

Ultraviolet Photoelectron Spectroscopy of Boranes and Carboranes. Five-, Six-, and Seven-Atom Frameworks

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Abstract: The He(I) and Ne(I) photoelectron spectra of 1,6-C₂B₄H₆, 1,5-C₂B₃H₅, 2,4-C₂B₅H₇, B₅H₉, and 2-CB₅H₉ and the He(I) spectra of B₆H₁₀, 2,3-C₂B₄H₈, B₅H₁₁, and B₆H₁₂ are reported. Spectra are assigned using observed band characteristics and existing calculations. By dividing each molecule into ring and polar fragments an empirical model is developed to rationalize the observed spectra of both those for which calculations exist and those for which calculations have yet to be reported. The model suggests that the partitioning of the cage orbitals into π and σ symmetry classes with respect to cage substituent bonds is a worthwhile generalization. In addition the model provides a simple interpretative tool such that the technique of photoelectron spectroscopy may be used by the experimental chemist to investigate the properties of other more complex cages.

One of the areas of contemporary inorganic chemistry that has caught the attention of synthetic,¹ structural,² and theoretical³ chemists is that of atom clusters. One reason for this interest is the potential significance of clusters in the area of catalysis.⁴ If history is a guide, the continued development of cluster chemistry will parallel the development in understanding the electronic states of these systems. The purpose of this work is to construct an experimental approach to a conceptually simple description of small clusters. In this paper an approximate, but useful, empirical model for small main group clusters as exemplified by the polyhedral boranes is developed.

The traditional approach to electronic structure is via quantum chemical calculations whose degree of sophistication varies inversely with the complexity of the problem. Progress toward a satisfactory description of the electronic structure of metal clusters has been slow, not for lack of effort, but simply because of the sheer difficulty of the problem.⁵ We feel that in this area the experimental technique of molecular photoelectron spectroscopy can make a significant contribution. With this method exact information on the electronic states of positive ions is produced.⁶ This information is easily translated into a one-electron molecular orbital description of the molecule⁶ which can then be directly compared with approximate, but more detailed, calculations. However, this is not the only way photoelectron spectra can be used. With even simple quantum chemical models as a language, it is possible for the experimental chemist to use the technique of photoelectron spectroscopy to reveal characteristic features of systems of interest.⁷ One objective of this work is to demonstrate this possibility for cluster systems.

The approach to complex clusters via borane systems has several advantages. First, the synthetic chemistry is sufficiently well worked out so that well-characterized series of compounds can be generated and studied.⁸ Second, the structures of many compounds are known and serve to clearly establish at least three distinct structural classes.^{9,10} The arrangement of heavy atoms in these clusters depends in a fundamental fashion on the number of electrons that can be associated with cluster bonding.¹¹ The simple working rules that have resulted from this discovery provide the experimental chemist with an excellent guide for the generation of structures from molecular formulas.¹² Finally, the compounds have been the subject of a continuing series of state of the art calculations so that the basic features of the electronic structures of the boranes are well understood.^{13,14} Thus, in approaching clusters in general from this direction, one begins with a firm base of established experimental and theoretical data from which one can explore the similarities and differences of more complex cluster systems.

In previous work we have presented some initial considerations of the photoelectron spectra of small closo carboranes¹⁵ and the effects of exo substituents on the photoelectron spectrum of a nido borane, B₅H₉.¹⁶ Others have reported the spectra of B₄H₁₀, B₅H₉, and B₁₀H₁₄ along with calculations.¹⁷ The discussion accompanying the latter work presented a correlation between the orbitals of the three boranes based on population analyses. In this paper a correlation is developed by a partitioning of the filled orbitals into three types. This model is used to present a simple rationale of both the photoelectron spectra and the results of existing quantum chemical calculations. Despite the approximate nature of the model, we show that it can be used to explain the basic features of the spectra of compounds for which calculations have not been carried out. In the following paper, the technique of photoelectron spectroscopy is used to characterize some clusters containing single iron atoms.

