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Electronic structures of the isolobal pair, $Ru_3(CO)_9(CH)_2$ and $(BH)_3(CH)_2$; the eighteen-electron rule versus skeletal electron-pair counting

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Abstract

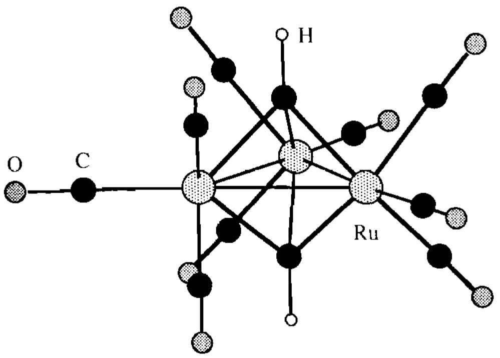
The isolobal relationship between $Ru(CO)_3$ and BH is explored through detailed comparisons of molecular-orbital calculations on the clusters, $Ru_3(CO)_9(CH)_2$ and $(BH)_3(CH)_2$. In addition to the principle bonds, which are the same as those one would predict from skeletal electron-pair counting (SEPC), the molecular-orbital calculations suggest that there are important secondary bonding interactions not predicted by SEPC. The most important of these are the interactions one would invoke if one enforced the 18-electron rule on Ru. Thus, the "t_{2g}" electron pairs, which SEPC views as spectator pairs, are actually involved in the bonding to a small degree.

Introduction

The 18-electron rule, or effective atomic number rule (EAN) [1], has found great success rationalizing the molecular structure, as well as correlating the structure and reactivity, of organometallic complexes. However, the efficacy of the method decreases rapidly as the nuclearity of the system increases [2]. These difficulties led to the development of other empirical electron counting rules such as skeletal electron-pair counting (SEPC) [3] and cluster valence electron counting (CVEC) [4]. SEPC has succeeded in main group clusters, especially in boranes and carboranes, and in transition metal clusters, by employing the isolobal principle [5].

Despite the usefulness of the empirical rules in both analyzing and predicting the structure of the cluster, they give somewhat different bonding schemes for the transition metal clusters. This difference arises because the EAN (18 e^-) rule assumes that the cluster is not electron deficient and thus one must form bonds to satisfy the full 18-electron count. On the other side, the SEPC assumes that the cluster can be electron deficient and makes no attempt to fill all transition metal valence orbitals. As we have shown, neither the SEPC nor the EAN rule alone reveals the full bonding nature of some dinuclear and trinuclear clusters [6–8].

Here we will investigate the bonding in the cluster, $Ru_3(CO)_9(CH)_2$, which may be viewed as a trigonal bipyramid with three Ru atoms around the equator and two C atoms forming the apexes, **1**. This hypothetical



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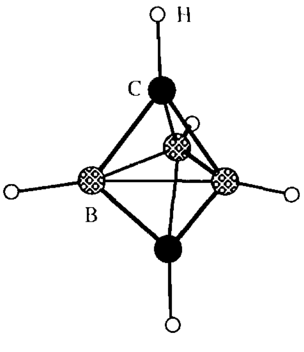

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cluster is a derivative of known trinuclear clusters, $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$ [9] or $H_3Os_3(CO)_9(CH)$ [10], the latter, in particular, makes an interesting analog for the mechanistic interpretation of reactions involving methyl groups and metal surfaces [11].

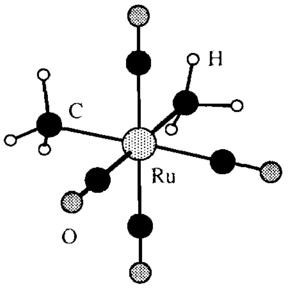
The cluster **1**, in light of the isolobal principle, should be equivalent to $B_5H_5^{2-}$ or 1,5-$C_2B_3H_5$ (**2**) in the aspect of skeletal bonding (see 'Discussion' below). The contradiction between EAN and SEPC rules will be more obvious through a comparison of these two clusters. The carborane **2** is clearly electron deficient and has only six pairs of electrons for cluster bonding. Likewise, the SEPC rules and isolobal principle require only six pairs of electrons to participate in cluster bonding for the ruthenium cluster. However, for the ruthenium cluster, the EAN rule predicts nine pairs of electrons to be involved in cluster bonding corresponding to the nine edges of the trigonal bipyramid.

Therefore a quantitative MO analysis of **1** and **2** could provide insight into how well each of the empirical rule describes the actual bonds.

