Journal of Organometallic Chemistry, *478* (1994) 49–55

Cluster isomerization. The case of M_4B_4 metallaboranes

Thomas P. Fehlner

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

(Received October 6, 1993)

Abstract

Approximate molecular orbital theory (Fenske–Hall) combined with fragment analysis is used to explore the relationship between geometric and electronic structure for metallaboranes containing M_4B_4 cluster cores. It is demonstrated that the isomers B,Fe-conjuncto-$\{Fe_2(CO)_6B_2H_4\}_2$ (I) and B,B-conjuncto-$\{Fe_2(CO)_6B_2H_4\}_2$ (II) are reasonably considered as either $Fe_2(CO)_6B_2H_4$ fragments joined by two three center-two electron bonds or chain and diamond shaped B_4H_8 moieties, respectively, coordinated by diiron fragments. However, the results also suggest that these compounds can be regarded as intermediates on the way to dodecahedral clusters similar to $\{(\eta^5\text{-}C_5H_5)M\}_4B_4H_4$, M = Co, Ni. The latter compounds are known to "violate" the cluster electron counting rules in that they have 8 and 10 cluster bonding pairs, respectively. A synthetic route to a dodecahedral M_4B_4 cluster containing 9 cluster bonding pairs is proposed.

Key words: Metallaborane; Molecular orbital calculations; Iron; Boron; Cobalt; Nickel

1. Introduction

The role of molecular orbital (MO) theory in the development of cluster chemistry has been prominent. From the origin and application of the idea of multicenter bonds [1] to tensor surface harmonic theory [2] the qualitative concepts derived from MO treatments have permitted many of the interesting structural features of clusters to be understood, thereby fostering more rapid evolution of the field [3]. Of particular note are the electron counting rules relating cluster formula to cluster geometry thus empowering a structural interpretation of spectroscopic data [4,5]. To some extent the success of these ideas has limited recognition of the large number of possible structures still allowed for a given cluster composition, *i.e.*, a given electron count. Cluster isomerization complicates matters but, at the same time, provides an opportunity for the development of a better understanding of the connection between composition and structure. Further, it provides an empirical way of attacking the problem of energetics in cluster systems[6].

In this contribution, the M_4B_4 cluster system is explored. The publication of the structures of $\{(\eta^5\text{-}C_5H_5)M\}_4B_4H_4$, M = Co, Ni [7–9] gave rise to three theoretical analyses. The reason is simple. Both compounds exhibit dodecahedral geometries (but with differing main group and metal atom positions) but neither has the proper electron count for a closo, eight vertex cluster (Fig. 1). Although varied in approach each of the three explanations of the failure of the counting rules has merit [10–12]. However, these explanations differ concerning the stability of a cluster structure with the proper electron count, *e.g.* the hypothetical $\{Fe(CO)_3\}_2\{Co(CO)_3\}_2B_4H_4$. Further they give no information on the relative stabilities of other possible geometries for clusters containing 8 or 10 formal skeletal bonding pairs. Note that the chemistry of these M_4B_4 clusters is unknown as they were isolated as minor products in a complex reaction system [7–9].

Most metallaboranes contain either a large number of boron atoms and one or two metal atoms or the reverse. In these limiting cases cluster properties are largely controlled by the bonding requirements of the more abundant cluster component [13–17]. However, there is a feature of clusters containing nearly equal numbers of main group and transition metal atoms that increases the possibility of observing metastable cluster structures. A consideration of the known properties of main group and transition element clusters reveals its origin. Main Group element clusters exhibit isomers of greatly differing energy connected by large barriers for

0022-328X/94/$7.00
SSDI 0022-328X(93)24299-K

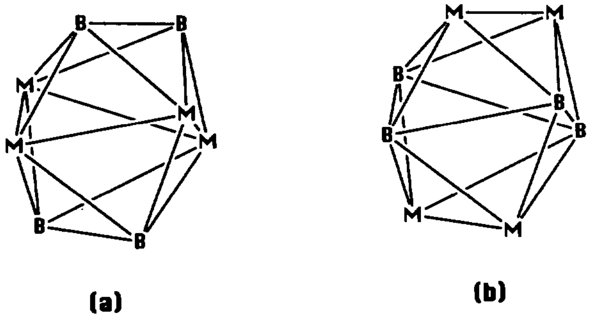


Fig. 1. Schematic representation of the structures of (a) $\{(\eta^5\text{-}C_5H_5)Co\}_4B_4H_4$ and (b) $\{(\eta^5\text{-}C_5H_5)Ni\}_4B_4H_4$.