The Ring-Polar Model. The LCAO approximation in which one-electron molecular orbitals are constructed from combinations of individual orbitals of the constituent atoms is well known to all chemists. A related approximate treatment which is becoming more popular both in qualitative¹⁸ and sophisticated¹⁹ considerations of the electronic structure of complicated molecules involves representing the molecule with orbitals derived from fragments containing more than one atom. In such a treatment fragment orbitals are classified into two types: those that interact strongly with other fragments and those that do not. The main advantage of such an approach is that the latter type of orbitals are largely transferable from molecule to molecule producing a net simplification of the problem. There is no unique way of dividing a molecule into fragments and the particular partitioning chosen results from an attempt to balance factors such as the number of fragment-fragment orbital interactions and the number of compounds a fragment can be used in. The fragments-in-molecules approach has already been used extensively in the analysis and interpretation of photoelectron spectra of a variety of chemical compounds²⁰ and is also adopted here for an approach to cluster structure via photoelectron spectroscopy.

For the detailed treatment of small clusters (five to seven heavy atoms) we propose that ring-polar partitioning originally presented as a physical factorization of the secular equation by Hoffmann and Lipscomb²¹ is appropriate. Here we restrict ourselves to clusters of heavy atoms each of which is bound to one hydrogen atom by normal covalent bonds.²² In the ring-polar model rings of three to five heavy atoms constitute one fragment. The polar fragments consist of two heavy atom-hydrogen atom fragments for bipyramids and one heavy atom-hydrogen atom fragment for pyramids. As schematically indicated in Figure 1, there are $2n$ (n = number of heavy atoms

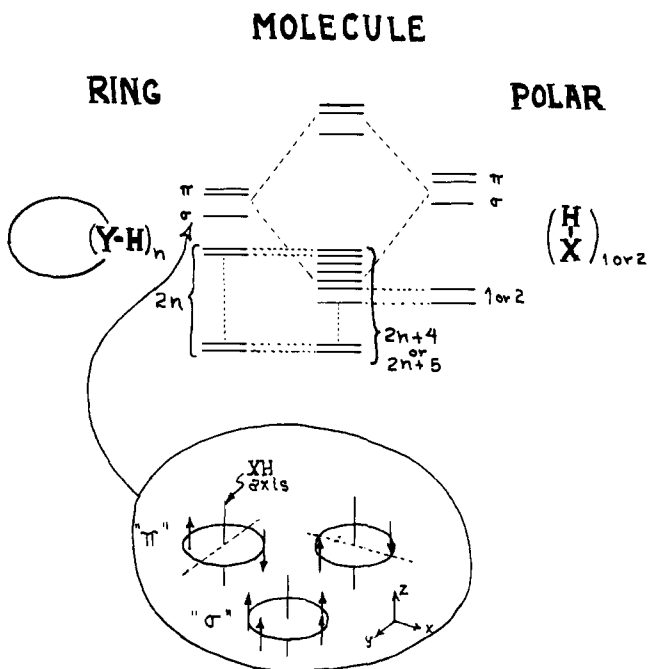


Figure 1. Schematic, qualitative representation of the ring polar model for the $(Y-H)_n(X-H)_2$ and $(Y-H)_n(X-H)$ molecules.

in the ring) transferable orbitals (those assumed not to interact with the polar fragments) in the ring fragment and one transferable orbital per polar fragment. The fragment-fragment interactions take place between three of the possible out-of-plane ring orbital combinations (one of σ symmetry with respect to the X-H axis of the polar fragment and two of π symmetry with respect to the same axis) and three orbitals or orbital combinations of the polar fragment(s) of matching symmetry. The net result is $2n + 4$ or $2n + 5$ filled orbitals for one and two polar fragments, respectively.

The major weakness of this model lies in the fact that more use is made of the orbitals in the ring fragment than of those in the polar fragment(s).²¹ Consequently, even approximate calculations indicate that more mixing than is permitted in the ring-polar separation occurs between ring and polar fragment orbitals. Thus, this particular factorization can fail even in predicting closed-shell species.²¹ However, here we take the number of filled orbitals in clusters of varying structure as a fact that has now been well established by the work of others.¹² Thus, in the following we do not use the formalism of the ring-polar model as a means of predicting closed shell species but rather as a representation of the basic features of the orbital structure of existing (therefore closed shell) compounds as revealed by the technique of photoelectron spectroscopy. Even though it is an approximate approach it not only provides a language for conveniently discussing the spectra for "known" systems, i.e., those for which good calculations exist, but also allows a reasonable assignment of "unknown" systems.