Models and method

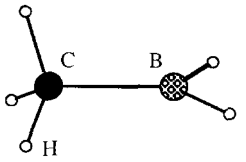
Fenske–Hall molecular orbital calculations [12] were performed on the Department of Chemistry's VAX 3400 computer. In the calculations, the Ru cluster **1** was idealized to a C_{3h} geometry. The $Ru(CO)_3$ fragment was treated as a part of an octahedral structure. The other structural parameters were set to the experimental data [9, 10]. A parallel calculation on the carborane **2** was carried out for the purpose of comparison. The structural parameters of **2** were taken from the crystal data [13]. Calculations were also performed on model compounds $RuMe_2(CO)_4$ (**3**), $Ru_2H_2(CO)_8$ (**4**), CBH_5 (**5**) and B_2H_4 (**6**) in order to determine the overlap populations corresponding to Ru–C, Ru–Ru, B–C and B–B single bonds, respectively. $RuMe_2(CO)_4$ and the $RuH(CO)_4$ fragments in **4** were restricted to a pseudooctahedral geometry, while the CH_3 and BH fragments in **3**, **5** or **6** were tetrahedral fragments. The values of Ru–Ru, Ru–C, B–C, B–B, B–H and C–O bond distances in **1** and **2** were utilized to fix the corresponding bond distances in **3**–**6**. The Ru–H bond lengths in **4** were determined by shortening the Ru–C bond length in **1** by the difference between standard C–C and C–H bond lengths [14]. The standard C–H bond length was also used to fix the C–H bond in the CH_3 fragments.

The Ru basis functions were taken from Richardson *et al.* [15] and augmented by 5s and 5p functions with exponents of 2.20. The carbon, oxygen, boron and hydrogen functions were taken from the double-ζ functions of Clementi [16] and fit to single-ζ functions [17], except for the p valence functions, which were retained in the double-ζ form. The atomic functions were made orthogonal by the Schmidt procedure. Mulliken population analysis [18] was used to determine the orbital populations as well as the individual atomic charges.



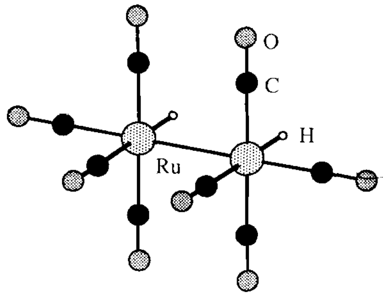
C_{2v}

3



C_s

5



C_{2v}

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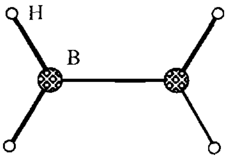


D_{2h}

6

Results and discussion

Significance of SEPC and isolobal analogy

$Ru_3(CO)_9(CH)_2$ can be viewed as a cluster formed from three $Ru(CO)_3$ and two CH fragments. Since $Ru(CO)_3$ and BH are isolobal fragments, their frontier orbitals should behave similarly in forming the $Ru_3(CO)_9(CH)_2$ and 1,5-$C_2B_3H_5$ clusters.

Due to its simplicity, the SEPC rule is a popular method for the analysis of cluster bonding. Here, we use the isolobal principle and expand on the analogy to the electron-deficient boron hybrids. As mentioned above, each $Ru(CO)_3$, which is isolobal to the BH fragment, contributes 3 orbitals and 2 electrons to cluster bonding. In the SEPC view the remaining 6 d electrons ('t_{2g}' set) on each Ru are not involved in the cluster bonding but are only involved in bonding to the carbonyls. Each CH fragment contributes 3 orbitals and 3 electrons. Thus, the $Ru_3(CO)_3(CH)_2$ cluster can be thought of as a 5 vertex polyhedron with 6 skeletal electron pairs. By analogy to the boron hydrides,

$Ru_3(CO)_9(CH)_2$ should be a *closo* cluster ($n+1$ pairs), and have a trigonal bipyramidal geometry. The $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$ compound provides an example of this *closo* structure.

Figures 1 and 2 show the MO diagrams of $Ru_3(CO)_9(CH)_2$ and $1,5\text{-}C_2B_3H_5$, respectively. The orbitals of either $Ru(CO)_3$ or BH are shown on the right, while those of CH are shown on the left. The low lying orbitals on each fragment are omitted from Fig. 1, since they contribute mainly to the fragment bonding rather than cluster bonding.

