Hypoelectronic Dimetallaboranes**

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Dedicated to Professor Thomas P. Fehlner
on the occasion of his 65th birthday

> *"There are no such things as electron-deficient compounds, only theory-deficient chemists."*
> R. E. Rundle[1]

Polyhedral boranes and their heteroatom-substituted derivatives have inspired an entire generation of chemists.[2] The great fascination of these compounds, which have demonstrated very few applications up to the present, lay and lies in the apparent complexity of the structures and their bonding schemes, which have resisted attempts at explanation for many years. Even after the pioneering work of H. C. Longuet-Higgins and W. N. Lipscomb,[3] the boranes and their bonding received little scientific attention. This situation changed drastically in the seventies when a simple set of electron-counting rules (the Wade–Mingos' rules)[4] were suddenly not only able to explain the bonding in nearly all the boranes and carboranes known at that time, but also proved extremely useful in the emerging area of metal-cluster complexes.[5]

Following the Wade–Mingos' rules from the boranes through to the transition-metal clusters metallaboranes play an important role. The very existence of metallaboranes provided encouragement and their adherence to the rules was explained later by the simple but powerful concept of the isolobal analogy.[6]

However, metallaboranes soon appeared that did not obey the rules. The problems began with a group of electron-deficient compounds that exhibited a closed deltahedron framework but that did not take on the form of the "canonical" polyhedron. Geometrically, their most obvious violation of the rules was that certain polyhedral vertices (occupied by metals) exhibited a higher connectivity at the cost of other positions. Depending on the counting method, the number of valence electrons (VE) in the cluster can be made to agree with the *closo* rule at least (*isocloso*-structure; the electron deficiency is localized on the metal),[7] or otherwise an electron deficiency delocalized in the cluster would have to be accepted (*hypercloso*-structure; cluster lacks 2 VE).[8]

This violation of the rules reached a climax with the recent preparation of a series of extremely electron-deficient metallaboranes, by T. P. Fehlner et al.[9] These are unusually stable compounds with elements from the manganese and iron subgroups, that are directly or indirectly accessible from (pentamethylcyclopentadienyl)metal halides and monoboranes. The salient features of the unusual structures of these complexes are the high coordination number of the metal centers and a metal–metal bond extending through the borane framework.

The new structure and bonding types are illustrated here by the homologous series of dirhenaboranes $[\{(C_5Me_5)Re\}_2B_nH_n]$ ($n = 6$—10; **1**–**5**; Figure 1, top). With the exception of **1**, which to date has only been isolated as the dichloro derivative $[\{(C_5Me_5)Re\}_2B_6H_4Cl_2]$ (**1a**), all the members of the series are well characterized, both spectroscopically and structurally (Figure 1, below).[10]

"Blind" application of the Wade–Mingos' rules classifies **1**–**5** as clusters with $p = n+2$ framework atoms and $(p-2)$ skeletal electron pairs (SEPs), since the nBH groups are expected to provide two electrons each for bonding in the cluster framework. The two 12 VE fragments $(C_5R_5)Re$ should not contribute any electrons to the cluster bonding (see below). According to the capping rule[5] the structures of **1**–**5** should be derived from $(p-3 = n-1)$-vertex canonical polyhedra in which three faces are additionally capped. For example, the structure of **2** should be a tricapped octahedron. The actual structures are, however, completely different. They are noncapped closed polyhedra that, as a result of their mostly low symmetry, show little similarity to the canonical deltahedra.

Even at an early stage it was recognized that the structures of the *isocloso*- (or *hypercloso*-) metallaboranes can be generated from the canonical *closo*-structure by diamond-square-diamond (DSD) framework rearrangements.[8,11] During any DSD rearrangement the connectivity of two of the four participating atoms increases by one while that of the other two decreases by one (Scheme 1). The overall connectivity of all the vertices (total vertex connectivity, TVC) of the cluster therefore remains constant; this quantity is the lowest common denominator for structures that either conform to or contravene the rules. The retention of a constant TVC can be used to limit the number of possible structures, but does not yield a more exact structural prediction. In addition a purely topological analysis such as this cannot provide any information about the electronic structure of the rearrangement product.

