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Localized Orbitals for Polyatomic Molecules. 5. The Closo Boron Hydrides $B_nH_n{}^{2-}$ and Carboranes $C_2B_{n-2}H_n$

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Abstract: Wave functions calculated in the approximation of partial retention of diatomic differential overlap (PRDDO) are presented for the closo boron hydrides $B_nH_n{}^{2-}$ and carboranes $C_2B_{n-2}H_n$ for n = 5–12. The wave functions are examined in terms of both the canonical molecular orbitals and localized molecular orbitals (LMO's) obtained by the Boys criterion. Reactivity predictions are based on various properties related to the atomic charge. Valencies and bond orders are also presented. The LMO's for each molecule are discussed, and for the same n are compared in order to examine the effects of placing the electronegative carbons in the cluster. The LMO's are also compared to topologically allowed structures and are, in general, found to correspond either to sums of topologically allowed structures or to delocalized topologically allowed structures.

As a class of compounds, the carboranes and boron hydrides are, perhaps, the family of molecules that has been most completely studied by rigorous theoretical methods.[1] Previous theoretical studies employing wave functions of nearly ab initio quality have been made of all of the open boron hydrides and carboranes whose structures have been determined experimentally.[2,3] In order to complete this phase of our work on this interesting family of molecules, we have extended our theoretical studies by the PRDDO molecular orbital method[4] to the closo boron hydrides[5c,g] and dicarbacarboranes.[5] (The acronym PRDDO refers to partial retention of diatomic differential overlap.) A number of semiempirical calculations using a variety of methods[6,7] have been performed on these molecules, but only a few ab initio calculations are available, and these are for the smaller carboranes and boron hydrides.[8] We believe that our calculations described below are the best available wave functions for most of these molecules.

The most extensively studied carborane series[5] is the series $C_2B_{n-2}H_n$ for $5 \leq n \leq 12$. Molecular structure parameters have been obtained from microwave spectroscopy for 1,5-$C_2B_3H_5$,[9] 1,2-$C_2B_4H_6$,[10] 1,6-$C_2B_4H_6$,[11] and 2,4-$C_2B_5H_7$;[12] these molecules have also been studied by ab initio methods.[8] The structures of the C,C′-dimethyl derivatives of 1,7-$C_2B_6H_8$,[13] 1,6-$C_2B_7H_9$,[14] 1,6-$C_2B_8H_{10}$,[15] and 2,3-$C_2B_9H_{11}$[16] have been determined by x-ray diffraction techniques. The structures of 1,2-[17] and 1,7-$C_2B_{10}H_{12}$[18] have been determined from x-ray diffraction studies while a combination of ^{11}B NMR[19] and electron diffraction[20] were used in determining the structure of 1,12-$C_2B_{10}H_{12}$. The chemistry of the largest members of this series, 1,2-, 1,7-, and 1,12-$C_2B_{10}H_{12}$, has been the most fully explored.

The dicarba-*closo*-carboranes are isoelectronic and isostructural with the remarkably stable doubly charged negative ions, $B_nH_n{}^{2-}$ (n = 6–12). At the time of Lipscomb's comprehensive survey of boron hydride chemistry in 1963,[1] only $B_{12}H_{12}{}^{2-}$ had been structurally characterized.[21] Since then the structures of $B_6H_6{}^{2-}$,[22] $B_8H_8{}^{2-}$,[23] $B_9H_9{}^{2-}$,[24] and $B_{10}H_{10}{}^{2-}$,[25] have determined by x-ray crystallographic methods. The molecules $B_7H_7{}^{2-}$ [26] and $B_{11}H_{11}{}^{2-}$ [27] have been partially characterized by ^{11}B NMR studies, but $B_5H_5{}^{2-}$ has not yet been observed. The basic geometric structures of the $B_nH_n{}^{2-}$ series are usually closed polyhedra with high symmetry. In all known cases, the isoelectronic dicarbacarborane has the same basic polyhedral shape, but the symmetry is usually much lower.

One of the major techniques for gaining insight into the structure of polyhedral boron hydrides has been the notion of the three-center bond. The central three-center BBB bond has been found in localized molecular orbitals (LMO's) from good wave functions using either the Boys[28] or Edmiston-Ruedenberg (ER) criteria.[29] The study of localized molecular orbitals in these polyhedra is of particular interest because (1) the number of pairs of electrons is greater than the number of centers by one and (2) there are some difficulties when these electron pairs are placed in an environment with high symmetry. The relationship of these LMO bonding structures to the simple topological structures is especially of interest for development of a general theory of bonding in these polyhedra. As previously discussed the Boys and ER criteria disagree for one type of bonding arrangement: the open BCB bond is found in 1,2-$C_2B_4H_6$ by the ER procedure, whereas the Boys procedure yields only central three-center bonds. However, the Boys method is computationally so efficient that we employ it, rather than the ER procedure, in this study.

We present in this paper PRDDO calculations[4] on the $B_nH_n{}^{2-}$ and $C_2B_{n-2}H_n$ series of molecules, and we discuss the reactivity and structures of these molecules in light of the canonical molecular orbitals. Localized molecular orbitals are obtained using the Boys criterion in order to examine the valence bonds in these molecules and to compare the LMO's with simple topological structures. These highly symmetric molecules are also interesting because they may yield multiple maxima on the LMO hypersurface. Comparison of the LMO's of the $B_nH_n{}^{2-}$ with those in the isoelectronic carboranes allows for the examination of the effects on the bonding of placing electronegative atoms into these clusters. These polyhedral

Table I. Carborane Energy Analysis

Molecule	Energy[a]	NRE[b]	KE[c]	NAE[d]	ERE[e]	Virial[f]
1,5-$C_2B_3H_5$	−152.528	124.785	152.754	−603.752	173.685	0.999
1,2-$C_2B_4H_6$	−177.763	176.318	177.957	−763.994	231.956	0.999
1,6-$C_2B_4H_6$	−177.785	180.526	178.263	−772.433	235.858	0.999
2,4-$C_2B_5H_7$	−203.101	227.490	203.241	−924.348	290.516	0.999
1,7-$C_2B_6H_8$	−228.371	285.624	228.583	−1098.386	355.807	0.999
1,6-$C_2B_7H_9$	−253.640	345.178	253.622	−1275.176	422.736	1.000
1,6-$C_2B_8H_{10}$	−278.925	415.497	278.830	−1473.374	500.121	1.000
2,3-$C_2B_9H_{11}$	−304.212	482.105	303.994	−1664.407	574.097	1.001
1,2-$C_2B_{10}H_{12}$	−329.499	567.331	329.174	−1891.891	665.887	1.001
1,7-$C_2B_{10}H_{12}$	−329.537	567.131	329.117	−1891.517	665.733	1.001
1,12-$C_2B_{10}H_{12}$	−329.545	567.003	329.087	−1891.243	665.607	1.001

[a] All energies in atomic units, 1 au = 627.5 kcal/mol. Total molecular energy. [b] Nuclear repulsion energy. [c] Kinetic energy. [d] Nuclear attraction energy. [e] Electron repulsion energy. [f] Value of the virial ratio ($-E/T$).

molecules are some of the simplest cluster-type molecules which have closed-shell ground states. Perhaps an understanding of the electronic structure of these molecules will be useful in making theoretical models of metal clusters.

Calculations

The wave functions were obtained using the PRDDO method, which explicitly includes all electrons in a minimum basis set of Slater orbitals. Exponents were taken from B_2H_6 for B and H_B and from ethane for C and H_C.[3a] Geometries for the carboranes were taken from the structural data and symmetrized to the molecular symmetry. Coordinates for the icosahedral carboranes were taken from those in our previous calculations.[7] The C–H distances were set at 1.10 Å and the B–H distances at 1.19 Å, thus compensating for apparent shortening of these bond distances in the x-ray method.[30] The framework geometries for the $B_nH_n^{2-}$ molecules except for n = 5, 7, and 11 were taken from the crystal data and then symmetrized. All unique B–B distances in these molecules were then subjected to a cycle of geometry optimization in order to provide more data on the gas-phase structures of these doubly negative ions and to account for the averaging due to symmetrization of the coordinates. Idealized D_{3h} and D_{5h} geometries were assumed for $B_5H_5^{2-}$ and $B_7H_7^{2-}$, and the boron–boron distances were taken from the isoelectronic dicarbacarborane structures. The two unique close B–B distances were then optimized for each molecule. For $B_{11}H_{11}^{2-}$, a C_{2v} structure was presumed to be the lowest state as evidenced by the ^{11}B NMR.[27] A comparison of the C_{5v} and C_{2v} geometries starting from idealized coordinates from $B_{12}H_{12}^{2-}$ showed the C_{2v} structure to be substantially more stable. The geometry of the C_{2v} structure was then optimized.[31]

Results and Discussion

Canonical Molecular Orbitals. We first discuss the wave functions for the carboranes and then discuss those of the *closo*-boron hydrides.

Carboranes. In Table I we present the energy analysis for the carboranes, while in Table II we give various one-electron properties. We note that 1,6-$C_2B_4H_6$ is 14 kcal/mol more stable than 1,2-$C_2B_4H_6$, in agreement with qualitative experiments.[32] The energy differences between the various isomers of the icosahedral carboranes are known experimentally and can be determined from the following rearrangements:[33]

$$1,2\text{-}C_2B_{10}H_{12}\ (o) \xrightarrow{450\ °C} 1,7\text{-}C_2B_{10}H_{12}\ (m) \xrightarrow{620\ °C} 1,12\text{-}C_2B_{10}H_{12}\ (p)$$

Experimentally, the para isomer is the most stable; the meta isomer is 16.8 kcal/mol less stable and the ortho isomer is 33.4 kcal/mol less stable than *p*-carborane. The PRDDO results also show that the para isomer is the most stable, but predicts the meta isomer to be only 5 kcal/mol less stable, and the ortho isomer to be 29 kcal/mol less stable. Thus the qualitative trends are again correctly predicted.

