

## Cyclopentadienyl Ruthenium, Rhodium, and Iridium Vertices in Metallaboranes: Geometry and Chemical Bonding

R. B. King\*

Department of Chemistry, University of Georgia, Athens, Georgia 30602

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Most cyclopentadienylmetallaboranes containing the vertex units CpM (M = Co, Rh, Ir; Cp =  $\eta^5$ -cyclopentadienyl ring, mainly  $\eta^5$ -Me<sub>5</sub>C<sub>5</sub>) and CpRu donating two and one skeletal electrons, respectively, have structures closely related to binary boranes or borane anions. Smaller clusters of this type, such as metallaborane analogues of *arachno*-B<sub>4</sub>H<sub>10</sub> (e.g., (CpIr)<sub>2</sub>B<sub>2</sub>H<sub>8</sub>), *nido*-B<sub>5</sub>H<sub>9</sub> (e.g., (CpRh)<sub>2</sub>B<sub>3</sub>H<sub>7</sub> and (CpRu)<sub>2</sub>B<sub>3</sub>H<sub>9</sub>), *arachno*-B<sub>5</sub>H<sub>11</sub> (e.g., CpIrB<sub>4</sub>H<sub>10</sub>), B<sub>6</sub>H<sub>6</sub><sup>2-</sup> (e.g., (CpCo)<sub>4</sub>B<sub>2</sub>H<sub>4</sub>), *nido*-B<sub>6</sub>H<sub>10</sub> (e.g., CpIrB<sub>5</sub>H<sub>9</sub> and (CpRu)<sub>2</sub>B<sub>4</sub>H<sub>10</sub>), and *arachno*-B<sub>6</sub>H<sub>12</sub> (e.g., (CpIr)<sub>2</sub>B<sub>4</sub>H<sub>10</sub>), have the same skeletal electron counts as those of the corresponding boranes. However, such clusters with eight or more vertices, such as metallaborane analogues of B<sub>8</sub>H<sub>8</sub><sup>2-</sup> (e.g., (CpCo)<sub>4</sub>B<sub>4</sub>H<sub>4</sub>), *arachno*-B<sub>8</sub>H<sub>14</sub> (e.g., (CpRu)<sub>2</sub>B<sub>6</sub>H<sub>12</sub>), and *nido*-B<sub>10</sub>H<sub>14</sub> (e.g., (CpRu)<sub>2</sub>B<sub>8</sub>H<sub>12</sub>), have two skeletal electrons less than those of the corresponding metal-free boranes, analogous to the skeletal electron counts of *isocloso* boranes relative to those of metal-free deltahedral boranes. Some metallaboranes have structures not analogous to metal-free boranes but instead analogous to metal carbonyl clusters such as 3-capped square pyramidal (CpRu)<sub>2</sub>B<sub>4</sub>H<sub>8</sub> and (CpRu)<sub>3</sub>B<sub>3</sub>H<sub>8</sub> analogous to H<sub>2</sub>Os<sub>6</sub>(CO)<sub>16</sub> and capped octahedral (CpRh)<sub>3</sub>B<sub>4</sub>H<sub>4</sub> analogous to Os<sub>7</sub>(CO)<sub>21</sub>. In the metallaborane structures closely related to metal-free boranes, the favored degrees of BH and CpM vertices appear to be 5 and 6, respectively.

## 1. Introduction

The basic building blocks of polyhedral borane chemistry are the most spherical deltahedra<sup>1,2</sup> namely, polyhedra in which all faces are triangles and all vertices are as nearly similar as possible. The Wade–Mingos rules<sup>3,4,5</sup> state that polyhedral boranes derived from such deltahedra are particularly stable if they contain  $2n + 2$  skeletal electrons, where  $n$  is the number of vertices in the underlying deltahedron. This special stability has been ascribed to three-dimensional aromaticity.<sup>6,7,8</sup> Thus the borane anions B<sub>*n*</sub>H<sub>*n*</sub><sup>2-</sup> ( $6 \leq n \leq 12$ ) are particularly stable and have structures based on  $n$ -vertex deltahedra in which all vertices have degrees 4 or 5 except for the single degree 6 vertex in B<sub>11</sub>H<sub>11</sub><sup>2-</sup> required by polyhedral topology.<sup>9</sup> In this connection, the degree of a vertex of a polyhedron refers to the number of polyhedral edges meeting at the vertex in question.

Hawthorne and co-workers<sup>10</sup> first showed that the vertices in deltahedral boranes and related carboranes could be replaced by isolobal transition metal vertices, typically units of the type CpM or M(CO)<sub>3</sub> (Cp = cyclopentadienyl; M = transition metal). During the course of this original work, the substitution of a light atom vertex (boron or carbon) in a polyhedral borane by a transition metal vertex was assumed not to affect the underlying deltahedral geometry. However, as metallaborane chemistry was developed further, particularly by Kennedy and co-workers,<sup>11–14</sup> a variety of deltahedral metallaborane structures were discovered based on deltahedra topologically distinct from the deltahedra found in simple boranes and carboranes. The introduction of a transition metal vertex in place of a light-element vertex (boron or carbon) was found sometimes to have the following effects:

\* Author to whom correspondence should be addressed. E-mail: rbking@sunchem.chem.uga.edu.

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(1) The geometry of the deltahedron changes to a “less spherical” geometry with a higher degree vertex (degree 6 or sometimes even 7) for the transition metal. Relatively electron-deficient early transition metal vertices (e.g., CpW and CpRe) were often found to have rather drastic effects on the underlying deltahedral geometry.

