bonding have considerably different structural and electronic consequences. Larger molecules, when compared in similar fashion, illustrate this point. For example, the benzyne molecule, C_6H_4 , with an in-plane localized double bond in addition to the out-of-plane π system can be compared with the isoelectronic $C_4B_2H_6$ molecule with a pentagonal pyramidal C_4B_2 core geometry and a delocalized cage bonding network (Scheme 2) [4]. The geometric consequences of multiple bonding and multicenter bonding are dramatically different.

The multicenter bonding required by borane and carborane cages was first successfully dealt with in a general sense by Lipscomb by utilizing localized two and three center bonds in the development of the 'styx' rules [5]. These ideas necessitated incorporation of resonance for symmetric structures and was of limited predictive use in terms of framework geometries. The contributions of Williams and coworker [6–9], Wade [10–13], and Mingos and coworkers [14–22] were focused first on the connection between cluster geometry and cluster valence electron count and, second, on the implications with respect to electronic structure. By doing so a requirement for $n + 1$ cluster bonding pairs for a cluster with a geometry based on a deltahedron of n vertices was identified. This key connection was later given fundamental theoretical justification by Stone [23,24]. Wade's rules, so-called, not only rationalize stoichiometry and structure but permit prediction of cluster structures based simply on knowledge of molecular formula. With the addition of the isolobal analogy [24], the connections with metal cluster chemistry, metallaborane and metallacarborane chemistry followed.

In the structural chemist's emphasis on the global minimum energy structure for a given set of atoms, other structures of higher energy that constitute true minima on the complex potential energy surface tend to be ignored. These structures are always of mechanistic interest, e.g. in terms of cluster rearrangement processes, but they can also play a role in ground state chemistry because in some cases the difference in en-



Scheme 2.

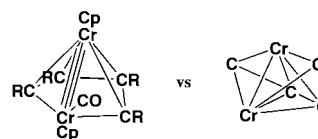


Scheme 3.

ergy between alternative structures is quite small, e.g. only very good calculations showed the energy of the known structure of B_4H_{10} to be less than that of a butadiene-like structure (Scheme 3) [25]. Thus, the perturbation of a heteroatom fragment might tip the balance and generate an exception to the rules.

Consider, then, some variants of structures predicted by Wade's rules. If the elements of H_2 are removed from a nido cluster network, these electron counting rules require rearrangement of the open structure into a closed deltahedron having one less vertex. An alternative structure is one with the same cage geometry but with a localized multiple bond, i.e. a cage with localized unsaturation. There is no evidence that such a structure is lower in energy in any homonuclear borane cage or carborane and, consequently, it would not normally be considered a viable structure. However, the situation could be considerably different in a metallaborane where isolobal metal and main group atom centers have significantly different properties. Localized multiple bonding between two adjacent metal centers in a metallaborane cage, for example, cannot so easily be ruled out.

Of particular pertinence is the ability of a transition metal fragment to adjust its electronic contribution to bonding. The example of the $CpM(CO)_2$ fragment is instructive [26,27]. The $CpFe(CO)_2$ fragment is isolobal with CH_3 , and $[CpFe(CO)_2]_2$ has a formal single bond and is isolobal with C_2H_6 . However, $[CpCr(CO)_2]_2$ has a formal triple bond and is isolobal with C_2H_2 . Thus, although simple counting suggests that the $CpCr(CO)_2$ fragment should be isolobal with CH_3^{2+} , it behaves as if it were isolobal with CH . In contrast to a main group fragment, a transition metal fragment has high-lying occupied d orbitals that may or may not participate in bonding. For Fe, these so-called ' t_{2g} ' orbitals lie at relatively low energy and are non-bonding. In the case of Cr they lie at higher energy, and for $CpCr(CO)_2$ two combine with the 'normal' single valence orbital of the $CpM(CO)_2$ fragment to form a set of three orbitals with appropriate symmetries and populations to form a CrCr triple bond. An interesting question then arises: will the



Scheme 4.