The dipole moments given by PRDDO (Table II) are too high as is usually found for most minimum basis set calculations. However, general trends are correctly predicted and the ratios of dipole moments are quite close to those found experimentally. (For the ratio μ (ortho)/μ (meta), experiment gives 1.55, while PRDDO gives 1.60.)

In Table II we also report the eigenvalues of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The negative of the HOMO eigenvalue is the ionization potential according to Koopmanns' theorem. The calculated ionization potentials range between 10.0 and 12.5 eV for the carboranes, and the largest ionization potentials are found for the $C_2B_{10}H_{12}$ isomers. The eigenvalue of the LUMO should correspond qualitatively to the ease of electron attachment and the formation of stable negative ions. The eigenvalue for the LUMO for 2,3-$C_2B_9H_{11}$ is unusually low, and therefore this molecule should form negative ions quite readily.

Much use of static reactivity indices has been made in predicting reactivity sites for electrophilic and nucleophilic attack in the boron hydrides with more than fair success. Only in cases where orbital symmetry may be involved do these predictions break down, although one may expect steric effects and complex mechanisms to play a role in some examples. The usual indices for describing reactivity are atomic charges, group charges, and inner shell eigenvalues (Table III), while another index that has been used is the sum of the populations in the n highest orbitals. However, studies of the *nido*-boranes has

Table II. One-Electron Properties for the Carboranes

Molecule	IP[a]	LUMO,[b] eV	μ,[c] D	μ (exp)[d]
1,5-$C_2B_3H_5$	11.29	6.15		
1,2-$C_2B_4H_6$	10.72	6.83	2.97	1.50
1,6-$C_2B_4H_6$	10.26	7.07		
2,4-$C_2B_5H_7$	10.69	7.21	1.82	1.32
1,7-$C_2B_6H_8$	11.43	3.70	2.02	
1,6-$C_2B_7H_9$	11.10	2.64	3.12	
1,6-$C_2B_8H_{10}$	11.62	3.73	2.80	
2,3-$C_2B_9H_{11}$	11.24	1.44	3.20	
1,2-$C_2B_{10}H_{12}$	12.03	4.33	6.21	4.31
1,7-$C_2B_{10}H_{12}$	12.13	4.73	3.88	2.78
1,12-$C_2B_{10}H_{12}$	12.30	4.70		

[a] Ionization potential from Koopmanns theorem in electron volts. [b] Eigenvalue for the lowest unoccupied molecular orbital in electron volts. [c] Calculated dipole moment in debye. [d] Experimental dipole moments.

Table III. Charges and Valencies for the Carboranes

Molecule	Atom	Valency	Charge[a]	Group charge[b]	Eigen[c]
1,5-$C_2B_3H_5$	C(1)	3.99	−0.12	−0.09	−11.190
	B(2)	3.53	0.14	0.06	−7.533
1,2-$C_2B_4H_6$	C(1)	3.97	−0.08	0.00	−11.277
	B(3)	3.69	0.07	0.01	−7.575
	B(4)	3.70	0.06	−0.01	−7.555
1,6-$C_2B_4H_6$	C(1)	3.99	−0.13	−0.06	−11.250
	B(2)	3.70	0.08	0.03	−7.581
2,4-$C_2B_5H_7$	C(2)	3.98	−0.12	−0.05	−11.256
	B(1)	3.65	0.11	0.04	−7.613
	B(3)	3.67	0.11	−0.06	−7.604
	B(5)	3.69	0.05	−0.02	−7.554
1,7-$C_2B_6H_8$	C(1)	3.96	−0.11	−0.03	−11.268
	B(2)	3.65	0.07	0.01	−7.578
	B(3)	3.65	0.11	0.06	−7.628
	B(5)	3.68	0.04	−0.03	−7.588
1,6-$C_2B_7H_9$	C(1)	3.99	−0.12	−0.04	−11.284
	B(2)	3.64	0.12	0.06	−7.646
	B(4)	3.67	0.07	0.00	−7.597
	B(8)	3.70	0.01	−0.06	−7.544
1,6-$C_2B_8H_{10}$	C(1)	3.99	−0.12	−0.03	−11.290
	C(6)	3.98	−0.06	0.02	−11.313
	B(2)	3.65	0.11	0.06	−7.646
	B(3)	3.68	0.06	0.00	−7.612
	B(7)	3.67	0.03	−0.03	−7.600
	B(8)	3.69	0.01	−0.06	−7.577
	B(10)	3.70	0.06	0.00	−7.581
2,3-$C_2B_9H_{11}$	C(2)	3.97	−0.08	0.00	−11.302
	B(1)	3.61	0.14	0.08	−7.673
	B(4)	3.67	0.08	0.02	−7.619
	B(8)	3.67	0.08	0.01	−7.613
	B(10)	3.72	−0.02	−0.09	−7.582
1,2-$C_2B_{10}H_{12}$	C(1)	3.96	−0.04	0.07	−11.390
	B(3)	3.66	0.07	0.03	−7.660
	B(4)	3.67	0.05	0.00	−7.622
	B(8)	3.71	0.01	−0.05	−7.580
	B(9)	3.71	0.02	−0.05	−7.571
1,7-$C_2B_{10}H_{12}$	C(1)	3.98	−0.06	0.03	−11.348
	B(2)	3.67	0.08	0.04	−7.662
	B(4)	3.69	0.04	−0.01	−7.622
	B(5)	3.68	0.06	0.00	−7.615
	B(9)	3.71	0.01	−0.05	−7.582
1,12-$C_2B_{10}H_{12}$	C(1)	3.98	−0.05	0.04	−11.342
	B(2)	3.69	0.05	−0.01	−7.622

[a] Atomic charge in electrons (e). [b] Group charge in electrons. The difference between the atomic and group charge is the hydrogen atom charge. [c] Inner-shell eigenvalue in atomic units.

shown that this latter index is not useful in predicting reactivity trends. The indices that we employ describe the charge on an atom. Electrophilic attack should occur at negative atoms (most positive inner shell eigenvalue), while nucleophilic attack occurs at positive atoms (most negative inner shell eigenvalue). The initial use of these indices for predicting reactivity sites was based on extended Hückel wave functions for the icosahedral carboranes where good experimental information is available. We now examine these indices with better wave functions.

For electrophilic halogenation of *o*-carborane by the Friedel-Crafts method for Cl, Br, and I, the experiments show that B(9) and B(12) are halogenated first followed by B(8) and B(10).[34] Electrophilic halogenation is not observed at the remaining boron sites which are attached to carbon, and is not observed at carbon. The group charges and inner shell eigenvalues suggest that both B(8) and B(9) should be susceptible to electrophilic attack, but we cannot predict at which of these two sites the attack should occur preferentially. The inner-shell eigenvalues do favor B(9), but we cannot place confidence in such a small difference. The group charges do show a nice effect in that the carbon is predicted to be positive and, thus, electrophilic attack should not occur here. The sums of atomic populations lead us to predict that, after six orbitals where the first major gap occurs (0.026 au), electrophilic attack should occur at B(9) and B(12) (1.36 e) before B(8) and B(10) (1.04 e).

The experimental evidence for electrophilic attack on *m*-carborane shows that attack occurs preferentially at B(9) and B(10), and next at B(4), B(6), B(8), and B(11).[35] Both the group charge and eigenvalue criteria show that B(9) (B(10)) is the preferred site for electrophilic attack and suggest that B(4) (B(6), B(8), B(11)) is the next site. Again the group charges show that the sites at which electrophilic substitution occurs are the only negatively charged sites in the cluster. The sums over atomic charges over the top five orbitals show that B(9) (B(10)) is the preferred site of electrophilic attack, but that the next site is B(5) (B(12)) not B(4) (B(6), B(8), and B(11)).

For *p*-carborane there is only one unique boron, so no predictions of the order of attack are necessary. The group charges do show that the carbons are positive, and thus electrophilic attack should not occur here, as has been experimentally verified. The rate of reactivity toward electrophilic halogenation, $o > m > p$, correlates with increasing ionization potential.

Photochemical chlorination of *o*-carborane is less selective.

