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# Three-Center Bonds in Electron-Deficient Compounds. The Localized Molecular Orbital Approach

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Having more valence atomic orbitals than valence electrons, electron-deficient compounds present ambiguities in the use of the paired electron bond. Molecular orbitals, at least of stable neutral compounds, are filled usually with a substantial energy gap to the lowest unoccupied excited orbital. However, molecular orbitals based upon the molecular symmetry group are delocalized. Moreover, they are not readily transferable to chemically closely related molecules.

Here, we seek a middle ground: nearly transferable multicenter bonds. We derive localized molecular orbitals (LMO's) objectively from accurate self-consistent field (SCF) molecular orbital (MO) theory. We explore the limits of transferability of these LMO's in the boranes, carboranes, and their related ionic species. Finally, we only begin to ask how these LMO's restrict the compositions, geometries, and reaction pathways in this area of chemistry.

## Localized Molecular Orbitals

Recent studies have considerably narrowed the gaps between resonance descriptions of these molecules[1,2] and molecular orbital results.[3,4] Extended Hückel theory, developed in this laboratory,[4,5] has been related[6,7,8] to rigorously defined SCF theory[9,10] of complex molecules. Leaving aside the severe limitations of SCF theory when electron correlation[11] is important, we note that it yields good approximations to electron density and to properties derived from one-electron operators,[12-14] like the dipole moment and nmr shielding constants.

Here, we start with symmetry MO's. Their conversion to localized chemical bonds is achieved by mixing MO's of different symmetries. For example, consider the double bond of ethylene, composed of a single $\sigma$ bond and a single $\pi$ bond. If we take the sum and difference of these two orbitals, we find two equivalent "banana" bonds, one above and the other below the molecular plane (Figure 1). This transformation leaves the total molecular electron density and the total energy invariant.[15-19] In one sense, it is a better description of electron-pair bonding, because (a) it maximizes the sum $D$ of repulsions of electrons within the same MO, $\phi_k$

$$D = \sum_k (kk|kk) = \sum_k \int \phi(i)\phi_k(j)\frac{1}{r_{ij}}\phi_k(i)\phi_k(j)\mathrm{d}V_i\mathrm{d}V_j$$

and (b) it minimizes both the exchange energy and the interorbital electron repulsion energy. We use this criterion below for obtaining localized bonds objectively from accurate and well-defined molecular orbital wave functions. Although we shall find that the three-center bond is alive and well, and residing in the laboratories of most boron chemists, we shall also find some important new developments.

How localized are these bonds, and how many centers occur in multicenter orbitals? Suppose that the LMO, $\phi^L$, resulting from the localization procedure given above, has obvious large components over three centers, for example, two borons and a hydro-

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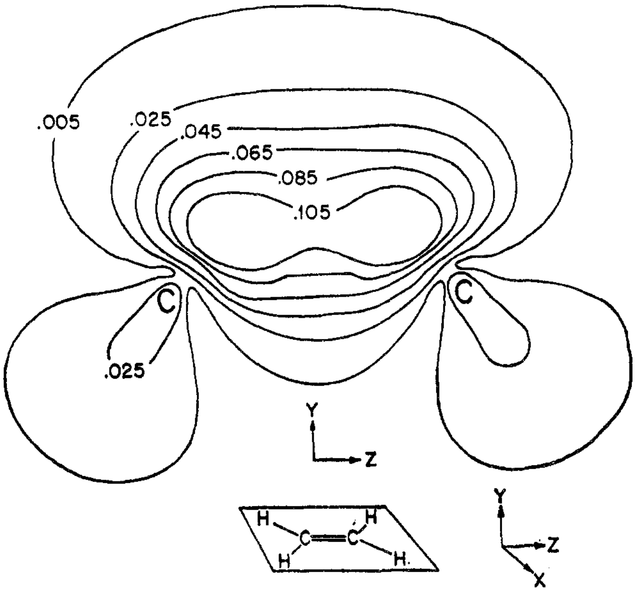

**Figure 1.** Localized C-C bond in ethylene. Contours are shown for the total density of one electron in electrons/au$^3$, where 1 au = 0.529 Å.