isomerization, *e.g.*, $C_2B_4H_6$ [18]. On the other hand, transition metal clusters exhibit isomeric forms which differ little in energy and possess relatively small barriers for rearrangement [19]. In certain cases the balance is fine enough that equilibria involving different cluster forms can be observed, *e.g.*, $Fe_3(CO)_9CH_4$ [20]. It follows that the mixed systems will exhibit a number of minima on the potential energy surface which do not differ greatly in energy and which are connected by barriers of modest heights. The practical consequence is that in these mixed systems the likelihood of the synthesis *and isolation* of metastable isomers is enhanced and an examination of their rearrangement to more stable forms is more easily accomplished.

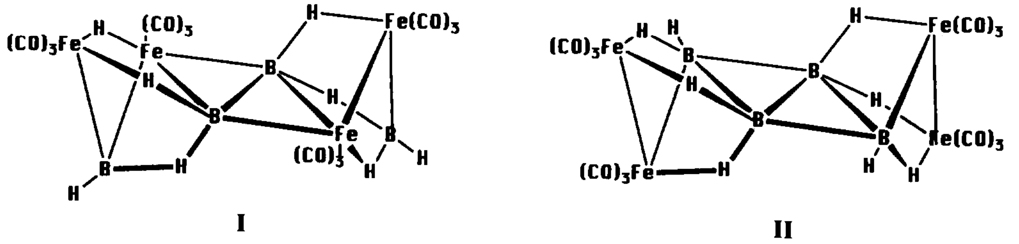
Recently we have reported the synthesis of a new M_4B_4 cluster system from the low temperature oxidative coupling of $[Fe_2(CO)_6B_2H_4]^{2-}$ [21,22]. The initial product is B,Fe-conjuncto-$\{Fe_2(CO)_6B_2H_4\}_2$ (**I**), which on heating leads to the formation of an equilibrium mixture of **I** and B,B-conjuncto-$\{Fe_2(CO)_6B_2H_4\}_2$ (**II**) (Fig. 2). The form of **I** in solution is the same as that in the solid state whereas **II** exists in three tautomeric forms in solution. The most abundant of these corresponds to the form found in the solid state. Further pyrolysis at higher temperatures results in the formation of metal borides and no evidence for the formation of other cluster species has been found. These two new isomeric M_4H_4 clusters have the same formal electron count as $\{(\eta^5\text{-}C_5H_5)Ni\}_4B_4H_4$. In the following, the electronic structures are modeled in order to explore the origins of the observed geometries as well as to seek eventual justification for an analysis of the cluster energetics in terms of a localized bonding model.

2. Inter M_2B_2 fragment bonding

Our original qualitative description of B,Fe-conjuncto-$\{Fe_2(CO)_6B_2H_4\}_2$ (**I**) consisted of two electron precise tetrahedral Fe_2B_2 clusters containing the normal 6 cluster bonding pairs joined across Fe–B edges by two three center-two electron bonds. For **II**, the same bonding description was applied except that the clusters are joined across B–B edges.

In the present study the purpose of the first analysis of the MO structures of **I** and **II** is to examine the validity of our previously proposed model. To do so, Fenske–Hall MO calculations [23,24] on **I** and **II** are transformed using as basis functions the MO's of two $Fe_2(CO)_6B_2H_4$ fragments with geometries corresponding to those found in **I** and **II**, respectively. The precision of the separation of fragment orbitals involved in intra-and inter-fragment bonding is used as a measure of the validity of the proposed bonding model. For a poor description the separation will not be a clean one and the MO's involved in inter-cluster bonding will be a complex mixture of many of the $Fe_2(CO)_6B_2H_4$ fragment orbitals.

