Table VI. Mulliken Population Analyses of $Pt(PH_3)_2$–C_2H_4 over the Molecular Orbitals on C_2H_4 and $Pt(PH_3)_2$ in the Two Conformations

conformation	populations					
	$8a_1$	π	$1b_1$	$2b_1$	$1b_2$	π^*
6	0.20	1,82	1.96	1.60	2.00	0.43
7	0.18	1.84	2.00	2.00	1.76	0.21

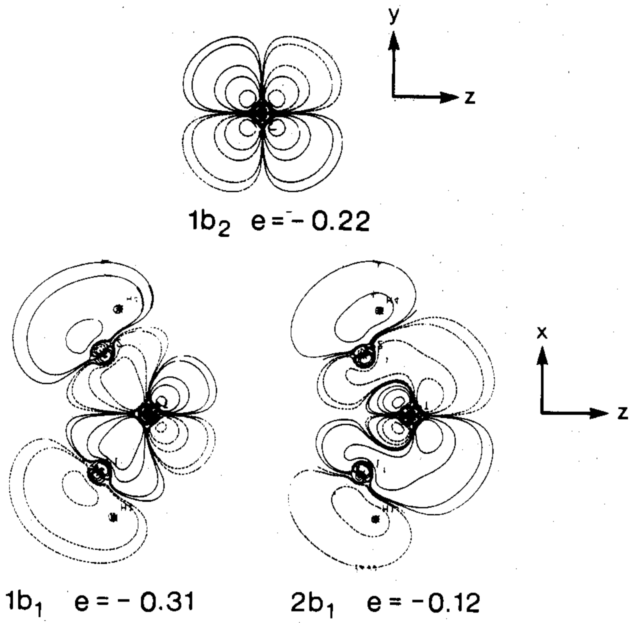

Figure 11. Shapes and orbital energies (in combined complex) of $1b_1$, $2b_1$, and $1b_2$. The orbital energy of π^* in the combined complex is –0.12 au.

involved in the two conformations confirm the descriptive account presented above and show a larger charge transfer from $2b_1$ to π^* in conformation **6** than from $1b_2$ to π^* in conformation **7**. The extent of the charge transfer in the former case (**6**) is graphically illustrated by the electron density difference map shown in Figure 10b.

In summary, the preferred conformation of ethylene in the d^8 system, Zeise's salt, $PtCl_3^-$–C_2H_4, in which the double bond is perpendicular to the $PtCl_3^-$ plane, **5**, arises largely as a consequence of dominant steric repulsions which are minimized in this conformation. The steric effects outweigh the bonding interactions, σ donation and π back-donation, both of which are more favorable for the in-plane conformation **4**. In the d^{10} system $Pt(CH_3)_2$–C_2H_4, the planar conformation **6** is preferred as a consequence of more favorable π back-donation. The steric interaction and σ donation are energetically very similar for the two conformations **6** and **7**.

Conclusions similar to ours have been developed independently by Hoffmann and co-workers[1] and by Norman.[11]

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Registry No. Cu^+-C_2H_4, 60203-82-9; Ag^+-C_2H_4, 35827-90-8; Au^+-C_2H_4, 69596-89-0; $PtCl_3^-$-C_2H_4, 12275-00-2; $Pt(PH_3)_2$-C_2H_4, 31941-73-8.

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Molecular Orbital Studies of *nido*-Beryllaboranes, $B_5H_{10}BeX$, Where X Is BH_4, B_5H_{10}, CH_3, or C_5H_5

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Molecular orbital studies are presented at the minimum basis set level for the beryllaboranes $B_5H_{10}BeBH_4$, $B_5H_{10}BeB_5H_{10}$, $B_5H_{10}BeCH_3$, and $B_5H_{10}BeC_5H_5$. The method, nearly at the SCF level, employs the PRDDO (partial retention of diatomic differential overlap) program. The bonding is analyzed in terms of charge stability, static reactivity indices, degrees of bonding, overlap populations, and fractional bonds obtained from localized molecular orbitals by using the criterion of Boys. The bonding within B_5H_{10} units is remarkably similar, although bonding about Be in $B_5H_{10}BeC_5H_5$ differs significantly from that in the other compounds. The relationships of these studies to the NMR spectra and to related chemistry are briefly indicated.

Introduction

The high toxicity of beryllium compounds[1] has limited studies in a very promising area of chemistry. Nevertheless, in the past decade a number of new beryllaboranes have been

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described. In most of these compounds, Be and B are linked through BeHB bridges,[2] including some direct Be···B bonding. However, a new area of chemistry is suggested by the closo structures[3] $B_9C_2H_{11}BeL$, where L is $O(C_2H_5)_2$ or $N(CH_3)_3$, and by the nido structures[4] $B_5H_{10}BeX$, where X is BH_4, B_5H_{10}, CH_3, C_5H_5, Cl, or Br. We present here theoretical studies of the first four of these nido structures of $B_5H_{10}BeX$ compounds.

The nature of electron-deficient bonding is particularly acute when beryllium is incorporated in the closo or nido framework of the boranes, because each Be supplies one less electron than does each B atom. While studies of localized molecular orbitals (LMO's) have supported three-center bond approximations to bonding, they have added the concept of fractional bonding as a consistent additional delocalization in boron hydrides and carboranes.[5,6] The expectation that bonding becomes even more fractional when Be is included, already indicated in $Be(BH_4)_2$[2a,7] and $Be(C_5H_5)_2$,[8] is clearly indicated by our results as described below. We shall show that the bonding in the B_5H_{10} regions is remarkably similar in these four $B_5H_{10}BeX$ compounds and that the bonding of π-C_5H_5 to the $B_5H_{10}Be$ fragment differs significantly from the bonding of BH_4, B_5H_{10}, or CH_3 to this fragment.