(2) The number of apparent skeletal electrons decreases from  $2n + 2$  to  $2n$  for a closed deltahedron having  $n$  vertices. This has been attributed to a change in the chemical bonding from the globally delocalized bonding characteristic of three-dimensional aromaticity<sup>6–8</sup> with a multicenter core bond to a set of three-center two-electron (3c-2e) bonds localized in some of the faces of the deltahedron.<sup>15</sup>

In recent years extensive work by Fehlner and co-workers<sup>16,17</sup> has greatly extended the scope of metallaboranes, particularly those with cyclopentadienylmetal vertices. In an earlier paper<sup>18</sup> I have discussed structure and bonding in such metallaboranes having cyclopentadienylmetal vertices of the early transition metals. In most cases such compounds were found to have closed deltahedral structures but often with more vertex nonequivalence than in the most spherical deltahedra found in metal-free boranes. This paper extends such analysis to metallaboranes with metal vertices of the following two types (Cp =  $\eta^5$ -cyclopentadienyl or substituted  $\eta^5$ -cyclopentadienyl, particularly  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>):

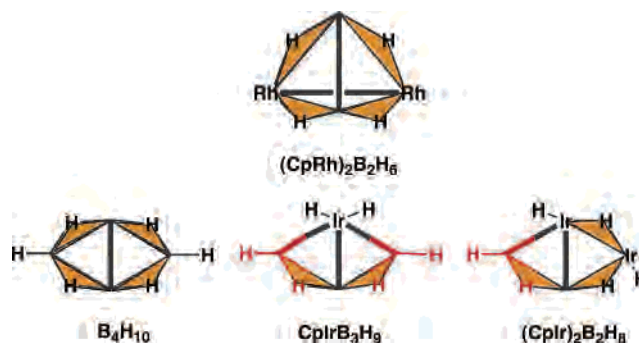
(1) CpCo, CpRh, and CpIr, which are donors of two skeletal electrons such as BH groups.

(2) CpFe, CpRu, and CpOs, which are donors of a single skeletal electron like a bare group 13 metal vertex, e. g., In or Tl.

Since these cyclopentadienylmetal vertices are more electron-rich than the early transition metal vertices discussed in the earlier paper,<sup>18</sup> structures analogous not only to closed deltahedral boranes but also to some of the more open *nido* and *arachno* boranes are also found. This detailed analysis of such metallaborane structures complements previously published work by the author on metal-free *nido*<sup>19</sup> and *arachno*<sup>20</sup> boranes.

## 2. Metallaboranes with Cyclopentadienylmetal Vertices of the Group 9 Metals (Co, Rh, Ir)

The metallaboranes with CpM vertices (M = Co, Rh, Ir) discussed in this paper are depicted in Figures 1–8, and some of their features are summarized in Table 1. In these and similar figures, triangular faces of polyhedra and polyhedral fragments containing 3c-2e bonds are depicted in yellow. Both 3c-2e and 4c-2e bonds involving  $\mu_2$ - or  $\mu_3$ -bridging hydrogen atoms, respectively, are depicted in orange. Vertices of degrees 3–7 are depicted in magenta, red, black, green, and blue, respectively. Edges corresponding to a 2c-2e bond are bold. Unmarked vertices are BH vertices and



**Figure 1.** (a) The tetrahedral (CpRh)<sub>2</sub>B<sub>2</sub>H<sub>6</sub>. (b) The B<sub>4</sub>H<sub>10</sub> analogues CpIrB<sub>3</sub>H<sub>9</sub> and (CpIr)<sub>2</sub>B<sub>2</sub>H<sub>8</sub>.

**Table 1.** Some Metallaboranes Containing CpM Units (M = Co, Rh, Ir)

formula	analogue	shape	no. of skeletal electrons	lit. ref.
(CpRh) <sub>2</sub> B <sub>2</sub> H <sub>6</sub>	B <sub>4</sub> R <sub>4</sub> (R = Cl, tBu)	tetrahedron	12	21
CpIrB <sub>3</sub> H <sub>9</sub>	<i>arachno</i> -B <sub>4</sub> H <sub>10</sub>	butterfly	14	22
(CpIr) <sub>2</sub> B <sub>2</sub> H <sub>8</sub>	<i>arachno</i> -B <sub>4</sub> H <sub>10</sub>	butterfly	14	22, 23
(CpCo) <sub>3</sub> B <sub>2</sub> H <sub>4</sub>	(CpCo) <sub>3</sub> C <sub>2</sub> R <sub>2</sub>	trigonal bipyramid	12	24
(CpRh) <sub>2</sub> B <sub>3</sub> H <sub>7</sub>	<i>nido</i> -B <sub>5</sub> H <sub>9</sub>	square pyramid	14	21, 28
CpIrB <sub>4</sub> H <sub>10</sub>	<i>arachno</i> -B <sub>5</sub> H <sub>11</sub>		16	25
(CpCo) <sub>4</sub> B <sub>2</sub> H <sub>4</sub>	B <sub>6</sub> H <sub>6</sub> <sup>2-</sup>	octahedron	14	29
(CpIr) <sub>2</sub> B <sub>4</sub> H <sub>8</sub>	<i>nido</i> -B <sub>6</sub> H <sub>10</sub>	pentagonal pyramid	16	23
(CpIr) <sub>2</sub> B <sub>4</sub> H <sub>10</sub>	<i>arachno</i> -B <sub>6</sub> H <sub>12</sub>		18	23, 30
(CpRh) <sub>3</sub> B <sub>4</sub> H <sub>4</sub>	Os <sub>7</sub> (CO) <sub>21</sub>	capped octahedron	14	29
(CpCo) <sub>4</sub> B <sub>4</sub> H <sub>4</sub>	B <sub>8</sub> H <sub>8</sub> <sup>2-</sup>	bisdisphenoid	16*	32

$\eta^5$ -Cp rings on transition metals are omitted for clarity. Skeletal electron counts corresponding to *isocloso* or analogous *isonido* and *isoarachno* metallaboranes<sup>15</sup> are starred. The CpM vertices (M = Co, Rh, Ir) in these structures are considered to be donors of two skeletal electrons similar to BH vertices.