To calibrate, as it were, the fragment analysis the examination of the MO's of B_2H_6 in terms of 2 BH_3 fragments is instructive. Diborane may be considered as two BH_3 fragments joined by two localized three center-two electron bonds. In a MO description one expects (Fig. 3(a)) to observe orbitals exhibiting the symmetric (a_g) and antisymmetric (b_{2u}) combination of these two equivalent bonds. However, the actual MO's can be more complex if they significantly mix with other orbitals of the same symmetry. In fact, three, not two, of the six filled MO's of B_2H_6 contain bridging hydrogen character. As may be appreciated from the fragment analysis in Fig. 3(b), these three orbitals



I

II

Fig. 2. Solid state structures of B,Fe-conjuncto-$\{Fe_2(CO)_6B_2H_4\}_2$ (I) and B,B-conjuncto-$\{Fe_2(CO)_6B_2H_4\}_2$ (II).

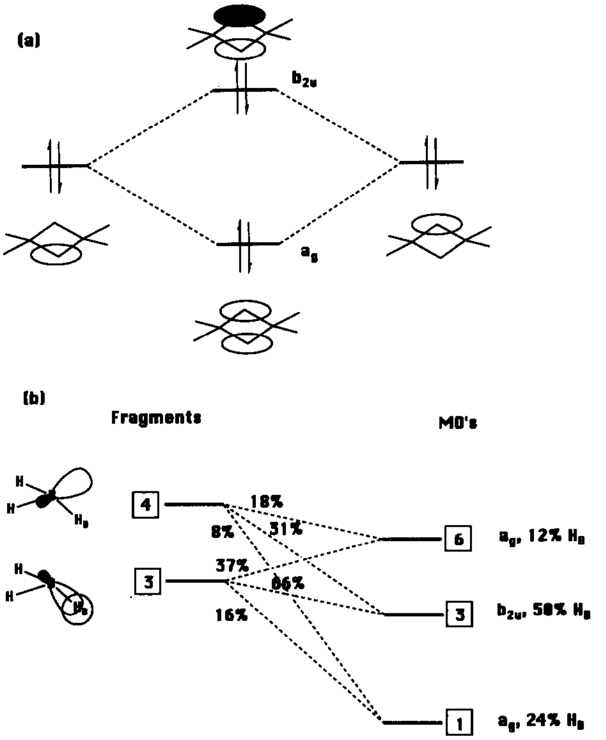


Fig. 3. (a) Filled orbital interaction diagram showing the generation of the MO's corresponding to the two equivalent localized three center-two electron bonds connecting the BH_3 fragments in B_2H_6. (b) Selected results from the fragment analysis of B_2H_6 in terms of two BH_3 fragments. The contributions from the HOMO and LUMO of BH_3 to the three filled MO's of B_2H_6 containing bridging hydrogen character are shown.

contain significant contributions from both the HOMO and LUMO of the BH_3 fragments. Because of its b_{2u} symmetry, MO 3 is "clean" and 97% of its character derives from the HOMO and LUMO of the BH_3 fragments. On the other hand, MO's 1 and 6 of a_g symmetry contain a significant amount of terminal as well as bridging hydrogen character. In any lower symmetry situation, *e.g.*, **I** and **II**, more mixing must be anticipated but the analog of the b_{2u} symmetry MO in diborane is a convenient measure of the validity of our original cluster bonding analysis.