Calculations and Results

The molecules are shown in Figure 1, where the numbering system, approximate geometry, and final results of bonding are also presented. Calculations were carried out by the PRDDO (partial retention of diatomic differential overlap) method,[9] which closely approximates the minimum basis SCF level.

For $B_5H_{10}BeBH_4$ and $B_5H_{10}BeB_5H_{10}$ the coordinates[4b] were symmetrized to molecular symmetries of C_s and C_2, respectively. These symmetrizations, which were shown to have negligible effects on the results, gave the coordinates in Table I.

The orbital exponents of Table II gave the energies listed in Table III. Pople exponents[10] (set B) gave energies which were considerably lower than those for Slater exponents (set A) for B and Be, probably because of contraction[11,12] of orbitals upon formation of these stable neutral molecules. All subsequent optimizations of exponents gave smaller improvements. Set C is that used earlier for $Be(BH_4)_2$.[7a] For $B_5H_{10}BeBH_4$ all exponents were optimized subject to the equality of 2s and 2p exponents for a type of atom (set E), yielding some additional contraction of the valence shell of B, and considerably more contraction for Be. Set D is an intermediate result for $B_5H_{10}BeBH_4$. For $B_5H_{10}BeB_5H_{10}$ the valence shell exponents of B and Be were reoptimized (set F), while other exponents were those of set E. Here, the B exponent did not change, while the Be exponent decreased considerably (set F). In general terms, the change of environment of Be results in large changes of its exponent, while even small changes in the valence shell exponent for B make relatively large changes in energy because of the relatively large number of boron atoms. Although optimization of exponents within the PRDDO approximation usually gives exponents which differ from SCF exponents by 0.1–0.2 au,[9] the extremely large exponent for Be is not an artifact of this approximation but occurs because of the very large positive charge on Be.

The $B_5H_{10}BeCH_3$ structure was assigned C_s symmetry and given the staggered configuration (Figure 1c). A rigid tetrahedral CH_3 group with bond angle 109.5° and CH distance 1.09 Å was assumed. Optimization was carried out on the coordinates of Be, H(7), H(11), and the methyl group and on the valence shell exponents of Be, C, and methyl hydrogen atoms. Convergence was found to a very flat minimum in these coordinates (Table I) and to a sharp minimum in the exponents (set G, Table II). Both Be and CH_3 moved toward the reader, and the local C_{3v} axis of the CH_3 group no longer passes through Be.

Table I. Coordinates (au)

atom	*x*	*y*	*z*
	$B_5H_{10}BeBH_4$ (C_s)		
B(1)	2.22995	0.0	1.77356
Be	5.63852	0.0	0.00001
B(3)	3.15022	2.78050	0.09498
B(4)	0.0	1.63595	0.0
B(5)	0.0	−1.63595	0.0
B(6)	3.15022	−2.78050	0.09498
B(7)	9.22048	0.0	0.49803
H(1)	2.09525	0.0	3.78691
H(3)	3.43094	4.54905	0.99839
H(4)	−1.57843	2.65979	0.69758
H(5)	−1.57843	−2.65979	0.69758
H(6)	3.43094	−4.54905	0.99839
H(7)	4.63442	2.39654	−1.44223
H(8)	1.36957	2.98920	−1.40288
H(9)	−0.62592	0.0	−1.62601
H(10)	1.36957	−2.98920	−1.40288
H(11)	4.63442	−2.39654	−1.44223
H(12)	7.57761	0.0	1.93974
H(13)	8.11440	0.0	−1.40652
H(14)	10.28989	−1.76148	0.72950
H(15)	10.28989	1.76148	0.72950
	$B_5H_{10}BeB_5H_{10}$ (C_2)		
Be	12.86806	0.48091	−13.06050
B(1)	13.60165	2.42637	−16.37600
B(3)	11.91111	−0.46878	−16.74779
B(4)	14.06456	0.61384	−19.06242
B(5)	16.63356	2.11301	−17.65127
B(6)	16.25288	1.97736	−14.31636
B(1′)	12.48442	2.16080	−9.54677
B(3′)	13.58783	−1.02653	−9.50756
B(4′)	11.65636	0.19041	−7.06720
B(5′)	9.43527	2.29550	−8.28127
B(6′)	9.81784	2.45082	−11.61510
H(1)	12.78648	4.23304	−16.58622
H(3)	9.94974	−0.50417	−17.44130
H(4)	13.40069	1.10902	−20.98296
H(5)	17.64756	3.48915	−18.74337
H(6)	17.03468	3.60734	−13.18289
H(7)	12.39393	−1.89019	−15.16344
H(8)	13.32907	−1.60783	−18.42628
H(9)	16.45551	0.11662	−18.90399
H(10)	17.88612	1.20709	−15.90602
H(11)	16.14284	0.10513	−13.28775
H(1′)	13.62695	3.74536	−9.15112
H(3′)	15.49911	−1.51003	−8.84243
H(4′)	12.38241	0.33946	−5.11144
H(5′)	8.69097	3.71359	−7.03638
H(6′)	9.37311	4.31272	−12.55764
H(7′)	12.85934	−2.15014	−11.23108
H(8′)	11.96124	−2.04878	−7.94725
H(9′)	9.21624	0.17837	−7.25347
H(10′)	8.05119	1.83903	−10.10102
H(11′)	9.57953	0.71425	−12.84105
	$B_5H_{10}BeCH_3$ (C_s)[a]		
Be	5.62547	0.0	0.38870
H(7)	4.72564	2.35856	−1.48722
H(11)	4.72564	−2.35856	−1.48722
C	8.56880	0.0	1.05837
H(12)	9.00215	1.68216	2.16539
H(13)	9.00215	−1.68216	2.16539
H(14)	9.69928	0.0	−0.66355
	$B_5H_{10}BeC_5H_5$ (C_s)[a]		
Be	5.63852	0.0	0.42000
C(1)	8.86866	0.0	−1.14796
C(2)	8.64991	2.16333	0.40850
C(3)	8.29598	1.33701	2.92689
C(4)	8.29598	−1.33701	2.92689
C(5)	8.64991	−2.16333	0.40850
H(12)	9.15533	0.0	−3.18776
H(13)	8.73850	4.12236	−0.22184
H(14)	8.06405	2.54776	4.57712
H(15)	8.06405	−2.54776	4.57712
H(16)	8.73850	−4.12236	−0.22184