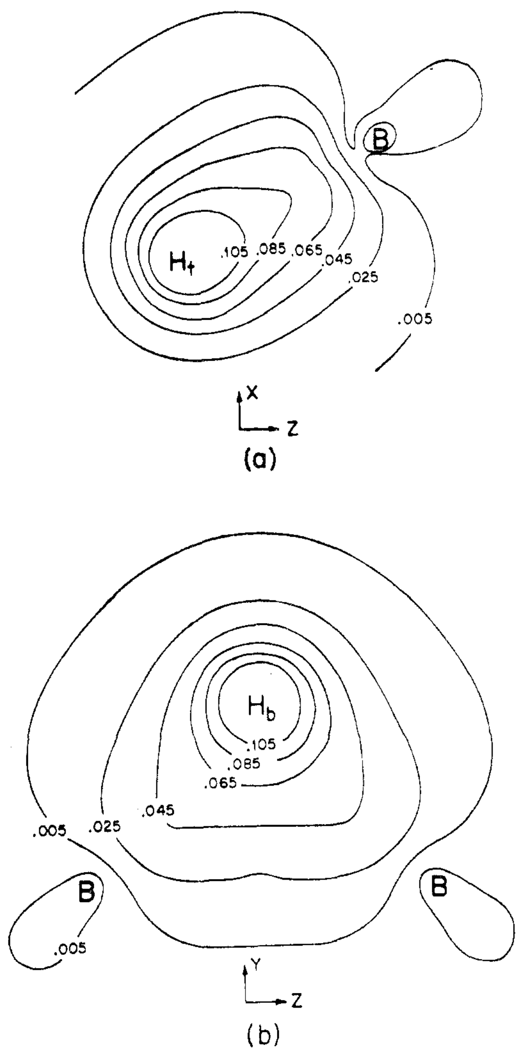

**Figure 2.** Density for one electron in electron/au$^3$ for (a) the B-H (terminal) bond and (b) the B-H-B bond in $B_2H_6$.

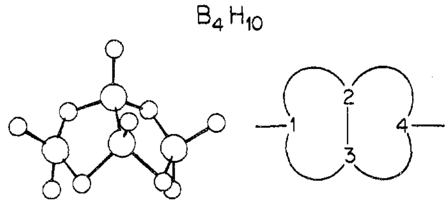

**Figure 3.** Geometrical and localized valence structure of $B_4H_{10}$. One terminal hydrogen is omitted from each boron (or, later, carbon) atom. The extra terminal H is indicated by a straight line, and the bridge hydrogen by a curved line.

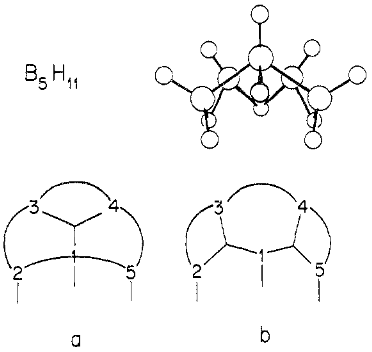

**Figure 4.** $B_5H_{11}$. Structure a, with an open three-center B(2)-B(1)-B(5) bond, is not favored by the localization, which yields central three-center bonds idealized in structure b.

gen of a bridge bond in diborane (Figure 2). It will also have small parts associated with all other atoms in the molecule. We obtain a truncated LMO, $\phi^T$, by omitting these small parts, and then renormalizing. Then the quantity[20,21]

$$d = 100[\tfrac{1}{2}\int(\phi^L - \phi^T)^2 dV]^{1/2}$$

defines a percentage delocalization, zero if the LMO is completely localized on the centers assumed and 100% if $\phi^L$ and $\phi^T$ are completely orthogonal. We suggest, at present, that a center be omitted from $\phi^T$ if it contributes less than about 0.2 electron to $\phi^L$.

## Boranes and Carboranes

The three-center bond has been widely used in boron compounds.[1,2,22,23] For example, in $B_6H_{10}$ there are 28 electrons and 34 valence orbitals. These 14 valence pairs may be accommodated in eight two-center bonds and six three-center bonds, thus accounting for all valence orbitals. The $B_6H_{10}$ structure has six terminal BH bonds and four hydrogen bridges. We then require two single BB bonds and two three-center BBB bonds. Similar rules apply to other boranes, carboranes, and their ions.

Some bonding arrangements are less favorable than others. For example, we exclude bonding of two adjacent B atoms by both a single bond and any type of three-center bond such as a bridge hydrogen, central BBB bond, or open BBB bond (see below). Even so, resonance hybrids are required for all but the simplest boranes ($B_2H_6$, $B_4H_{10}$) and carboranes. We show below that three-center bond theory is placed on a firm theoretical foundation[24] and that a

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(20) E. Switkes, W. N. Lipscomb, and M. D. Newton, *J. Amer. Chem. Soc.*, **92**, 3847 (1970).