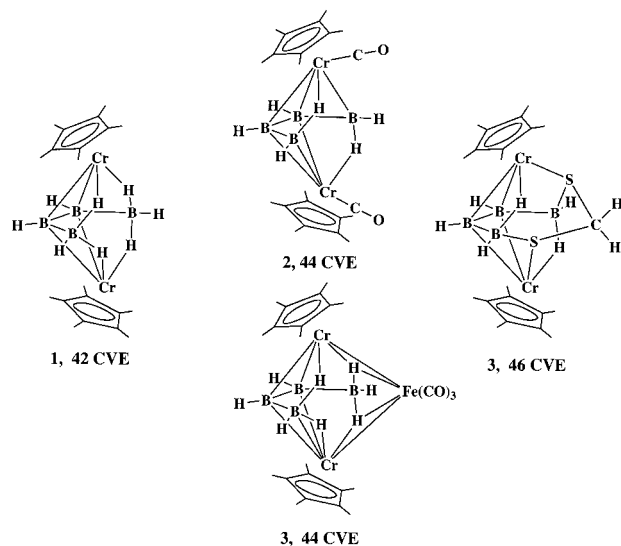


Fig. 1. Schematic drawings of the structures of $\text{Cp}_2^* \text{Cr}_2 \text{B}_4 \text{H}_8$ (**1**), $\text{Cp}_2^* \text{Cr}_2 (\text{CO})_2 \text{B}_4 \text{H}_6$ (**2**), $\text{Cp}_2^* \text{Cr}_2 \text{B}_4 \text{H}_8 \text{Fe} (\text{CO})_3$ (**3**) and $\text{Cp}_2^* \text{Cr}_2 \text{B}_4 \text{H}_6 (\text{S}_2 \text{CH}_2)$ (**4**) along with the two limiting geometric descriptions.

formal removal of the elements of H_2 from a dimetal-laborane cluster result in closing of the cluster, formation of a localized MM multiple bond, or something unanticipated by the above considerations?

For the known compound $\text{Cp}_2 \text{Cr}_2 (\text{CO}) \text{Ph}_4 \text{C}_4$, a nido-six atom cluster, it is clear that the second scenario obtains (Scheme 4) [28]. That is the Cr–Cr distance is consistent with an MM triple bond and the formal cluster electron count is two pairs short of the required eight pairs of a nido cluster structure based on a pentagonal bipyramid. The structure predicted by the cluster electron counting rules, a capped trigonal bipyramidal framework (the bicapped tetrahedron has the same connectivity) is not observed (Scheme 4).

In the case of dichromaboranes (Fig. 1) [29–32] it seems that neither cluster closing or localized multiple bond formation takes place. Unexpectedly, the set of related chromaboranes synthesized exhibit a geometric cluster structure seemingly independent of whether the number of available cluster bonding electrons is less than, equal to, or greater than the predicted number based on geometry and the electron counting rules. Thus, in the spirit of Wade's seminal contribution to our understanding of cluster bonding, the electronic structures of these stable, albeit reactive, chromaboranes are compared below with the guidance of approximate molecular orbital (MO) calculations.

2. Computational method

The molecular orbital calculations were carried out on $\text{Cp}_2 \text{Cr}_2 \text{B}_4 \text{H}_8$ (**1'**), $\text{Cp}_2 \text{Cr}_2 (\text{CO})_2 \text{B}_4 \text{H}_6$ (**2'**),

$\text{Cp}_2 \text{Cr}_2 \text{B}_4 \text{H}_8 \text{Fe} (\text{CO})_3$ (**3'**), and $\text{Cp}_2 \text{Cr}_2 \text{B}_4 \text{H}_6 (\text{S}_2 \text{CH}_2)$ (**4'**) ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) using the Fenske–Hall approximate MO method [33,34]. The 1988 version for Macintosh computers utilizing a minimal basis set was employed. For simplicity, an $\eta^5\text{-C}_5\text{H}_5$ ligand on the chromium atom was used in place of the $\eta^5\text{-C}_5\text{Me}_5$ (Cp^*) ligand found in the actual compounds **1–4** [29–32]. The structures of the four compounds are schematically shown in Fig. 1. Coordinates were taken from the published X-ray crystallographic data and idealized where appropriate. The positions of the bridging hydrogen atoms were problematic in **2**. In **3** the framework hydrogen atoms were located and refined; in **1** and **4** the hydrogens were located but not refined; in **2** they were not even located. However, the precisely defined structure of **3**, combined with known M–H–B metrics, permits them to be placed in reasonable positions in **2**.