Table IV. Overlap Populations and Degrees of Bonding for Carboranes

Molecule	Bond[a]	R^b	Degree of bonding	Overlap
1,5-$C_2B_3H_5$	C(1)-2	1.58	0.981	0.689
	2-3	1.86	0.285	0.028
1,2-$C_2B_4H_6$	C(1)-C(2)	1.54	0.785	0.528
	C(1)-3	1.63	0.685	0.461
	C(1)-4	1.61	0.727	0.524
	3-4	1.72	0.610	0.467
	4-6	1.75	0.658	0.503
1,6-$C_2B_4H_6$	C(1)-2	1.57	0.729	0.535
	2-3	1.69	0.563	0.413
2,4-$C_2B_5H_7$	1-C(2)	1.71	0.587	0.412
	1-3	1.82	0.410	0.286
	1-5	1.81	0.484	0.362
	C(2)-3	1.55	0.888	0.663
	C(2)-6	1.56	0.856	0.622
	5-6	1.65	0.805	0.643
1,7-$C_2B_6H_8$	C(1)-2	1.50	0.950	0.683
	C(1)-3	1.69	0.567	0.400
	C(1)-4	1.59	0.805	0.632
	2-3	1.77	0.447	0.341
	2-5	1.84	0.414	0.311
	2-6	1.70	0.747	0.625
	3-4	1.89	0.335	0.225
	3-6	1.84	0.427	0.308
1,6-$C_2B_7H_9$	C(1)-2	1.60	0.730	0.547
	C(1)-4	1.62	0.715	0.521
	2-3	1.77	0.379	0.231
	2-5	1.97	0.349	0.272
	4-5	1.78	0.444	0.308
	4-7	2.00	0.419	0.321
	4-8	1.72	0.646	0.512
1,6-$C_2B_8H_{10}$	C(1)-2	1.60	0.732	0.551
	C(1)-3	1.60	0.708	0.519
	2-3	1.81	0.440	0.304
	2-5	1.86	0.327	0.218
	2-C(6)	1.75	0.582	0.443
	2-7	1.79	0.508	0.415
	3-4	1.83	0.407	0.310
	3-7	1.80	0.546	0.462
	3-8	1.83	0.518	0.427
	C(6)-7	1.77	0.498	0.324
	C(6)-10	1.63	0.706	0.509
	7-8	1.84	0.452	0.343
	7-10	1.69	0.595	0.477
	8-10	1.68	0.678	0.544
2,3-$C_2B_9H_{11}$	1-C(2)	1.65	0.678	0.525
	1-4	2.04	0.288	0.190
	C(2)-4	1.59	0.808	0.603
	C(2)-8	1.68	0.554	0.387
	4-5	1.86	0.466	0.397
	4-8	1.80	0.445	0.334
	6-10	1.83	0.542	0.434
	8-10	1.78	0.561	0.467
	10-11	1.84	0.432	0.334
1,2-$C_2B_{10}H_{12}$	C(1)-C(2)	1.67	0.622	0.412
	C(1)-3	1.72	0.537	0.377
	C(1)-4	1.72	0.571	0.411
	3-4	1.77	0.476	0.384
	3-8	1.77	0.537	0.436
	4-5	1.77	0.488	0.387
	4-8	1.77	0.523	0.424
	4-9	1.77	0.525	0.432
	8-9	1.77	0.522	0.423
	9-12	1.77	0.528	0.435
1,7-$C_2B_{10}H_{12}$	C(1)-2	1.72	0.575	0.422
	C(1)-4	1.72	0.572	0.409
	C(1)-5	1.72	0.571	0.415
	2-3	1.77	0.442	0.345
	2-6	1.77	0.493	0.393
	4-5	1.77	0.484	0.390
	4-8	1.77	0.521	0.431
	4-9	1.77	0.526	0.425
	5-9	1.77	0.527	0.434
	9-10	1.77	0.522	0.415
1,12-$C_2B_{10}H_{12}$	C(1)-4	1.72	0.575	0.420
	3-5	1.77	0.484	0.380
	3-8	1.77	0.529	0.436

[a] Numbers with no letter are boron atoms. [b] Bond distance in Å.

Table V. Energy Analysis for the Boron Hydrides[a]

Molecule	Energy	NRE	KE	NAE	ERE	Virial
$B_5H_5^{2-}$	−125.890	108.975	128.347	−527.680	164.407	0.981
$B_6H_6^{2-}$	−151.292	153.617	153.224	−676.448	218.314	0.987
$B_7H_7^{2-}$	−176.623	205.765	178.781	−840.749	279.579	0.988
$B_8H_8^{2-}$	−201.901	261.579	204.099	−1012.058	344.479	0.989
$B_9H_9^{2-}$	−227.237	319.912	229.134	−1188.083	411.800	0.992
$B_{10}H_{10}^{2-}$	−252.588	392.369	254.613	−1392.439	492.868	0.992
$B_{11}H_{11}^{2-}$	−277.823	453.617	279.584	−1573.972	562.948	0.994
$B_{12}H_{12}^{2-}$	−303.314	538.173	304.597	−1801.763	655.608	0.996

[a] Energies in atomic units. See Table I for explanation of column headings.

Table VI. Relative Energies for the Boron Hydrides

Molecule	HOMO[a]	$-E/n$[b]	Δ[c]
$B_5H_5^{2-}$	0.177	25.178	−23.2
$B_6H_6^{2-}$	0.122	25.215	0
$B_7H_7^{2-}$	0.061	25.232	10.7
$B_8H_8^{2-}$	0.104	25.238	14.4
$B_9H_9^{2-}$	0.068	25.249	21.3
$B_{10}H_{10}^{2-}$	0.004	25.259	27.6
$B_{11}H_{11}^{2-}$	0.023	25.257	26.4
$B_{12}H_{12}^{2-}$	−0.077	25.276	38.3

[a] Highest occupied molecular orbital eigenvalue in atomic units. [b] Negative of the total energy divided by the number of borons in atomic units. [c] $E(B_6H_6^{2-})/6 - E(B_nH_n^{2-})/n = \Delta$ in kilocalories per mole.

All sites are halogenated in the order from most negative to most positive; the final site is at B(3) as predicted by PRDDO. For *m*-carborane photochemical chlorination leads to two monochloro isomers, and is less selective than electrophilic substitution. Photochemical chlorination of *p*-carborane is random. We also note that fluorine attack leads to decafluorocarboranes nonselectively. These results are in agreement with our PRDDO predictions that the carbons are positively charged. Thus, electrophilic attack should not occur at these sites.

For the other carboranes that we have studied there are few experimental results. Electrophilic attack occurs at B(8), the apex, in $C_2B_7H_9$.[36] The PRDDO prediction is that electrophilic attack should be at this apex for all of the different indices. The remaining order is B(4) > B(2). For 1,7-$C_2B_6H_8$ the order is predicted to be B(5) > B(2) > B(3) based on group charges, but the eigenvalues do not corroborate this order. The molecule 1,6-$C_2B_8H_{10}$ has the order B(8) > B(7) > B(10) ~ B(3) > B(2) based on group charges, but again the eigenvalue differences are too small to be used in making these predictions. The order for electrophilic attack is B(10) > B(8) ~ B(4) > B(1) in 2,3-$C_2B_9H_{11}$ according to both the charge and eigenvalue criteria.

The group charges for carbon show some variation. In the smaller polyhedra the carbons are more negative than in the icosahedral carboranes. Thus the hydrogens on the carbons in the smaller molecules should be more acidic than the hydrogens in the larger molecules. For 1,6-$C_2B_8H_{10}$ where there are two unique carbons we predict C(1) to be more susceptible to electrophilic attack than C(6), while the hydrogen on C(1) should be more acidic and could be easily lost.[33a]

The concept of quantitative bond indices and valencies has been introduced by Armstrong et al.[37] and used by Pepperberg et al.[38] in a discussion of bonding in small boron hydrides. The valency of atom a, V_a, is defined as the sum of the degrees of bonding, B_{ab}, between a and all other atoms, b,

$$V_a = \sum_{a\neq b} B_{ab} = \sum_{a\neq b}\sum_{i_a}\sum_{j_b} P_{i_a j_b}{}^2$$

The quantity B_{ab} is the sum of the squares of the elements of the density matrix P_{ij} over orthogonalized atomic orbitals. The valency is given in Table III, while bond distances, degrees of bonding, and overlap populations are given in Table IV for the carboranes.

For the carboranes, the valencies are approximately 4 for all carbons (Armstrong et al.,[37] from CNDO calculations, give a valency of 3.95 for CH_4) and thus the carbons have normal valencies. The borons have valencies averaging about 3.6–3.7 as compared to a valency of 2.98 in BH_3. An exception occurs in 1,5-$C_2B_3H_5$, where the valency is very low, 3.53, and, as seen in the LMO's discussed below, leads to a different type of bonding. A general trend, not strictly adhered to, is that the more negative borons have higher valencies.

The values for the degree of bonding correlate well with the overlap populations showing the same trends, except that larger differences are observed in the values of B_{ab}. Short boron–carbon distances tend to have high degrees of bonding, near 1.0, which is the value found for the C–C bond in ethane; such bonds usually have distances <1.60 Å. The degree of bonding for the C–C bond in 1,2-$C_2B_{10}H_{12}$ is low and as seen in the LMO's this bond is quite delocalized. Most boron–boron bonds have values between 0.40 and 0.70 which correlate reasonably well with bond length: short bonds have higher degrees of overlap than do long bonds.

Boron Hydride Ions. The energy analysis is given in Table V for the boron hydrides. In order to examine the stability of these closo boron hydride polyhedra we have calculated the average energy for each BH group in an ion and then compared it to the average energy of the BH group in $B_6H_6^{2-}$, the smallest known dianion (Table VI). For example, a BH group in $B_7H_7^{2-}$ is more stable than a BH group in $B_6H_6^{2-}$ by 10.7 kcal/mol. The results do show $B_5H_5^{2-}$ to be quite unstable by −23.2 kcal/mol for each BH group, while $B_{12}H_{12}^{2-}$ is the most stable at 38.3 kcal/mol. The calculations seem to predict that $B_7H_7^{2-}$ is more stable than is observed. A most interesting comparison between $B_{10}H_{10}^{2-}$ and $B_{11}H_{11}^{2-}$ shows that the BH group in $B_{11}H_{11}^{2-}$ is *less* stable than the BH group in $B_{10}H_{10}^{2-}$. $B_{11}H_{11}^{2-}$ is the only $B_nH_n^{2-}$ dianion not to have a highly symmetric closed polyhedron; this instability shows up in this comparison.