[a] Atoms not listed are given the same coordinates as those in the appropriate fragment of $B_5H_{10}BeBH_4$.

Table II. Exponents for Orbitals

Set A	
Be_{1s}	3.7
Be_{2s}	0.975
Be_{2p}	0.975
B_{1s}	4.7
B_{2s}	1.3
B_{2p}	1.3
H	1.2

Set B	
Be_{1s}	3.68
Be_{2s}	1.10
Be_{2p}	1.10
B_{1s}	4.68
B_{2s}	1.45
B_{2p}	1.45
H	1.24

Set C[a]	
Be_{1s}	3.7
Be_{2s}	1.24
Be_{2p}	1.24
B_{1s}	4.688
B_{2s}	1.44
B_{2p}	1.45
$B-H_t$	1.13
$B-H_b-B$	1.209
$B-H_b-Be$	1.10

Set D[b]	
Be_{2s}	1.24
Be_{2p}	1.24

Set E[a]	
Be_{1s}	3.7
Be_{2s}	1.5
Be_{2p}	1.5
B_{1s}	4.688
B_{2s}	1.514
B_{2p}	1.514
$B-H_t$	1.11
$B-H_b-B$	1.169
$B-H_b-Be$	1.08

Set F[b]	
Be_{2s}	1.31
Be_{2p}	1.31

Set G[a,b]	
Be_{2s}	1.389
Be_{2p}	1.389
C_{1s}	5.67263
C_{2s}	1.69
C_{2p}	1.69
$C-H_t$	1.13

Set H[a,b]	
Be_{2s}	1.18
Be_{2p}	1.18
C_{1s}	5.67263
C_{2s}	1.72
C_{2p}	1.72
$C-H_t$	1.13

[a] When more than one atom is listed, the exponent belongs to H. [b] Exponents not listed are taken from set E.

The barrier to rotation of the methyl group was found to be only 0.9 kcal/mol, in a calculation at angles of 15, 30, 45, and 60° from the orientation shown in Figure 1c. The distances between the hydrogens of the BeH_bB bridges and those of the CH_3 group decreased from 2.945 to 2.701 Å in this rotation of 60° from the staggered to the eclipsed conformation. Because no further optimizations were made in this study, it is possible that the barrier is even smaller than 0.9 kcal/mol.

In $B_5H_{10}BeC_5H_5$, the C_5H_5 group was taken as rigid, and C–H distances were set at 1.09 Å and C–C distances at 1.415 Å.[13] The exponent for H is the same as that assumed above for H in CH_3. Within the further constraints of C_s symmetry and a staggered configuration of C_5H_5 relative to the BeH_bB hydrogen bridges (Figure 1d), a limited optimization was made of the coordinates of the C_5H_5 group, the z coordinate of Be, and the valence shell exponents of Be and C. Here, no study was made of the rotational barrier, which is expected to be very small. Throughout these optimizations the C_5H_5 group remained as a π-bonded η^5 [14] ligand. There seemed to be no tendency for C(1) to approach Be much more closely than did the other C atoms, although we may have biased this tendency by maintaining a strictly planar C_5H_5 group. Edge bonding has been described in the structure of $Be(C_5H_5)_2$.[8,15] Coordinates, exponents (set H), and energetics for $B_5H_{10}BeC_5H_5$ are given in Tables I–III. Here, the environment of Be is somewhat different from that for X = BH_4, B_5H_{10}, and CH_3, as suggested by the comparatively small valence shell exponent of 1.18 for X = C_5H_5. We now turn to a more detailed analysis of these optimized wave functions, calculated for the final coordinates listed in Table I, and exponent sets E, F, G, and H of Table II for X = BH_4, B_5H_{10}, CH_3, and C_5H_5, respectively.

Discussion

Valencies, atomic charges, and inner-shell eigenvalues (Table IV) are sometimes useful as static reactivity indices, and may become useful if the reaction chemistry[4a] extends beyond substitution at Be. Here, we comment only on the information they provide about the nature of the electron distribution. The valency[16] of an atom in a molecule is defined as the sum of the degrees of bonding[16] of that atom to all other atoms. This index of covalent bonding and the atomic charges and inner-shell eigenvalues are frequently correlated: the more negative the atomic charge, the less negative is the inner-shell eigenvalue because of repulsion between these valence and inner-shell electrons. If correlation corrections (not included here) are made, the inner-shell eigenvalues become observables,[11] although atomic charges and valencies are less directly related to experiment.