3. Results and discussion

Although the geometries of **1** and **2** are nearly the same, the number of cluster bonding electrons differ by two. In the Wade method, which considers CpCr as a three orbital, -1 electron contributor to cluster bonding [11], **1** has five and **2** has six skeletal electron pairs (sep). In terms of cluster valence electrons (cve), in which the external ligands and all metal electrons are included in the count [24], **1** has 42 and **2** has 44. MO calculations on **1** and **2** are able to rationalize their electronic structures [30]. In this previous work attention was focused on (a) MO justification for the existence of a Cr–Cr bond in **1** and **2**, (b) the contrast between **1** and its hypothetical, but realistic, Co analog, illustrating the important role of metal nuclear charge and the noncoplanarity of the Cp rings, and (c) the perturbation in the framework of **1** caused by the addition of a CO ligand to each Cr center in **2**. However, the analysis of these two compounds alone was insufficient to address the ultimate origin of the insensitivity of cluster structure to the number of cluster bonding electrons or, indeed, whether **1** is more than simply an odd exception to the rules with no general implication for the cluster structure problem. Whatever the case, it seemed clear that there was no simple isolobal version of the CpCr fragment that would generate correspondence between the composition and geometry of **1** and the cluster electron counting rules. On the other hand, it was also clear that the behavior of this system is rooted in the nature of the CpCr fragments and in their interaction with the borane fragment.

The situation was further complicated when it was found that **4**, with seven sep (46 cve) also exhibited the same $\text{Cr}_2 \text{B}_4$ framework of **1** and **2** [32]. Some suggestion that these compounds do illustrate a general phe-

nomenon came from the characterization of **3** with six sep (44 cve) and, again, the same Cr_2B_4 framework [31]. That is, as long as one counts the CpCr fragment in the same way, the series **1–4** presents four clusters with qualitatively similar geometries but three different cluster electron counts. For these reasons, this set of compounds has now been more thoroughly analyzed both in terms of geometry and MO descriptions of the electronic structures.

3.1. MO considerations

Selected MO parameters for the Cp derivatives, **1'–4'** are given in Table 1. Although there are differences, the calculated parameters are sensibly constant for this set of closely related compounds. The calculated ionization potentials are in the expected energy region for a stable compound, the HOMO–LUMO gaps are reasonably large, the charges on Cr suggest Cr(II) (which is appropriate considering the compounds are derived from $[\text{Cp}^*\text{CrCl}_2]_2$), the Cr–Cr interactions are bonding (the Co analog of **1** gives an antibonding Co–Co overlap population for the same cluster geometry [30]), and the Cr–B overlap populations are sensitive to the presence or absence of a bridging atom. In short, based on the usual MO criteria for stability, all four molecules have an electron count appropriate for their electronic structures. Taken individually one finds nothing out of the ordinary in the MO descriptions.

In examining the electronic structure of **3'**, the MO properties of $\text{Cp}_2\text{Cr}_2\text{B}_4\text{H}_8$ in the experimental geometry in which it is found in **3'** were calculated and compared to those found for the free molecule **1'**. A portion of the eigenvalue spectrum for each geometry is shown in Fig. 2 where it may be seen that the rather small, experimentally determined, changes in this fragment in going from **1'** to **3'** (see also below) lead to a large change in the frontier orbital energies of $\text{Cp}_2\text{Cr}_2\text{B}_4\text{H}_8$, e.g. the HOMO. The gaps in the MO energy levels for the distorted geometry might suggest stability for 40, 44, or 46 cve. In this particular case the geometric change adjusts the HOMO and LUMO of $\text{Cp}_2\text{Cr}_2\text{B}_4\text{H}_8$ to approximately the same energy such that they develop properties appropriate for interaction with the π symmetry frontier orbitals of the $\text{Fe}(\text{CO})_3$

