Electronic Considerations in Metalloboranes

By CHRISTOPHER J. JONES, WILLIAM J. EVANS, and M. FREDERICK HAWTHORNE*
(*Department of Chemistry, University of California, Los Angeles, California* 90024)

Summary A $2n + 14$ electron rule is proposed for *closo* n-vertex polyhedral heteroboranes containing one transition-metal vertex; *nido*-polyhedra of this type require $2n + 16$ electrons while *closo*-polyhedra with two transition metal vertices require $2n + 26$ electrons.

A LARGE portion of organo-transition-metal chemistry may be rationalized in terms of the 18-electron rule.[1] However, despite the wide variety of metalloborane species which are known, no simple electron counting method has been described to cover polyhedral metalloboranes. The electronic requirement for a closed n-vertex polyhedral metalloborane may be derived as follows. A total of $2n + 2$ electrons are required for bonding within the polyhedral framework[2] while 18 electrons are required to establish an 'inert-gas configuration' for the metal. Since six electrons are shared[3] between the metal vertex and the remaining polyhedral fragment, a total of $2n + 2 + 18 - 6 = 2n + 14$ electrons are required by the metalloborane framework. For example, $[(\pi\text{-}C_5H_5)CoC_2B_9H_{11}]$ has a total of 60 electrons, counting $\pi\text{-}C_5H_5$ as a 5-electron donor, as in application of the 18-electron rule, and the polyhedral atoms boron, carbon, and cobalt as 3, 4, and 9 electron donors respectively. After subtracting 22 electrons for exopolyhedral CH and BH bonds, 38 electrons remain, *i.e.* $2n + 14$ for a 12 vertex polyhedron. Similar reasoning leads to a $2n + 16$ electron rule for *nido*-heteroboranes with one transition-metal vertex while closed polyhedra with two transition metal vertices require $2n + 26$ electrons. For *commo*-compounds in which two *closo*-polyhedra are fused at the metal atom a more complex situation exists. Thus the total number of vertices, n, of a *commo*-compound comprised of two polyhedra of n_1 and n_2 vertices respectively is given by $n = n_1 + n_2 - 1$. The electronic requirement for polyhedral bonding is then $2n_1 + 2 + 2n_2 + 2$; inclusion of 18 electrons for the metal gives a total of $2n_1 + 2n_2 + 22$ electrons from which 12 electrons shared between the metal and the remaining fragments must be subtracted. Restating this total in terms of n gives a $2n + 12$ electron rule for *commo*-metalloboranes with two *closo*-polyhedra. Systems with one nido- and one *closo*-polyhedron require $2n + 14$ electrons while those with two *nido*-polyhedra require $2n + 16$ electrons.

The compounds $[(\pi\text{-}Ph_4C_4)PdC_2B_9H_{11}]$, $[(Ph_3P)_2HPtSB_9H_{10}]$, $[(\pi\text{-}C_5H_5)_2NiCoCB_7H_8]$, $[C_2B_9H_{11}$-*commo*-$Ni\text{-}C_2B_9H_{11}]$, and $[C_2B_9H_{11}$-*commo*-$Co\text{-}C_5H_5N\text{-}C_2B_8H_{10}]^-$ serve[4–6] as examples of the above rules which are found to apply to the majority of known metalloboranes. However, since these proposals incorporate the 18 electron rule exceptions may be expected to occur as is found for the 18 electron rule itself; for example one might compare $[(\pi\text{-}C_5H_5)_2Fe]^+$ and $[(\pi\text{-}C_5H_5)_2Fe]$ with $[(\pi\text{-}C_5H_5)FeC_2B_9H_{11}]$ and $[(\pi\text{-}C_5H_5)FeC_2B_9H_{11}]^-$.

In considering the chemical reactions of a metalloborane, additional factors such as the formal oxidation state of the metal and the overall molecular charge must be taken into account. Metalloboranes with low molecular charges and metals in common formal oxidation states may be expected to exhibit greater chemical stability than those with high molecular charge or metals in unusual formal oxidation states. This is essentially a statement about the compatibility of the metal–ligand fragment with the borane framework. High molecular charges relative to the parent borane or carborane along with unusual formal oxidation states for the metal are indications that the metal–ligand fragment itself is unable to satisfy the electronic requirements of the polyhedral framework. These requirements may be restated in terms of Wade's comparison[2] between $\{(CO)_3Ru\}$ and $\{BH\}$. Using such reasoning it can be deduced that $\{(\pi\text{-}C_5H_5)Co\}$, like $\{BH\}$ may contribute three orbitals and two electrons to the polyhedral bonding, while $\{(\pi\text{-}C_5H_5)Ni\}$, like $\{CH\}$ may contribute three orbitals and three electrons. Thus, one might expect $\{(\pi\text{-}C_5H_5)Co\}$ and $\{(\pi\text{-}C_5H_5)Ni\}$ to replace $\{BH\}$ and $\{CH\}$ respectively in a polyhedral environment to give stable carborane analogues.

Use of the above proposals has already led to the discovery[5] of $[(\pi\text{-}C_5H_5)_2NiCoCB_7H_8]$ which undergoes thermal rearrangements like $C_2B_8H_{10}$ and $[(\pi\text{-}C_5H_5)CoC_2B_7H_9]$. One might also expect $[(CO)_3\text{-}FeC_2B_9H_{11}]$ to be an air-stable carborane analogue by comparison with the known $[(CO)_2\text{-}1,2,3\text{-}FeC_2B_9H_{11}]_2^{2-}$ which oxidizes in air. Hopefully, further examination of the chemistry of the metalloboranes in the context of these proposals will lead to a more complete understanding of the electronic requirements of this unique class of compounds.

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Added in proof: The orbitals and electrons available for polyhedral bonding of various metal–ligand fragments have been enumerated recently (D. M. P. Mingos, *Nature Phys. Sci.*, 1972, **236**, 99).

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