Experimental Section

The photoelectron spectra of 1,5- $C_2B_3H_5$, 1,6- $C_2B_4H_6$, 2,4- $C_2B_5H_7$, B_5H_9 , 2- CB_5H_9 , B_6H_{10} , 2,3- $C_2B_4H_8$, B_5H_{11} , and B_6H_{12} have been recorded in the gaseous state using He(I) (21.2 eV) and, in some cases, Ne(I) (16.8 eV) radiation.²³ The spectrometer used¹⁵ has a resolution of 20 meV (fwhm) at 5 eV electron energy. A mixture of xenon and argon was used as an internal calibrant. Samples were gifts (B_5H_{11} ,²⁴ B_6H_{12} ,²⁴ and CB_5H_9);²⁵ were purchased (1,5- $C_2B_3H_5$,²⁶ 1,6- $C_2B_4H_6$,²⁶ 2,4- $C_2B_5H_7$,²⁶ and B_5H_9);²⁷ or were prepared according to published procedures (B_6H_{10} ²⁸ and 2,3- $C_2B_4H_8$).²⁹ Purity of samples was checked by mass spectrometric analysis and in some cases by ^{11}B NMR. B_5H_{11} was run with the sample reservoir at $-78^\circ C$ to reduce decomposition.

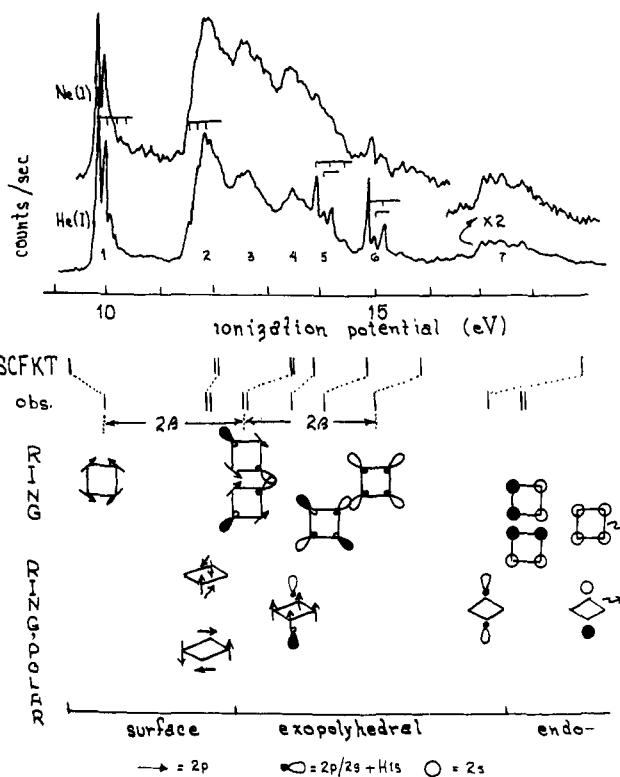


Figure 2. The photoelectron spectra of 1,6- $C_2B_4H_6$ and the band assignments in terms of ring, polar, and ring-polar interaction orbitals. The SCF orbital energies are taken from ref 32.

Photoelectron Spectra. The data are presented in Figures 2-9 and Table I. Ideally each band in the photoelectron spectrum corresponds to an electronic state of the molecular ion; however, many bands are obviously complex and represent more than one state. Band shape and vibrational fine structure, when observed, reflect differences between the structure of the molecule in the ground electronic state and the particular state of the ion reached by photoionization. In terms of Koopmans' theorem,⁶ each individual band arises from the ionization of a filled molecular orbital and, thus, band structure also reflects molecular orbital characteristics. For ionization of orbitals of similar composition and energy, band area reflects orbital occupancy.³⁰ Finally, the dependence of the cross section on photon energy for ionization of orbitals situated on atoms of differing nuclear charge will be different.³¹ Variable frequency photoionization thus allows one to distinguish individual ionizations in complex bands and allows qualitative conclusions concerning the atomic makeup of a molecular orbital to be drawn.²⁰

Applications

Bipyramidal (Closely) Structures. 1,6- $C_2B_4H_6$. This molecule has been the subject of a previous study¹⁵ and the old and new data are summarized in Figure 2 and Table I. Briefly, on the basis of vibrational fine structure bands 1 and 2 are assigned to ionization of molecular orbitals associated with the framework. Similarly, bands 5 and 6 are assigned to orbitals primarily involved in heavy atom hydrogen bonding, i.e., exopolyhedral bonds. Band areas or shapes indicate that bands 1, 4, 5, and 6 are due to the ionization of single occupied molecular orbitals while 2 and 3 are due to ionization of doubly degenerate orbitals. The calculated dependence of atomic orbital cross sections on energy indicates that ionization from boron orbitals increases in intensity relative to carbon orbitals as the photon energy is changed from 21.2 to 16.8 eV.²⁰ On this basis the spectra suggest greater carbon character for band 2 than band 3. It is also observed that the bands known to be associated with exo-polyhedral hydrogen bonds (5 and 6) decrease sharply in intensity with lower energy photons.