The charge on Be is highly positive (close to +1 for X = BH_4) for the three ligands BH_4, B_5H_{10}, or CH_3 but slightly negative for X = C_5H_5 (comparable to structure II of ref 8 for $Be(C_5H_5)_2$). The order of charges on Be is also consistent with the order of exponents for the valence shell of Be, smallest for set H and largest for set E. Also, the valency of Be is smallest in $B_5H_{10}BeBH_4$ and largest in $B_5H_{10}BeC_5H_5$, while the other two compounds have intermediate values closer to that in $B_5H_{10}BeBH_4$. Thus, also by this valency criterion, Be is more covalently bonded in $B_5H_{10}BeC_5H_5$ than in the other three compounds.

Of the boron atoms, B(1) is always negative, and B(4) and B(5) are always positive, while B(3) and B(6) have intermediate charges. To a good approximation, the more negative boron atoms have a larger valency, an indication that the additional electron density is largely involved in the bonding regions.

Charges on terminal (t) and bridge (b) hydrogen atoms generally follow the order $q(H_t,B) < q(H_b,BBe) < 0 < q(H_t,C) < q(H_b,BB)$. The one exception is in $B_5H_{10}BeBH_4$, where,

Table III. Energetics[a]

structure	set	NRE[b]	KE[c]	NAE[d]	ERE[e]	E[f]	VR[g]	$\lvert\Delta E\rvert$[h]
$B_5H_{10}BeBH_4$ (C_s)	A	233.190	170.416	−852.009	278.005	−170.398	1.000	
	B	233.190	171.816	−857.208	281.627	−170.575	0.993	0.177
	C	233.190	171.198	−854.938	279.948	−170.602	0.997	0.027
	D	233.190	171.679	−855.710	280.204	−170.637	0.994	0.035
	E	233.190	171.812	−855.986	280.335	−170.649	0.993	0.012
$B_5H_{10}BeB_5H_{10}$ (C_2)	A	479.899	272.029	−1578.272	553.872	−272.472	1.002	
	B	479.899	274.276	−1586.422	559.555	−272.692	0.994	0.220
	C	479.899	273.520	−1583.170	557.023	−272.729	0.997	0.037
	E	479.899	274.573	−1584.686	557.457	−272.757	0.993	0.028
	F	479.899	274.431	−1584.511	557.412	−272.769	0.994	0.012
$B_5H_{10}BeCH_3$ (C_s)	G	233.800	184.233	−888.682	287.383	−183.266	0.995	
$B_5H_{10}BeC_5H_5$ (C_s)	H	518.219	336.139	−1811.963	621.922	−335.683	0.999	

[a] All energies are in au. [b] Nuclear repulsion energy. [c] Kinetic energy. [d] Nuclear attraction energy. [e] Electron repulsion energy. [f] Total energy. [g] Virial ratio ($-E/T$). [h] Absolute value of the difference in the energies of two successively listed calculations for the same structure.

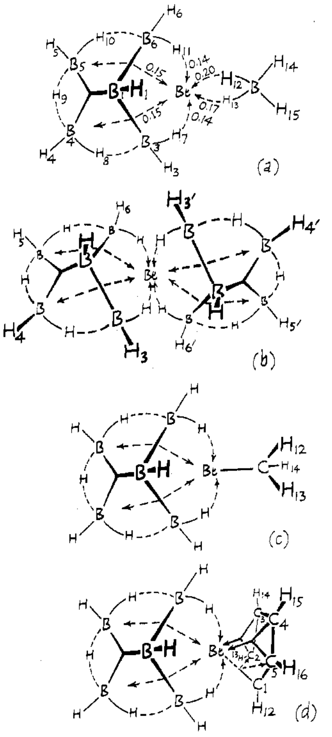

Figure 1. The molecules examined, the numbering systems used, and the LMO structures: (a) $B_5H_{10}BeBH_4$, (b) $B_5H_{10}BeB_5H_{10}$, (c) $B_5H_{10}BeCH_3$, (d) $B_5H_{10}BeC_5H_5$. The numbering of the $B_5H_{10}Be$ fragment,[4] which is the same for all four molecules, is only shown for $B_5H_{10}BeBH_4$. Bond notation in the LMO structures: —, >0.50 e; - - -, 0.36–0.50 e; →, 0.26–0.35 e; - - ->, 0.09–0.25 e. In (a) we show electron donations along dotted arrows in the six fractional bonds to Be.

on the average, $q(H_b,BBe) < q(H_t,B)$. A qualification is that there is some difficulty in comparing charge allocation for H_t, bonded to one atom, with that for H_b, bonded to two atoms. Nevertheless, these trends are consistent with the exponents (sets E and G). Thus, the less electronegative the atom to which H is attached, the more negative is the H itself as the electrons shift toward this H atom. Consequently, the $H_b(BBe)$'s are more negative than the acidic $H_b(BB)$'s.

Overall charges on the ligands X are −0.16 to −0.21 for B_5H_{10}, −0.48 for BH_4, −0.22 for CH_3, and +0.17 for C_5H_5, again placing the C_5H_5 group in a different category. The BH_4 group is comparatively anionic in this analysis.

The less negative inner-shell eigenvalues are well correlated with the more negatively charged atoms, although exceptions can be found for Be and B when different molecules are compared.

The gap between the highest occupied and lowest unoccupied molecular orbitals is 0.546, 0.521, 0.545 and 0.459 au for X = BH_4, B_5H_{10}, CH_3, and C_5H_5, respectively. These large values are indicative of some resistance to oxidation or reduction. The charge stability for the $B_5H_{10}BeC_5H_5$ is somewhat less than that for the other three compounds.

