1989, *28*, 3210), the position of a proton and the centroid of electron density associated with it for a hydrogen atom bound to another atom do *not* coincide; a disparity of 0.15 Å is typical for a M-H bond. The average Re-H distance in the X-ray structure determination of ReH$_5$(PPh$_3$)$_3$ was 1.54 [5] Å,[8c] and this can be compared to the average Re-H distance of 1.688 [5] Å determined by neutron diffraction in ReH$_5$(PMePh$_2$)$_3$ (Emge, T. J.; Koetzle, T. F.; Bruno, J. W.; Caulton, K. G. *Inorg. Chem.* **1984**, *23*, 4012). Correcting for the X-ray-determined H···H distances for ReH$_5$(PPh$_3$)$_3$ and applying the DD calculation[17] lead to the significantly larger T_1(min) value of 259 ms at 400 MHz. Thus, with T_1^{-1} depending on r_{HH}^{-6}, such discrepancies introduce serious errors.

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Supplementary Material Available: Figures containing the variable-temperature spectra of complexes **1**, **3**, and **4** and variable-temperature spectra for Re$_2$H/D$_{8-n}$(PR$_3$)$_4$ (PR$_3$ = PEt$_2$Ph, PMe$_2$Ph) (5 pages). Ordering information is given on any current masthead page.

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Bonding in Clusters. 11.[†] Gas-Phase Photoelectron Spectra of the 12-Apex Closo Systems 1,12-$B_{12}H_{10}(CO)_2$, 1,2- and 1,7-$C_2B_{10}H_{12}$, and Related Main Group V and VI Heteroboranes and -carboranes. The Electronic Structure of $B_{12}H_{12}^{2-}$

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The He I and He II photoelectron spectra of 1,12-B$_{12}$H$_{10}$(CO)$_2$ and 1,2- and 1,7-C$_2$B$_{10}$H$_{12}$ are assigned in terms of correspondence of bands to BH bonding or cluster-localized orbitals. The experimental assignments are found to agree excellently with MNDO calculations on the molecules, which allows assignment of the cluster orbitals and ionizations in terms of Stone's theory of *closo*-boranes. Spectra of the related *closo*-heteroboranes 1,2-X(CH)B$_{10}$H$_{10}$ (X = P, As, Sb), X$_2$B$_{10}$H$_{10}$ (X = As, Sb), and SeB$_{11}$H$_{11}$ are found to be very similar, also agreeing with calculated results. The lone pairs of the heteroatoms are found to be localized in the valence s atomic orbital. An orbital diagram for B$_{12}$H$_{12}^{2-}$ is extrapolated from these results, which shows it to be distinctly different from the smaller *closo*-borane anions.

The electronic structure and bonding of boranes have attracted an enormous amount of attention since the basic set of chemical/geometric types became established by structural techniques. The interest stemmed initially from a general appreciation that the molecules presented a "soluble problem" in molecular bonding whose solution involved "nonclassical" bonding ideas. It received more purpose when equivalent structural types of molecules were identified in heteroborane, metallaborane, and all-metal clusters. The vast majority of this interest is represented by theoretical considerations of the nature of the bonding ranging in sophistication from the powerful, largely heuristic, approaches of Lipscomb's *styx* rules[1] and Wade's rules[2] to full ab initio calculations on individual molecules. In recent years Stone has presented[3,4] a general theory of the electronic structure of the *closo*-borane anions, which may be considered as the parent molecules for all the structural types,[4,5] which has been extensively adopted as the framework for the discussion of the properties of all related molecules. There is, in comparison with all this theoretical work, a distinct paucity of experimental data on the molecules, other than structure determinations.

One of the most useful experimental techniques applied to these compounds is photoelectron (pe) spectroscopy. The available studies are distributed widely across the various types of clusters, and as much of the work was performed before the advent of Stone's theory, they lack the organization provided by a consistent framework. Further, very few of the studies are on the closo compounds, which are the most tractable theoretically, and those that are usually involve the introduction of heteroatoms into the cage to compensate for the anionic charge of the parent *closo*-B$_n$H$_n^{2-}$ systems. The only study of a volatile compound with an intact *closo*-borane cage is an earlier paper in this series[6] on 1,10-B$_{10}$H$_8$(N$_2$)$_2$.

In this paper we report the pe spectra of a number of 12-apex closo compounds and are able to provide a consistent assignment of all features observed. The assignment is found to agree remarkably well with the results of MNDO calculations[7] of the electronic structure of the molecules. We also compare the MNDO-optimized geometries with structural data where available, again finding very good agreement. In general, the MNDO calculations appear to provide a very accurate description of these molecules. We extrapolate from the experimental data an energy level diagram for the parent B$_{12}$H$_{12}^{2-}$ anion, which again agrees with calculation and which provides an explanation for the remarkable thermal and hydrolytic stability of the anion.

The discussion and assignments use Stone's theory labeling. The theory shows that the molecular orbitals of the near-spherical systems B$_n$H$_n^{2-}$ have distributions and degeneracies (as close as molecular symmetry permits) that are characterizable by atomic orbital labels. Thus, in B$_{12}$H$_{12}^{2-}$, the 13 cluster orbitals are labeled $S^\sigma(a_{1g})$, $P^\sigma(t_{1u})$, $D^\pi(h_g)$, and $F^\pi(t_{2u})$, the σ and π superscripts indicating predominantly B 2s and B 2p (tangential to the surface of the sphere) composition, respectively. Similarly the 12 BH bonding orbitals can be labeled $S^x(a_{1g})$, $P^x(t_{1u})$, $D^x(h_g)$, and $F^x(g_u)$, these having large percentage B 2p (radial to the sphere) composition. In a recent paper[8] we have shown that the σ/x orbitals

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[†] Part 10 is ref 8; Part 9 is ref 5.