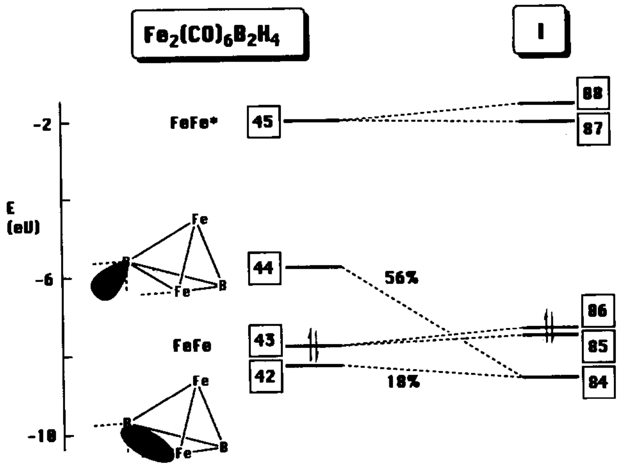


Fig. 4. Sketches of selected frontier orbitals of the $Fe_2(CO)_6B_2H_4$ fragments and fragment analysis of the frontier orbitals of B,Fe-conjuncto-$\{Fe_2(CO)_6B_2H_4\}_2$ (**I**) according to the Fenske–Hall technique.

The results are summarized in Fig. 4 for **I** and Fig. 5 for **II**. The MO structure of $Fe_2(CO)_6B_2H_6$ and related anions has been discussed previously [25,26] and the MO's of the $Fe_2(CO)_6B_2H_4$ fragment are closely related. As expected, the LUMO for a $Fe_2(CO)_6B_2H_4$ fragment is predominantly an empty orbital centered on a boron atom and pointing towards the space usually occupied by a terminal hydrogen atom. However, note that this orbital contains significant metal character (25% for the fragment derived from **I** and 28% for that derived from **II**). The HOMO of the Fe_2B_2 fragment is a Fe–Fe bonding orbital and the SHOMO has, in the case of **I**, Fe–B bonding character and, in the case of **II**, B–B bonding character. Like the LUMO, the SHOMO contains significant contributions from the other atoms in the fragment which are far from negligible (31% for **I** and 65% for **II**). Hence, this orbital is not simply a highly localized Fe–B or B–B edge bonding orbital, respectively, and is better described as a cluster bonding orbital. Note, however, that the twisting of the $Fe(CO)_3$ fragments along the Fe–Fe vector with respect to each other in **I** and, to some extent, in **II** results in more localization of this orbital in the pertinent Fe–B or B–B edge than is

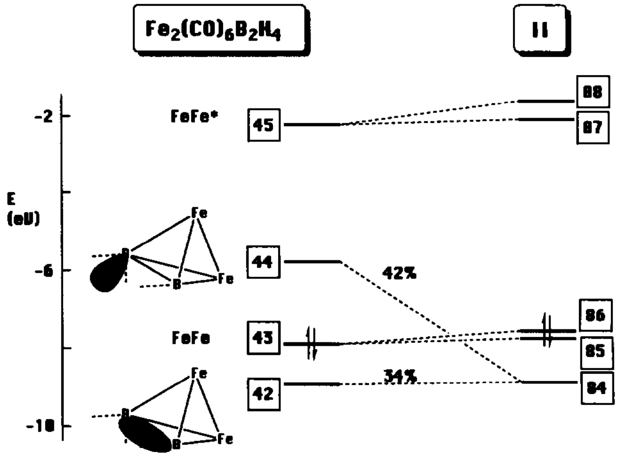


Fig. 5. Sketches of selected frontier orbitals of the $Fe_2(CO)_6B_2H_4$ fragments and fragment analysis of the frontier orbitals of B,B-conjuncto-$\{Fe_2(CO)_6B_2H_4\}_2$ (**II**) according to the Fenske–Hall technique.

present in a $[Fe_2(CO)_6B_2H_5]^-$ ion with C_2 symmetry. Qualitatively, one can easily envision the formation of two inter-fragment three center bonds from the combination of the LUMO of one $Fe_2(CO)_6B_2H_4$ and SHOMO of the other $Fe_2(CO)_6B_2H_4$ fragment and the reverse. This is essentially the qualitative model we have used previously [21,22].