The high-lying orbitals of $Ru(CO)_3$ retain much of their octahedral parentage [19], and thus are labelled (in the ascending order of energy) as 't_{2g}', 'e_g' and 'a_1'. As shown in Table 2, 't_{2g}' correspond to the three 4d orbitals stabilized by backbonding with the carbonyls' π^* (π acceptor orbital), while 'e_g' are derived from the remaining two 4d orbitals, which mix with high-lying 5p orbitals and negatively overlap with the carbonyl's σ donor orbitals. Orbital 'a_1' is the 5s/5p hybrid. There are six electrons in the 't_{2g}' orbitals and two electrons in the 'e_g' orbitals. The 15 lowest lying valence molecular orbitals of the $Ru(CO)_3$ fragment consist of the symmetry-adapted combinations of the carbonyl 3σ, 4σ and 1π orbitals and the Ru–CO σ bonds formed by donation from the carbonyl 5σ orbitals to the metal orbitals.

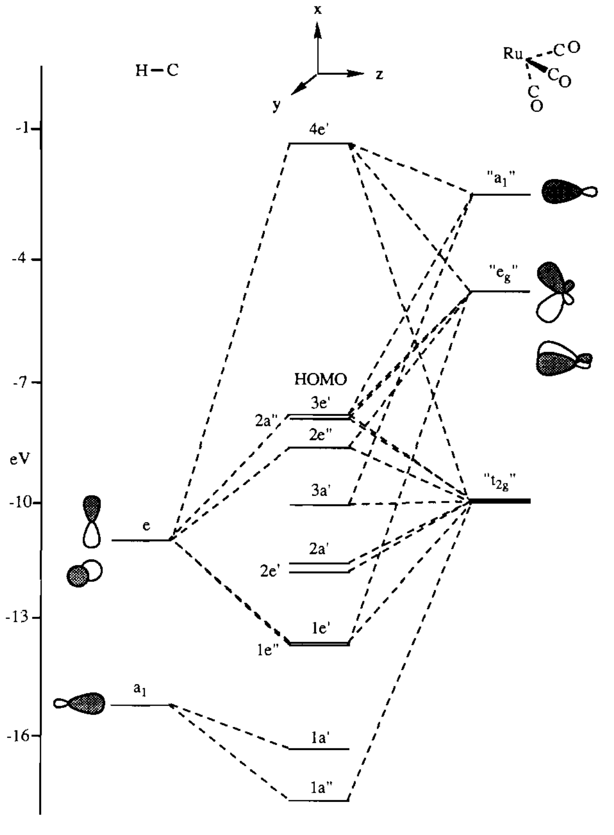


Fig. 1. Molecular orbital diagram of $Ru_3(CO)_9(CH)_2$, constructed from $Ru(CO)_3$ and CH fragments.

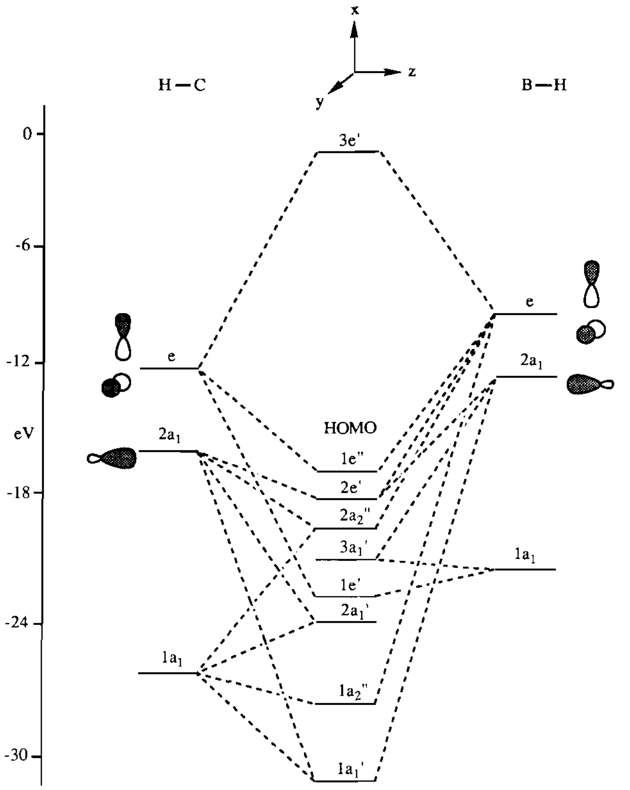


Fig. 2. Molecular orbital diagram of $1,5\text{-}C_2B_3H_5$, constructed from BH and CH fragments.