A simple count of the bonding contacts (the blue and red lines in Figure 1) shows that the structures **1**–**5** have the same overall connectivity as the corresponding canonical *closo*-polyhedra with 8–12 vertices (Table 1). Therefore, it is no surprise that they can be transformed from one to the other by means of the DSD rearrangement: In a thought experiment the corresponding canonical *closo*-structure types can be

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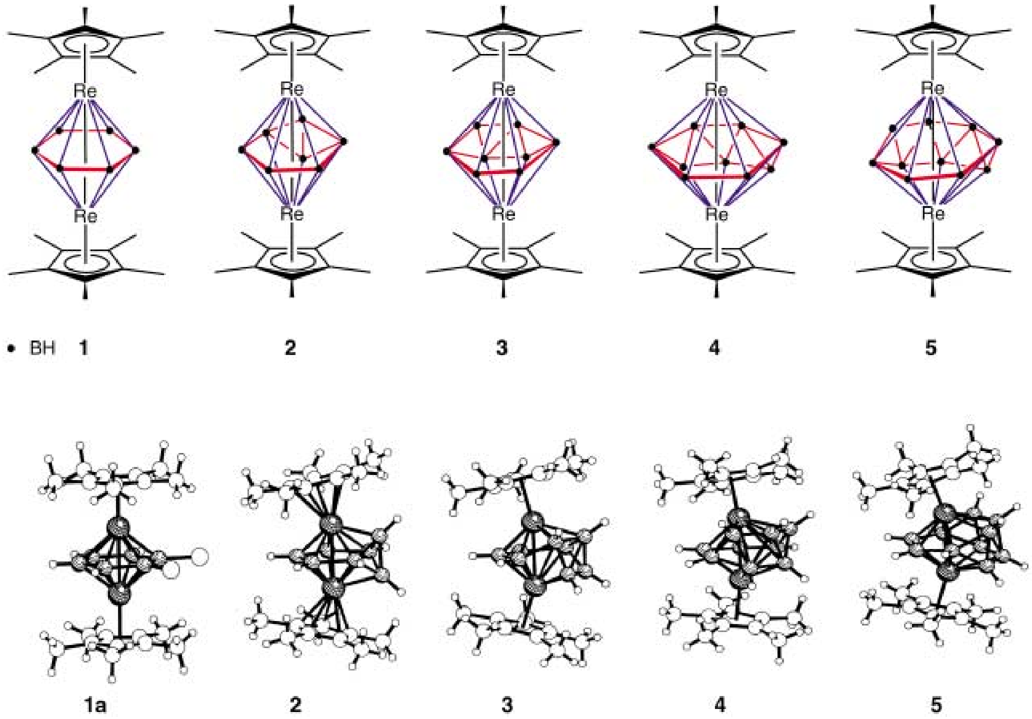
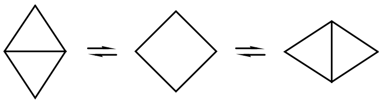


Figure 1. Formulae and molecular structures of the dirhenaboranes **1**–**5**. For $n = 6$ only the dichloro derivative **1a** has been structurally characterized.



Scheme 1. Schematic representation of the diamond-square-diamond (DSD) rearrangement.

Table 1. Electron count and cluster connectivity for the dirhenaboranes **1**–**5**.