Trends in degrees of bonding and overlap populations (Table V) are parallel and indicate in a striking way the near constancy of bonding in the $B_5H_{10}Be$ unit among these four compounds. The largest variations occur in the Be–B(1) bond and in the molecule $B_5H_{10}BeC_5H_5$. Within the $B_5H_{10}Be$ unit, the bond strengths are in the order (B(1)–B(3)) > (B(1)–B(4)) > (B(4)–B(5)) > (B(3)–B(4)) > (Be–B(1)) > (Be–B(3)). The B–H_t bonds are stronger than the B–H_b fragment of B–H_b–Be bonds, and this fragment is stronger than the B–H_b fragment of B–H_b–B bonds. The extreme relative weakness of the Be–H_b fragment is due to the electronegativity difference between B amd Be. Also, this Be–H_b fragment in these molecules has a much smaller overlap population than that (0.310) calculated[2a] for the doubly bridged structure of $Be(BH_4)_2$. With respect to bonds involving C, the σ bond between Be and C in $B_5H_{10}BeCH_3$ is a strong single bond, and the C–C bonds in the C_5H_5 unit of $B_5H_{10}BeC_5H_5$ have an

Table IV. Atomic Charges, Valencies, and Inner-Shell Eigenvalues

atom[a]	AC[b]	V[c]	ISE[d]
	$B_5H_{10}BeBH_4$ (C_s)		
B(1)	−0.121	3.774	−7.525
Be	0.685	2.176	−4.762
B(3)	−0.014	3.673	−7.613
B(4)	0.144	3.585	−7.671
B(7)	−0.045	3.702	−7.534
H(1)	−0.094	0.991	
H(3)	−0.074	0.994	
H(4)	−0.065	0.996	
H(7)	−0.067	0.996	
H(8)	0.058	0.997	
H(9)	0.039	0.998	
H(12)	−0.099	0.990	
H(13)	−0.122	0.985	
H(14)	−0.105	0.989	
	$B_5H_{10}BeB_5H_{10}$ (C_2)		
Be	0.424	2.488	−4.744
B(1)	−0.109	3.768	−7.501
B(3)	0.048	3.640	−7.595
B(4)	0.145	3.592	−7.640
B(5)	0.106	3.621	−7.633
B(6)	0.037	3.640	−7.584
H(1)	−0.094	0.991	
H(3)	−0.093	0.991	
H(4)	−0.080	0.994	
H(5)	−0.078	0.994	
H(6)	−0.088	0.992	
H(7)	−0.073	0.995	
H(8)	0.047	0.998	
H(9)	0.036	0.999	
H(10)	0.054	0.997	
H(11)	−0.069	0.995	
	$B_5H_{10}BeCH_3$ (C_s)		
B(1)	−0.120	3.776	−7.509
Be	0.402	2.387	−4.613
B(3)	0.024	3.658	−7.596
B(4)	0.142	3.588	−7.659
C	−0.263	3.905	−11.127
H(1)	−0.096	0.991	
H(3)	−0.083	0.993	
H(4)	−0.068	0.995	
H(7)	−0.071	0.995	
H(8)	0.054	0.997	
H(9)	0.040	0.998	
H(12)	0.015	1.000	
H(14)	0.008	1.000	
	$B_5H_{10}BeC_5H_5$ (C_s)		
B(1)	−0.075	3.757	−7.492
Be	−0.008	2.991	−4.660
B(3)	0.020	3.657	−7.562
B(4)	0.126	3.604	−7.627
C(1)	−0.005	3.988	−11.218
C(2)	0.023	3.991	−11.223
C(3)	0.020	3.992	−11.221
H(1)	−0.098	0.990	
H(3)	−0.094	0.991	
H(4)	−0.080	0.994	
H(7)	−0.036	0.999	
H(8)	0.053	0.997	
H(9)	0.033	0.999	
H(12)	0.014	1.000	
~~H(13)~~	~~0.020~~	~~1.000~~	
H(14)	0.019	1.000	

[a] Only unique atoms are listed. [b] Atomic charge in electrons. [c] Valency. [d] Inner-shell eigenvalue for B, Be, or C in au.