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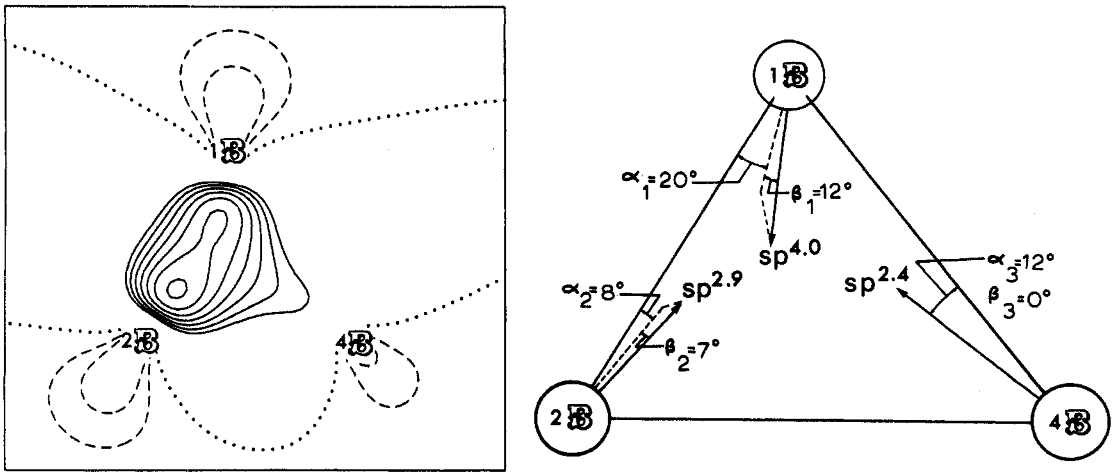

**Figure 5.** (a) One of the two localized three-center orbitals in the boron framework of $B_5H_{11}$. The electron density is obtained by squaring this function. (b) Hybrids resulting from the localization procedure.

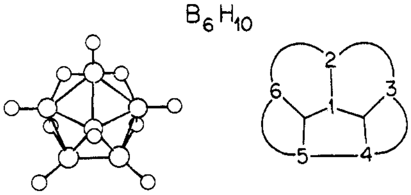

**Figure 6.** $B_6H_{10}$, which localizes uniquely.

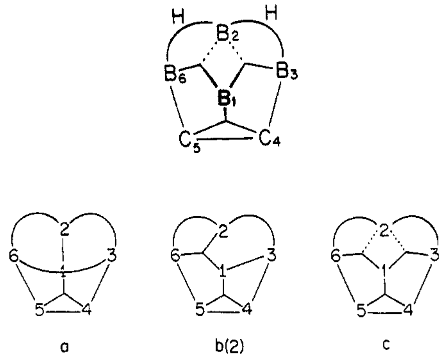

**Figure 7.** $C_2B_4H_8$, which localizes differently from $B_6H_{10}$ and yields two fractional three-center bonds having partial orbital contributions to $B_2$. Alternate, nearly equivalent, descriptions a and b (a hybrid of two) are not favored by the localization.

new level of detail is obtained including distinctions between bonding rules between boranes and carboranes.

Bridge and terminal hydrogens, with a few interesting exceptions, are very similar in our LMO results. Their delocalization percentages (d) are about 14 and 10, respectively. For comparison, we observe that inner shells have percentages of 5.0, 4.5, 1.3, and 0.8 for B, C, N, and O, respectively. Central three-center BBB bonds range from 15 to 24%, and the bent bonds of ethylene (Figure 1), butadiene, and benzene have *d* values of 6, 8 and 19%, respectively.[25] We comment below on unusual *d* values.

Proceeding now to $B_4H_{10}$[20] (Figure 3), $B_5H_{11}$[20] (Figures 4 and 5), and $B_6H_{10}$[26] (Figure 6), we see that in each case a single preferred valence structure occurs upon localization of each SCF wave function. In $B_5H_{11}$, the LMO's indicate a preference for central three-center BBB bonds (Figure 4b) over the structure involving an open three-center BBB bond (Figure 4a). The three-center bond itself is unsymmetrical (Figure 5a), having hybrids shown in Figure 5b. The unusual nonexternal H atom in the symmetry plane of $B_5H_{11}$ is 20% delocalized toward $B_2$ and $B_5$. Nevertheless, its bonding localizes as a terminal bond, even though it has some bridge properties.