Muetterties and Knoth[39] have related the energy of the highest occupied molecular orbital (HOMO) to the susceptibility of the closo dianions to oxidative processes. Since oxidative processes correspond to the removal of an electron, the more positive the value of the HOMO, the more easy it is to remove an electron. Polarographic studies indicate that the stability toward oxidative processes decreases in the order $B_{12}H_{12}^{2-} > B_{10}H_{10}^{2-} > B_{11}H_{11}^{2-} \gg B_9H_9^{2-} > B_8H_8^{2-}$, while qualitative observation of oxidation of ions in solutions yields the order $B_{12}H_{12}^{2-}$, $B_{10}H_{10}^{2-}$, $B_{11}H_{11}^{2-} > B_6H_6^{2-} > B_9H_9^{2-} \sim B_8H_8^{2-} > B_7H_7^{2-}$. The ordering given by PRDDO (Table VI) is $B_{12}H_{12}^{2-} > B_{10}H_{10}^{2-} > B_{11}H_{11}^{2-} > B_9H_9^{2-} \sim B_7H_7^{2-} > B_8H_8^{2-} > B_6H_6^{2-} > B_5H_5^{2-}$. However, whether such correspondences have true predictive value is subject to

Table VII. Valencies and Charges for the Boron Hydrides

		Valency	Atom charge[a]	Group charge[b]	Eigen[c]
$B_5H_5^{2-}$	B(1)	3.88	−0.23	−0.48	−6.918
	B(2)	3.66	−0.11	−0.34	−6.979
$B_6H_6^{2-}$	B(1)	3.82	−0.11	−0.33	−7.020
$B_7H_7^{2-}$	B(1)	3.75	−0.01	−0.21	−7.101
	B(2)	3.79	−0.11	−0.32	−7.044
$B_8H_8^{2-}$	B(1)	3.77	−0.03	−0.21	−7.074
	B(3)	3.75	−0.10	−0.28	−7.118
$B_9H_9^{2-}$	B(1)	3.80	−0.10	−0.28	−7.099
	B(2)	3.74	−0.01	−0.19	−7.143
$B_{10}H_{10}^{2-}$	B(1)	3.80	−0.08	−0.25	−7.122
	B(2)	3.74	−0.03	−0.19	−7.162
$B_{11}H_{11}^{2-}$	B(1)	3.55	0.07	−0.07	−7.217
	B(2)	3.80	−0.10	−0.28	−7.139
	B(4)	3.73	−0.01	−0.17	−7.188
	B(8)	3.76	−0.03	−0.19	−7.180
	B(10)	3.74	−0.01	−0.16	−7.200
$B_{12}H_{12}^{2-}$	B(1)	3.75	−0.02	−0.17	−7.192

[a] Atomic charge in electrons. [b] group charge in electrons. [c] Inner-shell eigenvalue in atomic units.

Table VIII. Overlap Populations and Degrees of Bonding in the Boron Hydrides

Molecule	Bond	R^a	Degree of bonding	Overlap
$B_5H_5^{2-}$	1-2	1.59	0.959	0.733
	2-3	1.83	0.389	0.167
$B_6H_6^{2-}$	1-2	1.70	0.691	0.533
$B_7H_7^{2-}$	1-2	1.76	0.540	0.419
	2-3	1.59	0.849	0.682
$B_8H_8^{2-}$	1-2	1.55 (1.56)	0.918	0.694
	1-3	1.72 (1.76)	0.535	0.430
	1-4	1.68 (1.72)	0.728	0.605
	3-4	1.84 (1.93)	0.462	0.346
$B_9H_9^{2-}$	1-2	1.66 (1.71)	0.682	0.552
	2-3	1.78 (1.81)	0.474	0.344
	2-4	1.92 (1.93)	0.421	0.342
$B_{10}H_{10}^{2-}$	1-2	1.63 (1.73)	0.680	0.555
	2-3	1.79 (1.86)	0.455	0.354
	2-6	1.74 (1.81)	0.555	0.473
$B_{11}H_{11}^{2-}$	1-2	1.59	0.776	0.582
	1-4	2.21	0.250	0.151
	2-4	1.69	0.722	0.583
	2-8	1.74	0.480	0.376
	4-5	1.81	0.520	0.441
	4-8	1.68	0.578	0.480
	6-10	1.74	0.556	0.445
	8-10	1.74	0.537	0.444
	10-11	1.74	0.502	0.426
$B_{12}H_{12}^{2-}$	1-2	1.74 (1.77)	0.540	0.446

[a] Bond length in Å. Experimental values in parentheses.

question, since for these doubly negative species, there are positive eigenvalues at the minimum basis set level for all moelcules except $B_{12}H_{12}^{2-}$. The molecule $B_{12}H_{12}^{2-}$ can more easily stabilize its excess negative charge because of the larger number of centers and, thus, all of the eigenvalues are bound. Stability toward oxidative processes is more likely due to the size of the molecule except in cases where special stability is conferred because of the aromatic-like molecular orbital character of the molecule, e.g., in $B_{10}H_{10}^{2-}$. Also, we note that the PRDDO method does not give the correct ordering for $B_6H_6^{2-}$, which is too small to stabilize the excess charge when only a minimum basis set is used.

Reactivity predictions in the closo-dianion boron hydrides are less complicated because, except for $B_{11}H_{11}^{2-}$, there are at most two different sites which are apical or equatorial. The various reactivity indices are given in Table VII. For these molecules, electrophilic attack should occur at apical borons before equatorial borons. These predictions are based on both the eigenvalue and group charge criteria. For $B_{11}H_{11}^{2-}$, the order for electrophilic attack is expected to be B(2) > B(8) ~ B(4) ~ B(10) > B(1). For $B_{11}H_{11}^{2-}$ we note that nucleophilic attack is predicted at the apex in contrast to the other boron hydrides. For $B_{10}H_{10}^{2-}$, experimental evidence[40] suggests that factors other than charge may govern the site of electrophilic attack since hydroxylamine-*o*-sulfonic acid gives only equatorial-substituted products instead of the predicted apical substitution. Thus some other mechanism could be operating. The only exception to nucleophilic attack at equatorial positions is the acid-catalyzed reaction of $B_{10}H_{10}^{2-}$ with acetonitrile, which again may proceed by another mechanism.

The valencies in the boron hydrides are shown in Table VII and the bond distances, degrees of bonding and overlap populations are shown in Table VIII. The valencies of the boron atoms in the closo boron hydrides tend to be higher than those in the respective carboranes. The bond distances calculated by PRDDO tend to show a shortening of 0.03–0.05 Å over the

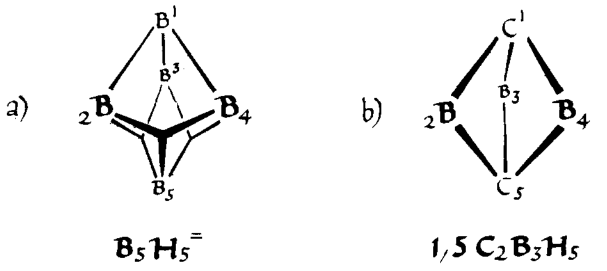

Figure 1. LMO structures for $n = 5$: (a) LMO's for $B_5H_5^{2-}$ corresponding to a normal TA structure; (b) LMO's for $C_2B_3H_5$ corresponding to a forbidden TA structure.

crystal structure distances obtained from the crystal structures, but the general trends in bond lengths are retained. As in the carboranes, the degrees of bonding tend to fall between 0.40 and 0.70, and short bonds tend to have high degrees of bonding.

Localized Molecular Orbitals. The localized molecular orbitals (LMO's) were obtained using the Boys criteria.[2b,28] Twenty-five iterations were preformed which gave reasonable convergence. All structures had negative second derivatives, thus demonstrating that the LMO's have converged to a maximum on the LMO hypersurface. In certain cases the eigenvector of the highest eigenvalue on the second derivative test is followed to assure convergence to a maximum.[2b] The LMO's are discussed below and compared with their simple topologically allowed (TA) structures which are all of the type $(0, n - 2, 3, 0)$.[41]

Localized molecular orbitals for many of the closo carboranes have been obtained by Guest and Hillier[8d] using the ER criteria with INDO wave functions. In general our results, where they can be compared, agree reasonably well with their results. We note that the ER-INDO LMO's must be viewed with some care, as the LMO's for $1,2\text{-}C_2B_4H_6$ obtained by the ER criteria for INDO wave functions do not yield two open BCB bonds and two B-C bonds which we found from the ER procedure using an ab initio wave function. Rather their results correspond to the LMO's obtained with the Boys criteria, which show four central BCB bonds and two fractional centers.

$B_5H_5^{2-}$ and $1,5\text{-}C_2B_3H_5$. The LMO's for $B_5H_5^{2-}$ are given in Figure 1a and have threefold symmetry. However, the LMO's do not have D_{3h} symmetry and, thus, there are other equivalent molecular orbital structures related by symmetry. In contrast to the LMO structure of $B_5H_5^{2-}$, the LMO's for $1,5\text{-}C_2B_3H_5$ (Figure 1b) have a classical structure with four bonds to carbon and only three bonds (including the $B\text{-}H_t$ bond) to boron. This valence structure was predicted by Beaudet[9a] based on the long B-B basal bond. However, the B-B bond in $1,5\text{-}C_2B_3H_5$ is only slightly longer than the corresponding bond in $B_5H_5^{2-}$ and, as we have noted, this classical localization is not found in $B_5H_5^{2-}$. Since the apex-equatorial distances are comparable in both molecules, effects due to the replacement of C for B must be important in changing the localization. Thus, geometry alone cannot explain the results. In terms of topological theory, the LMO's for $B_5H_5^{2-}$ correspond to the simple TA structure (0330) show in Figure 1a, while the LMO's for $C_2B_3H_5$ do not correspond to a TA structure.