The actual fragment analysis shows that the two higher occupied MO's of the two conjuncto-$\{Fe_2(CO)_6B_2H_4\}_2$ isomers are derived nearly completely from the HOMO's of the fragments and correspond to the unbridged Fe–Fe interactions in each Fe_2B_2 fragment. In both **I** and **II** the next lowest lying MO (84) is made up of nearly equal mixtures of the LUMO's and SHOMO's of the Fe_2B_2 fragments and is the analog of the b_{2u} MO of diborane illustrated in Fig. 3(b). Although other Fe_2B_2 fragment orbitals contribute 26% (in the case of **I**) and 24% (in the case of **II**) this must be considered a reasonably clean separation for the complex molecule. However, MO 84 is the only MO that contains significant contributions from both the LUMO's and SHOMO's of the fragments, *i.e.*, the next highest is MO 77 with 2% LUMO and 6% SHOMO contributions for **I** and MO 75 with 2% LUMO and 2% SHOMO contributions for **II**. Clearly the inter M_2B_2 fragment interaction is strongly mixed with the intra M_2B_2 cage bonding.

The fragment analysis shows that the view of conjuncto-$\{Fe_2(CO)_6B_2H_4\}_2$ clusters as electron precise Fe_2B_2 tetrahedral clusters joined by two three center bonds is not only a convenient and useful description but one that finds considerable justification by a fragment analysis. On the other hand, the multicentered interactions in this Fe_4B_4 system, which are demanded by the fact that the number of available valence electrons is less than the number of valence functions, are significantly spread over the whole Fe_4B_4 cluster and not just localized in the inter-Fe_2B_2 cluster interaction. The implication is that **I** and **II** should be viewed as coupled M_2B_2 clusters and species well on their way towards single M_4B_4 clusters.

3. Borane vs. metal fragments

One wonders whether another fragment analysis might be more appropriate. The AO basis results for **I** shows MO 84 to contain nearly equal contributions from the boron atoms making up the B_4 chain. In addition, the overall Mulliken charge on the B_4H_8 fragment is −1.39. Viewing the B_4 chain in **I** as $[B_4H_8]^{2-}$ leads one to recall the early postulated structure of B_4H_{10} as an analog of butadiene (Fig. 6). The diamond motif of the B_4 fragment in **II** is thus seen as related to the known structure of B_4H_{10} which is

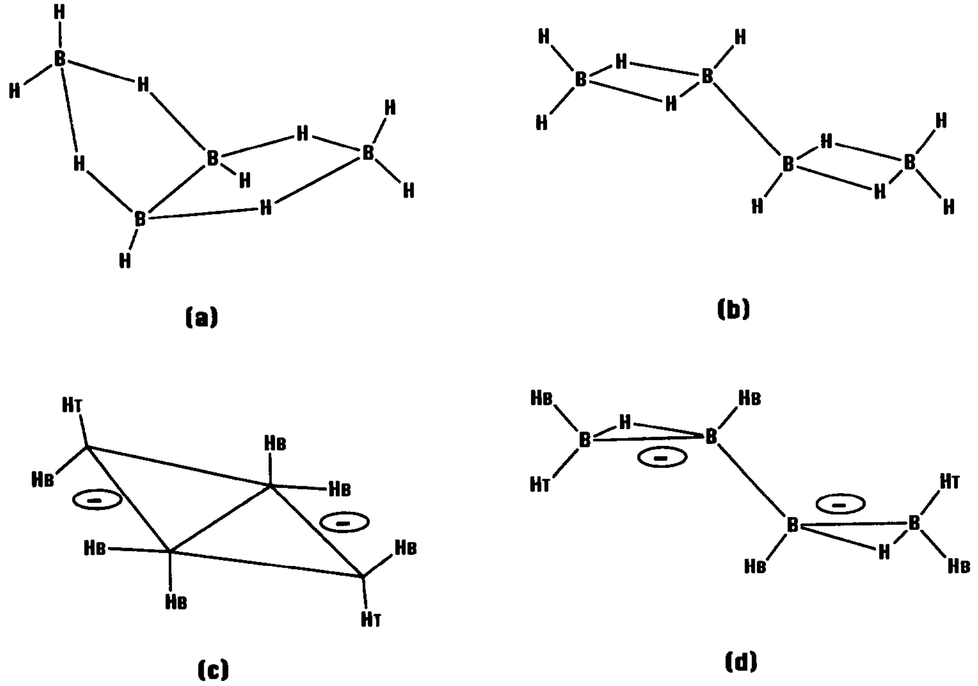


Fig. 6. B_4 boranes: (a) known "bicyclobutane" structure of B_4H_{10}, (b) "1,3-butadiene" structure of B_4H_{10}, (c) the planar$[B_4H_8]^{2-}$ fragment in **II** and (d) $[B_4H_8]^{2-}$ fragment in **I**. H_T and H_B refer to terminal and bridging hydrogens, respectively, in the metalated compound.