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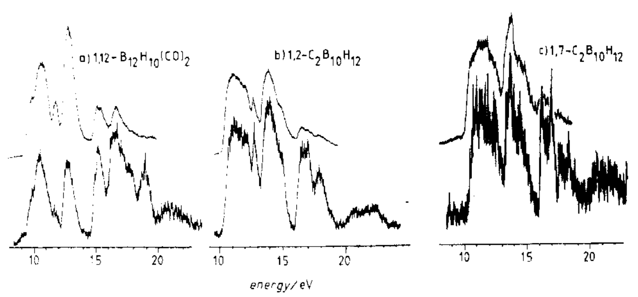
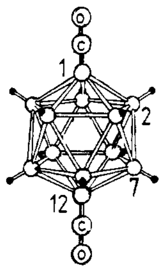


Figure 1. He I and He II photoelectron spectra of 1,12-$B_{12}H_{10}(CO)_2$, 1,2-$C_2B_{10}H_{12}$, and 1,7-$C_2B_{10}H_{12}$.

can be accurately considered as being constructed from $sp^{1/2}/sp^2$ radially directed hybrids of the B atoms of the clusters.

Experimental Section

The compounds studied were all prepared by literature methods.[9,10] The preparation[9] of 1,12-$B_{12}H_{10}(CO)_2$ (structure I) was adapted to a



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25-mL-volume high-pressure bomb that was not silver lined. The yield was 18%, and the compound was identified by its infrared spectrum, which was identical with an authenticated sample provided by Prof. Knoth of Du Pont.

The photoelectron spectra were measured on a Perkin-Elmer PS16/18 spectrometer. The samples were introduced as solids into the ionization region and heated to produce sufficient vapor pressure. For 1,12-$B_{12}H_{10}(CO)_2$ the optimum temperature was 120 °C and the maximum count rates were 4000 counts s^{-1} for He I and 400 counts s^{-1} for He II (120,4000,400). The conditions for the other samples were as follows: 1,2-$C_2B_{10}H_{12}$, 60,4000,400; 1,2-$P(CH)B_{10}H_{10}$, 94,1000,400; 1,7-$C_2B_{10}H_{12}$, 65,1000,100; 1,2-$As(CH)B_{10}H_{10}$, 80,1000,40; 1,2-$Sb(CH)B_{10}H_{10}$, 128,1000,400; $As_2B_{10}H_{10}$, 100,1000,100; $Sb_2B_{10}H_{10}$, 205,4000,100; $SeB_{11}H_{11}$, 83,1000,100. The spectra were calibrated by using Ar and N_2 standards. The He I spectra appeared to suffer from reduced sensitivity, compared to that normally expected, at energies higher than 18 eV. This serves to prohibit observation of any bands in the 18–21-eV region and to over emphasise the apparent He I and He II intensity variations of the spectra.

The MNDO program was used as supplied by QCPE with full optimization, without symmetry restriction, of all $3N-6$ variable geometric parameters in all cases, which, for example, for 1,12-$B_{12}H_{10}(CO)_2$ required the optimization of 72 parameters. Local minima for the structure, other than that calculated, were not searched for. We have made such searches in earlier work on closo systems and have never found alternative structures close enough in energy to be worth consideration. The assignments of the molecular orbitals of low-symmetry species presented something of a problem, which was aided by the calculation of the localized orbitals. The B(C)–H localized bonds so determined were all shared 55% B(C)–45% H with very little variation. In analyzing the canonical orbitals, we therefore took $1 + {}^{55}/_{45} = 2.25 \times$ H component as the fraction of B(C)–H bonding in any one orbital and the residual B(C) component as cluster bonding. We accepted 70% of one distinct bonding type as a clear assignment (most orbitals have much higher percentages). If the majority composition is 60–70%, the assignment is given in brackets in the tables.

Results and Discussion

Photoelectron Spectra. 1,12-$B_{12}H_{10}(CO)_2$. The photoelectron spectra of this compound are shown in Figure 1a. The 33 valence molecular orbitals, and hence ionizations, of this molecule should correspond to 13 cluster, 10 BH σ, 2 BC σ, 4 CO π, 2 lone-pair (which are equivalent to the 4σ orbital of free CO), and 2 CO σ (equivalent to the 3σ of free CO), localized orbitals. Of these the two CO σ's will be outside the range of the spectra of Figure 1a. There is no fundamental reason to expect a good one-to-one correspondence between the localized and canonical orbitals; all canonical orbitals with the same molecular symmetry are capable of mixing. In fact we find strong evidence for such a correspondence and retain these convenient labels in the following discussion. We can identify orbitals/ionizations that involve the CO groups through comparison with the spectra of BH_3CO,[11] free CO, and ketene.[12]

The band with intensity maximum at 19.0 eV in the He II spectrum (not observed in He I) can be assigned to the oxygen axial lone pairs. It has the sharpest band shape in the spectrum, indicating nonbonding character, and its equivalent is found at 18.5 (adiabatic)–19.5 eV in BH_3CO and at 19.5 eV (adiabatic) in free CO. Further, there is no corresponding band in the carborane spectra (Figure 1b,c), suggesting that this is a carbonyl-localized ionization.