$B_6H_6^{2-}$, $1,6\text{-}C_2B_4H_6$, and $1,2\text{-}C_2B_4H_6$. The octahedral molecule $B_6H_6^{2-}$ has an interesting localization (Figure 2a) that has threefold symmetry (centers 1, 3, and 4 are related as are 2, 5, and 6). We note that there are three equivalent fractional centers. The orbitals in this highly symmetric molecule arrange themselves with four orbitals in the upper cap and three orbitals in the lower cap. As found in $B_5H_5^{2-}$ there are symmetry equivalent structures and, in general, a number of *symmetry equivalent* multiple maxima are observed on the LMO hypersurface for these polyhedral molecules. For $B_6H_6^{2-}$, there are eight such structures.

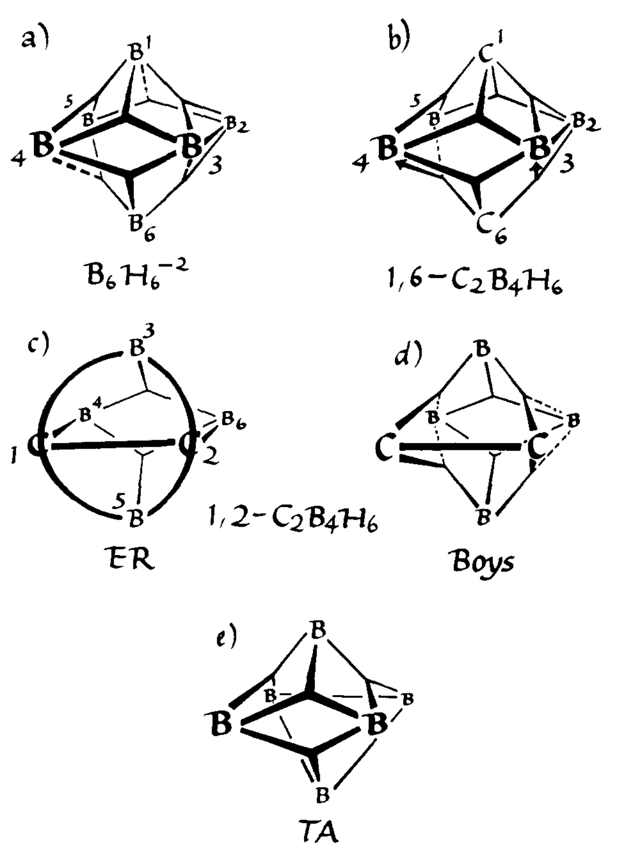

Figure 2. LMO structures for $n = 6$. Bonding conventions from ref 3 are (1) ⇢ 0.15-0.25 e, (2) → 0.25-0.35 e, (3) - - - 0.35-0.50 e, and (4) — population >0.50 e. (a) LMO's for $B_6H_6^{2-}$; (b) LMO's for $1,6\text{-}C_2B_4H_6$; (c) LMO's for $1,2\text{-}C_2B_4H_6$ as determined from the Edmiston-Ruedenberg criterion; (d) LMO's for $1,2\text{-}C_2B_4H_6$ as determined by the Boys criterion; (e) TA structure most like the LMO structures.

In Figure 2b, the LMO's for the 1,6 isomer of $C_2B_4H_6$ are shown and the LMO's are quite similar to those for $B_6H_6^{2-}$. The main differences are that the 1-2-5 fractional bond in $B_6H_6^{2-}$ has increased its contribution to the apex, and the bonding from the 6-2 and 6-4 bonds to 3 and 4, respectively, has decreased substantially. Thus the LMO's only have C_s symmetry, yet there are still only eight symmetry equivalent maxima. We note here that C(1) is a true fractional center with five bonds. Substitution of carbons in the 1,6 position has not dramatically altered the LMO's.

The LMO's for the 1,2 isomer (Figure 2d) are still quite similar. The 2-5-1 three-center bond in $B_6H_6^{2-}$ now is a C-C bond (assume that we substitute the carbons at B(2) and B(5) in Figure 2a) and the remaining LMO's change only slightly. Borons 3 and 4 remain as fractional centers and the LMO's in the top and bottom caps become equivalent and the overall LMO's exhibit the molecular symmetry. For this isomer there are no other symmetrical maxima on the LMO hypersurface. However, for this series even substitution of the carbons in adjacent positions where they form a strongly localized C-C bond does not significantly alter the localization pattern for seven orbitals distributed among the six centers in the octahedron.

The Boys and ER methods show different LMO structures for $1,2\text{-}C_2B_4H_6$. The ER structure is shown in Figure 2c, and rather than having all central three-center bonds, two open BCB bonds are found along with two B-C single bonds. These four bonds replace the four central three-center BCB fractional bonds found by the Boys method. The ER structure has a

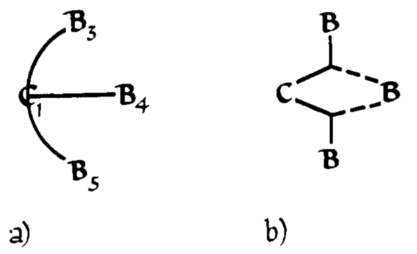

Figure 3. The possible LMO bonding patterns for a carbon and three adjacent borons: (a) LMO's from the ER criterion; (b) LMO's from the Boys criterion. Note the formal equivalence of these two structures as described in ref 2b.

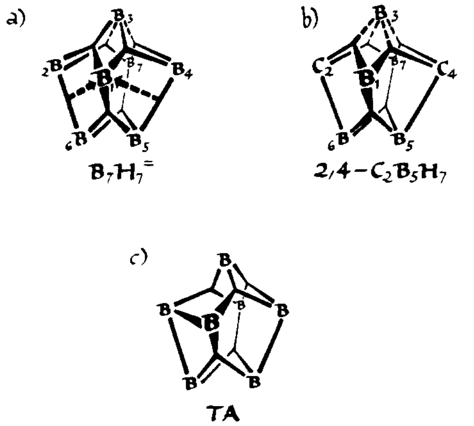

Figure 4. LMO structures for $n = 7$: (a) LMO's for $B_7H_7^{2-}$; (b) LMO's for 2,4-$C_2B_5H_7$; (c) one of the equivalent TA structures contributing to the LMO's.

higher self-energy than the Boys structure, but in the Boys structure the centroids are maximally separated. The Boys structure is a saddle point on the ER surface and vice versa. We note that the preference of Boys method for equivalent, central three-center bonds, relative to open three-center BCB bonds, is very similar to the preference of the ER method for fractional bonding relative to open three-center BBB bonds in boron hydrides. In both cases an identical geometrical configuration of four atoms is involved (Figures 3a and 3b), making possible reasonably accurate predictions of situations where open bonds might occur, if ab initio wave functions were localized by the ER method.

The relationship of the topological theory to the $C_2B_4H_6$ isomers has been previously discussed in detail.[8b] The topological structure most like the LMO's for $B_6H_6^{2-}$ is shown in Figure 2e. The single bonds of the TA structure show donation to adjacent centers in the LMO description. Thus, the LMO's are more highly delocalized in order to give a more nearly even charge distribution.

$B_7H_7^{2-}$ and 2,4-$C_2B_5H_7$. The LMO's for $B_7H_7^{2-}$, shown in Figure 4a, have only C_s symmetry as the two cap borons do not have equivalent bonding in this structure. We note that B(3) is a fractional center with less bonding from B(7) than from B(1). The B(2)-B(6) and B(4)-B(5) single bonds show some donation to B(1) and the three-center bonds involving B(1) and B(3) consequently have a larger contribution from B(3). Since the ER and Boys localizations on 2,4-$C_2B_5H_7$ had previously been reported to have C_{2v} symmetry, a careful check on the convergence of the localization using the eigenvector-following technique was made for this ion. However, only the C_s structure was found and, in fact, the C_{2v} type structure led to the C_s structure. Even though there is an absence of nonequivalent multiple maxima, there are 14 symmetry-related maxima on the LMO hypersurface.

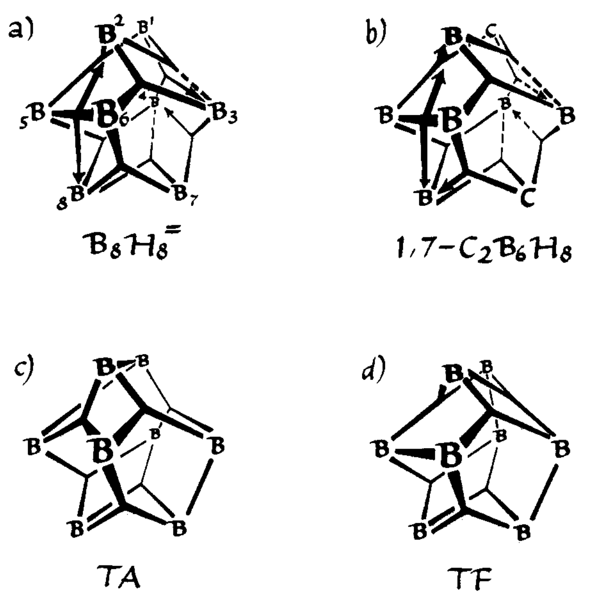

Figure 5. LMO structures for $n = 8$: (a) LMO's for $B_8H_8^{2-}$; (b) LMO's for 1,7-$C_2B_6H_8$; (c) TA structure most like the LMO's; (d) the LMO's actually correspond to this topologically forbidden (TF) structure.