	1	**2**	**3**	**4**	**5**
d(Re-Re) [Å]	2.689	2.787	2.835	2.860	2.819
n	6	7	8	9	10
p	8	9	10	11	12
SEP (found)[a] ($p-2$)	6	7	8	9	10
SEP (canon.)[b] ($p+1$)	9	10	11	12	13
point group (canon.)[c]	D_{2d}	D_{3h}	D_{4d}	C_{2v}	I_h
TVC	36	42	48	54	60
Connectivity (found)[a,d,e]	$2^{(6)}6^{(4)}$	$2^{(6)}2^{(5)}5^{(4)}$	$2^{(6)}4^{(5)}4^{(4)}$	$1^{(7)}1^{(6)}5^{(5)}4^{(4)}$	$2^{(7)}6^{(5)}4^{(4)}$
Connectivity (canon.)[b,d]	$4^{(5)}4^{(4)}$	$6^{(5)}3^{(4)}$	$8^{(5)}2^{(4)}$	$6^{(1)}8^{(5)}4^{(2)}$	$12^{(5)}$

[a] Actual value. [b] Canonical value for a *closo*-structure derived from the Wade–Mingos' rules. [c] Symmetry of the canonical deltahedron. [d] In the form: number of vertices$^{\text{(connectivity)}}$; the connectivity of a vertex is related to the cluster framework only. [e] The metals always occupy the sites of highest connectivity.

unraveled to generate the open B_nH_n "bridging ligands" that are capped by highly coordinated rhenium atoms in **1**–**5** and which have not been observed in the free state. In fact, it has been shown that, apart from for **5**, two steps are sufficient.[10] The number of SEPs are reduced by three from $p+1$ (canonical *closo*) to $p-2$ (in **1**–**5**). One electron pair is compensated by the formation of the metal–metal bond so that each DSD process in **1**–**4** apparently "costs" one electron pair (i.e. one CbMO is lost).

But why is it that the structures of the rhenaboranes **1**–**5** (and many other hypoelectronic metallaboranes) do not conform to the Wade–Mingos' rules? It is not a deficiency of the rules because they were not conceived for such a situation! They require that the framework atoms lie approximately on the surface of a sphere.[12] In polyhedral boranes, two p orbitals (π symmetry with respect to the radius vector) and one sp-hybrid orbital (σ symmetry) from each BH group participate in the bonding (the second sp-hybrid orbital forms a two-center-two electron (2c–2e) bond to the *exo*-hydrogen atom). The "magic" electron counts are determined by the number of molecular orbitals that are *not* available for occupation by electrons (or electron pairs from ligands). The classical example of the octahedral $[B_6H_6]^{2-}$ ion ($p = 6$) illustrates the ($p+1$)-SEP rule for *closo*-clusters: Of the allowed 18 linear combinations of atomic orbitals, 11 have high energy so that only one σ orbital oriented to the center of the cluster and six π orbitals on the cluster surface can be occupied by $p+1 = 7$ electron pairs. In general the Wade–Mingos' rules only apply when each framework atom provides three valence orbitals for bonding in the cluster and when both the σ and π interactions are significant.[13]

The isolobal concept relates the CH_{4-x} fragments derived from CH_4 with metal-complex fragments that are formally generated from electronically saturated complexes $d^m[ML_n]$ by homolysis of M–L bonds.[6] This approach leads to well-known isolobal relationships such as $CH_3 \underset{\circ}{\longleftrightarrow} d^7\,ML_5$, $CH_2 \underset{\circ}{\longleftrightarrow} d^8\,ML_4$, and $CH \underset{\circ}{\longleftrightarrow} d^9\,ML_3 \underset{\circ}{\longleftrightarrow} d^{10}\,M(C_5R_5)$, in which the fragments to the left and right of the isolobal arrow have a similar number of frontier orbitals with similar symmetry characteristics and energy. The same applies to $BH \underset{\circ}{\longleftrightarrow} d^8\,ML_3 \underset{\circ}{\longleftrightarrow} d^9\,M(C_5R_5)$. These conical metal-complex fragments provide, as in BH, exactly three frontier orbitals ($1\sigma + 2\pi$) and two valence electrons and are therefore able to represent BH in clusters. If the remaining requirements are fulfilled, the Wade–Mingos' rules will apply. Different "rule-breaking" electron counts are found in clusters in which σ interactions dominate (such as alkali-metal and gold clusters), or in clusters in which δ orbitals are involved (e.g. $[M_6Cl_8L_6]^{4+}$ (M = Mo) W and $[M_6Cl_{12}L_6]^{2+}$ (M = Nb, Ta)). The latter situation can be easily understood for systems lacking π-acceptor ligands.[14]