The $B_6H_{10}$ structure has isoelectronic analogs $CB_5H_9$, $C_2B_4H_8$, $C_3B_3H_7$, and $C_2B_4H_8$. A LMO study[27] of $C_2B_4H_8$ shows two differences in bonding when compared to $B_6H_{10}$. First, the LMO's join the two carbons with both a single bond and a central three-center bond (Figure 7), a feature not, so far, found in boranes. Second, the LMO's give new bonds, best described as fractional three-center bonds (Figure 7c), avoiding the more conventional possibilities (Figure 7a or 7b). We designate dotted legs in the central three-center bond toward the atom ($B_2$) which appears to have five bonds, including the terminal H atom. However, the exclusion principle is not violated, because only fractions of an atomic orbital are used in these bonds. Atomic populations are 0.74 on $B_1$, 0.50 on $B_2$, and 0.65 on $B_3$ (or $B_6$) from each of the fractional bonds. The bonding relationships shown in Figures 7a, 7b and 7c among these four atoms will emerge as a general principle for fractional three-center bonds below. The high value of 24% for *d* for the B(1)-B(2) bond in $B_6H_{10}$ may be a symptom of this change in bonding as one goes to the carborane $C_2B_4H_8$.

Localization in $B_5H_9$ is ambiguous, yielding two different results depending upon the starting orbitals.[19] It is therefore recommended that localization should be carried out only after the starting set has been subjected to unitary transformations based upon random numbers. In set A, Table I, the B(1)-B(2)-B(3) bond is central three-center, while the B(1)-B(5) and B(1)-B(4) bonds are nearly single bonds. Set B has a single B(1)-B(4) bond, and fractional three-center bonds B(1)-B(2)-B(3) and B(1)-B(5)-B(2) as shown in Figure 8. All of these bonds have a *d* percentage of about 22. We refer below to this occurrence of fractional three-center bonds when

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(25) M. D. Newton and E. Switkes, *J. Chem. Phys.*, **54**, 3179 (1971).

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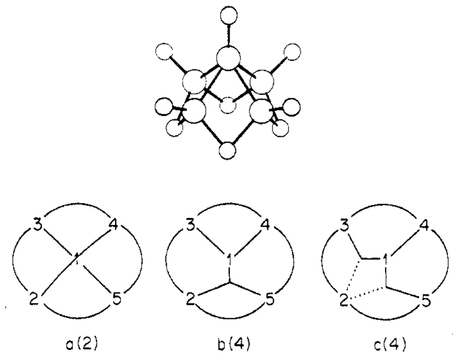
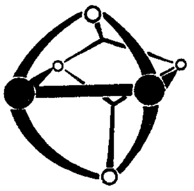


**Figure 8.** $B_5H_9$. Localized structures b and c are obtained upon localizing from different randomized sets of orthogonal molecular orbitals, but structure a is not favored. The full molecular symmetry ($C_{4v}$) is obtained from the number of equivalent resonance hybrids indicated in parentheses.



1,2-$C_2B_4H_6$

**Figure 9.** Localized orbitals in 1,2-$C_2B_4H_6$. Open three-center bonds pass through the carbon atoms, which are also joined by a single bond. The topology is 0430, indicating no bridge hydrogens, four three-center bonds, three single bonds, and no $BH_2$ groups.

**Table I**
**Localized Framework Orbitals in $B_5H_9$**

| | Atoms | Populations | | |
|---|---|---|---|---|
| Set A | B(1)-B(2)-B(3) | 0.71 | 0.63 | 0.65 |
| | B(1)-B(5)-B(2) | 0.71 | 0.85 | 0.33 |
| | B(1)-B(3)-B(4) | 0.71 | 0.31 | 0.86 |
| Set B | B(1)-B(2)-B(3) | 0.71 | 0.55 | 0.72 |
| | B(1)-B(5)-B(2) | 0.71 | 0.81 | 0.42 |
| | B(1)-B(3)-B(4) | 0.72 | 0.23 | 0.88 |

high symmetry is present, and when the number of bonding pairs does not match the order of a principal axis of the molecule.