The orbitals of the ring-polar model as described above are easily generated. There will be two sets of four transferable

Table I. Vertical Ionization Potentials, Relative Band Areas, and Band Assignments

Molecule	Band ^a	IP, ^b eV	A/E ^c (rel)	A/E (736 Å) A/E (584 Å)	IP per band (min)	IP per band (assigned)	Assignment ^d
1,6-C ₂ B ₄ H ₆	1	9.9	0.1	1.0	1	1	S,R; B2p
	2	11.8	0.2	1.1	1	2	S,R-P; B2p,C2p
	3	12.5	0.2	1.3	1	2	Ex,R; B2p,H1s
	4	13.4	0.2	1.3	1	1	Ex,R-P; B2p,C2p,H1s
	5	14.0			1	1	Ex,R; B2s,H1s
	6	15.0			1	1	Ex,R; B2p,H1s
	7	17.5			1	3	1Ex,P; C2p,H1s 2Ed,R; B2s
1,5-C ₂ B ₃ H ₅	1	10.9	0.4	1.0	1	2	S,RP; B2p,C2p
	2	11.7	0.4	1.4	2	2	Ex,R; B2p,H1s
		12.1 sh					
	3	13.5	0.4	1.4	1	1	Ex,RP; B2p,C2p,H1s
	4	14.5	0.2	1.7	1	1	Ex,R; B2p,H1s
	5	16.0			1	1	Ex,P; C2p,H1s
2,4-C ₂ B ₅ H ₇	6	16.9			2	2	Ed,R; B2s
		17.5 sh					
	1	10.6	0.3	1.0	2	2	S,R; B2p,C2p
	2	11.6	0.4	1.0	2	2	S,R-P; B2p S,R-P; B2p,C2p S,R; B2p,C2p
	3	12.8	0.2	1.8	1	1	Ex,R-P; B2p,C2p,H1s
	4	13.8	0.3	1.0	1	2	Ex,R; B2p,C2p,H1s
	5	14.2			1	1	Ex,R; B2s,C2s,H1s
	6	15.0			1	1	Ex,R; B2s,C2s,H1s
B ₅ H ₉	7	15.4			1	1	Ex,P; B2p,H1s
	8	17.4			1	1	Ex,R; B2p,C2p,H1s
	1	10.5	0.4	0.9	1	2	S,RP; B2p
	2	12.7	0.7	1.0	2	3	1Ex,RP; B2p,H1s 2Ex,R; B2p,H1s
	3	14.6	0.8	0.3	2	3	2Ex,R; B2p,B2s,H1s Sp,R; B2p,H1s
2,CB ₅ H ₉	4	16.4			1	1	Ed,P; B2s
	5	18.6			1	2	Ed,R; B2s
	1	10.4	0.2	1.0	2	2	S,RP; B2p,C2p
	2	12.4	0.4	1.2	3	5	1Ex,RP; B2p,C2p,H1s 2Ex,R; B2p,C2p,H1s
		11.8 sh 12.2 sh					2Sp,R; B2p,C2p,H1s
B ₆ H ₁₀	3	14.9			2	2	2Ex,R; B2s,C2s,H1s
	4	14.7 sh					1Ex,R; B2p,H1s
		16.1 16.6 sh			2	2	Ed,P; B2s
	1	9.4	1.0		1	1	S,RP; B2p
	2	12.2	6.5		4	6	1S,RP; B2p 1Ex,RP; B2p,H1s Ex,R; B2p,H1s 2Sp,R; B2p,H1s
2,3-C ₂ B ₄ H ₈	3	14.6	0.9		1	1	Ex,R; B2p,H1s
	1	9.6	1.0		1	1	S,RP; B2p,C2p
	2	12.3	6.2		4	6	1S,RP; B2p,C2p 1Ex,RP; B2p,C2p,H1s 2Ex,R; B2p,C2p,H1s 2Sp,R; B2p,C2p,H1s
B ₅ H ₁₁		11.3 sh 11.7 sh					
	3	14.9	0.4		1	1	Ex,R; B2p,C2p,H1s
	1	10.7	1.0		1	1	Ex,R; B2p,C2p,H1s S,RP; B2p
	2	12.2	5.8		3	5 or 6	
B ₆ H ₁₂		11.7 sh 12.5 sh					
	3	14.0	0.8		1	1	
	4	14.8	0.5		1	1	
	1	10.2	1.0		1	1	S,RP; B2p
	2	12.1	6.2		2	6	
		11.5 sh					
	3	13.7	1.7		1	2	
	4	14.9	1.1		1	1	