**2.1. Four-Vortex Structures.** The structure of (CpRh)<sub>2</sub>B<sub>2</sub>H<sub>6</sub> (Figure 1a)<sup>21</sup> is based on a Rh<sub>2</sub>B<sub>2</sub> tetrahedron with the 12 skeletal electrons required for two-electron bonds along each of its six edges. However, four of these edges are bridged by the “extra” hydrogen atoms so that four of these “edge bonds” are 3c-2e bonds (orange triangles in Figure 1a) and the other two edges (bold in Figure 1a) have simple 2c-2e bonds. All four vertices in (CpRh)<sub>2</sub>B<sub>2</sub>H<sub>6</sub> are of degree 5, counting the bonds to the *bridging* hydrogen atoms in addition to the actual edges of the Rh<sub>2</sub>B<sub>2</sub> tetrahedron.

The heavier congener of rhodium, namely, iridium, forms a different type of four-vertex metallaborane, namely, (CpIr)<sub>2</sub>B<sub>2</sub>H<sub>8</sub>, with a butterfly-like structure of two triangular “wings” sharing an edge, i.e., the “body” of the butterfly (Figure 1b).<sup>22,23</sup> This butterfly structure of (CpIr)<sub>2</sub>B<sub>2</sub>H<sub>8</sub> is closely related to that of the simplest *arachno* borane B<sub>4</sub>H<sub>10</sub>, and both structures have 14 skeletal electrons. An intermediate CpIrB<sub>3</sub>H<sub>9</sub> is also known,<sup>22,23</sup> but it has not been structurally characterized since it decomposed in the X-ray beam.

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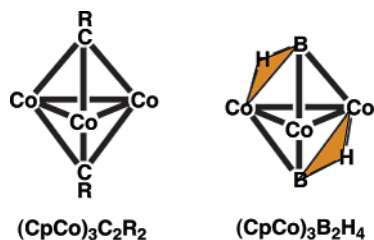


Figure 2. The trigonal bipyramidal  $(\text{CpCo})_3\text{C}_2\text{R}_2$  and  $(\text{CpCo})_3\text{B}_2\text{H}_4$ .

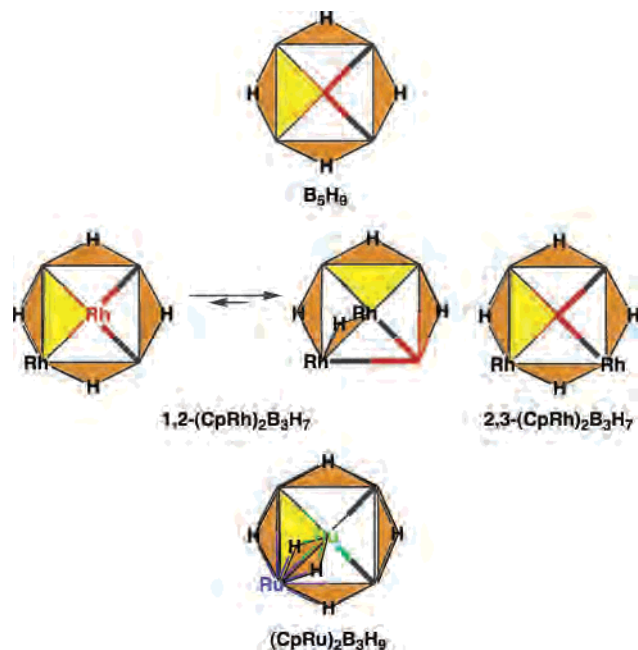


Figure 3. Square pyramidal boranes and metallaboranes: (a)  $\text{B}_5\text{H}_9$ . (b) The three isomers of  $(\text{CpRh})_2\text{B}_3\text{H}_7$  and (c)  $(\text{CpRu})_2\text{B}_3\text{H}_9$ .

**2.2. Five-Vertex Structures.** Both trigonal bipyramidal and square pyramidal five-vertex structures are known in this series of metallaboranes. The trigonal bipyramidal cobalt complex  $(\text{CpCo})_3\text{B}_2\text{H}_4$  (ref 24) is isoelectronic and isostructural with the biscarbyne cobalt complexes<sup>26,27</sup>  $(\text{CpCo})_3\text{C}_2\text{R}_2$  (Figure 2). However,  $(\text{CpCo})_3\text{B}_2\text{H}_4$  has 3c-2e Co–H–B bonds along two of its axial–equatorial edges.<sup>24</sup>

Three isomers of the square pyramidal rhodium complex  $(\text{CpRh})_2\text{B}_3\text{H}_7$  are known analogous to  $\text{B}_5\text{H}_9$  (Figure 3).<sup>21,28</sup> Reaction of  $[(\eta^5\text{-Me}_5\text{C}_5)\text{RhCl}]_2$  ( $\text{Cp} = \eta^5\text{-Me}_5\text{C}_5$ ) with  $\text{LiBH}_4$  followed by addition of  $\text{THF}\cdot\text{BH}_3$  first gives a mixture of two 1,2- $(\text{CpRh})_2\text{B}_3\text{H}_7$  tautomers with one rhodium atom at the apex and the other rhodium atom at the base of the square pyramid (Figure 3b).<sup>28</sup> One of these tautomers has four 3c-2e bonds, namely, two B–H–B and two Rh–H–B bonds, along the edges of the basal square of the pyramid. The other more stable tautomer has only three basal 3c-2e B–H–B bonds and one 3c-2e Rh–H–Rh bond connecting the two rhodium atoms so that both rhodium atoms are