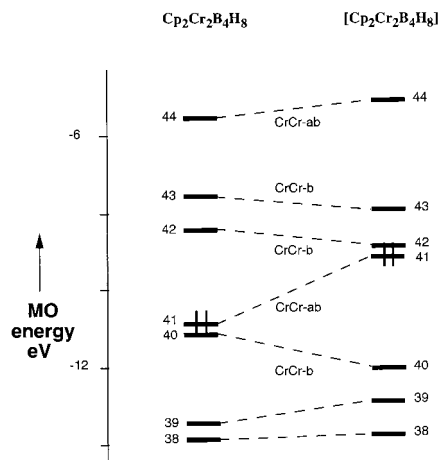


Fig. 2. A comparison of the frontier MO energies of $\text{Cp}_2\text{Cr}_2\text{B}_4\text{H}_8$ (**1'**) and the $\text{Cp}_2\text{Cr}_2\text{B}_4\text{H}_8$ fragment from **3'**.

fragment. However, the important point is that the frontier orbitals are sensitive to small changes in cluster geometry not involving cluster opening or closing by loss or gain of edge bonding interactions.

This sensitivity of the metal-based frontier orbitals to details of geometry suggests that rather small changes in geometry can lower the energy of an unoccupied orbital into the range of the filled orbitals or, alternatively, raise the energy of an occupied orbital into the range of unfilled orbitals. This observation suggests a more careful examination of the measured structural parameters of **1–4** might well be informative.

3.2. Geometric considerations

The structures of **1–4** (Fig. 1) can be considered to be based on either a pentagonal bipyramid with an unoccupied equatorial vertex (no metal–metal bond and required eight sep or cve of 48) or an M_2B_2 tetrahedron with two face-capping boron vertices (metal–metal bond and required six sep or cve of 44). As described in the earlier study of **1** and **2**, the MO evidence and the diamagnetism of the compounds are consistent with the presence of a metal–metal bond. Hence, the geometry of each cluster was designated as a bicapped tetrahedron. Independently of which description of geometry

Table 1

Selected MO parameters of $\text{Cp}_2\text{Cr}_2\text{B}_4\text{H}_8$ (**1'**), $\text{Cp}_2\text{Cr}_2(\text{CO})_2\text{B}_4\text{H}_6$ (**2'**), $\text{Cp}_2\text{Cr}_2\text{B}_4\text{H}_8\text{Fe}(\text{CO})_3$ (**3'**) and $\text{Cp}_2\text{Cr}_2\text{B}_4\text{H}_6(\text{S}_2\text{CH}_2)$ (**4'**)

Compound	HOMO (eV)	HOMO – LUMO gap (eV)	$q\text{Cr}_2^a$	$q\text{B}_4^a$	Mulliken overlap population	
					Cr_2	Cr–B^b
1'	–10.8	2.4	2.9	–1.8	0.06	0.05
2'	–9.5	3.0	2.7	–2.0	0.03	0.15
3'	–9.0	1.4	2.6	–2.0	0.11	0.01
4'	–8.6	3.8	2.4	–1.9	0.04	0.01

^a Mulliken population.

^b For a Cr–H–B edge in **1'**; for a Cr–B edge in **2'**; for a Cr, Fe–H–B edge in **3'**; for a Cr–S–B edge in **4'**.