The CO π ionization energies are very insensitive to environment in a variety of compounds composed of light atoms. They are found in a 16.0–17.5-eV band in BH_3CO, the same in ketene, even though there is extensive delocalization due to C–C π bonding, and at 16.5–17.5 eV in free CO. They can be confidently associated with one of the features in the 16–18-eV region (most clearly seen in the He II spectrum), probably with the first one with the sharp rising edge at 16.5 eV. Interestingly, the same ionizations show a marked sensitivity to environment in metal carbonyl compounds.[13] This simply reflects the much greater polarizability of the metal d^n orbitals compared with the borane cage or organic carbon framework orbitals.

The BC σ-bond ionization of BH_3CO was assigned to a broad band of maximum intensity at 14.8 eV. The energy of this orbital in related compounds will be very sensitive to environment, unlike those discussed above. The equivalent orbital in ketene is calculated (MNDO) to have an energy of −16.34 eV corresponding to a broad feature in the spectrum at 16.5 eV, which was incorrectly assigned[12] as the dissociation continuum of a lower energy (16.08 eV) structured band. As the B–C bonding in 1,12-$B_{12}H_{10}(CO)_2$ is considerably stronger than that in BH_3CO, but is unlikely to be as strong as the C–C bonding in ketene, we can take these values as limits on its ionization energy. This identifies it firmly as all or part of the band between 15 and 16 eV that appears to have two components. Again, there is no equivalent band in the carborane spectrum, supporting this assignment.

The cluster and BH σ ionizations therefore account for all the features observed at energies between 9.5 and 14 eV and for some part of the region between 16.5 and 19 eV. These are very much the same regions covered by the whole spectrum of the carboranes, which contains only these types of ionizations, allowing that CH will be fairly similar to BH.

If the shoulder at 9.8 eV is taken as corresponding to one of the many doubly degenerate orbital/ionizations to be accounted for, then intensity comparisons suggest that the band with a maximum at 10.8 eV contains two such events and that with a maximum at 11.8 eV one more. The two components of the 10.8-eV band are distinguished by the intensity variations between He I and He II, in that the high-energy side of the band loses intensity compared to the low-energy side. This is only just discernible in Figure 1a but is clear on the original data. The band between 12.5 and 14 eV corresponds to numerous ionizations.

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Table I. Experimental Assignment of Pe Bands of 1,12-$B_{12}H_{10}(CO)_2$ Compared with the MNDO-calculated Orbitals

exptl		calcd		
energy/eV	assignt[a]	–energy/eV	assignt[b]	% BH
9.8 (sh)	cluster	11.05	e_{2u}, F^π	0
10.8	cluster	11.59	e_{1u}, F^π	0
	BH	11.73	e_{2g}, D^x	75
11.8	BH	11.78	e_{1g}, D^x	77
		13.39	a_{1g}	35
13.2	BH	14.04	e_{1u}, (P^x)	53
	many ionizations	14.42	a_{2u}, P^x/F^x	86
		15.48	e_{2u}, F^x	94
15.5	B–C	18.82[c]	a_{2u}, B–C	
		20.33[c]	a_{1g}, B–C	
16.5	CO π	17.77	e_{2g}, CO π	
		18.12	e_{2u}, CO π	
17.1		18.18	a_{1g}	64
17.7	cluster	20.05	e_{2g}, (D^π)	33
(18.2)		20.43	e_{1g}, D^π	24
19.0	O lp	23.09	a_{2u}, O lp	
		27.24	a_{1g}, O lp	
		28.00	e_{1u}, P^σ	
		30.65	a_{2u}, P^σ	
		38.65	a_{1g}, S^σ	
		47.65	a_{1g}, a_{2u}, CO σ	

[a] Based on comparisons with other spectra and intensity variations—see text. [b] For assignment criteria see Experimental Section. [c] Shifted out of calculated energy order for purpose of comparison—see text.

Considering the intensity variations between He I and He II, we find the whole of this high-energy band, the 11.8-eV peak, and the high-energy side of the 10.8-eV band lose intensity on He II excitation compared with the 9.8-eV shoulder and the low-energy side of the 10.8-eV band. These differences should correspond to the difference between cluster and BH orbitals, and it is logical that those losing intensity will be the BH bonding ones. These involve the large radius H 1s atomic orbitals, which are the most sensitive to photon energy.

Finally, the features in the 16–18-eV region not accounted for by CO π can be assigned as more cluster orbitals. The entire region shows a large enhancement of intensity between He I and He II, and this is extremely unlikely to be a property of BH bonding orbitals.

These experimental assignments are summarized in Table I, where they are compared with the results of a MNDO calculation and show very good agreement. Between the onset of ionization and the CO π ionizations, i.e. for the first 7 eV below onset, the calculated energies need to be corrected by 1.5 eV, and the oxygen lone pairs (lp's) show that this error increases to ~4 eV at 12 eV below onset. The only large error is in the BC bonding orbitals, which are calculated to be ~2 eV too stable and on the wrong side of the CO π's. Computationally, these are the most difficult orbitals due to the unusual bonding of the carbonyl groups to the cage. The calculated orbitals contain a large component of CO bonding as well as BC, which would certainly serve to stabilize the energy. The extent of this mixing is probably overestimated by the calculation.