TABLE 1. Molecular composition of $Ru_3(CO)_9(CH)_2$

Orbital	Fragment composition (%)			
	't_{2g}'	'e_g'	'a_1'	CH
4e′	13	45	11	22
3e′	40	33	13	14
2a″	50	43		6
2e″	43	42		15
3a′	82		10	7
2a′	91	4	4	
2e′	90	3	2	3
1e′	52	6	7	29
1e″	47	11		37
1a′	7	7	6	31
1a″	22	8		42

According to SEPC and the isolobal principle, both BH and $Ru(CO)_3$ provide two electrons and three orbitals to cluster bonding. Each CH fragment contributes three orbitals and three electrons to cluster bonding. In this view, the 't_{2g}' set of the $Ru(CO)_3$ fragment participates primarily in Ru–CO bonding through π backdonation.

However, the spectator role of the 't_{2g}' orbitals is not entirely clear. As demonstrated in Tables 1 and 2,

TABLE 2. Mulliken overlap populations of $Ru_3(CO)_9(CH)_2$ by molecular orbital

Orbital	Overlap populations										
	Ru–Ru							Ru–CH			
	‘t_{2g}’–t_{2g}’	‘t_{2g}’–‘e_g’	‘t_{2g}’–‘a_1’	‘e_g’–‘e_g’	‘e_g’–‘a_1’	‘a_1’–‘a_1’	Total	‘t_{2g}’–CH	‘e_g’–CH	‘a_1’–CH	Total
3e′	−0.032	−0.100	−0.160	0.035	0.392	−0.116	0.019	−0.370	0.393	0.284	0.307
2a″	0.062	−0.231		0.133			−0.036	−0.202	0.214		0.012
2e″	−0.050	0.098		−0.126			−0.078	−0.312	0.621		0.309
3a′	−0.025	0.055	0.009	−0.001	−0.037	0.057	0.058	−0.092	−0.039	0.184	0.053
2a′	0.079	0.008	0.007	−0.004	0.034	0.017	0.141	0.003	−0.007	−0.010	−0.014
2e′	−0.010	0.084	0.043	0.003	0.035	−0.010	0.145	0.025	−0.015	0.008	0.018
1e′	−0.014	0.048	0.098	0.006	−0.006	−0.005	0.127	0.511	0.125	0.253	0.889
1e″	−0.045	−0.030		−0.024			−0.099	0.469	0.450		0.919
1a′	0.005	0.019	−0.002	−0.004	0.032	0.014	0.064	0.051	0.142	0.182	0.375
1a″	0.017	0.042		0.016			0.075	0.249	0.172		0.421

TABLE 3. Mulliken overlap populations for $Ru_3(CO)_9(CH)_2$

	Overlap populations									
	‘t_{2g}’–‘t_{2g}’	‘t_{2g}’–‘e_g’	‘t_{2g}’–‘a_1’	‘e_g’–‘e_g’	‘e_g’–‘a_1’	‘a_1’–‘a_1’	‘t_{2g}’–CH	‘e_g’–CH	‘a_1’–CH	Total
Ru–Ru	−0.004	0.023	−0.002	0.037	0.464	−0.092				0.426
Ru–CH							0.487	2.216	1.050	3.753

TABLE 4. Mulliken gross populations and net populations of $Ru_3(CO)_9(CH)_2$ by fragment orbital

Fragment orbital	Mulliken population	Net population	Dν
‘t_{2g}’	5.499	5.415	0.084
‘e_g’ (xz)	0.663	0.453	0.210
‘e_g’ (yz)	1.060	0.852	0.208
‘a_1’	0.451	0.280	0.171
C---H	1.326	1.042	0.284
C_{Px}	1.070	0.815	0.255
C_{Py}	1.070	0.815	0.255

TABLE 5. Mulliken gross populations and net populations of 1,5-$C_2B_3H_5$ by fragment orbital

Fragment orbital	Mulliken population	Net population	Dν
B–H	1.938	2.047	−0.109
B---H	0.625	0.371	0.254
B_{Px}	0.467	0.229	0.238
B_{Py}	0.809	0.554	0.255
C---H	1.133	0.897	0.236
C_{Px}	1.106	0.799	0.307
C_{Py}	1.106	0.799	0.307

there exists strong mixing of the ‘t_{2g}’, ‘e_g’ and ‘a_1’ orbitals. The ‘t_{2g}’ set contributes significantly to both of the frontier orbitals. The HOMO, 3e′, contains 40% ‘t_{2g}’ character. The mixing of ‘t_{2g}’, ‘e_g’ and ‘a_1’ is also considerable in the lower energy orbitals. For instance, it can be seen from Table 2 that the overlap population between ‘t_{2g}’ and ‘e_g’ or ‘a_1’ in the 2e′ orbital is even larger than that among the three orbitals in ‘t_{2g}’ set itself. We should point out that such mixing will be important to the cluster bonding only if it produces a net bonding (antibonding) contribution. As shown in Table 2, even though the ‘t_{2g}’ orbitals contribute significantly to the Ru–C bonding in the lower six orbitals (1a″–1e′), the majority of this bonding contribution is cancelled out by the ‘t_{2g}’–C antibonding contribution from the upper orbitals. Since all molecular orbitals derived from the ‘t_{2g}’ orbitals are filled, the net contribution of the ‘t_{2g}’ orbitals to metal–metal bonding is also relatively small. Based on the results listed in Table 3, it can be judged that for both the Ru–Ru and Ru–C bonds the net bonding interaction is principally from the ‘e_g’ and ‘a_1’ orbitals, i.e. the isolobal analogues of the frontier orbitals of the BH fragment.