viewed as an analog of bicyclobutane. It is interesting to note that high level calculations are required in order to place the energy minimum of the observed "bicyclobutane" structure of B_4H_{10} below that of the unobserved "butadiene" structure [27]. These considerations suggest a fragment analysis of the MO's of **I** and **II** in terms of the B_4 fragments plus two Fe_2 fragments might be instructive. To keep an even number of electrons on each of the three fragments the analysis was done in terms of B_4H_8 and two $Fe_2(CO)_6$ fragments.

The results of this fragment analysis are summarized in Table 1 for **I** and **II**. The orbital structure of the $Fe_2(CO)_6$ fragment has been detailed earlier [28] and those of the chain and ring forms of B_4H_8 fragments are reminiscent of butadiene and bicyclobutane, respectively [29]. Table 1 shows that the 12 borane fragment orbitals of lowest energy are substantial contributors to the MO's of **I** and **II**. For the neutral borane fragments there are 10 filled orbitals and, thus, the LUMO and the filled orbitals of $[B_4H_8]^{2-}$ contribute significantly to the MO structure of **I** and **II**. However, principally because of the large number of B–H–Fe interactions, this fragment analysis is not substantially better than the one involving two $Fe_2(CO)_6B_2H_4$ fragments which was presented above. Despite this, the fragment analysis draws some interesting parallels between free and "coordinated" B_4 fragments. Thus, the fact that the stability of **II** is only slightly larger than that of **I** (22) may well be related to the similar stabilities of B_4H_{10} calculated for the bicyclobutane and 1,3-butadiene isomeric forms.

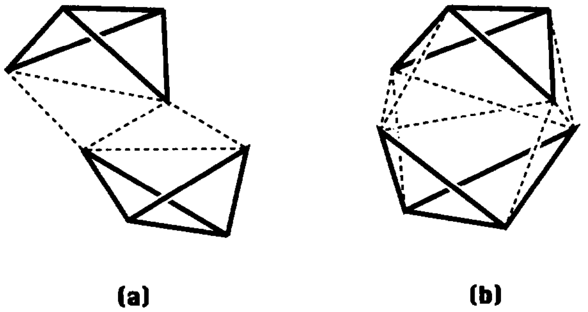


Fig. 7. The "synthesis" of (a) conjuncto-$\{Fe_2(CO)_6B_2H_4\}_2$ and (b) $\{(\eta^5\text{-}C_5H_5)Co\}_4B_4H_4$ from tetrahedral M_2B_2 fragments. The vertices can be variously metal or boron atoms depending on the molecule described.

4. Discussion

What, then, is the relationship of **I** and **II** to $\{(\eta^5\text{-}C_5H_5)M\}_4B_4H_4$, M = Co, Ni? The nickel compound might be viewed as two M_4B_4 tetrahedra fused across two B–B edges in a perpendicular fashion rather than a parallel one as in **II** (Fig. 7). In doing so the original B–B interaction is lost and is replaced by new Ni–B and B–B interactions thereby generating a puckered

TABLE 1. Fragment analysis of **I** and **II** in terms of $[B_4H_8]$ fragments (Fig. 6) showing the largest fragment orbital contributions to the MOs