The only orbitals not clearly accounted for by Table I are the two a_{1g}'s, calculated at –13.39 and –18.18 eV, which are both formally of D type. Their energies would appear to indicate an assignment of –13.39 eV as D^x and –18.18 eV as D^π simply by comparison with other orbitals of these types. The higher energy orbital, however, has less BH component, 35%, than the lower energy one, 64%. Extensive mixing of these two axially directed orbitals has occurred, reversing their original bonding types presumably due to the axial perturbation induced by the carbonyl groups. This mixing is probably also complicated by the fate of the formally a_{1g}, S^x orbital, which is involved with B–C bonding in this molecule. It has not affected the e_{1g} and e_{2g} partners of either D^x or D^π and would not apply in the $B_{12}H_{12}^{2-}$ parent.

Finally, we note that there is a broad pe feature at high energy, maximum intensity 21 eV, which from Table I could correspond to the stabilized O 1p orbital and/or the p^σ orbitals (e_{1u} or e_{1u}, a_{2u}). Bands have been reported in this region of the pe spectra of carbonyl-containing compounds, particularly metal carbonyls, that are in-fact "shake-up" resonances. Although this is a possible explanation in this case, we suspect that the P^σ's are actually involved to some extent, as an equivalent band is seen in the carborane spectrum, which, of course, has no carbonyl groups. This assignment is also supported by the calculation as shown in Table I.

It is worth noting that the percentages of BH character identified in Table I sum to more than 90% of the total expected, indicating the small extent of mixing between the F^π, D^π, and BH and the S^σ, P^σ, and CO groups of orbitals.

1,2-$C_2B_{10}H_{12}$. This molecule (structure II; A, B = CH) is potentially simpler than the dicarbonylborane, as the valence orbitals/ionizations are just the 13 cluster, 10 BH and 2 CH localized ones. However the spectrum (Figure 1b) shows far less structure and prohibits a similarly detailed analysis. The reduced symmetry, C_{2v}, removes all the degeneracies of the previous case, causing an apparent broadening due to overlapping of the ionization events. An additional cause for the increased width of bands is an effect of the presence of two carbon atoms in the cage. Any group of related orbitals, F^π, D^π, D^x, etc., with similar energies, will have one or two of their number stabilized to some extent due to their carbon atom component, producing a wider spread of energies for the group. Thus, for example, the cluster/BH orbitals of 1,12-$B_{12}H_{10}(CO)_2$ covered by the 10–11.5-eV band spread to the 10–13.5-eV band of 1,2-$C_2B_{10}H_{12}$. The sharp feature at 12.8 eV can be assigned therefore to orbitals with a large carbon component and of cluster type on the basis of its sharpness and increased relative intensity on changing to He II excitation.

Similarly, the 12.5–14-eV band of the carbonyl compound widens to the 13.5–15.5-eV band of the carborane and loses maximum intensity while developing a high-energy shoulder at 15.0 eV. This shoulder should arise from ionization of CH bonding orbitals. The variation in intensity between He I and He II of those bands below 15 eV is far less dramatic than that in the carbonyl compound, most notable being a gain in intensity of the 13.5–15.5-eV band rather than a loss. From our discussion above this suggests a predominantly cluster character for the related orbitals, whereas the assignment was BH bonding in the carbonyl. The inference is that extensive mixing of cluster and BH orbitals has occurred in the low symmetry of the carborane. One effect of this is to "even-out" the atomic orbital structure of all the molecular orbitals, reducing the extent of intensity variations with change in ionizing-radiation wavelength. Another is to stabilize the cluster bonding orbitals at the expense of the BH bonding component.

The high-energy bands at 16–19 eV cover the same region as the cluster bonding orbitals assigned in the carbonyl spectrum (after deletion of carbonyl-localized ones) and show the same very large increase in intensity from He I to He II, and we propose the same, predominantly D^π, assignment. The band at 20–23 eV is again assigned as P^*, with the broader shape arising from the splitting of the D_{5d} degeneracy.

1,7-$C_2B_{10}H_{12}$. The spectrum of this compound is shown in Figure 1c and is very similar to that of 1,2-$C_2B_{10}H_{12}$ except for the higher intensity of the 13.5–14.5-eV band, which makes it similar in appearance to the equivalent band of the carbonyl compound. The shoulder at 14.5 eV is more pronounced than that in the 1,2-compound and represents a clear separation of BH and CH bonding orbitals. The He II spectrum shows that this shoulder gains in intensity compared with the main band, consistent with C composition and with features in the 1,2-compound spectrum, but unfortunately the He II spectrum is of rather poor quality and no more can be deduced from it. The He I spectra of both the low-symmetry carboranes have been previously reported,[14] and our spectra are identical. The He I spectrum of the

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Table II. MNDO-Calculated Orbital Energies (eV) of the $C_2B_{10}H_{12}$ Carboranes[a]