The 1,2-$C_2B_4H_6$ structure localizes beautifully to the unique valence structure[28] shown in Figure 9. The open three-center bond has, so far, been found by these localization procedures only when C is the middle atom. The orbital on C is almost pure $\pi$, so that the bonding open three-center orbital changes sign at the C atom.

The ideas of these last three paragraphs are partially summarized in the principle shown in Figure 10. Of the many bonding situations where one might expect fractional three-center bonds, we consider only a few, including now $B_{10}H_{14}$ and $B_{10}H_{14}^{2-}$.

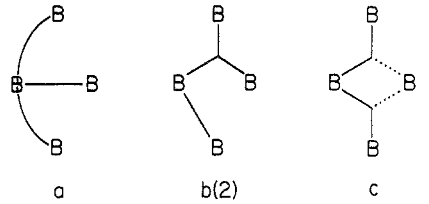


**Figure 10.** One important principle of near-equivalence of bond types. Structure a is favored only if the atom at the middle of the three-center bond is carbon, and usually structure c is favored over a or the hybrid (b) when all atoms are boron, as suggested above for 4,5-$C_2B_4H_8$ and $B_5H_9$.

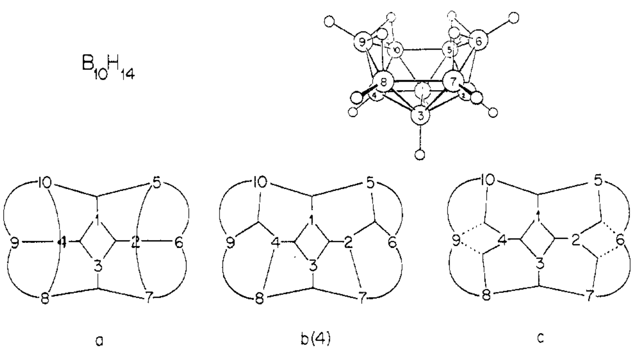


**Figure 11.** $B_{10}H_{14}$. (c) The favored localized valence structure extrapolated from structure a or the hybrid (b) using the general principle shown in Figure 10. This localized structure is an excellent approximation to a localized orbital analysis of a wave function for $B_{10}H_{14}$ obtained by the INDO method.

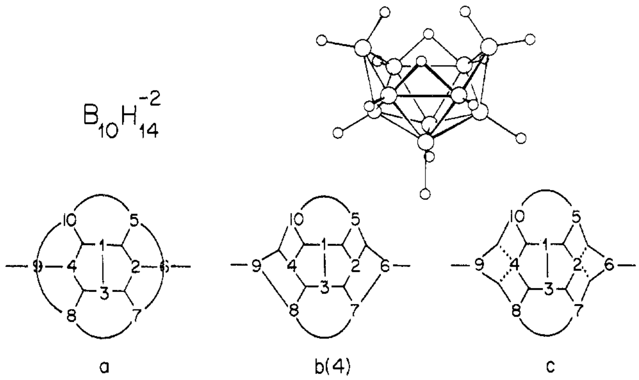


**Figure 12.** $B_{10}H_{14}^{2-}$. Valence structure a or the hybrid (b) extrapolate using the principle of Figure 10 to the favored valence structure (c).

The predicted[29] LMO structure (Figure 11c) for $B_{10}H_{14}$ avoids the problems associated earlier with the 24 resonance structures[30] or with the open three-center BBB bonds[23] (Figure 11a). This unique LMO structure has recently been found by localization of an INDO wave function.[31] The reactive orbitals of the new SCF wave function[29] for $B_{10}H_{14}$ are consistent with preferred electrophilic attack at B(2) (B(4)), then at B(1) (B(3)), then at B(5) (B(7)), B(8), B(10)), and finally at B(6) (B)9)). This order, and the reverse order for nucleophilic attack, would apply only if the transition state is dominated by the ground-state wave function. Most substitution reactions agree with these theoretical results.

Using the same principle (Figure 10) we predict[32] fractional three-center bonds for $B_{10}H_{14}^{2-}$ (Figure 12c). Again, we can avoid a hybrid of 24 valence structures.[2] If $B_{10}H_{14}^{2-}$ had the hydrogen arrangement of $B_{10}H_{14}$, or conversely, there would be only

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[28] I. R. Epstein, D. S. Marynick, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **95**, 1760 (1973).