Isomer I				Isomer II			
MO #	E_{MO} (eV)	Fragment orbital #	% in MO	MO #	E_{MO} (eV)	Fragment orbital #	% in MO
84	−8.56	12	16	84	−8.75	12	23
71	−12.51	10	47	71	−12.09	11	38
70	−12.62	11	45	70	−14.23	10	46
69	−15.05	9	42	69	−14.99	9	18
						8	22
						7	17
68	−15.61	8	13				
67	−15.76	8	15	67	−15.60	8	20
						7	11
				65	−15.99	6	19
63	−16.29	7	22				
62	−16.38	6	35	62	−16.6	5	26
57	−17.65	5	38				
52	−19.61	4	41				
				49	−19.90	3	43
				47	−20.09	4	38
38	−20.90	3	27				
				36	−21.18	2	19
				35	−21.35	2	20
22	−23.72	2	32				
20	−23.85	2	36				
15	−24.90	1	96	15	−24.27	1	87

ring of boron atoms and an overall dodecahedral cluster geometry. In the same fashion $\{(\eta^5\text{-}C_5H_5)Co\}_4B_4H_4$ can be viewed as two Co_4B_4 tetrahedra fused across the Co-Co edges and yielding, after arrangement, a puckered ring of Co atoms and a dodecahedral cluster geometry. One can adopt the explanation advanced by O'Neill and Wade to rationalize the difference in the electron counts of the Ni and Co systems, *i.e.*, for a dodecahedral cluster there is a set of two low-lying non-degenerate orbitals that can be empty (8 skeletal pairs) or filled (9 or 10 skeletal pairs) [11]. Comparing this notional "synthesis" with that of **I** or **II** we see that the essential difference between these cluster bonding systems is that, in going from the structure of **I** or **II** to the dodecahedral cluster, five inter-M_2B_2 fragment interactions are converted into eight. Thus, the conversion of **I** or **II** into a dodecahedral cluster would cause an increase in the extent of delocalized bonding.

Unfortunately **I** and **II** show no tendency for rearrangement into a dodecahedral cluster. However, cluster **II** has 6 bridging hydrogens whereas $\{(\eta^5\text{-}C_5H_5)Ni\}_4B_4H_4$ has none and bridging hydrogens are known to have a structural role in cluster chemistry. Although these "extra" hydrogens are ignored in the electron counting rules except in so far as they contribute electrons to the skeletal bonding count, it has been suggested that such bridging hydrogens enhance the stability of more localized bonding networks, *e.g.*, **I** and **II** relative to delocalized networks, *e.g.*, $\{(\eta^5\text{-}C_5H_5)M\}_4B_4H_4$ [30]. Certainly it is known that bridging hydrogens are generally found in association with cluster atoms of low coordination number in nido and arachno structures [11].

This, then, suggests that if the number of bridging hydrogens can be reduced, preferably to zero, structures similar to **I** or **II** might readily rearrange to a dodecahedral form. Based on our work with $[Fe_2(CO)_6B_2H_4]^{2-}$, the oxidative fusion of $[CoFe(CO)_6B_2H_3]^{2-}$, a presently unknown anion that might be obtained from the recently synthesized $CoFe(CO)_6B_2H_5$ mixed metal metallaborane [31], would result in the formation of $\{(CO)_3Fe\}_2\{(CO)_3Co\}_2B_4H_6$. This compound has 10 formal skeletal pairs but only two "extra" hydrogens. Naturally the structure of this compound would be intrinsically interesting but in this case H_2 loss might be facile enough such that $\{(CO)_3Fe\}_2\{(CO)_3Co\}_2B_4H_4$ would form at a temperature below the cluster degradation temperature. This cluster has 9 formal skeletal pairs which is the proper count for a dodecahedral M_4B_4 *closo*-cluster. The successful preparation and characterization of this compound would imply that $\{(\eta^5\text{-}C_5H_5)Ni\}_4B_4H_4$ should be easily oxidized and $\{(\eta^5\text{-}C_5H_5)Co\}_4B_4H_4$ should be easily reduced thereby reopening the question of the skeletal electron count of the most stable form of the M_4B_4 single cage.

5. Calculations

The molecular orbital calculations were completed on a MacII computer using a Macintosh version of the Fenske–Hall approximate MO method [32]. Interatomic distances and angles were idealized from X-ray crystallographic data. A minimal basis set was employed in these calculations using the functions included in the program. These are functions generated by the numerical $X\alpha$ atomic orbital program of Herman and Skillman [33] used in conjunction with the $X\alpha$-to-Slater basis program of Bursten and Fenske [34,35].