1,12-compd	1,7-compd	1,2-compd	pe spectrum
12.12 e cl (0)	12.12 (7)	12.18 (11)	10–13-eV band, cl/BH
	12.27 (30)	12.20 (33)	
12.69 e BH (82)	12.46 (39)	12.86 (40)	
	12.64 (46)	12.37 (44)	
13.11 e BH[c] (77)	12.76 (81)	12.71 (44)	
	12.91[c] (44)	12.93 (78)	
13.19 e cl[b] (3)	13.15[c] (72)	13.15[c] (52)	
	13.40[b] (48)	13.24[b] (40)	12.8-eV sh cl C local
13.39 a BH[b] (71)	13.40[b] (54)	13.68[b] (38)	
15.07 e BH (91)	15.13 (92)	15.10 (90)	13.5–14.5-eV band, BH
	15.15 (92)	15.43[c] (88)	
15.61 a BH[b] (86)	15.55[b] (85)	15.43 (86)	
16.21 e BH (96)	16.24 (96)	16.26 (96)	
	16.55 (93)	16.56 (93)	
17.43 a BH[c] (93)	16.96 (91)	17.07[c] (85)	14.5-eV sh, CH
18.80 a BH (82)	18.86 (81)	18.96[b] (81)	
20.88 e cl (31)	20.93 (32)	20.98 (32)	16–19-eV band, D^π
	21.01 (32)	21.01 (32)	
21.11 e cl (31)	21.09 (33)	21.07 (31)	
	22.25[c] (33)	21.69 (35)	
24.23 a cl[b] (36)	22.37 (32)	23.18[c] (36)	
28.86 e P^σ (22)	28.92 (23)	28.72 (25)	P^σ
	20.19 (13)	31.82 (14)	
35.45 a $P^{\sigma b}$ (17)	34.55[b] (18)	31.92[b] (17)	
43.99 a $S^{\sigma b}$ (5)	44.18[b] (5)	44.88[b] (7)	S^σ

[a] The figure in parentheses is the percentage of BH component in each orbital; for 1,12-$C_2B_{10}H_{12}$ the D_{5d} degeneracies e or a and the assignment cluster (cl) or BH bond (BH) are given. [b] Indicates large C atom composition, 10–20%. [c] Indicates significant C atom composition less than 10%.

1,12-carborane has been reported only once[15] and surprisingly, given the D_{5d} symmetry of the molecule, shows hardly any more detail than the two spectra presented here. The general features are the same, and the 10–13-eV band is somewhat more structured, but there appears to be no additional information in the spectrum.

The MNDO-calculated orbital energies of all three carboranes are compared in Table II with the experimental assignments made above. Facile correlation of the orbitals across the molecules as listed in Table II is achieved from the fractional composition of BH character given and, for some orbitals, from localization on the C atoms. The only significant difference is that the top eight orbitals of the 1,12-compounds, which are very clearly BH or cluster, mix quite extensively in the lower symmetry 1,7- and 1,2-compounds. This agrees with the observation of considerably less variation of intensity of their low-energy pe bands with photon energy compared with that of the equivalent bands of the dicarbonyl. We therefore predict that 1,12-$C_2B_{10}H_{12}$ will exhibit greater intensity variations, as its high symmetry should maintain the separation of cluster/BH character of the orbitals. All the experimental assignments are supported by the calculation. From Table II it is surprising that the spectrum of the 1,12-compound is not better resolved than is found. This could be a consequence of Jahn–Teller splitting of all degenerate ion states, but this is unlikely to be of the same magnitude in all cases. Other than a general energy shift between theory and experiment, of the same magnitude as applied for the dicarbonyl compound, we find good agreement between theory and experiment for the carboranes. Details of MNDO calculations on the two low-symmetry carboranes have been reported previously[14] and are very similar to ours. Reference 14 compared the calculations with the He I spectrum and therefore ignored orbitals of binding energies greater than 19 eV. The conclusions derived are fundamentally the same as ours, mainly that in the top orbitals there is extensive mixing of cluster and BH bonding orbitals, although this is rather overemphasized in ref 14.

The main general points derived from the above analysis of the spectra and comparison with calculations are (a) that orbitals clearly retain their cluster or BH character in the high-symmetry compounds, even if mixing is symmetry allowed, and (b) that in the limit of clear separation of these types the orbital energy order is

$$S^\sigma < P^\sigma < D^\pi < S^x \sim P^x, F^x < D^x < F^\pi$$

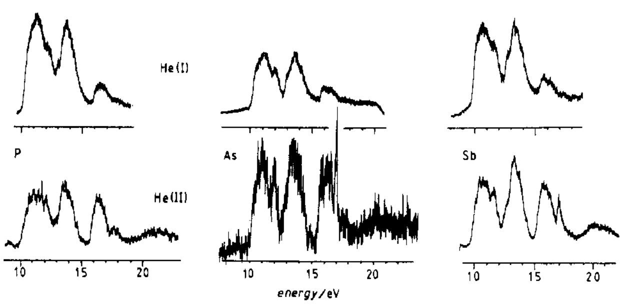
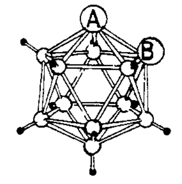


Figure 2. He I and He II photoelectron spectra of $X(CH)B_{10}H_{10}$ (X = P, As, Sb).