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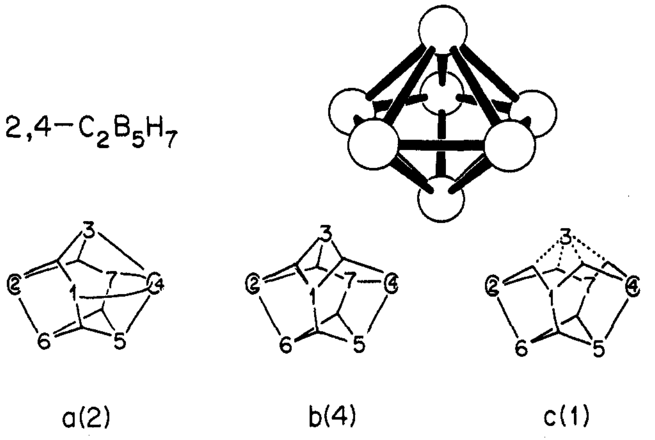

**Figure 13.** 2,4-$C_2B_5H_7$. This compact structure localizes surprisingly well to the fractional three-center bond description c, which has approximate equivalents in the less favored hybrids a and b.

one three-center bond structure. Thus, the preferred, but different, H arrangements in $B_{10}H_{14}$ and $B_{10}H_{14}^{2-}$ are perhaps related to a resonance stabilization when described by central three-center bond theory. An alternative statement is that a geometrical structure having a fractional three-center bond description is probably preferred over an isomeric structure having a very small number of central three-center valence structures. The substitution chemistry of $B_{10}H_{14}^{2-}$ is almost unknown, because its reactions are dominated by electron loss, consistent with the effect of electron repulsions in raising all SCF eigenvalues by about 0.4 au over those in $B_{10}H_{14}$.[33]

A carborane of low symmetry, 2,4-$C_2B_5H_7$ ($C_{2v}$), has a simple and symmetrical LMO result. The four fractional bonds dotted toward B(3) (Figure 13c) are most simply related to equivalent descriptions (Figures 13a and 13b) which are only a small fraction of possible resonance structures. The SCF wave function[34] suggests nucleophilic reactivity first at B(3), then at B(1), and finally at B(5). The reverse order applies to electrophilic substitution. We note that B(5) is attached to only one C, while B(3) and B(1) are attached to two C atoms. Of B(3) and B(1) the former has fewer neighbors.[35]

More symmetrical structures give rather complex LMO descriptions. In 1,6-$C_2B_4H_6$ ($D_{4h}$)[28] the number of framework pairs (seven) does not match the rotational order (eight). Hence, localization to a single valence structure is not possible. In hypothetical $B_4H_4$ ($T_d$) the electron density has tetrahedral symmetry, of course, but the framework LMO's surprisingly tend to localize as rather unsymmetrical central three-center bonds.[36] However, the nonexistence of this compound is probably associated with a vacant molecular orbital than with this pathological localization.

More efficient localization procedures may allow the study of more complex boranes and carboranes. Until then, an acceptable procedure is to use the principles of the studies here, in conjunction with a complete search for appropriate standard three-center bond structures, in order to discover the most appropriate bond representation in a molecule or a reaction intermediate. An example of a prediction is shown in Figure 14 for $m$-$C_2B_{10}H_{12}$ and $o$-$C_2B_{10}H_{12}$.

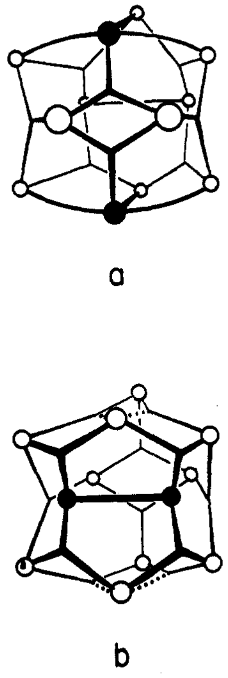

**Figure 14.** Three-center localization guesses for 1,7-$C_2B_{10}H_{12}$ in structure a and 1,2-$C_2B_{10}H_{12}$ in b. Structure b is the reversed diagram of a modified at the top and bottom to use fractional three-center bonds in b in place of the single bond and open three-center bond at carbon in a.