This isolobal relationship between the $Ru(CO)_3$ and BH fragments can also be observed in Tables 4 and 5, where Dν is defined as the difference between the Mulliken population and net population of the fragment orbital ν. Thus, Dν is the total overlap population between orbital ν and all the other fragment orbitals. The values of Dν exhibit a similar pattern for the frontier orbitals of the $Ru(CO)_3$ and BH fragments, a result consistent with the isolobal analogy.

In the final clusters, one can find orbitals of 1,5-$C_2B_3H_5$, for which the corresponding molecular orbitals of $Ru_3(CO)_9(CH)_2$ show a dramatic resemblance (Fig. 3). However, this correspondence is ambiguous in other molecular orbitals of $Ru_3(CO)_9(CH)_2$ and 1,5-$C_2B_3H_5$ due to the strong mixing of the 't_{2g}' with the 'e_g' and 'a_1' fragment orbitals in the ruthenium system.

Localized bonding and the EAN rule

On the basis of the $18e^-$ rule ($8e^-$ at the main group atoms and $18e^-$ at the metal atoms) and common formal oxidation state conventions, Ru and C may be treated as Ru^{2+} (d^6) and C^{3-}, respectively. Based on these initial assumptions, one could draw the dominant resonance structure as shown in **7** with the bonds designated as dative bonds (arrows). Such an assignment of the formal oxidation state probably deviates severely from the actual charge distribution, since it exaggerates the ionic contributions. At the other extreme we may construct another resonance form by assigning all Ru–C as covalent bonds, **8**. The true ground state wavefunction must be a mixture of these two extreme forms and the many intermediate ones.

Now we shall examine in more detail the use of the 't_{2g}' orbitals of the Ru centers in cluster bonding. In both resonance patterns mentioned above, it is essential to have nine 2-center, 2-electron ($2c$–$2e^-$) bonds. To make these bonds in **7** and **8**, each Ru center has used one of its 't_{2g}' electron pairs in the cluster bonding. Thus, invoking the 't_{2g}' orbital in the cluster bonding is the key characteristic for the enforcement of the $18e^-$ rule on systems which are electron deficient ($3c$–$2e^-$ bonds) in SEPC.

In small clusters one can often arrive at a localized bonding picture by following the prescription of Lipscomb [20]. In $B_5H_5^{2-}$, the triangular base of the pyramid could be bonded by the three $2c$–$2e^-$ B–B bonds and the two capping BH groups bonded to each base through the three open $3c$–$2e^-$ bonds as shown by **9** [21]. Different arrangements of the three $2c$–$2e^-$ and three $3c$–$2e^-$ bonds are also possible. For example, we can have three central type $3c$–$2e^-$ bonds in the lower cap, and three $2c$–$2e^-$ B–B bonds in the upper cap as shown