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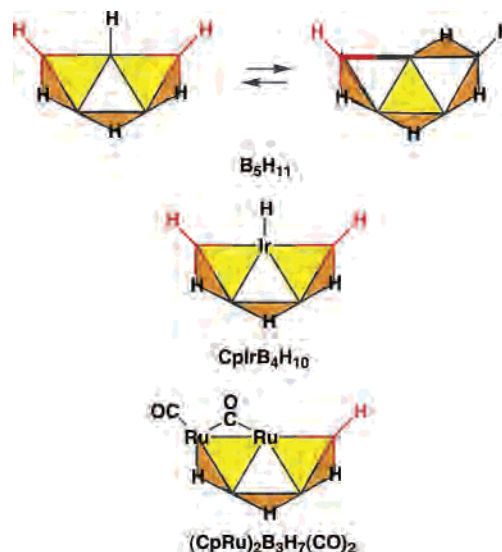


Figure 4.  $\text{B}_5\text{H}_{11}$  and analogous metallaboranes: (a)  $\text{B}_5\text{H}_{11}$ ; (b)  $\text{CpIrB}_4\text{H}_{10}$ ; (c)  $(\text{CpRu})_2\text{B}_3\text{H}_7(\text{CO})_2$ .

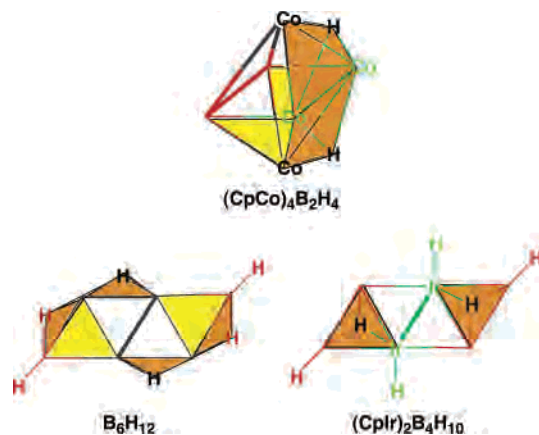


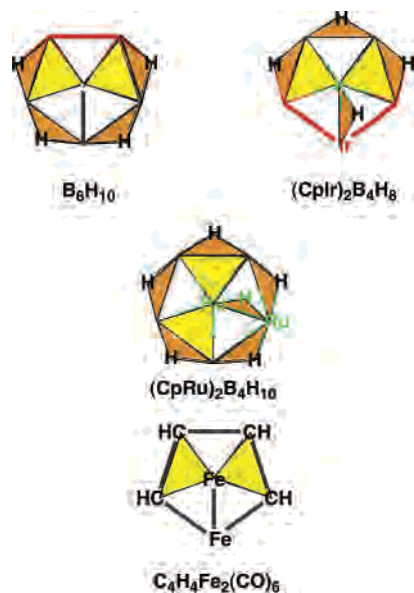
Figure 5. (a) The octahedral  $(\text{CpCo})_4\text{B}_2\text{H}_4$ . (b) The  $\text{B}_6\text{H}_{12}$  analogue  $(\text{CpIr})_2\text{B}_4\text{H}_{10}$ .

located at degree 5 vertices counting the bridging hydrogen atoms. Further reaction leads to a more stable 2,3- $(\text{CpRh})_2\text{B}_3\text{H}_7$  isomer with both rhodium atoms on the base of the square pyramid.

A CpIr analogue of *arachno*- $\text{B}_5\text{H}_{11}$ , namely,  $\text{CpIrB}_4\text{H}_{10}$ , is also known (Figure 4), which has the expected 16 skeletal electrons for an *arachno* five-vertex structure.<sup>23,25</sup> The iridium atom and two of the boron atoms in  $\text{CpIrB}_4\text{H}_{10}$  are located at degree 5 vertices whereas the other two boron atoms are located at degree 4 vertices. NMR studies on  $\text{CpIrB}_4\text{H}_{10}$  (Figure 4b) indicate that the hydrogen atom bonded to the iridium atom remains a terminal hydrogen atom rather than bridging to an adjacent degree 4 boron atom to increase the degree of the latter from 4 to the more favorable 5.

**2.3. Six-Vertex Structures.** There are three six-vertex structures found in this series of metallaboranes. The octahedral cobalt complex  $(\text{CpCo})_4\text{B}_2\text{H}_4$  has the expected 14 skeletal electrons for a globally delocalized octahedron (Figure 5a).<sup>29</sup> Two adjacent faces of the  $\text{Co}_4\text{B}_2$  octahedron are capped by  $\mu_3$ -hydrogen atoms. The iridium complex

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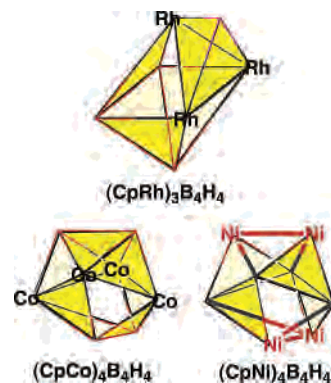


**Figure 6.** Pentagonal pyramidal boranes and related compounds. (a) A comparison of  $B_6H_{10}$  with  $(CpIr)_2B_4H_8$  and (b)  $(CpRu)_2B_4H_{10}$ . (c) The related ferrole-iron tricarbonyl  $C_4H_4Fe_2(CO)_6$ .

$(CpIr)_2B_4H_8$  has 16 skeletal electrons.<sup>23</sup> This complex has the same skeleton as the isoelectronic pentagonal pyramidal *nido* borane  $B_6H_{10}$  but with a different arrangement of hydrogen atoms, including a hydrogen bridge across the apical-basal Ir-Ir edge (Figure 6a). The iridium complex  $(CpIr)_2B_4H_{10}$  has 18 skeletal electrons and is isoelectronic with the *arachno* borane  $B_6H_{12}$  (Figure 5b).<sup>30</sup> However, the arrangement of the six “extra” hydrogen atoms in  $(CpIr)_2B_4H_{10}$  is quite different than that in  $B_6H_{12}$  leading to an effective degree 6 for each of the CpIr vertices.