The LMO's for 2,4-$C_2B_5H_7$ (Figure 4b) are similar to those of $B_7H_7^{2-}$, but have the higher molecular C_{2v} symmetry. The B-C bonds are more highly localized and do not donate significantly to the apical borons. Thus, B(1) and B(7) have the same kinds of bonds to B(3), the fractional center, and the LMO's have C_{2v} symmetry.

The relationship of the LMO's for 2,4-$C_2B_5H_7$ to the TA structures has been discussed previously.[8c] For $B_7H_7^{2-}$, a similar relationship of summing two TA structures (Figure 4c) to give the fractional center at B(3) is also found.

$B_8H_8^{2-}$ and $C_2B_6H_8$. The LMO's for $B_8H_8^{2-}$, shown in Figure 5a, are not as easy to visualize as are those in the smaller polyhedra. The LMO's show C_2 symmetry and, thus, there are four symmetry-related structures. There are four centers receiving significant amounts of donation, two equatorial and two apical. The bonds are arranged such that there are four three-center bonds in each cap and one B-B bond in the equatorial regions. The equatorial single bond is delocalized toward the apices. The LMO structure shows how the nine orbitals can best arrange themselves among eight centers with fourfold symmetry.

The LMO's for 1,7-$C_2B_6H_8$ (Figure 5b) are remarkably similar to the LMO's for $B_8H_8^{2-}$ and exhibit the C_2 symmetry of the molecule. The only modifications are that certain orbitals change in their contributions to various centers. The delocalization in the 3-7 and 1-4 bonds decreases in going to the carborane, while the 6-7-8 and 1-5-2 bonds in the carborane decrease in their contributions to 8 and 2. Substitution of the carbons in apical positions significantly lowers the symmetry of the molecule, but only minor changes are observed in the LMO's.

For $B_8H_8^{2-}$, the topological structure most like the LMO's is shown in Figure 5c. However, the LMO's actually correspond to a delocalized topologically forbidden structure in which B(3) and B(4) are not connected (Figure 5d). Thus the LMO's for $B_8H_8^{2-}$ and 1,7-$C_2B_6H_8$ do not correspond to a simple form of a topological structure.

$B_9H_9^{2-}$ and $C_2B_7H_9$. The LMO's for $B_9H_9^{2-}$ (Figure 6a) show threefold symmetry and thus there is only one other symmetry-related maximum on the hypersurface. The three borons in one triangular face are fractional centers and the other triangular face has no fractional centers; the three apical

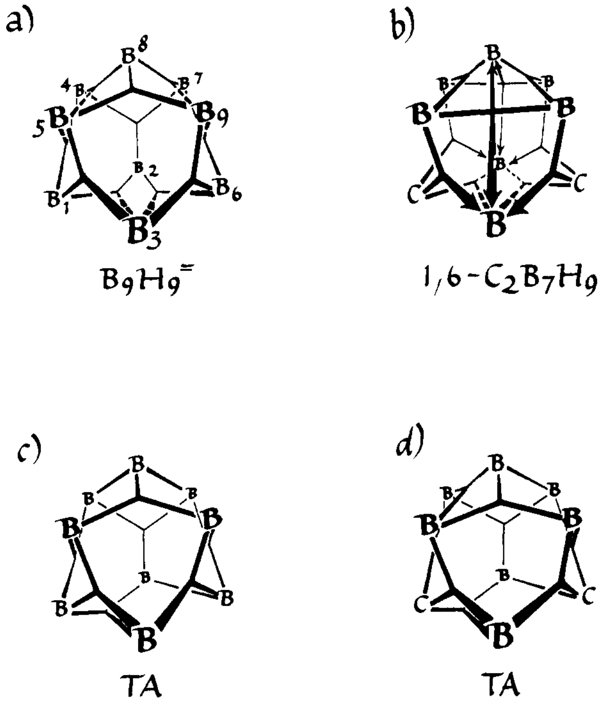

Figure 6. LMO structures for n = 9: (a) LMO's for $B_9H_9^{2-}$; (b) LMO's for 1,6-$C_2B_7H_9$; (c) TA structure for $B_9H_9^{2-}$; (d) TA structure for 1,6-$C_2B_7H_9$.

borons are also normally bonded. The fractional bonds are those that interconnect the two triangles with an apex. Normal bonds are found for bonds connecting an apex with two borons on the same triangular face.

The LMO's in $C_2B_7H_9$ (Figure 6b) are quite different from those found for $B_9H_9^{2-}$ because the introduction of the two carbons causes the molecular symmetry of $C_2B_7H_9$ to be lower than the LMO symmetry of $B_9H_9^{2-}$, and the LMO's have to change. The LMO's for $C_2B_7H_9$ have C_{2v} symmetry and the bonds show significant amounts of delocalization. The four equivalent BCB bonds show low populations on the two borons adjacent to the two carbons. This deficiency is made up by the delocalization of the B-B single bonds. Thus B(2) and B(3) are fractional centers participating in five framework bonds. The apex boron, B(8), is also a fractional center, participating in two normal BBB bonds and in delocalization from the two B-B single bonds.

As in $B_6H_6^{2-}$, the LMO's for $B_9H_9^{2-}$ correspond to a delocalized topological structure (Figure 6c). More adjustment of the TA structure occurs in order to give the high symmetry of the LMO's. The localized orbitals of $C_2B_7H_9$ correspond to a sum of four topological structures, one of which is shown in Figure 7d.

$B_{10}H_{10}^{2-}$ and $C_2B_8H_{10}$. There are two different LMO structures for $B_{10}H_{10}^{2-}$, shown in Figure 7. Both structures are relative maxima on the LMO hypersurface. Attempts to interconvert the two structures by following the $\gamma_{\max}$ eigenvector lead to symmetry-related maxima of the same type. There are eight symmetry-related structures for each structure and thus there are a total of 16 truncated LMO structures that describe the total density of $B_{10}H_{10}^{2-}$. The structures are described as 4,4,3 and 3,5,3 structures depending on the number of bonds which join the apices to the equatorial borons (first and third integers) and the number joining the two equatorial rings (second integer). Both structures have only C_s symmetry. The 3,5,3 structure has three delocalized single bonds and five fractional centers, all of which are equatorial borons. We also note that two of the three single bonds join the equatorial rings. The 4,4,3 structure has only one single bond which connects an apical boron to an equatorial ring. There are only four fractional centers, one apical boron and three equatorial. As in the 3,5,3 structure, one fractional center has five framework bonds.

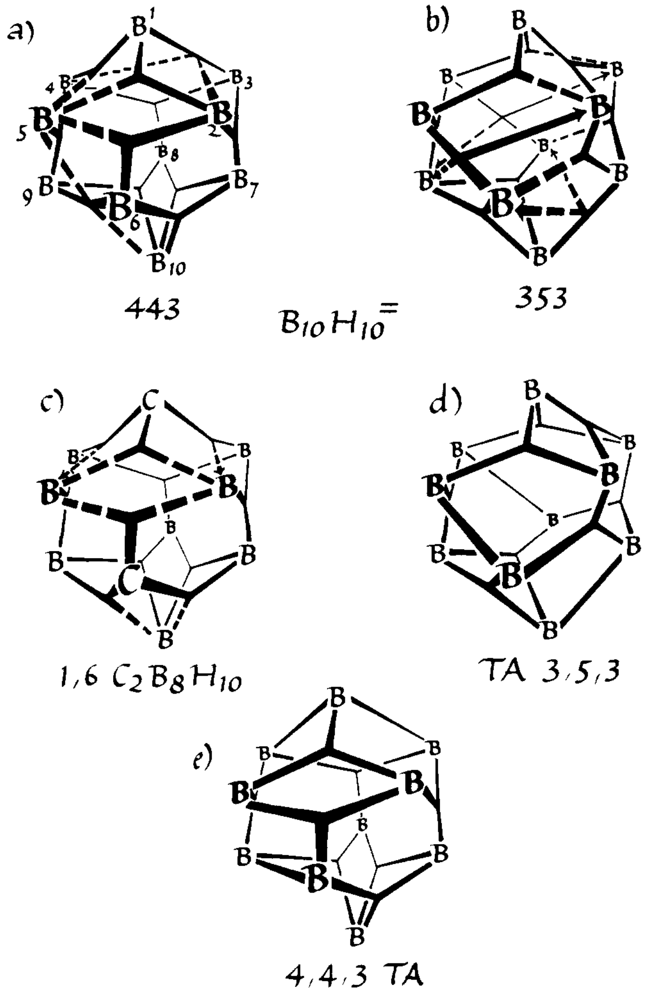

Figure 7. LMO's for n = 10: (a) LMO's for $B_{10}H_{10}^{2-}$, 4,4,3 structure; (b) LMO's for $B_{10}H_{10}^{2-}$, 3,5,3 structure; (c) LMO's for 1,6-$C_2B_8H_{10}$; (d) TA structure most like the 3,5,3 LMO structure; (e) TA structure most like the 4,4,3 LMO structure.

The carborane 1,6-$C_2B_8H_{10}$ has the carbons arranged in C_s symmetry and thus the LMO's could be the same as in $B_{10}H_{10}^{2-}$. However, the LMO's for 1,6-$C_2B_8H_{10}$ (Figure 7c) are somewhat different. A 3,4,4 structure with C_s symmetry is found. However, in this structure only three fractional centers are found with one at the apex. The major change in going from $B_{10}H_{10}^{2-}$ to 1,6-$C_2B_8H_{10}$ is that the delocalized 1-3 bond only delocalizes to one center (2) in 1,6-$C_2B_8H_{10}$ instead of two centers. The 9-6-10 bond shows no delocalization to B(5) in 1,6-$C_2B_8H_{10}$ as it did in $B_{10}H_{10}^{2-}$. Even though the LMO's are qualitatively the same in the 4,4,3 structure of $B_{10}H_{10}^{2-}$ and 1,6-$C_2B_8H_{10}$, the plane of symmetry is different, showing the complexity of the valence bonding in these polyhedral molecules.