Table V. Unique Bonds

bond	BL[a]	DOB[b]	OP[c]
$B_5H_{10}BeBH_4$ (C_s)			
Be-B(1)	2.033	0.291	0.244
Be-B(3)	1.975	0.282	0.194
Be-B(7)	1.914	0.326	0.149
B(1)-B(3)	1.786	0.658	0.538
B(1)-B(4)	1.739	0.568	0.444
B(3)-B(4)	1.774	0.452	0.329
B(4)-B(5)	1.731	0.534	0.403
B(1)-H(1)	1.068	0.976	0.815
B(3)-H(3)	1.061	0.978	0.836
B(4)-H(4)	1.062	0.979	0.843
B(7)-H(14)	1.097	0.971	0.814
Be-H(7)	1.573	0.199	0.120
Be-H(12)	1.451	0.286	0.219
Be-H(13)	1.507	0.240	0.189
B(3)-H(7)	1.149	0.755	0.633
B(3)-H(8)	1.236	0.467	0.360
B(4)-H(8)	1.261	0.487	0.425
B(4)-H(9)	1.265	0.479	0.383
B(7)-H(12)	1.157	0.686	0.556
B(7)-H(13)	1.165	0.718	0.583
$B_5H_{10}BeB_5H_{10}$ (C_2)			
Be-B(1)	2.071	0.344	0.317
Be-B(3)	2.078	0.260	0.191
Be-B(6)	2.068	0.269	0.198
B(1)-B(3)	1.785	0.628	0.513
B(1)-B(4)	1.732	0.570	0.449
B(1)-B(5)	1.748	0.566	0.443
B(1)-B(6)	1.792	0.627	0.508
B(3)-B(4)	1.768	0.469	0.350
B(4)-B(5)	1.742	0.512	0.387
B(5)-B(6)	1.778	0.454	0.333
Be-H(7)	1.696	0.169	0.097
Be-H(11)	1.748	0.142	0.066
B(3)-H(7)	1.155	0.777	0.668
B(3)-H(8)	1.310	0.436	0.323
B(4)-H(8)	1.283	0.516	0.445
B(4)-H(9)	1.295	0.458	0.364
B(5)-H(9)	1.251	0.497	0.398
B(5)-H(10)	1.234	0.529	0.465
B(6)-H(10)	1.273	0.421	0.312
B(6)-H(11)	1.132	0.805	0.695
B(1)-H(1)	1.055	0.973	0.817
B(3)-H(3)	1.101	0.977	0.825
B(4)-H(4)	1.107	0.978	0.829
B(5)-H(5)	1.073	0.976	0.834
B(6)-H(6)	1.129	0.978	0.822
$B_5H_{10}BeCH_3$ (C_s)			
Be-B(1)	1.940	0.352	0.301
Be-B(3)	1.976	0.290	0.198
Be-C	1.597	0.963	0.739
B(1)-B(3)	1.786	0.630	0.517
B(1)-B(4)	1.739	0.571	0.450
B(3)-B(4)	1.774	0.456	0.330
B(4)-B(5)	1.731	0.523	0.393
B(1)-H(1)	1.068	0.972	0.811
B(3)-H(3)	1.061	0.978	0.830
B(4)-H(4)	1.062	0.979	0.842
C-H(12)	1.090	0.976	0.754
C-H(14)	1.090	0.975	0.754
Be-H(7)	1.664	0.183	0.099
B(3)-H(7)	1.202	0.770	0.653
B(3)-H(8)	1.236	0.462	0.354
B(4)-H(8)	1.261	0.494	0.430
B(4)-H(9)	1.265	0.479	0.385
$B_5H_{10}BeC_5H_5$ (C_s)			
Be-B(1)	1.941	0.384	0.362
Be-B(3)	1.982	0.279	0.185
Be-C(1)	1.900	0.397	0.242
Be-C(2)	1.962	0.328	0.193
Be-C(3)	2.059	0.319	0.160
B(1)-B(3)	1.786	0.599	0.482
B(1)-B(4)	1.739	0.573	0.457
B(3)-B(4)	1.774	0.454	0.331
B(4)-B(5)	1.731	0.523	0.397
C(1)-C(2)	1.415	1.223	0.945
C(2)-C(3)	1.415	1.294	0.973
C(3)-C(4)	1.415	1.250	0.957
B(1)-H(1)	1.068	0.967	0.813
B(3)-H(3)	1.061	0.975	0.830
B(4)-H(4)	1.062	0.977	0.834
C(1)-H(12)	1.090	0.982	0.785
C(2)-H(13)	1.090	0.984	0.790
C(3)-H(14)	1.090	0.985	0.785
Be-H(7)	1.692	0.153	0.024
B(3)-H(7)	1.202	0.793	0.734
B(3)-H(8)	1.236	0.449	0.335
B(4)-H(8)	1.261	0.506	0.449
B(4)-H(9)	1.265	0.479	0.382

[a] Bond length in Å. [b] Degree of bonding. [c] Overlap population.

average degree of bonding (1.257) characteristic of substantial aromatic character.

Localized molecular orbital (LMO) studies, which have illuminated the chemistry of the boranes and carboranes,[17c] have yielded the results shown in Figure 1 and Table VI, where we have used the criterion of Boys.[17a,b] Each LMO structure was shown by the second-derivative test[18] to be a minimum, not a saddle point on the LMO hypersurface. Convergence, which was slowest by far for $B_5H_{10}BeC_5H_5$, was assumed by use of up to 20 iterations. Several independent localizations for each molecule showed each set of LMO's to be unique. We would not be surprised if, after further optimization of $B_5H_{10}BeC_5H_5$, we were to find nearly equivalent LMO's which differ only in the redistribution of bonds in the BeC_5 fragment where local C_{5v} symmetry nearly exists. The most striking results are that the $B_5H_{10}Be$ fragment is very similar in all of these molecules and that the Be is bonded to B_5H_{10} only through fractional bonds. Some of these LMO's contribute so little to Be that we lowered the threshold for such contributions to 0.09 e in order to classify all B–H_b–Be bonds as bridges. Thus, Be is capable of forming many fractional bonds, from five in $B_5H_{10}BeCH_3$ to eight in $B_5H_{10}BeB_5H_{10}$. The effects of relative electronegativities,[19] C > H > B > Be, are that (1) H has the highest population in all B–H_t or B–H_b–B bonds, (2) the order of populations is H_b > B > Be in all B–H_b–Be bonds, and (3) the largest population is at two B's in all bonds involving B and Be only and at C in bonds involving Be and C only.