**2.4. The Seven-Vertex Structure  $(CpRh)_3B_4H_4$ .** Capped deltahedra are not found in metal-free boranes since a BH vertex in a deltahedron does not have an “extra” orbital in its  $sp^3$  bonding orbital manifold available for bonding to a capping atom after allowing for the three internal orbitals required for the deltahedral skeletal bonding and the external orbital for bonding to the hydrogen atom. However, replacing a  $B_3$  triangular face in a deltahedron with a  $M_3$  triangular face ( $M$  = transition metal) provides orbitals that can bond to a capping atom since transition metals, unlike boron, use a nine-orbital  $sp^3d^5$  manifold. In capped octahedral  $(CpRh)_3B_4H_4$  (Figure 7a) a degree 3 BH vertex caps the  $Rh_3$  face of the underlying octahedron.<sup>28</sup> A similar capped octahedral structure is found in the homoleptic osmium carbonyl  $Os_7(CO)_{21}$  (ref 31). Both  $(CpRh)_3B_4H_4$  and  $Os_7(CO)_{21}$  have the 14 skeletal electrons expected for a capped octahedral structure.

**2.5. The Eight-Vertex Structure  $(CpCo)_4B_4H_4$ .** In 1982 I presented skeletal bonding models for the related bisdisphenoidal eight-vertex clusters  $(CpM)_4B_4H_4$  ( $M$  = Co,<sup>32</sup> Ni<sup>33,34</sup>) having apparent skeletal electron counts differing by



**Figure 7.** (a) The capped octahedral  $(CpRh)_3B_4H_4$ . (b) The contrasting structures of bisdisphenoidal  $(CpCo)_4B_4H_4$  and  $(CpNi)_4B_4H_4$ .

four.<sup>35</sup> Additional aspects of the chemical bonding in these compounds were discussed later by Fehlner.<sup>36</sup> The subsequent work on *isocloso* cluster compounds<sup>15</sup> suggests that  $(CpCo)_4B_4H_4$  can be regarded as an *isocloso* compound with  $2n = 16$  skeletal electrons and a skeletal bonding topology consisting of eight 3c-2e bonds. This is exactly the chemical bonding model that was derived in 1982 by a different method.<sup>35</sup>

In  $(CpCo)_4B_4H_4$  the CpCo groups occupy the four degree 5 vertices, and the BH groups occupy the four degree 4 vertices,<sup>32</sup> in accord with the general preference of transition metals for higher degree vertices than BH vertices (Figure 7b). This pattern is reversed for the nickel analogue  $(CpNi)_4B_4H_4$ , in which the CpNi groups occupy the four degree 4 vertices and the BH groups occupy the four degree 5 vertices.<sup>33,34</sup> This difference may ultimately relate to the fact that a CpNi vertex requires one electron less than a CpCo vertex to achieve the favored 18-electron rare gas configuration.

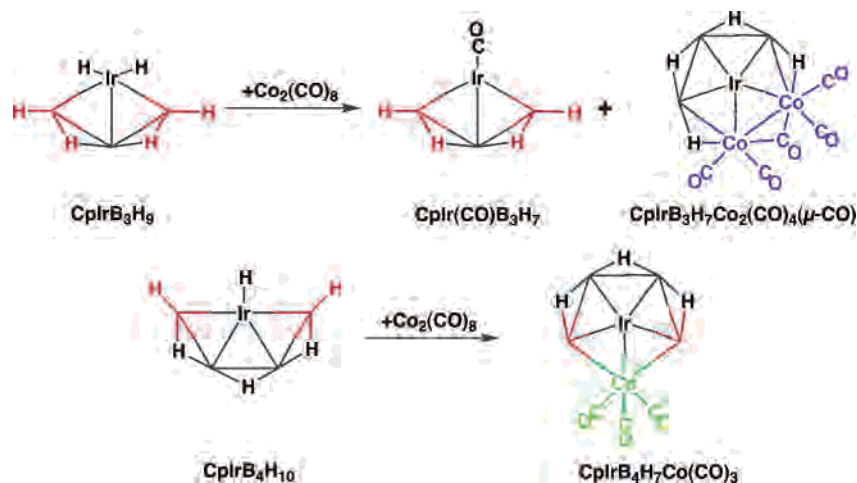
**2.6. Reactions of Cyclopentadienyliridaboranes with Cobalt Carbonyls.** Some interesting mixed metal clusters have been obtained by allowing cyclopentadienyliridaboranes having relatively open four- and five-vertex *arachno* structures to react with  $Co_2(CO)_8$  to add cobalt vertices to the cluster structure to give pentagonal pyramidal *nido*- $B_6H_{10}$  analogues. Thus reaction of the *arachno*-tetraborane analogue  $CpIrB_3H_9$  with  $Co_2(CO)_8$  gives a mixture of the  $\eta^3$ -“boraallyl” derivative  $CpIr(CO)(\eta^3-B_3H_7)$  isoelectronic with  $B_4H_{10}$  and the *nido*-hexaborane analogue  $CpIrB_3H_7Co_2(CO)_5$ , having the expected 16 skeletal electrons (Figure 8a).<sup>23</sup> Reaction of the *arachno*-pentaborane analogue  $CpIrB_4H_{10}$  with  $Co_2(CO)_8$  also gives a pentagonal pyramidal derivative, namely, the *nido*-hexaborane analogue  $CpIrB_4H_7Co(CO)_3$ , again having the expected 16 skeletal electrons (Figure 8b).<sup>23</sup>

### 3. Metallaboranes with Cyclopentadienylruthenium Vertices

The metallaboranes with CpRu vertices discussed in this paper are depicted in Figures 3–9 and some of their features

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**Figure 8.** Reactions of *arachno*-iridaboranes with  $\text{Co}_2(\text{CO})_8$  to give pentagonal pyramidal derivatives: (a) Reaction of  $\text{CpIrB}_3\text{H}_9$  with  $\text{Co}_2(\text{CO})_8$ . (b) Reaction of  $\text{CpIrB}_4\text{H}_{10}$  with  $\text{Co}_2(\text{CO})_8$ .