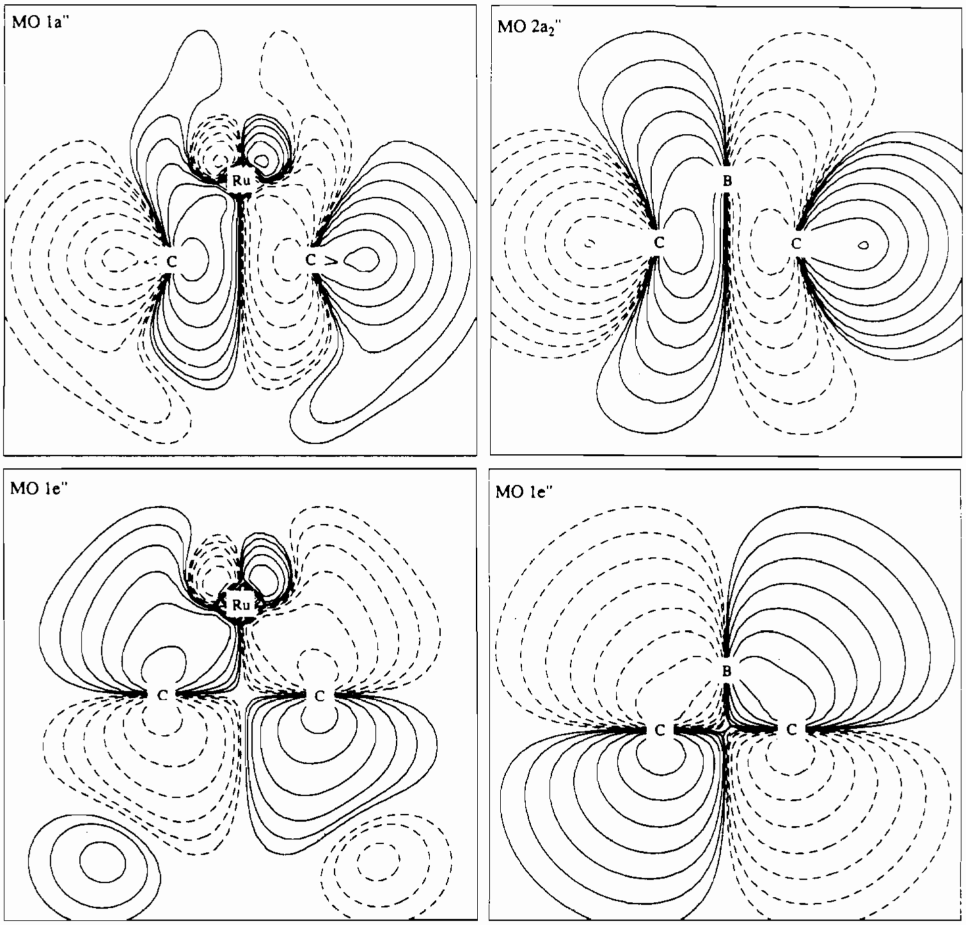
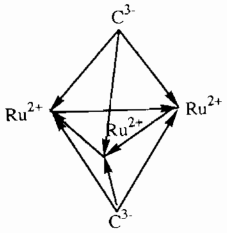


Fig. 3. Contour plots for selected orbitals of $Ru_3(CO)_9(CH)_2$ and 1,5-$C_2B_3H_5$ in the C–Ru–C plane or C–B–C plane. The lowest contour values are 0.00195 (e Å^{-3})$^{1/2}$ and each succeeding contour differs from the previous one by a factor of 2.0.



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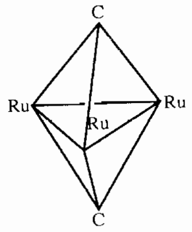

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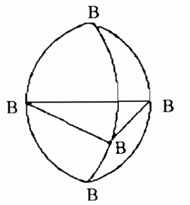

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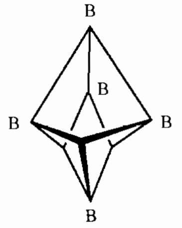

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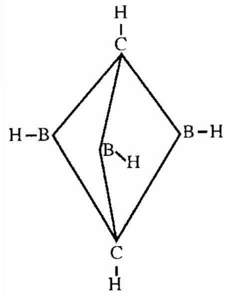

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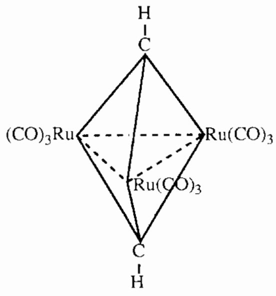

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by **10** [22]. Similar localized bonding schemes for the Ru cluster can be obtained by replacing the apical BH and basal BH fragments with CH and $Ru(CO)_3$ groups, respectively.

It can be concluded that the primary contradiction between the 18-electron prediction and the SEPC prediction is the number of electron pairs utilized in cluster bonding. The focus of the argument is whether some of the 't_{2g}' pairs will be involved in cluster bonding or only involved in bonding to the carbonyls.

Because of the delocalized character of the calculated molecular orbitals, it is often difficult to identify molecular orbitals with a particular localized bonding pattern. Various criteria have been utilized to obtain the localized molecular orbitals for 1,5-$C_2B_3H_5$ [22, 23]; here we will use an alternative method. We will determine the strength of the cluster bonds by means of an analysis of relative overlap population. Thus, bonding schemes are described on the bases of the strength of the cluster bonds. Model compounds **3**, **4**, **5** and **6** were used to determine the overlap populations corresponding to typical B–C, B–B, Ru–C and Ru–Ru single bonds, respectively. The results are summarized in Table 6 together with the corresponding overlap populations in $Ru_3(CO)_9(CH)_2$ and 1,5-$C_2B_3H_5$.