We are now attempting to study LMO's and reaction pathways in the initial stages of the pyrolysis of $B_2H_6$. The near-Hartree–Fock limit for the $2BH_3$ to $B_2H_6$ reaction is −19.0 kcal obtained from an extended Slater basis set.[37] An appropriate correlation correction has not been made, but the single and double excitations from a minimum Slater basis set give a correlation correction of −10.6 kcal. A recent experimental value is −35.5 kcal for $\Delta H_f$. So far, the best transition state is centrosymmetric, having two very unsymmetrical bridge hydrogens, only slightly distorted $BH_3$ units, a B···B distance of 3.0 Å, and an energy greater than $2BH_3$'s by 2.6 kcal (Figure 15). The LMO's show very little three-center bonding in this transition state.[38] Further studies are in progress on $B_3H_7$ (Figure 16), $B_3H_9$, $B_4H_8$, $B_4H_{12}$, and of course on the stable hydrides produced in these reactions.

## Summary

(a) No open three-center bonds have been found in localized molecular orbitals of boranes.

(b) Carboranes, but not boranes, may have open three-center bonds, where C is the central atom, and may have an adjacent pair of C atoms (or an adjacent B and C) joined by both a single bond and a central three-center bond.

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(33) D. S. Marynick, J. H. Hall, Jr., and W. N. Lipscomb, to be published.

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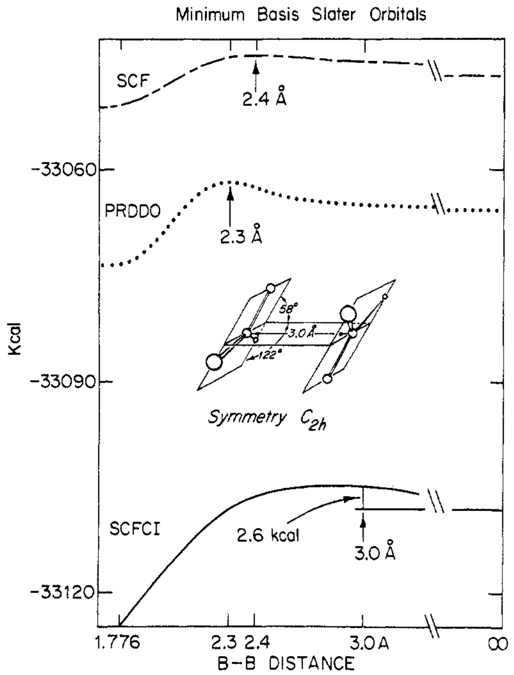

**Figure 15.** The formation of $B_2H_6$ from two $BH_3$ molecules, as a function of the B···B distance. The favored transition state has symmetry $C_{2h}$ and consists of $BH_3$ units which are nearly planar with nearly equal BH bond lengths and which are less stable than two isolated $BH_3$'s by 2.6 kcal. For the PRDDO method see ref 8.

(c) Unique preferred three-center bonds exist in valence structures of $B_2H_6$, $B_4H_{10}$, $B_5H_{11}$, $B_6H_{10}$, and 1,2-$C_2B_4H_6$.

(d) Structures for which three-center bonds can be drawn are preferred over those which cannot be so expressed. For example, $B_{11}H_{11}^{2-}$ of $C_{2v}$ symmetry is preferred over the $C_{5v}$ structure.

(e) Of alternative geometries for an isomer, the structure having the larger number of nearly equivalent three-center bond structures is preferred. This argument takes precedence over which choice has the more favorable charge distribution.

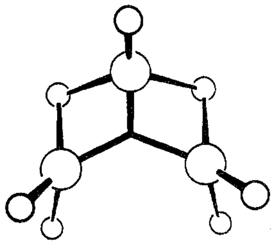

**Figure 16.** Hypothetical geometrical and valence structure for $B_3H_7$.

(f) Unique fractional three-center bond descriptions exist for 4,5-$C_2B_4H_8$ and probably also for $B_{10}H_{14}$, $B_{10}H_{14}^{2-}$, and $B_9H_{13}L$.

(g) Fractional three-center bonds occur replacing an open three-center bond and a single bond from the central atom to a fourth atom, except when C is the central atom.

(h) It is probable that valence structures having a vacant orbital which can easily be incorporated into three-center bond structures are preferred over those which cannot.

In more general terms we see now differences in the valence rules as they apply to boron and carbon in the boranes and carboranes. In addition to the early objectives of deciding what stable "electron-deficient" species are stable in the sense that all orbitals are filled to the valence level, we now hope that a hierarchy of rules at different levels of detail can be derived from rigorous self-consistent field methods in such a way that charge distributions, reaction intermediates, and reaction pathways can be found.

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