Table 2

Selected structural parameters of $\text{Cp}_2^* \text{Cr}_2 \text{B}_4 \text{H}_8$ (**1**), $\text{Cp}_2^* \text{Cr}_2 (\text{CO})_2 \text{B}_4 \text{H}_6$ (**2**), $\text{Cp}_2^* \text{Cr}_2 \text{B}_4 \text{H}_8 \text{Fe} (\text{CO})_3$ (**3**) and $\text{Cp}_2^* \text{Cr}_2 \text{B}_4 \text{H}_6 (\text{S}_2 \text{CH}_2)$ (**4**)

Compound	sep	$d(\text{Cr}-\text{Cr})$ (Å)	Av. $d(\text{Cr}-\text{B})$ (Å)	Av. $d(\text{B}-\text{B})$ (Å)	Av. $\angle \text{B}-\text{B}-\text{B}$ (deg)
1	5	2.87	2.06	1.70	112
		long	short	short	small
2	6	2.79	2.14	1.65	120
		short	long	short	large
3	6	2.71	2.17	1.72	121
		short	long	short	large
4	7	2.92	2.16	1.81	114
		long	long	long	small

chosen, the four observed structures would be judged the same in terms of a Wade's rules analysis.

There are, however, measurable differences in the structural parameters associated with the core geometries and four such structural parameters are gathered in Table 2. Those examined are the Cr–Cr distance, the average Cr–B distance, the average B–B distance, and the average B–B–B angle. These parameters are not independent. For discussion purposes they have been classified as long (large) or short (small) as shown in the table. The qualitative agreement between the parameters of **2** and **3** relative to **1** and **4** provides justification for suggesting a distinctive cluster core geometric pattern for each of the three electron counts. In turn, one expects that the geometric changes observed in going from **1** to **2** or **3** should correlate with the properties of the lowest unoccupied MO (LUMO) of **1'** relative to those of the HOMO. Similarly, the changes in going from **2** or **3** to **4** should correlate with the properties of the second lowest unoccupied MO of **1'**. These three orbitals all have high Cr characters (ca. 60%), and the confirmation of a correlation between geometry and MO properties would suggest a prominent role of the $\text{Cp}_2 \text{Cr}_2$ fragment in the observed behavior.

3.3. Correlation of geometry and MO characters

The pertinent MOs in **1'** were examined and the bonding characters with respect to the same atom–atom interactions chosen to describe the geometric changes are given in Table 3. The character of the HOMO (MO 41) constitutes the base-line relative to changes on populating the LUMO, i.e. the addition of a pair of cluster bonding electrons to MO 42 in going from **1'** to

2' or **3'**. The correlation is very good, i.e. Cr–Cr, long \rightarrow short, antibonding to bonding; Cr–B, short \rightarrow long, bonding to antibonding; B–B, short \rightarrow short, bonding to bonding; $\angle \text{B}-\text{B}-\text{B}$, small \rightarrow large, little angle dependence to bonding at $\angle = 135^\circ$. In going from **2'** or **3'** to **4'** by the addition of a pair of electrons to MO 43, the correlation is almost as good, i.e. Cr–B, long \rightarrow long, antibonding to antibonding; B–B, short \rightarrow long, bonding to antibonding; $\angle \text{B}-\text{B}-\text{B}$, large \rightarrow small, bonding at $\angle 135^\circ$ to bonding at $\angle = 90^\circ$ and antibonding at 180° . The exception is Cr–Cr, short \rightarrow long, bonding to bonding. A possible explanation of this discrepancy is that the smaller B–B–B angle with a long Cr–B distance probably forces a long Cr–Cr distance. As the boron character of the MOs increases from 8% to 17% to 26% in going from MO 41 to 42 to 43, it is reasonable that the B–B and Cr–B interactions will become increasingly more dominant.

It seems clear that the small changes in cluster geometry in the set of compounds, plus the perturbation of the added ligands, lead to large changes in the frontier orbital properties. This permits the accommodation of two fewer and two more skeletal electrons relative to the number required by Wade's rules without either a closing or opening of the framework deltahedron, i.e. no skeletal bond formation or breaking. Compound **1** is electron poor relative to the Wade standard and we have viewed it as exhibiting delocalized electronic unsaturation [30]. Its chemical reactivity justifies this designation. Compound **3** is electron rich relative to the same standard and these 'extra' electrons are also delocalized over the cluster framework; however, its reactivity has not yet been explored.