**Table 2.** Some Metallaboranes Containing CpRu Units

formula	analogue	shape	no. of skeletal electrons	lit. ref.
$(\text{CpRu})_2\text{B}_3\text{H}_9$	<i>nido</i> - $\text{B}_5\text{H}_9$	square pyramid	14	21
$(\text{CpRu})_2\text{B}_4\text{H}_8$ $(\text{CpRu})_3\text{B}_3\text{H}_8$	$\text{H}_2\text{Os}_6(\text{CO})_{18}$ structure	3-capped square pyramid	14	21, 39
$(\text{CpRu})_2\text{B}_4\text{H}_{10}$	<i>nido</i> - $\text{B}_6\text{H}_{10}$	pentagonal pyramid	16	21
$(\text{CpRu})_2\text{B}_6\text{H}_{12}$	<i>arachno</i> - $\text{B}_8\text{H}_{14}$		20*	41
$(\text{CpRu})_2\text{B}_8\text{H}_{12}$	<i>nido</i> - $\text{B}_{10}\text{H}_{14}$		22*	41

are summarized in Table 2. The CpRu vertices in these structures are considered to be donors of a single skeletal electron like bare vertices of group 13 atoms, particularly indium and thallium.

**3.1. Five- and Six-Vertex Structures.** The simplest CpRu borane is the pentaborane analogue  $(\text{CpRu})_2\text{B}_3\text{H}_9$ , which has the expected 14 skeletal electrons (Figure 3c).<sup>21</sup> As in the pentaborane analogue  $(\text{CpRh})_2\text{B}_3\text{H}_7$ , four of the extra hydrogens in  $(\text{CpRu})_2\text{B}_3\text{H}_9$  bridge the basal edges of the  $\text{M}_2\text{B}_3$  square pyramid. The remaining two “extra” hydrogens in  $(\text{CpRu})_2\text{B}_3\text{H}_9$  bridge the Ru–Ru edge, which is an apical-basal edge of the square pyramid. In this structure (Figure 3c) the three BH vertices all have the favored degree of 5 whereas the two CpRu vertices have degrees 6 (green) and 7 (blue).

An interesting reaction of  $(\text{CpRu})_2\text{B}_3\text{H}_9$  is its carbonylation with  $\text{Co}_2(\text{CO})_8$  to give a dicarbonyl of stoichiometry  $(\text{CpRu})_2\text{B}_3\text{H}_7(\text{CO})_2$  (Figure 4c).<sup>37</sup> This reaction results in the addition of two CO groups (+4 electrons) and the elimination of  $\text{H}_2$  (−2 electrons), corresponding to a net addition of two skeletal electrons. Therefore the  $(\text{CpRu})_2\text{B}_3\text{H}_7(\text{CO})_2$  product has 16 skeletal electrons and is isoelectronic with *arachno*- $\text{B}_5\text{H}_{11}$ . It is therefore not surprising that the structure of  $(\text{CpRu})_2\text{B}_3\text{H}_7(\text{CO})_2$  consists of a network of three fused triangles similar to that of  $\text{B}_5\text{H}_{11}$  (Figure 4).

Several six-vertex ruthenaboranes are known. The pentagonal pyramidal  $(\text{CpRu})_2\text{B}_4\text{H}_{10}$  has 16 skeletal electrons such as its close relative *nido*- $\text{B}_6\text{H}_{10}$  (Figure 6b).<sup>21</sup> Five of the six extra hydrogens in  $(\text{CpRu})_2\text{B}_4\text{H}_{10}$  bridge the basal edges. The sixth “extra” hydrogen in  $(\text{CpRu})_2\text{B}_4\text{H}_{10}$  bridges the Ru–Ru edge, which is one of the apical-basal edges of

the pentagonal pyramid. In this structure of  $(\text{CpRu})_2\text{B}_4\text{H}_{10}$  the BH and CpRu vertices, all have the favored degrees of 5 and 6, respectively. The structure of  $(\text{CpRu})_2\text{B}_4\text{H}_{10}$  can also be considered to be closely related to the “ferrole” derivatives  $\text{R}_4\text{C}_4\text{Fe}_2(\text{CO})_6$  (Figure 6c), obtained from alkynes and iron carbonyls.<sup>38</sup>

The remaining six-vertex ruthenaboranes, namely,  $(\text{CpRu})_2\text{B}_4\text{H}_8$  and  $(\text{CpRu})_3\text{B}_3\text{H}_8$ , both have the 14 skeletal electrons consistent with octahedral clusters.<sup>21,39</sup> However, in both cases the cluster structures are not octahedra but instead square pyramids capped on a triangular face similar to the isoelectronic  $\text{H}_2\text{Os}_6(\text{CO})_{18}$  (Figure 9).<sup>40</sup> As in  $\text{H}_2\text{Os}_6(\text{CO})_{18}$ , this 3-capped square pyramidal structure appears to be more stable than the octahedron because of the need of an “open” face (i.e., the uncapped square face) to accommodate some of the hydrogen atoms as bridges along the square edges. In the case of both  $(\text{CpRu})_2\text{B}_4\text{H}_8$  and  $(\text{CpRu})_3\text{B}_3\text{H}_8$ , the “open” square face of the 3-capped square pyramid has bridging hydrogen atoms along all of its four edges (Figure 9). In  $(\text{CpRu})_3\text{B}_3\text{H}_8$  the fifth bridging hydrogen bridges one of the two Ru–Ru edges connecting the apical ruthenium atoms to a basal ruthenium atom.