The approximate average hybridizations (sp^h), related to the percent s character at each center for each LMO by $h = (100 - \%s)/\%s$, are shown in Table VII. These values are exact averages for the Be–Cp ($X = C_5H_5$) and the C–H_t ($X = CH_3$) bonds, as well as for the bonds within C_5H_5. For the other bonds, they are qualitative values around which h is centered for each participating atom. Some observations are as follows: (i) the hybrids ($sp^{6.7}$) for C in C_5H_5···Be bonds are essentially of the π type in $B_5H_{10}BeC_5H_5$, while C–C bonds within this C_5H_5 group are $sp^{2.0}$; (ii) the Be hybrids ($sp^{4.3}$) toward C_5H_5 have more p character than bonds to the boron framework ($sp^{1.4}$) or the Be–C bond ($sp^{1.3}$) in $B_5H_{10}BeCH_3$; (iii) the largest deviation from tetrahedral hybridization at C in $B_5H_{10}BeCH_3$ occurs in the Be–C bond ($sp^{2.2}$), perhaps for

Table VI. Boys Localized Molecular Orbitals[a]

centers[b]				populations at centers			
A	B	C	D	A	B	C	D
$B_5H_{10}BeBH_4$ (C_s)							
B(1)	B(4)	B(5)		0.67	0.65	0.65	
B(3)	B(1)	B(4)	Be	0.88	0.78	0.19	0.15
H(7)	B(3)	Be		1.22	0.67	0.14	
H(12)	B(7)	Be		1.29	0.55	0.20	
H(13)	B(7)	Be		1.31	0.57	0.17	
H(8)	B(4)	B(3)		1.05	0.52	0.46	
H(9)	B(4)	B(5)		1.08	0.47	0.47	
H(1)	B(1)			1.17	0.85		
H(3)	B(3)			1.14	0.88		
H(4)	B(4)			1.12	0.90		
H(14)	B(7)			1.19	0.83		
$B_5H_{10}BeB_5H_{10}$ (C_2)							
B(5)	B(1)	B(4)		0.68	0.66	0.61	
B(3)	B(1)	B(4)	Be	0.85	0.77	0.24	0.15
B(6)	B(1)	Be	B(5)	0.82	0.80	0.23	0.15
H(7)	B(3)	Be		1.22	0.69	0.12	
H(11)	B(6)	Be		1.21	0.71	0.10	
H(8)	B(4)	B(3)		1.05	0.55	0.43	
H(9)	B(5)	B(4)		1.08	0.49	0.45	
H(10)	B(5)	B(6)		1.05	0.57	0.41	
H(1)	B(1)			1.17	0.84		
H(3)	B(3)			1.16	0.86		
H(4)	B(4)			1.14	0.88		
H(5)	B(5)			1.14	0.88		
H(6)	B(6)			1.15	0.87		
$B_5H_{10}BeCH_3$ (C_s)							
B(1)	B(4)	B(5)		0.68	0.65	0.65	
B(3)	B(1)	B(4)	Be	0.85	0.79	0.19	0.17
H(7)	B(3)	Be		1.20	0.70	0.11	
H(8)	B(4)	B(3)		1.06	0.53	0.45	
H(9)	B(4)	B(5)		1.08	0.47	0.47	
C	Be			1.42	0.63		
H(12)	C			1.02	1.01		
H(14)	C			1.03	0.99		
H(1)	B(1)			1.17	0.84		
H(3)	B(3)			1.15	0.87		
H(4)	B(4)			1.12	0.89		
$B_5H_{10}BeC_5H_5$ (C_s)							
B(1)	B(4)	B(5)		0.66	0.66	0.66	
B(3)	B(1)	Be	B(4)	0.81	0.77	0.23	0.19
H(7)	B(3)	Be		1.18	0.75	0.09	
H(8)	B(4)	B(3)		1.06	0.55	0.43	
H(9)	B(4)	B(5)		1.08	0.47	0.47	
C(1)	Be	C(2)	C(5)	1.02	0.43	0.24	0.24
C(3)	C(2)	Be		0.88	0.71	0.33	
C(3)	C(4)			1.02	1.02		
C(1)	C(2)			1.03	1.01		
C(3)	C(2)			1.02	0.98		
C(1)	H(12)			1.02	1.00		
C(2)	H(13)			1.03	0.99		
C(3)	H(14)			1.03	0.99		
H(1)	B(1)			1.18	0.84		
H(3)	B(3)			1.18	0.85		
H(4)	B(4)			1.14	0.87		

[a] Only unique LMO's have been listed. The others can be obtained by applying the appropriate symmetry operation. [b] Centers contributing at least 0.09 e to a given LMO have been listed.

Table VII. Approximate "Average" Hybridizations[a] in $B_5H_{10}BeX$

atom	bond type	h_{av}
B	B-H_t	2.2
B(3)	B(3)-H_b-B(4)	6.1
B(4)	B(3)-H_b-B(4)	3.1
B(4)	B(4)-H_b-B(5)	4.4
B	B-H_b-Be	3.3
B	framework[b]	2.4
(with the exception in the following line)		
B(1)	B(1)-B(4)-B(5)	6.3
Be	B-H_b-Be	4.0
Be	framework[b]	1.4
Be	Be-C (X = CH_3)	1.3
Be	Be-Cp (X = C_5H_5)	4.3
C	C-H_t (X = CH_3)	2.7
C	Be-C (X = CH_3)	2.2
C	Be-Cp (X = C_5H_5)	6.7
C	C-C (X = C_5H_5)	2.0
C	C-H_t (X = C_5H_5)	1.8

[a] The hybridization, h, is the power of p in sp^h. h_{av} is determined for each type of bond as described in the text. [b] Not involving C or H.

the same reasons as in ethane[20] where C–C is $sp^{2.4}$; (iv) the B(1)–B(4)–B(5) bond has $sp^{6.3}$ hybrids from B(1), i.e., a surprisingly large percentage of p character.

In $B_5H_{10}BeB_5H_{10}$, which has only C_2 symmetry, B(3) and B(6), or B(4) and B(5), are not equivalent. However, the asymmetries involved (Tables IV–VI) are too small to warrant a separate discussion.