The relative magnitudes of the perturbation of the metal orbitals by cluster geometry vs. the external ligands is not known, but it certainly would be worth investigating whether **1** could be easily reduced, i.e. whether an added electron could be stabilized by a rather minor change in cluster geometry without new metal ligands. The calculations based on the experimental structures of **1** and **3** suggest that additional external ligands may not be necessary and that this could be accomplished by a slight squashing of the cluster frame-

Table 3

Selected frontier orbital parameters of $\text{Cp}_2 \text{Cr}_2 \text{B}_4 \text{H}_8$ (**1'**)

MO	Cr–Cr ^a	Cr–B ^a	B–B for B–B–B angle ^a
HOMO (41)	ab	b	b, independent of angle
LUMO (42)	b	ab	b, $\angle = 135^\circ$
(43)	b	ab	b for $\angle = 90^\circ$; ab for $\angle 180^\circ$

^a b = bonding, ab = antibonding relative to the atoms specified.

work as illustrated in an exaggerated manner in Scheme 5.

3.4. Electron counting

These results show that the unique properties of the transition metal can add another dimension to cluster electron counting in metallaboranes. Although the isolobal principle is extremely valuable, it is least ambiguous when the 't_{2g}' set is highly stabilized by the external ligands and the intrinsic metal nuclear charge, e.g. Fe(CO)₃, or the reverse, e.g. Mo(OR)₃ [35,36]. In the case of the compounds discussed here, the metal ligand and metal nuclear charge places the 't_{2g}' orbitals right smack in the center of the typical frontier orbital energy range. Hence, not only do they have properties appropriate for cluster bonding but they are also easily perturbed, thereby effectively changing the metal fragment contribution to cluster bonding. In these compounds the 't_{2g}' orbitals plus electrons constitute a reservoir which can be accessed by rather small geometric changes. If the Wade count is low, a small cluster distortion raises the energy of a cluster orbital that would normally be filled into the region of unoccupied orbitals. If the Wade count is high, a different distortion lowers the energy of a normally unfilled orbital into the region of occupied orbitals. Neither of these orbitals is uniquely identifiable with one CpCr fragment and there is no obvious way to adjust the formal cluster electron 'count' to make Wade's rules fit. In fact, to the extent demonstrated by these chromaboranes the overall delta-hedral structure observed appears to be decoupled from electron count.

This work suggests that the addition of the appropriate number and types of transition metal fragments to a borane framework permits the manifold of alternate geometries, ordinarily lying energetically well above the Wade structures, to be accessed. The significance of the work lies not in the apparent 'violation' of Wade's rules but in the ability to construct compounds containing a hybrid electronic structure in which elements of non-classical cluster bonding compete with elements of classical bonding associated with the dimetal fragment of the cluster. Compound **1** should have a Cr–Cr localized double bond but instead exhibits a cluster structure in which the expected unsaturation is distributed over metal

and boron centers. The unique electronic features are expected to be coupled with equally interesting chemical reactivity. This is the case for **1**. However, additional reactions need be investigated and new analogs of **1** are required in order to more fully establish these ideas.

4. Conclusions

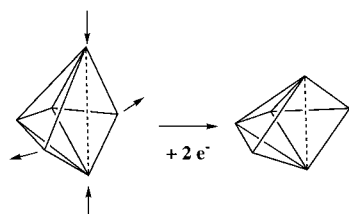
The original publications on cluster bonding authored by Ken Wade pointed out that an analysis of boranes, compounds that broke the existing rules, revealed new rules—the cluster electron counting rules. Here, in turn, the pattern defined by the cluster electron counting rules in competition with the patterns defined by rules for multiple bonding leads to new cluster forms and permits the definition of delocalized cluster electronic unsaturation and supersaturation in dichromaboranes. The observations brings to mind the comment he inserted, with apologies to Shakespeare, into one of our joint publications that "... there are more shapes in the heaven and earth of cluster chemistry than are dreamt of in our current electron counting philosophy" [37]. Yet his modesty cannot gainsay the fact that it is the context provided by the cluster electron counting rules that permits these shapes to be identified as new and which leads, ultimately, to an understanding of their origin.

Acknowledgements

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Scheme 5.

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