^a See figures for numbering. ^b Energies refer to band centers. Shoulders on bands are indicated by sh following the energy. Two errors in the data in Table I of ref 15 should be noted. The band listed at 19.77 eV for C₂B₄H₆ is not confirmed in this work. The band in C₂B₅H₇ assigned to ionization of the 12a₁ and 1a₂ orbitals has a band center at 10.6 eV as stated here. The values 10.9 and 11.2 eV in ref 15 are incorrect. ^c Band area, He(I), over mean electron energy. ^d S = surface orbital, Ex = exo-polyhedral orbital, Ed = endo-polyhedral orbital, R = ring orbital, RP = ring-polar interaction orbital, P = polar orbital, Sp = protonated surface orbital.

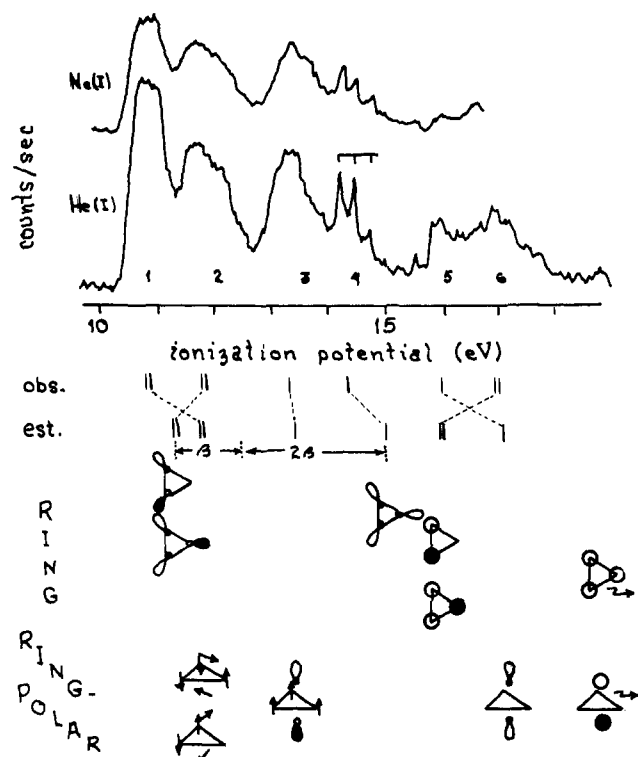


Figure 3. The photoelectron spectra of 1,5-C₂B₃H₅ and the band assignments using the ring-polar model. Correlations between observed and estimated levels are made on the basis of observed band characteristics.

orbitals associated with the ring and constructed out of B2p and 2s and H1s, and three orbitals associated with the interaction of the fragments. Although it is known that for the valence region the higher energy orbitals will be predominantly 2p, the next lower energy orbitals 2p, 2s, and H1s, and the lowest mainly 2s and that the relative ordering of the orbital sets will depend on the number of nodes in the orbital (the most symmetric being at lowest energy), an unambiguous assignment is not possible without the aid of calculations. As SCF calculations have been published³² these are used to make the assignment schematically illustrated in Figure 2, one that also agrees with the experimental observations summarized above.

This "calibration" results in several simple "rules". The higher energy set of four ring fragment orbitals is constructed from in-plane 2p orbitals while the lower set of four ring fragment orbitals and the transferable polar fragment orbitals are formed from 2s orbitals. The ring-polar interactions result from out-of-plane 2p_z ring orbitals and polar 2p_x and 2p_y orbitals. H1s are then assigned to the six (one per cluster atom) highest energy orbitals for which such interactions are allowed by symmetry. It is noted that the highest occupied molecular orbitals in this system are constructed strictly from 2p functions that lie in the surface of the polyhedron. As these orbitals are the analogue of π systems in other classes of compounds,³³ they are appropriately denoted as π -endo-polyhedral orbitals or surface orbitals. The six orbitals lying below the surface orbitals are involved mainly in σ -exo-polyhedral interactions while the last four orbitals of the valence shell are σ -endo-polyhedral in nature. These ten orbitals represent the σ system of the cluster. Thus, π -endo-, σ -exo-, and σ -endo-polyhedral designations constitute a more general, but less detailed, partitioning of the cage molecular orbital structure.