The topological structures for the two LMO structures are shown in Figure 7d and 7e for the 4,4,3 and 3,5,3 structures, respectively. In order to obtain the LMO's of $C_2B_8H_{10}$, two of the 4,4,3 structures must be summed.

$B_{11}H_{11}^{2-}$ and $C_2B_9H_{11}$. The LMO's for $B_{11}H_{11}^{2-}$ (Figure 8a) show that there are two centers with unique bonding arrangements. The apex is a fractional center with four framework bonds which involve two bonds containing B(2) and two bonds containing B(3). These two centers are quite close to the apex, and a strong interaction is expected. Boron B(11) has five

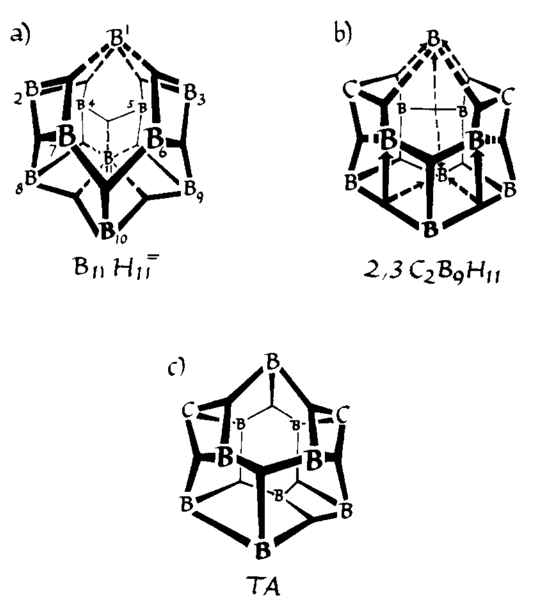

Figure 8. LMO's for n = 11: (a) LMO's for $B_{11}H_{11}^{2-}$; (b) LMO's for $2,3\text{-}C_2B_9H_{11}$; (c) TA structure most like the LMO's of $2,3\text{-}C_2B_9H_{11}$.

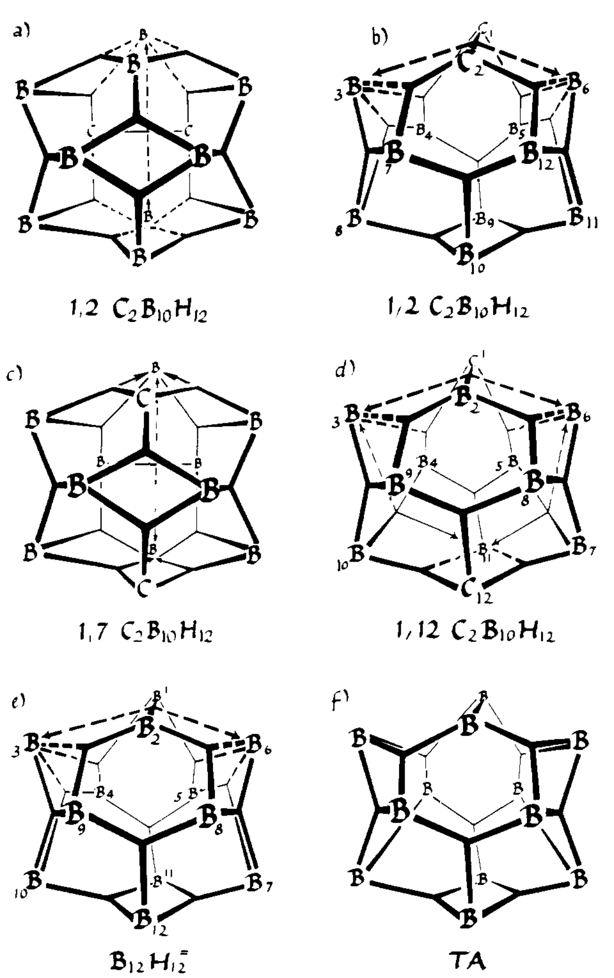

Figure 9. LMO's for n = 12: (a) LMO's for $1,2\text{-}C_2B_{10}H_{12}$; (b) rotated view of the LMO's given in Figure 9a to the same orientation as given for $1,12\text{-}C_2B_{10}H_{12}$; (c) LMO's for $1,7\text{-}C_2B_{10}H_{12}$; (d) LMO's for $1,12\text{-}C_2B_{10}H_{12}$; (e) LMO's for $B_{12}H_{12}^{2-}$; (f) basic TA structure for all the LMO's given in this figure.

framework bonds; such a fractional center with five equivalent framework bonds has been found in $B_{11}H_{13}^{2-}$. Since the molecule has C_{2v} symmetry and the LMO's have only C_s symmetry, there is another symmetry-related maximum.

Because the carbons in $2,3\text{-}C_2B_9H_{11}$ are placed so that the molecular symmetry is retained, the LMO's do not change greatly. Since the carbons that are being added (Figure 8b) have more electrons, however, the orbitals and their amounts on specific atoms change somewhat. As the carbons donate about three electrons to the framework bonds, the LMO's involved with carbon tend to force the boron atoms to have lower populations in bonds involving carbons than those found when borons are substituted at those positions. Thus, the C(2)-8-7 and C(3)-9-6 bonds have lower populations on B(7) and B(6). To account for this effect, the B(8)-B(10)-B(11) and B(9)-B(10)-B(11) bonds in $B_{11}H_{11}^{2-}$ and $C_2B_9H_{11}$ become delocalized B(8)-B(10) and B(9)-B(10) single bonds with delocalization to B(7) and B(11) and to B(6) and B(11), respectively. As a consequence the B(8)-B(4)-B(11) and B(9)-B(5)-B(11) bonds increase their density on B(11). The B(4)-B(5)-B(11) bond in $B_{11}H_{11}^{2-}$ becomes another delocalized single bond (B(4)-B(5)) with delocalization to B(11) and B(1) in $2,3\text{-}C_2B_9H_{11}$. The delocalization from this bond helps to account for the loss of density to B(1) from the C(2)-B(4)-B(1) and C(3)-B(5)-B(1). Borons 1 and 11 are still fractional centers, but the introduction of the carbons in $C_2B_9H_{11}$ has changed the quantitative aspects, although the LMO's remain qualitatively the same as in $B_{11}H_{11}^{2-}$. Again the LMO's have only C_s symmetry and another symmetry-related maximum is present.

The LMO's in $B_{11}H_{11}^{2-}$ do not correspond to a TA structure or to a sum of TA structures. The TA structure most similar to the LMO's is shown in Figure 8c. The usual combination[8c] of an adjacent B-B and BBB bond is made, giving B(11) as a fractional center. A similar combination of the 2-4 (3-5) and 1-2-7 (1-3-6) bonds is not possible as the three-center bonds in the other TA structures with 2-7 and 3-6 bonds do not remain the same. However, the possibility of such combinations suggests that B(1) should be a fractional center. In order to make B(1) a fractional center, the 4-5-1 bond becomes a 4-5-11 bond with fractional bonding to B(11) and the 2-4 and 3-5 bonds become 1-2-4 and 1-3-5 three-center bonds, giving a unique set of LMO's to this molecule. In $2,3\text{-}C_2B_9H_{11}$, the LMO's correspond to a delocalized version of the TA structure shown in Figure 8c. Substitution of carbons at the 2 and 3 positions forces the 1-2-4 and 1-3-5 bonds to be more localized between 2 and 4 and 3 and 5, having only donation from the apical boron to these bonds. The 1-4-5 bond in the TA structure, thus, becomes more like a delocalized 4-5 two-center bond with donation to B(1) and B(11).

$B_{12}H_{12}^{2-}$ and $C_2H_{10}H_{12}$. The icosahedral molecules have well-behaved localized structures. We discuss the LMO's of the ortho and meta isomers first, and then turn our attention to the more symmetrical *p*-carborane and $B_{12}H_{12}^{2-}$.

The LMO's for $1,2\text{-}C_2B_{10}H_{12}$ (Figure 9) are quite similar to the results proposed by Lipscomb.[1c] The only change is that the C-C single bond delocalizes to the two borons that are adjacent to both carbons. These borons are fractional centers, and the electron rich carbon region donates charge to these electron-deficient sites. Otherwise the bonding is quite normal. The LMO's display the C_{2v} symmetry of the molecule. Another view of the molecule is given in Figure 9b for later comparative purposes.

The LMO's for $1,7\text{-}C_2B_{10}H_{12}$ (Figure 9c) are remarkably similar to the LMO's of *o*-carborane, although the carbons are in different positions. The LMO's exhibit the same C_{2v} symmetry as found in the ortho isomer. However, as we have observed before, the quantitative aspects of the LMO's change with the introduction of the carbons. The B-B single bond delocalizes to the two fractional centers as did the C-C single bond. The fractional bonds do not show as nearly equal bonding to the fractional centers as they did in $1,2\text{-}C_2B_{10}H_{12}$, but other than this minor change the LMO's are the same. As predicted by Lipscomb[1b] the ER localization may yield a combination of open BCB bonds and B-C bonds rather than four central BCB bonds with fractional centers. The relationship is the same as found for 1,2-$C_2B_4H_6$.