However, in the case of the *isocloso*-metallaboranes it is not really clear why the typical organometallic fragments (e.g. $(C_5H_5)Fe$, (arene)Ru) that are part of the framework of these clusters, should contribute a number of orbitals and electron pairs that deviate from the isolobal rule. R. B. King made a proposal that only requires three skeletal orbitals per metal:[15] Canonical *closo* clusters are characterized by a radial σ orbital over *p* centers and *p* 2c–2e bonds on the surface, but in this case only *p* 3c–2e bonds in *p* of the $(2p-4)$ triangular faces of the *isocloso*-polyhedron can be present. It is not, however, clear if such topological considerations can be used for the even less symmetrical compounds **1**–**5**.

An alternative description of the metallaboranes **1**–**5** considers these as triple-decker sandwich complexes that have increasingly complicated bridging ligands as the number of boron atoms increases (marked red in Figure 1). This viewpoint is particularly compelling for **1**. The 18 VE rule (d electrons of the metal + π electrons of the decks) for sandwich complexes can be extended to a 30 VE electron rule for triple-decker complexes.[16] Triple-decker complexes with 30 VE conform to the Wade–Mingos' rules for the central $M_2(\mu_2\text{-}\eta^n{:}\eta^n\text{-}cyclo\text{-}X_n)$ unit. The $(p=n+2)$-vertex *closo*-polyhedra then have $p+1=n+3$ SEPs (8 SEPs for $n=5$, 9 SEPs for $n=6$). With 24 VE $(\pi^5+d^7+\pi^0+d^7+\pi^5)$ however, the complexes **1**–**5** do not conform to the VE rule for triple-decker-sandwich complexes either. The geometrically simplest case, complex **1**, is in fact the most electron deficient of all triple-decker complexes currently known with a planar middle deck!

The apparent electron deficiency of the triple-decker complex **1** can be convincingly explained by simple arguments. All triple-decker-sandwich complexes are based on the qualitative frontier orbital scheme for the $[\{(C_5H_5)Ni\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_5)]^+$ ion (Figure 2, left).[17] The HOMO of this complex (e_1') is derived from the d_{xz} and d_{yz} orbitals of the two metal atoms (or the $(C_5H_5)M$ fragments). Since the bridging ligand has no π orbitals of suitable symmetry, these orbitals are essentially nonbonding. At larger metal–metal distances a lower-lying group of six molecular orbitals, often designated t_{2g}, (d_{xy}, $d_{x^2-y^2}$, and d_{z^2}) participate in the bonding to the bridging ligand to a lesser extent. A (30–34) VE rule can be derived from the occupancy of the e_1' orbitals. With 30 VE ($[(C_5Me_5)_3Ru_2]^+$), these orbitals are empty, with 34 VE they are fully occupied ($[(C_5H_5)_3Ni_2]^+$). Triple-decker-sandwich complexes with 31–33 VE are paramagnetic.

If the bridging ligand of a triple-decker complex has a large diameter, the metal atoms can approach each other to bonding distance without their bonds to the bridging ligand becoming too short. The short metal–metal distance causes the a_1' (d_{z^2}, M–M bonding) and a_2'' orbitals (d_{z^2}, M–M antibonding) to be strongly split; the later orbital now lies so high that it can no longer be occupied. The e_1' set (d_{xz}, d_{yz}) is also raised (interaction with σ orbitals of the bridge) and always remains unoccupied. The magic electron count is now 28 (e.g. $[\{(C_5Me_5)Mo\}_2(\mu\text{-}\eta^6{:}\eta^6\text{-}P_6)]$[19]).[20] The electronic structure can also be described on the basis of a 30 VE triple-decker complex in which an electron pair has been removed from the valence shell by the formation of a metal–metal σ bond.