The ^{11}B chemical shift of the apex boron B(1) is at a much higher field in $B_5H_{10}BeC_5H_5$[4a] than it is in the other three molecules (X = BH_4, B_5H_{10}, and CH_3), even though B(1) is less negatively charged in this molecule than it is in the other three (Table IV). Of course, paramagnetic shifts are large, and often dominant, in boron chemistry and require coupled Hartree–Fock theory,[21] or a near-equivalent. Arguments based only on charges are known to give poor results, e.g., for 6,9-$B_{10}H_{12}L_2$ compounds.[22]

The relative coupling constants[2b,c,4a] J between ^{11}B and ^1H have some correlation with the percent s character in the hybrid orbital of B which bonds to H.[22] We caution, however, that the contact term is not the only source of the coupling constants, inasmuch as there are a dipolar interaction with the electron spin and also an orbital interaction with the magnetic field due to the orbital motion of the electron involved in the coupling of nuclear spins.[23] There is some general correlation between ^{11}B and ^1H in the sense that J is largest when H is H_t (small h, large %s), intermediate when H is H_b connecting B and Be, and smallest when H is H_b connecting two B's (large h, small %; see Table VII). However, h_{av} varies from 6.1 for B(3) to 3.1 for B(4) in B(3)–H_b–B(4) bonds. Also, indicative that other effects besides the contact term are important is that J for B(3)–H(7) is unusually large and J for B(1)–H(1) is unusually small for $B_5H_{10}BeC_5H_5$ as compared with $B_5H_{10}BeCH_3$. However, the percent s character at B(3) and B(1) in these bonds is comparable in these two molecules.

The degrees of bonding and overlap populations (Table V) often predict the same trends in strengths of bonding as those suggested[4a] from the NMR data. For example, overlap populations show that the Be–B(1) interaction is strongest and the Be–B(3) and Be–B(6) interactions are weakest in $B_5H_{10}BeC_5H_5$. On the average, in these molecules, the B–H overlap populations, degrees of bonding and percent s character at B tend to decrease in the series B–H_t, B–H_b–Be, and B–H_b–B. Furthermore, the degrees of bonding and overlap populations for the various B–H_b–B bonds also vary as the percent s character at B, although these variations are comparatively small.

Finally, we comment on related molecular species which may merit further study. (i) Besides the four compounds studied here, two more are known,[4a] $B_5H_{10}BeCl$ and $B_5H_{10}BeBr$. Perhaps $B_5H_{10}BeF$ and $B_5H_{10}BeI$ can be made. The adducts with X = $N(CH_3)_3$ or $O(C_2H_5)_2$ would be positive ions, which would be expected to lose H^+ from a bridge BH_bB bond. Perhaps the positive ion could be restored, as it was added[24] to B_6H_{10} to make $B_6H_{11}^+$. Syntheses have been attempted[4a] for $B_5H_{10}BeH$ and $B_5H_{10}BeB_3H_8$. Our calculations on $B_5H_{10}BeH$ show great absolute stability (E = −144.275 au) and a large energy gap (0.558 au) between the highest filled and lowest unfilled molecular orbitals. However, the added hydrogen is very negative (−0.342 e; optimized Be–H distance = 1.264 Å; optimized exponent = 0.93), and the Be is very positive (+0.485 e). Also, the valency of this H atom is only 0.883 (cf. Table IV). An extremely hydridic hydrogen may be reactive with other parts of this hypothetical $B_5H_{10}BeH$ molecule. If $B_5H_{10}BeB_3H_8$ can be prepared, it would probably not have a plane of symmetry if the bonding of B_3H_8 to Be is similar to that in $Be(B_3H_8)_2$,[2d] but a few unsymmetrical boron hydrides are known.[25] (ii) A "triple sandwich" type[26] complex may exist, for example $B_5H_{10}Be(B_3C_2H_5)CoC_5H_5^-$ or $B_5H_{10}Be(B_3C_2H_5)Fe(CO)_3^-$. (iii) Perhaps Mg can be substituted for Be in these compounds, although Mg may be reluctant to stabilize hydrogen bridges. Perhaps the valence structure which is most closely related to these $B_5H_{10}BeX$ compounds is that of $C_2B_4H_8$.[27] Therefore, possibly metallo adducts might be made from $B_5H_9BeX^-$ in the way that $C_2B_4H_7^-$ reacts with [1,2-bis(diphenylphosphino)ethane]nickel(II) chloride to give (π-2,3-$C_2B_4H_6$)Ni[$(C_6H_5)_2PCH_2]_2$.[28] Perhaps other types[29,30] of metalloderivatives analogous to $Zn(B_{10}H_{12})_2^{2-}$ and $Ni(B_{10}H_{12})_2^{2-}$ could be made, although this is a larger extrapolation. (iv) Closo derivatives may also exist and may stabilize the reactivity of Be, as in $B_9C_2H_{11}BeL$.[3] Here, a study of isomerization and preferred positions of Be (or more than one Be) relative to B and C would be interesting. *closo*-Beryllaboranes with other elements are conceivable, as well as those with metals. Finally, polymeric products may be formed from closo derivatives by coupling through Be–H_b–B bridges, as in $[3\text{-Be-1,2-}B_9C_2H_{11}]_n$.[3b]

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Registry No. $B_5H_{10}BeBH_4$, 60923-64-0; $B_5H_{10}BeB_5H_{10}$, 65762-38-1; $B_5H_{10}BeCH_3$, 65859-18-9; $B_5H_{10}BeC_5H_5$, 65760-50-1.

References and Notes

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