The 1,12 isomer (Figure 9d) rapidly converges to an LMO structure that exhibits C_s symmetry, giving a total of ten symmetry-related maxima on the LMO hypersurface. There are three fractional centers, two in the upper pentagon and one in the lower pentagon. The three delocalized single bonds, one B-C and two B-B bonds, all donate to the fractional centers. The B-C bond connects an apex to a pentagon, while the two other B-B bonds connect the two pentagons. The 13 bonds are arranged so that three bonds connect each of the apices to the pentagons and the remaining seven bonds connect the two equatorial pentagons giving a 3,7,3 type structure. The LMO structure for the 1,12 isomer is essentially the same as for the other icosahedral carboranes (rotate the 1,2 isomer to place C(1) at an apex (Figure 9b)). The only changes are that the delocalized 4-10 and 5-7 single bonds in the 1,12 isomer become three-center fractional bonds to B(3) and B(6) and do not donate to B(11) in the 1,2 and 1,7 isomers, which gives higher symmetry to the LMO's. The 12-10-11 and 12-7-11 bonds have a higher density on B(11) in the ortho and meta isomers than in the para isomer. Thus, even though the carbons are placed in different positions, the LMO's (with a C at an apex) are all basically the same and all correspond to a 3,7,3 type structure.

The LMO structure for $B_{12}H_{12}^{2-}$ (Figure 9e) has the same structure as that found for the 1,2-$C_2B_{10}H_{12}$ isomer. Thus the structure has C_{2v} symmetry and there are three fractional centers. Again this is basically a 3,7,3 structure. There are 30 equivalent structures showing the large number of valence structures needed to describe the density.

The topological structure most like the LMO's for $B_{12}H_{12}^{2-}$ is shown in Figure 9f. The LMO's for this molecule and the carborane isomers are delocalized versions of this structure.

Conclusions

We have examined the electronic structure of the closo boron hydride dianions and the closo carboranes in terms of both canonical (CMO's) and localized molecular orbitals. The value of the CMO's lies in examining molecular properties such as ionization potentials and reactivity sites based on charges. For example, the charge predictions show that the preferred positions of carbons occur at sites in the corresponding boron hydride that have the highest negative charge or valency in agreement with simple predictions.

The use of LMO's allows us to examine the relationship of these rigorously defined valence structures to the simple valence bond structures predicted by the topological theory. The LMO's in general correspond to delocalized topological structures or to sums of TA structures. In the first case, the TA structures are delocalized in order to give a more nearly even charge distribution. For the second case, the summing of different TA structures is necessary to give fractional centers and a certain symmetry to the LMO's. The summing of structures necessary to give the LMO's follows the prescriptions given by Marynick and Lipscomb[8c] for 2,4-$C_2B_5H_7$. The LMO's for 1,5-$C_2B_3H_5$ and $B_8H_8^{2-}$ do not correspond to TA structures but correspond, instead, to a "classical" structure with only three bonds to boron for 1,5-$C_2B_3H_5$ and a forbidden topological structure for $B_8H_8^{2-}$. For $B_{11}H_{11}^{2-}$ the LMO's are similar to a sum of TA structures, but the resulting fractional bonding causes a change in the remaining bonds so that the LMO's do not correspond to a delocalized TA structure or to a sum of TA structures.

In general the LMO's have a lower symmetry than does the molecule and thus a number of symmetry-equivalent multiple maxima are present on the LMO hypersurface. As in the topological theory, these various structures must be summed to give the appropriate molecular density. Each LMO diagram is described in terms of truncated localized bonds, where smaller contributions to atoms other than those connected are omitted. Hence, the sum is required in order to obtain the full molecular symmetry. Actually, if the LMO wave function is not truncated, any one of these LMO structures has a total electron density with the correct molecular symmetry. For $B_{10}H_{10}^{2-}$, however, a new type of behavior of the hypersurface was observed in that two different maxima were found on the surface each of which corresponded to a different TA structure; the two structures could not be interconverted.

Carbon substitution, even though it usually lowers the molecular symmetry and significantly changes the charge distribution, does not radically change the LMO's except for $n = 9$. Proceeding from $B_9H_9^{2-}$ to $C_2B_7H_9$, the molecular symmetry becomes lower than the symmetry of the LMO's and the LMO's consequently change so that a different TA structure becomes dominant. It is, of course, extremely satisfying that only one TA structure is needed to describe the bonding in $B_{12}H_{12}^{2-}$ and the carborane isomers.

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Addition Compounds of Alkali Metal Hydrides. 14. The Reaction of Trialkylboranes with Lithium Trialkylborohydrides

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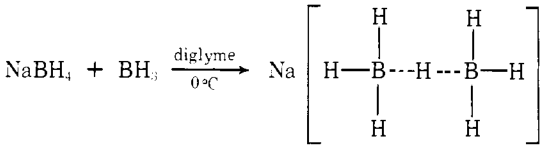
Abstract: Lithium hydride reacts with trimethylborane in solvents such as ethyl ether, *n*-butyl ether, etc., to form lithium trimethylborohydride (1:1 adduct, $\mathrm{LiMe_3BH}$). Further addition of trimethylborane does not result in the formation of lithium hexamethyldiborohydride [1:2 adduct, $\mathrm{LiMe_3BHBMe_3}$]. However, in solvents such as tetrahydrofuran, monoglyme, diglyme, etc., the corresponding reaction gives either lithium trimethylborohydride or lithium hexamethyldiborohydride, depending upon the amount of trimethylborane. The following explanation nicely accounts for this major effect of solvent upon the reaction course. In solvents such as ethyl ether, which are relatively poor solvating media for the lithium ion, the borohydride anion must be strongly associated with the lithium ion and is thus not free to add the additional trialkylborane. However, in solvents such as tetrahydrofuran, which solvate lithium ion strongly, the association is much weaker if it occurs at all. Then borohydride anions are relatively free to interact with trialkylboranes to form 1:2 addition compounds. The rates of reductions of alkyl halides with lithium triethylborohydride in various solvents, together with infrared and ^{11}B NMR studies, strongly support the above results and interpretations.

Addition compound formation between sodium borohydride and borane was first discovered[2] in 1957. It was observed that sodium borohydride solution in diethylene glycol dimethyl ether (diglyme) would absorb 1 molar equiv of borane to give a 1:1 stable adduct, $\mathrm{NaBH_4{\cdot}BH_3}$ ($\mathrm{NaB_2H_7}$). The formation of $\mathrm{NaB_2H_7}$ was found to be highly solvent dependent and failed to occur in ethyl ether or tetrahydrofuran (THF). The bonding in such adducts is believed to be related to the bonding in other electron-deficient compounds, such as trimethylaluminum dimer, diborane, etc.[3] A structure involving a single hydrogen bridge between the two boron atoms was proposed for this compound (eq 1).



$$\mathrm{NaBH_4} + \mathrm{BH_3} \xrightarrow[0\,^\circ\mathrm{C}]{\text{diglyme}} \mathrm{Na}\left[\begin{array}{ccccc} & \mathrm{H} & & \mathrm{H} & \\ & | & & | & \\ \mathrm{H}— & \mathrm{B} & \cdots\mathrm{H}\cdots & \mathrm{B} & —\mathrm{H} \\ & | & & | & \\ & \mathrm{H} & & \mathrm{H} & \end{array}\right] \qquad (1)$$

Since this first observation, the topic of single hydrogen bridged boron compounds has been the subject of numerous investigations.[4] Recent developments in our laboratory have led to the development of a number of modified borohydrides, particularly trialkylborohydrides. A number of these have emerged as highly attractive reducing agents.[5] Unlike the parent borohydride, trialkylborohydrides have only one B-H bond, and are far more powerful reducing agents. Consequently, it was of interest to examine the interactions between trialkylborohydride and trialkylborane.

Accordingly, we undertook to examine lithium trimethylborohydride-trimethylborane and lithium triethylborohydride-triethylborane systems by means of various physical and chemical tools, such as vapor pressure-composition studies, chemical reactivity studies, infrared, ^{11}B NMR, etc. The systems were examined in various solvents, such as ethyl ether, tetrahydrofuran, monoglyme, diglyme, and benzene, to understand the influence of solvents on the adduct formation. The results of this investigation are reported in the present paper.

Results and Discussion

Vapor Pressure Composition Studies. (A) Lithium Hydride–Trimethylborane–Ethyl Ether System. It has been recognized earlier that trimethylborane reacts with lithium hydride in the presence of ethyl ether either at 0 or −80 °C to form the 1:1 complex, lithium trimethylborohydride (Figure 1).[6] Further addition of trimethylborane did not result in the uptake of additional trimethylborane as required for the formation of lithium hexamethyldiborohydride.

$$\mathrm{LiH + Me_3B \rightarrow LiMe_3BH} \qquad (2)$$

$$\mathrm{LiMe_3BH + Me_3B \nrightarrow LiH{\cdot}2Me_3B} \qquad (3)$$

Similar results were realized in *n*-butyl ether.

(B) Lithium Hydride–Trimethylborane–Tetrahydrofuran System. Lithium hydride reacts with trimethylborane in the presence of tetrahydrofuran at 0 °C to form the 1:1 complex, lithium trimethylborohydride. Here, additional trimethylborane is taken up, leading to the formation of a 1:2 complex, lithium hexamethyldiborohydride.

$$\mathrm{LiH + Me_3B \xrightarrow[0\,^\circ C]{THF} LiMe_3BH} \qquad (4)$$

$$\mathrm{LiMe_3BH + Me_3B \rightarrow LiH{\cdot}2Me_3B} \qquad (5)$$

The results, summarized in Table I and Figure 2, clearly in-

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