1,2-$X(CH)B_{10}H_{10}$ (X = P, As, Sb). These molecules (structure II; A = X, B = CH) are isoelectronic with the carborane discussed above. Their He I and He II pe spectra are shown in Figure 2, and their overall appearance is remarkably similar to that of the carboranes. In fact, very much the same analysis and assignment applies—with one interesting exception—so we simply reiterate these without going again through the criteria. The first two bands, lower than 15 eV, are extremely similar in all three compounds and account for mixed-cluster (F^π) and BH,CH bonding orbitals/ionizations with the cluster orbitals concentrated in the higher energy band. The high-energy shoulders on both bands are attributed to orbitals with significant carbon character. The intensity variations between He I and He II of these bands is even less than in the 1,2-carborane case, and we deduce from this that the mixing has largely evened-out the amount of B/C/H contribution to the orbitals with the exception of the shoulders. The same must also be true of any X-atom contributions to the cluster-bonding parts of these orbitals, as we see no distinctive bands or unusual intensity variations that could be associated with X localization.



II

The next band in energy, 15–17 eV, is again assigned to the D^π cluster orbitals. It shows the expected large variation in intensity, and it has the same energy as the equivalent bands in the carbonyl and carborane cases. The only difference is the loss of distinct maxima, which is certainly due to the very low symmetry of these molecules. Finally, in the direct comparison with the carborane, the highest energy He II band, assigned to P^σ in the other cases, is present at the same energy, 20–23 eV, in the phosphorus compound and shows a steady decrease in binding energy on going to As, 19–22 eV, and Sb, 19–21 eV.

The most distinctive features of these spectra are the sharp bands in the He II spectra at 17.2 eV in Sb and 17.1 eV in As, which have a broad equivalent at maximum 17.8 eV in P and which are not observed in the He I spectra. They can only be the lone pair ionizations of the heteroatoms. The band shapes in As and Sb are too sharp for any other assignment. The energies of these bands show that the lone pairs are localized in the valence s atomic orbital of the heteroatoms. This is made clear by comparison with the spectra of the $(CH_3)_3X$ molecules, which have been completely assigned.[16] In these the ionization corresponding to the X–C bonding orbital but largely localized on the X valence

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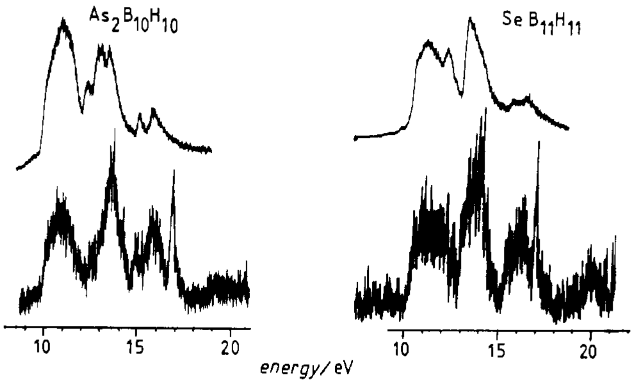

Figure 3. He I and He II photoelectron spectra of $As_2B_{10}H_{10}$ and $SeB_{11}H_{11}$.

s atomic orbital is found at ~17 eV in all the molecules. The appearance of the ionizations only in the He II spectra is understandable when one considers photoionization cross-section data on the group V atoms themselves.[17] This shows that the valence s atomic orbitals have a higher cross section for He II compared to He I, by a factor of 3 for the P 3s, 100 for As 4s, and 5 for Sb 5s. We have previously proposed[18] this localized valence s atomic orbital assignment for the lone pairs of the group VI heteroboranes such as $YB_{11}H_{11}$ (Y = S, Se, Te) but only on the evidence of calculations. This assignment means that the lone-pair density is chemically unavailable, both in energy and spatial distribution, and that the heteroboranes should not demonstrate any Lewis-base properties due to the heteroatoms.

Figure 3 shows the pe spectra of $As_2B_{10}H_{10}$ (structure II; A, B = As) and $SeB_{11}H_{11}$ (structure II; A = Se, B = BH), which strongly support the above assignment. In the He II spectrum of the diarsenic compound the lone-pair band is again very sharp and, although not noticeably more intense than the same band in Figure 2, has a greater area, being significantly wider—the two lone-pair ionizations are more or less degenerate. Also, the high-energy shoulder of the low-energy band of Figure 2, assigned to carbon-localized cluster orbitals, has disappeared—as expected. The spectra of $Sb_2B_{10}H_{10}$ were also obtained, but due to the very high temperature required to volatilize this compound they were of poor quality; however, they show evidence of both of the effects noted above.

We have reported the He I spectra of the $YB_{11}H_{11}$ (Y = Se, Te) and related compounds previously,[19] but these contained no evidence of the lone-pair ionization. The spectra of the selenaborane (Figure 3) show that this ionization is observable in the He II spectrum at 16.8 eV, as expected. This also supports our earlier assignment of calcogen lone pairs to valence s atomic orbitals in *closo*-heteroboranes.[18] The earlier He I spectra were recorded on a spectrometer that did not suffer from low sensitivity at energies higher than 18 eV. We therefore suspect that the lone-pair ionizations of all these group V and VI heteroboranes are only observable with He II radiation.

Table III lists the calculated molecular orbitals of the phosphorus compound and shows percentage compositions and overall assignments where the mixing allows. Almost all our experimentally proposed assignments are supported by the calculation. The only point that needs discussion is that there is no one canonical orbital that corresponds to the phosphorus lone pair. It is mixed/spread out among a number of orbitals in the −18 to −22 eV region. This is consistent with the broad band observed in the 17-eV region compared to the sharp bands in the As and Sb spectra. A calculation of the localized orbitals of the molecule finds the lone pair in an orbital of 92% 3s composition. The evidence of the spectra of the heavier atom congeners is that a one-to-one correspondence between localized and canonical orbitals applies in these cases.