It can be seen that the overlap population between boron and carbon in 1,5-$C_2B_3H_5$ is close to that of a B–C single bond, whereas the overlap population between two boron atoms in 1,5-$C_2B_3H_5$ is much weaker than that of a B–B single bond. Therefore, 1,5-$C_2B_3H_5$ can be viewed as a 'classical structure' with six B–C single bonds and no B–B bond as shown in **11**. Substitution of carbon for boron apparently caused a dramatic change in the bonding picture of $B_5H_5^{2-}$. This change is primarily due to the stronger electronegativity of carbon. Similar results have been found previously by the other semiempirical [22, 23] and *ab initio* studies [23a, 24].

For the ruthenium case, the overlap population between ruthenium and carbon in $Ru_3(CO)_9(CH)_2$ is comparable with that of a Ru–C single bond, whereas, the overlap population between two ruthenium atoms in $Ru_3(CO)_9(CH)_2$ is only 18% of that of a Ru–Ru single bond. This analysis suggests that $Ru_3(CO)_9(CH)_2$ may also be roughly viewed as a 'classical structure' with six strong Ru–C bonds and three much weaker Ru–Ru bonds (see **12**). We note again the similarity of $Ru_3(CO)_9(CH)_2$ and 1,5-$C_2B_3H_5$ in the cluster bonding scheme.

Role of t_{2g}-like electrons

Although the isolobal principle and SEPC rules have provided a basically correct bonding picture for the $Ru_3(CO)_9(CH)_2$ cluster, the weak Ru–Ru bonds are stronger than the corresponding B–B bonds. This result could arise from other SEPC bonding contributions such as **9** and **10** in addition to **11**, or from an involvement of 't_{2g}' pairs as suggested by the $18e^-$ rule.

The difference in cluster bond strength between the ruthenium and carborane systems is unique to transition metal clusters. This kind of difference can be further observed in an analysis of the atomic charge of the carbon atom (see Table 7). For 1,5-$C_2B_3H_5$, the Mulliken atomic charge of a carbon atom is −0.31, which is easily explained as a donation of p electrons from the frontier orbitals of the more electropositive BH fragments. In contrast to the carborane case, the Mulliken atomic charge of a carbon atom in $Ru_3(CO)_9(CH)_2$ is

TABLE 6. Mulliken overlap populations of 1,5-$C_2B_3H_5$ and $Ru_3(CO)_9(CH)_2$

	Overlap population			
	B–B	B–C	Ru–Ru	Ru–C
1,5-$C_2B_3H_5$	0.089	0.738		
$Ru_3(CO)_9(CH)_2$			0.046	0.490
Single bond	0.766	0.757	0.257	0.383

TABLE 7. Mulliken populations and atomic charges of $Ru_3(CO)_9(CH)_2$ and 1,5-$C_2B_3H_5$

	Mulliken populations						Atomic charge	
	't_{2g}'	'e_g'	'a_1'	$1a_1$	$2a_1$	e	C	H
$Ru(CO)_3$	6	2	0					
$Ru_3(CO)_9(CH)_2$	5.499	1.723	0.451				−0.511	0.034
Difference	−0.501	−0.277	0.451					
BH				2	2	0		
1,5-$C_2B_3H_5$				1.938	0.625	1.276	−0.268	0.045
Difference				0.062	−1.375	1.276		

−0.51, where only 7% is provided by the hydrogen atom. According to the SEPC rule, the remaining 0.48 electrons on the carbon atom should come from the frontier orbitals of the $Ru(CO)_3$ fragments. However, instead of losing 0.48 electrons to the carbon atom, each set of 'e_g' and 'a_1' orbitals gains 0.17 electrons from the other fragment orbitals during construction of the $Ru_3(CO)_9(CH)_2$ cluster. Therefore, the SEPC theory is unable to account for a total of 1.47 electrons obtained by the two CH fragments and the three sets of the 'e_g' and 'a_1' orbitals of the $Ru(CO)_3$ fragments.

We note that the three 't_{2g}' sets of the $Ru(CO)_3$ fragments lose 1.50 electrons in forming the ruthenium cluster. A possible explanation could be that these 't_{2g}' electrons are donated to the carbon atoms as well as to the other 'e_g' and 'a_1' orbitals, i.e. the 't_{2g}' electrons are involved in cluster bonding. This bonding picture favors contributions from those resonance structures derived from the $18e^-$ rule, **7** and **8**. This possibility is also consistent with the results of Table 3, where the 't_{2g}'–'e_g' and 't_{2g}'–CH overlap populations have significant values relative to the 'e_g'–'e_g' and 'a_1'–CH overlap populations. Therefore, involvement of the 't_{2g}' electrons strengthens the Ru–Ru and Ru–C bonds in the sense of a secondary bonding interaction. The role of the 't_{2g}' electrons reveals the electron-rich character of ruthenium atom, which is not properly reflected by the isolobal principle and SEPC rules.