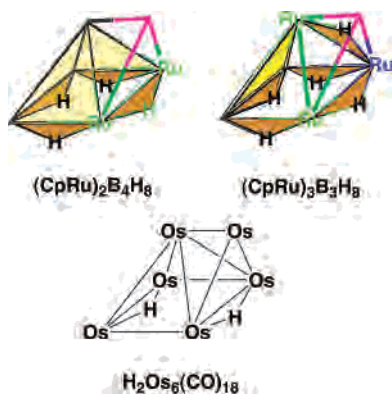
**3.2. Structures with More than Six Vertices.** The eight-vertex ruthenaborane  $(\text{CpRu})_2\text{B}_6\text{H}_{12}$  has a structure very similar to that of the isomer of *arachno*- $\text{B}_8\text{H}_{14}$  having the six extra hydrogens bridging the edges of the open hexagonal face (Figure 10a).<sup>41</sup> The six B vertices and the two CpRu

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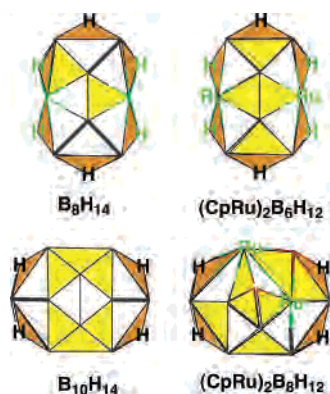
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**Figure 9.** (a) The 3-capped square pyramidal  $(\text{CpRu})_2\text{B}_4\text{H}_8$  and  $(\text{CpRu})_3\text{B}_3\text{H}_8$ . (b) The 3-capped square pyramidal metal carbonyl cluster  $\text{H}_2\text{Os}_6(\text{CO})_{18}$ .

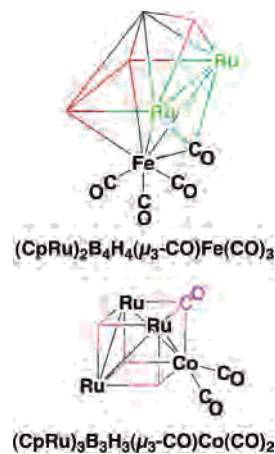


**Figure 10.** (a) A comparison of  $\text{B}_8\text{H}_{14}$  and  $(\text{CpRu})_2\text{B}_6\text{H}_{12}$ . (b) A comparison of  $\text{B}_{10}\text{H}_{14}$  and  $(\text{CpRu})_2\text{B}_8\text{H}_{12}$ .

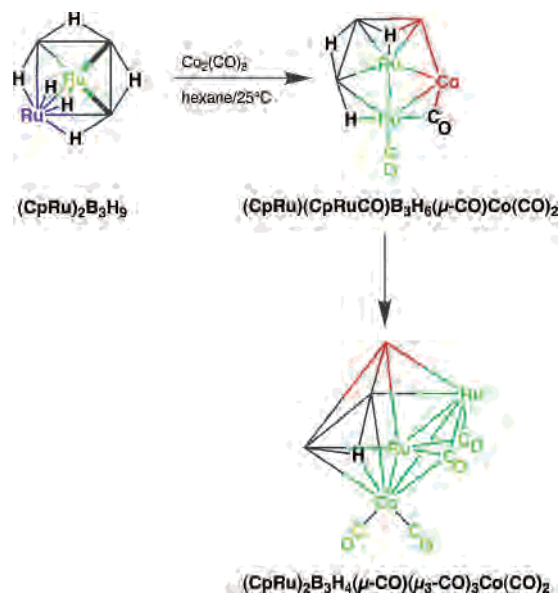
vertices have the favored degrees of 5 and 6, respectively. The skeletal electron count of 20 for  $(\text{CpRu})_2\text{B}_6\text{H}_{12}$  is two less than the skeletal electron count of 22 for  $\text{B}_8\text{H}_{14}$ . This means that the three 2c-2e bonds in  $\text{B}_8\text{H}_{14}$  (bold lines in Figure 8a) are replaced by two 3c-2e bonds in  $(\text{CpRu})_2\text{B}_6\text{H}_{12}$  in order to balance the change in skeletal electron count. This decrease of two skeletal electrons from a simple borane such as  $\text{B}_8\text{H}_{14}$  to a metallaborane such as  $(\text{CpRu})_2\text{B}_6\text{H}_{12}$  is similar that found in going from the deltahedral boranes  $\text{B}_n\text{H}_n^{2-}$  ( $6 \leq n \leq 12$ ) with  $2n + 2$  skeletal electrons to deltahedral *isocloso* metallaboranes [e.g., ( $\eta^6$ -arene)  $\text{RuB}_{10}\text{H}_{10}$ ] with only  $2n$  skeletal electrons.<sup>15</sup>

The 10-vertex ruthenaborane  $(\text{CpRu})_2\text{B}_8\text{H}_{12}$  has a structure closely related to that of the very stable *nido*- $\text{B}_{10}\text{H}_{14}$  but with a diamond-square-diamond (dsd) process providing vertices of degree 6 for the two CpRu groups (Figure 10b).<sup>41</sup> The skeletal electron count of 22 for  $(\text{CpRu})_2\text{B}_8\text{H}_{12}$  is two less than that of 24 for  $\text{B}_{10}\text{H}_{14}$  so that  $(\text{CpRu})_2\text{B}_8\text{H}_{12}$  can be considered to be an *isonido* compound.<sup>15</sup>

**3.3. Reactions of Cyclopentadienylruthenaboranes with Metal Carbonyls.** Many of the cyclopentadienylruthenaboranes have open faces that can be capped by additional metal atoms to form closed structures. Metal carbonyl reagents are often useful for such transformations. Reactions of this type have been observed for the 3-capped square



**Figure 11.** (a)  $(\text{CpRu})_2\text{B}_4\text{H}_4(\mu_3\text{-CO})\text{Fe}(\text{CO})_3$ ; (b)  $(\text{CpRu})_3\text{B}_3\text{H}_3(\mu_3\text{-CO})\text{Co}(\text{CO})_2$ .