Table III. Assignment of the MNDO-Calculated Molecular Orbitals of $1,2\text{-}P(CH)B_{10}H_{10}$ and Comparison with Experiment

	% compn				
−energy/eV	cluster	P	BH	assignt	exptl assignt
12.18	(36.9	29.4)	28.1	(cluster)	11.5-eV band
12.38	55.7		37.7		
12.45	86.1	5.1	2.4	cluster	
12.50	54.5	2.5	39.8		
12.56	43.2		49.0		
12.85	9.2	1.1	76.8	BH	
12.90	(23.1	33.1)	39.8		
13.37	51.1[a]		38.5	(cluster)	12.2-eV sh, C local
13.54	(40.0[a]	21.6)	27.4	(cluster)	
14.47	9.5	20.8	63.5	(BH)	14-eV band
15.10	6.2		88.3	BH	
15.41	11.0		81.1	BH	
16.38			93.2	BH	
16.48		15.0	71.5	BH	
16.92	7.7	5.9	80.1	BH	
18.56	4.5	3.7	77.4	BH	16.5-eV band, D^{π}
21.07	(53.5	9.0)	31.7	(cluster)	
21.17	(54.7	14.7)	22.7	(cluster)	
21.23	60.6		31.9	(cluster)	
21.26	48.0	20.1	23.3	(cluster)	
22.44	(54.7	8.6)	28.4	(cluster)	
28.56	(66.3	18.7)	2.5	P^{σ}	22-eV band
28.86	76.2	2.3	7.0	P^{σ}	
31.96	78.8[a]	1.8	8.7	P_z^{σ}	
41.77	79.3[a]	6.1	3.8	S^{σ}	

[a] Indicates large C atom component.

Table III also shows that even in these heteroborane molecules, which represent a large distortion from the parent $B_{12}H_{12}^{2-}$ closo system, there are five orbitals of predominantly (65–75%) cluster character, the D^{π}'s, at low binding energy.

MNDO Structure Comparisons. The structure of the carboranes have been determined, and the theoretical values for the bond lengths are compared with experimental ones in Table IV. The experimental values are from electron diffraction[20] data, and therefore not all bond lengths could be uniquely determined for the 1,7- and 1,2-compounds. The best values reported from various parametric fits are compared with averages of the individual calculated values, averaged to mimic the parameters used in the experimental analysis. In all cases the calculated values are longer than experiment by typically 0.035 Å, but otherwise the comparison is extremely good. Only the C–C bond of the 1,2-compound shows an unusually large error, the calculation finding this bond to be almost exactly the same length as the adjacent B–C bonds.

The only phosphaborane structure known[21] is that of $9,10\text{-}Cl_2\text{-}1,7\text{-}P(CH)B_{10}H_8$. The agreement between an MNDO-calculated structure for this molecule and the experimental data is very good. C–B bond lengths, which have experimental values between 1.70 and 1.75 Å are calculated at 1.731–1.769 Å. Values for P–B are 2.01–2.04 Å (experimental) and 1.992–2.018 Å (calculated) the 20 B–B bonds, 1.74–1.82 Å (experimental) and 1.796–1.861 Å (calculated), show the largest error, but only of the same magnitude as that found in the carboranes. Values for B–Cl are 1.772 and 1.803 Å (experimental) and 1.795 Å (calculated). It seems reasonable to assume that the same agreement applies for the structure of the 1,2-phosphacarborane discussed in the pes section.

Numerous attempts to grow crystals of $1,12\text{-}B_{12}H_{10}(CO)_2$ both from solutions and by sublimation have failed to yield any of adequate quality. The MNDO calculation gives a D_{5d} geometry with bond lengths $B_{eq}\text{–}B_{ap}$ = 1.822 Å, $B_{eq}\text{–}B_{eq}$ 1.865 Å, $B_{eq}\text{–}B_{eq}'$ = 1.786 Å, B–C = 1.486 Å, and C–O = 1.159 Å. The MNDO-calculated B–B bond length of $B_{12}H_{12}^{2-}$ is 1.816 Å and

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Table IV. Comparison between the Experimental and MNDO-Calculated (in Parentheses) Bond Lengths (Å) of the Carboranes

compd	C–B	B–B	B–B	C–C
1,12-$C_2B_{10}H_{12}$	1.710 (1.758)	1.792 (1.833)	1.772 (1.806)	
1,7-$C_2B_{10}H_{12}$	1.719 (1.750)	1.790 (1.813)	1.828 (1.824)	
1,2-$C_2B_{10}H_{12}$	1.708 (1.748)	1.800 (1.837)	1.787 (1.848)	1.676 (1.743)

shows that the carbonyl substitution has produced only a small perturbation of the parent geometry. This is despite the different charge distribution necessitated by the conversion to a neutral species. The BH groups of $B_{12}H_{12}^{2-}$ carry charges of 0.166, those of 1,12-$B_{12}H_{10}(CO)_2$ are calculated to have −0.04, and the BCO groups' +0.20 charge is distributed as B, −0.32, C, +0.58, and O, −0.06. This suggests a valence bond structure for the group of a B–C single bond and a C–O triple bond, which is reflected in the bond lengths given. This is rather different from the BN_2 groups of $B_{10}H_8(N_2)_2$, where evidence for greater delocalization over the three atoms was found.[6]