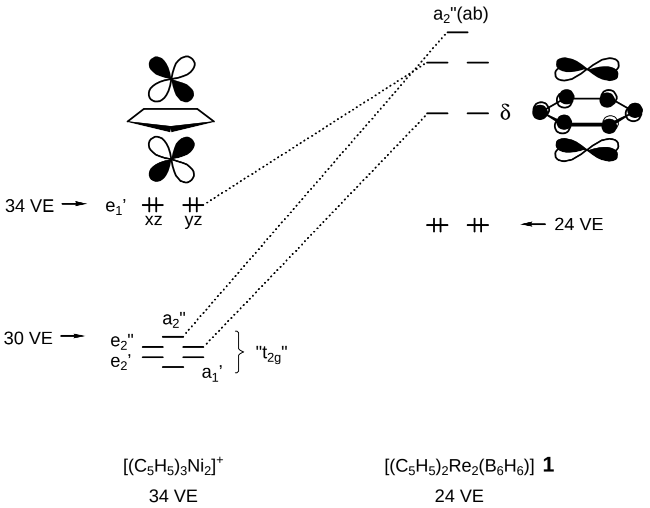


Figure 2. Qualitative MO scheme for $[\{(C_5H_5)Ni\}_2\{\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_5)\}]$[17] and $[\{(C_5H_5)Re\}_2\{\mu\text{-}\eta^6{:}\eta^6\text{-}(B_6H_6)\}]$ **1**.[18] Only the most important frontier orbitals are shown.

Further reinforcement of the interaction between the metal center and the bridging ligand, for example, by increased proximity and/or more diffuse metal orbitals, results in even more orbitals leaving the "t_{2g}" set. This phenomenon involves the e_2' combinations ($d_{x^2-y^2}$, d_{xy}; M–M bonding with δ symmetry) that are extensively destabilized by an antibonding interaction with bonding σ orbitals in the plane of the bridging ligand.[20c] This effect is shown in Figure 2 (right) for **1**. The electron count is further reduced by four to 24 VE. Corresponding bonding combinations with δ symmetry are of course stabilized. For **1** this means that the Re–Re and Re–B bonds strengthen at the cost of the B–B bonds (an Re–Re antibonding (a_2'') and two Re–B antibonding, B–B bonding orbitals (e_2') are emptied).

So are the rule-breakers **1**–**5** dimetallaborane clusters or triple-decker-sandwich complexes? The answer to this question could be the following: What is the difference? In fact the structural principle of a triple-decker—an equatorial ring and two apical (polar) fragments—was already used for the factorization of the secular equation for boron cages a long time ago.[21] Boranes and carboranes lack, of course, energetically accessible orbitals with δ symmetry in the axial direction; the canonical structures are highly preferred. There are also no known metallaboranes structurally analogous to **1**–**5** with the later (electron rich) transition metals (e.g. with $Ni(C_5R_5)$ which is isolobal to CH). In the present case all the metal-centered δ orbitals are filled so that any interaction with (filled) δ orbitals of the borane fragment would be repulsive. The "rule-breaking" structures of complexes such as **1**–**5** are therefore only possible with the early transition metals.

There is the danger with successful models that their potential is overestimated. There are many cases where a simple (and within its limitations very successful) concept inhibited further development of our understanding. To cite only one example from chemistry, neither the boranes or the noble gas compounds could exist if only the 2c–2e bond model was to apply. With such "bad news for successful models"[22] we should be grateful for the "good news about rule violations".

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[5] In a simplified form, the rules require p-vertex deltahedra as the basic form of the *closo*-polyhedral framework; these have $(p+1)$ cluster-bonding MOs (CbMOs). The sequential removal of m vertices ($m = 1-3$) leads to *nido- arachno-*, and *hypho*-structures with $p' = p - m$ vertices and $(p' + 1 + m)$ CbMOs. Capping the l faces ($l = 1-4$) results in $(p' + 1 - l)$ CbMOs ($p' = p + l$; "capping" rule). The general formula for the number x of CbMOs in any given cluster with p' framework atoms is therefore $x = p' + m - l + 1$.

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