Conclusions

The isolobal relationship between the $Ru(CO)_3$ and BH fragments can be seen in the calculated results. The principle bonding can be explained by application of the isolobal principal and skeletal electron-pair counting rule. The 'e_g' and 'a_1' fragment orbitals make the major net contribution to the ruthenium cluster bonding. Both 1,5-$C_2B_3H_5$ and $Ru_3(CO)_9(CH)_2$ are grossly described by a 'classical' bonding picture with six B–C or Ru–C bonds (2c–2e$^-$).

However, the SEPC rule alone cannot account for the weak Ru–Ru bonds nor for the Mulliken atomic charge of the carbon atoms in the ruthenium cluster. The explanation requires invoking contributions from the $18e^-$ resonance structures, i.e. including the 't_{2g}' electrons in the cluster bonding.

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References

1 N.V. Sidgwick, *The Electronic Theory of Valency*, Cornell University Press, Ithaca, New York, 1927.
2 M.B. Hall, in J.P. Fackler Jr. (ed.), *Metal–Metal Bonds and Clusters in Chemistry and Catalysis*, Plenum, New York, 1990, p. 265.
3 (a) K. Wade, *Adv. Inorg. Radiochem.*, *18* (1976) 1; (b) D.M.P. Mingos, *Acct. Chem. Res.*, *17* (1984) 311.
4 (a) J.W. Lauher, *J. Am. Chem. Soc.*, *100* (1978) 5305; (b) J.W. Lauher, *J. Am. Chem. Soc.*, *101* (1979) 2604.
5 (a) M. Elian and R. Hoffmann, *Inorg. Chem.*, *14* (1975) 365; (b) R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, *21* (1982) 711.
6 D.E. Sherwood, Jr. and M.B. Hall, *Inorg. Chem.*, *21* (1982) 3458.
7 G.L. Griewe and M.B.Hall, *Inorg. Chem.*, *27* (1988) 2250.
8 G.L. Griewe and M.B. Hall, *Organometallics*, *7* (1988) 1923.
9 W. Yeh, J.R. Shapley, J.W. Ziller and M.R. Churchill, *Organometallics*, *5* (1986) 1757.
10 A.G. Orpen and T.F. Koetzler, *Acta Crystallogr., Sect. B*, *40* (1984) 606.
11 R.B. Calvert and J.R. Shapley, *J. Am. Chem. Soc.*, *99* (1977) 5225.
12 M.B. Hall and R.F. Fenske, *Inorg. Chem.*, *11* (1972) 768.
13 E.A. McNeill, F.R. Gallaher, F.R. Scholer and S.H. Bauer, *Inorg. Chem.*, *12* (1973) 2108.
14 J.A. Pople and M. Gordon, *J. Am. Chem. Soc.*, *89* (1967) 4253.
15 J.W. Richardson, M.J. Blackman and J.E. Ranochak, *J. Chem. Phys.*, *58* (1973) 3010.

16 (a) E.J. Clementi, *J. Chem. Phys., 40* (1964) 1944; (b) *IBM J. Res. Dev., 9* (1965) 2.

17 R.F. Fenske and D.D. Radtke, *Inorg. Chem., 7* (1968) 479.

18 R.S. Mulliken, *J. Chem. Phys., 23* (1955) 1833, 1841.

19 M. Elian, M.-L. Chen, D.M.P. Mingos and R. Hoffmann, *J. Am. Chem. Soc., 98* (1976) 7240.

20 W.N. Lipscomb, *Boron Hydrides,* Benjamin, New York, 1963.

21 E.B. Moore, Jr., L.L. Lohr, Jr. and W.N. Lipscomb, *J. Chem. Phys., 35* (1961) 1329.

22 D.A. Dixon, D.A. Kleier, T.A. Halgren, J.H. Hall and W.N. Lipscomb, *J. Am. Chem. Soc., 99* (1977) 6226.

23 (a) M.F. Guest and I.H. Hillier, *Mol. Phys., 26* (1973) 435; (b) G.D. Graham, D.S. Marynick and W.N. Lipscomb, *J. Am. Chem. Soc., 102* (1980) 2939.

24 N.J. Fitzpatrick and M.O. Fanning, *J. Mol. Struct., 40* (1977) 271.