Electronic Structure of $B_{12}H_{12}^{2-}$. The consistency of the spectroscopic analysis and the calculations of the variety of 12-apex closo compounds presented above allows us to extrapolate to an orbital diagram for the $B_{12}H_{12}^{2-}$ anion. The orbital types and symmetries are listed in the introduction, and the question we can now address is the extent to which orbitals of the same I_h symmetry but different cluster and BH character mix. All of the compounds considered are of lower symmetry, represent different degrees of perturbation of the parent borane, and must allow greater opportunity for mixing to occur. From the above therefore we are confident that $B_{12}H_{12}^{2-}$ will have an orbital energy order of

$$S^{\sigma}(a_{1g}) < P^{\sigma}(t_{1u}) < D^{\pi}(h_g) < S^{x}(a_{1g}) < P^{x}(t_{1u}) \sim F^{x}(g_u) < D^{x}(h_g) < F^{\pi}(t_{2u})$$

with perhaps some uncertainty in the position of S^x. Of these the D^{π} and D^x orbitals show a much greater tendency to mix under low-symmetry perturbations than any other atomic label related pair. This would account for the D^x's being out of the logical S < P < D < F order. Figure 4 illustrates the results of an MNDO calculation on the anion that, not surprisingly, shows the predicted order of orbitals.

What is surprising is that this is not the order we would have predicted from earlier work on *closo*-boranes. We have reported ab-initio[22,23] and MNDO[5,23] calculations on $B_6H_6^{2-}$, MNDO[5] on $B_7H_7^{2-}$, and photoelectron data and MNDO results[6] on $B_{10}H_{10}(N_2)_2$, a compound closely related to 1,12-$B_{12}H_{10}(CO)_2$. In all of these the energy order has consistently been $S^{\sigma} < P^{\sigma} < n, x < D^{\pi}, F^{\pi}$, for the $2n + 1$ orbitals of $B_nH_n^{2-}$. The evidence of the current work is that the D^{π}'s drop dramatically in energy between $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$, with the result that the D^x and D^{π}'s of $B_{12}H_{12}^{2-}$ have been misassigned in an earlier paper in this series.[24]

We have reported details of MNDO calculations[5] on $B_{11}H_{11}^{2-}$ and the related *nido*-$B_{10}H_{14}$, which in fact show an intermediate stage of the D^{π} stabilization. They are the first orbitals in energy above S^{σ} and P^{σ} but are close in energy to the BH orbitals. The proximity in energy and the low symmetry of these molecules causes extensive mixing of the BH and D^{π} type orbitals, which inhibited us from drawing any definite conclusions on D^{π} stabilization in that work. Stone's[3,4] energy equation for the π orbitals has the D^{π}'s reducing in energy with increasing $B_nH_n^{2-}$ cluster size for n = 2–10 but increasing for n > 10. Fowler and Porterfield have presented a more detailed analysis of this equation using EHT calculations[25] that has the D^{π} energies more or less constant across the range of cluster sizes. As neither of these theoretical approaches include the BH bonding orbitals, and, particularly as Stone has π and σ energies on separate, unrelated scales, it is not possible to fully compare them with the results above.

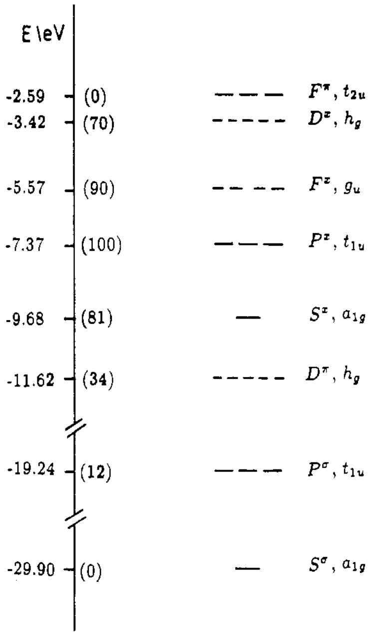

Figure 4. MNDO-calculated occupied molecular orbitals of $B_{12}H_{12}^{2-}$. The number in parentheses is the calculated percentage of BH bonding character.

It is tempting to suggest that the anomalous stability of the D^{π}'s in $B_{12}H_{12}^{2-}$ is in some way related to the capacity of the I_h symmetry to accommodate the five orbitals in their atomic degeneracy. There is, of course, no such clear correlation between symmetry and energy. It is more realistic to propose that their stability does correlate with the renowned chemical stability of $B_{12}H_{12}^{2-}$. The reactivity of the closo anions is a function of the surface-distributed, cluster-bonding, electron density rather than the BH bonding density. In $B_{12}H_{12}^{2-}$, 22 of 26 cluster-bonding electrons are deep in energy and very unlikely to be involved in chemical reactions; in general they will serve to maintain the integrity of the structure.

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Registry No. 1,12-$B_{12}H_{10}(CO)_2$, 12541-42-3; 1,2-$C_2B_{10}H_{12}$, 16872-09-6; 1,7-$C_2B_{10}H_{12}$, 16986-24-6; $P(CH)B_{10}H_{10}$, 30112-97-1; $As(CH)B_{10}H_{10}$, 23231-66-5; $Sb(CH)B_{10}H_{10}$, 28883-32-1; $As_2B_{10}H_{10}$, 51292-90-1; $SeB_{11}H_{11}$, 68027-10-1; $B_{12}H_{12}^{2-}$, 12356-13-7.

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