**Figure 12.** The reaction of square pyramidal  $(\text{CpRu})_2\text{B}_3\text{H}_9$  with  $\text{Co}_2(\text{CO})_8$  to give pentagonal pyramidal  $(\text{CpRu})(\text{CpRuCO})\text{B}_3\text{H}_6(\mu\text{-CO})\text{Co}(\text{CO})_2$  followed by its conversion to octahedral  $(\text{CpRu})_2\text{B}_3\text{H}_4(\mu\text{-CO})(\mu_3\text{-CO})_3\text{Co}(\text{CO})_2$ .

pyramidal six-vertex cyclopentadienylruthenaboranes  $(\text{CpRu})_2\text{B}_4\text{H}_8$  and  $(\text{CpRu})_3\text{B}_3\text{H}_8$  (Figure 3c) with iron and cobalt carbonyls.

The reaction of  $(\text{CpRu})_2\text{B}_4\text{H}_8$  (Figure 9) with  $\text{Fe}(\text{CO})_5$  results in the expected capping of the square face of  $(\text{CpRu})_2\text{B}_4\text{H}_8$  to give the capped octahedral  $\text{Ru}_2\text{FeB}_4$  cluster  $(\text{CpRu})_2\text{B}_4\text{H}_4(\mu_3\text{-CO})\text{Fe}(\text{CO})_3$  (Figure 11a) having the 14 skeletal electrons required for the underlying octahedron. The  $\mu_3\text{-CO}$  group and the degree 3 BH vertex cap  $\text{Ru}_2\text{Fe}$  and  $\text{Ru}_2\text{B}$  faces, respectively, of the underlying octahedron. A similar reaction of  $(\text{CpRu})_3\text{B}_3\text{H}_8$  (Figure 9) with  $\text{Co}_2(\text{CO})_8$  results in a more complicated geometrical transformation to give the tricapped tetrahedral  $\text{Ru}_3\text{CoB}_3$  cluster  $(\text{CpRu})_3\text{B}_3\text{H}_3(\mu_3\text{-CO})\text{Co}(\text{CO})_2$  with the 12 skeletal electrons required for the underlying  $\text{Ru}_3\text{Co}$  tetrahedron (Figure 11b).<sup>42</sup> Three of the four faces of this underlying tetrahedron are capped by BH groups and the fourth face by the  $\mu\text{-CO}$  group leading

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to a cubane-like structure. Note that the metal carbonyl reaction of the original cluster richer in CpRu vertices, which donate only one skeletal electron each, gives a more condensed structure requiring fewer skeletal electrons. Furthermore, all of the bridging hydrogen atoms are lost in both of these reactions involving the six-vertex 3-capped square pyramidal clusters.

The reaction of the simpler square pyramidal cyclopentadienylruthenaborane (CpRu)<sub>2</sub>B<sub>3</sub>H<sub>9</sub> with Co<sub>2</sub>(CO)<sub>8</sub> follows a different course (Figure 12) to give pentagonal pyramidal (CpRu)(CpRuCO)B<sub>3</sub>H<sub>6</sub>(μ<sub>3</sub>-CO)Co(CO)<sub>2</sub> with the expected 16 skeletal electrons for the *nido* structure ( $16 = 2n + 4$  for  $n = 6$ ) related to *nido*-B<sub>6</sub>H<sub>10</sub> (Figure 6a).<sup>21</sup> In this case the metal carbonyl moiety does not cap the open square face of the original square pyramid but expands the base of the pyramid from a square to a pentagon. In addition, three of the six bridging hydrogen atoms of (CpRu)<sub>2</sub>B<sub>3</sub>H<sub>9</sub> are retained. The μ-CO group bridges the unique Ru–Co basal edge of this pentagonal pyramid. In this case the presence of bridging hydrogen atoms along all of the edges of the basal square in (CpRu)<sub>2</sub>B<sub>3</sub>H<sub>9</sub> (Figure 2) probably blocks access of the metal carbon moiety to this open face.

Mild heating of (CpRu)(CpRuCO)B<sub>3</sub>H<sub>6</sub>(μ<sub>3</sub>-CO)Co(CO)<sub>2</sub> results in loss of H<sub>2</sub> with rearrangement of the underlying Ru<sub>2</sub>CoB<sub>3</sub> cluster to octahedral (CpRu)<sub>2</sub>B<sub>3</sub>H<sub>4</sub>(μ-CO)(μ<sub>3</sub>-CO)-

Co(CO)<sub>2</sub> with the 14 skeletal electrons expected for an octahedron (Figure 12).<sup>21</sup>

#### 4. Summary

This paper shows how the cyclopentadienylmetallaboranes containing the vertex units CpM (M = Co, Rh, Ir) and CpRu donating two and one skeletal electrons, respectively, have structures closely related to binary boranes or borane anions or, in some cases, metal carbonyl clusters such as Os<sub>7</sub>(CO)<sub>21</sub> and H<sub>2</sub>Os<sub>6</sub>(CO)<sub>18</sub>. For the smaller clusters of this type, the skeletal electron counts are the same as those of the corresponding boranes. However, metallaborane clusters with eight or more vertices have two skeletal electrons less than the corresponding metal-free boranes analogous to the skeletal electron counts of *isocloso* metallaboranes versus those of metal-free deltahedral boranes.<sup>15</sup> In the metallaborane structures closely related to metal-free boranes, the favored degrees of BH and CpM vertices appear to be 5 and 6, respectively, similar to clusters discussed in previous papers.<sup>15,18,19,20</sup>

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