Acknowledgments

The support of National Science Foundation is gratefully acknowledged.

References

1 W.N. Lipscomb, *Boron Hydrides*, Benjamin, New York, 1963.
2 A.J. Stone, *Molec. Phys., 41* (1980) 1339.
3 D.M.P. Mingos and D.J. Wales, *Introduction to Cluster Chemistry*, Prentice Hall, New York, 1990.
4 K. Wade, *Adv. Inorg. Chem. Radiochem, 18* (1976) 1.
5 D.M.P. Mingos, *Acc. Chem. Res., 17* (1984) 311.
6 J.A. Connor, in B.C. Gates, L. Guczi and H. Knözinger (eds.), *Metal Clusters in Catalysis*, Elsevier, Amsterdam, 1986.
7 J.R. Pipal and R.N. Grimes, *Inorg. Chem., 18* (1979) 257.
8 J.R. Bowser and R.N. Grimes, *J. Am. Chem. Soc., 100* (1978) 4623.
9 J.R. Bowser, A. Bonny, J.R. Pipal and R.N. Grimes, *J. Am. Chem. Soc., 101* (1979) 6229.
10 D.N. Cox, D.M.P. Mingos and R. Hoffmann, *J. Chem. Soc., Dalton Trans.,* (1981) 1788.
11 M.E. O'Neill and K. Wade, *Inorg. Chem., 21* (1982) 461.
12 R.B. King, *Polyhedron, 1* (1982) 132.
13 C.E. Housecroft and T.P. Fehlner, *Adv. Organomet. Chem., 21* (1982) 57.
14 J.D. Kennedy, *Prog. Inorg. Chem., 32* (1984) 519.
15 J.D. Kennedy, *Prog. Inorg. Chem., 34* (1986) 211.
16 R.N. Grimes, in R.N. Grimes, (ed.), *Metal Interactions with Boron Clusters,* Plenum, New York, 1982, p. 269.
17 T.P. Fehlner, *Inorganometallic Chemistry*, Plenum, New York, 1992.
18 T. Onak, *Organoborane Chemistry*, Academic Press, New York, 1975.
19 C.P. Horwitz and D.F. Shriver, *Organometallics, 3* (1984) 756.
20 T.K. Dutta, J.V. Vites, G.B. Jacobsen and T.P. Fehlner, *Organometallics, 6* (1987) 842.
21 C.-S. Jun, X. Meng, K.J. Haller and T.P. Fehlner, *J. Am. Chem. Soc., 113* (1991) 3603.
22 C.-S. Jun, D.R. Powell, K.J. Haller and T.P. Fehlner, *Inorg. Chem., 32* (1993) 5071.
23 R.F. Fenske, *Pure Appl. Chem., 27* (1988) 61.
24 M.B. Hall and R.F. Fenske, *Inorg. Chem., 11* (1972) 768.

25 G.B. Jacobsen, et al., *Inorg. Chem., 26* (1987) 4040.
26 E.L. Andersen, R.L. DeKock and T.P. Fehlner, *Inorg. Chem., 20* (1981) 3291.
27 B.J. Morris-Sherwood and M.B. Hall, *Chem. Phys. Lett., 84* (1981) 194.
28 D.L. Thorn, R. Hoffmann, *Inorg. Chem., 17* (1978) 126.
29 W.L. Jorgensen and L. Salem, *The Organic Chemist's Book of Orbitals*, Academic Press, New York, 1973.
30 M.A. Cavanaugh, T.P. Fehlner, R. Stramel, M.E. O'Neill and K. Wade, *Polyhedron, 4* (1985) 687.
31 C.-S. Jun, Ph.D. thesis, University of Notre Dame, Indiana, USA 1993.
32 Available from M.B. Hall, Texas A&M University.
33 F. Herman and S. Skillman, *Atomic Structure Calculations,* Prentice-Hall, Englewood Cliffs, NJ. 1963.
34 B.E. Bursten and R.F. Fenske, *J. Chem. Phys., 67* (1977) 3138.
35 B.E. Bursten, R.J. Jensen and R.F. Fenske, *J. Chem. Phys., 68* (1978) 3320.