1,5-C₂B₃H₅. This molecule constitutes the first test of the usefulness of the ring-polar model. The polar fragment orbitals as well as the ring-polar interaction orbitals factored from the results on C₂B₄H₆ may be directly carried over to C₂B₃H₅. The

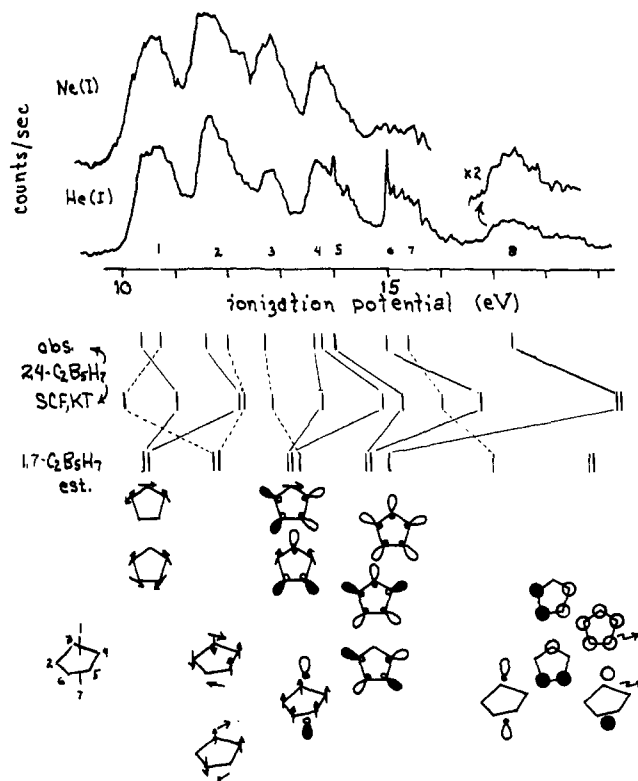


Figure 4. The photoelectron spectra of 2,4-C₂B₅H₇, the estimated band positions for 2,4-C₂B₅H₇ using SCF orbital energies³⁵ and Koopmans' theorem, and the estimated band positions for 1,7-C₂B₅H₇ using the ring-polar model.

ring orbitals must be modified. This is easily done by considering each of the two sets of ring orbitals as if they were isolated systems. In the case of a four-member ring the relative energies of each set are $\alpha - \beta$, α , α , and $\alpha + 2\beta$, while for a three-member ring they are $\alpha - \beta$, $\alpha - \beta$, and $\alpha + 2\beta$, where α and β are parameters.³⁴ Using α 's and β 's from C₂B₄H₆ for each set of orbitals ($\alpha_1 = -12.4$, $\beta_1 = -1.3$, $\alpha_2 = -17.5$, $\beta_2 = -1.7$ eV) yields the predicted spectrum indicated in Figure 3. The experimental results allow some testing of the predictions.

On the basis of fine structure band 4 is clearly exo-polyhedral while on the basis of area bands 1 and 2 involve the ionization of doubly degenerate orbitals. The change in relative intensity upon changing photon energy²⁰ suggests that band 1 has greater carbon 2p character than band 2 and, thus, is associated with ring-polar interactions. These data allow the correlation between estimated and observed energy levels for bands 1-4. Bands 5 and 6 are assigned by difference. The model generates qualitative orbital types and approximate positions so that the spectrum is quickly assigned. SCF calculations of the orbital energies of this molecule have not been published.

2,4-C₂B₅H₇. This molecule consists of a five-atom ring and two polar groups; however, the carbon atoms are now in the ring and the polar fragments are now BH rather than CH. The observed fine structure identifies bands 5 and 6 as exo-polyhedral ionizations. Relative band areas suggest that bands 1, 2, 4, and 7 involve the ionization of more than one molecular orbital. In bands 1 and 2 this is clearly evident from the definite change in band contour as photon energy is reduced. In each case the higher component seems to be associated with an orbital having higher boron content.

The ring-polar model can be used to predict the spectrum of the 1,7-C₂B₅H₇ but not 2,4-C₂B₅H₇ because in the latter case all the degeneracies will be removed and there is no way to estimate the splitting involved. Taking a different tack, the

observed spectrum and the SCF computational results³⁵ on the 2,4 isomer when compared to the predicted spectrum of the 1,7 isomer will show the sensitivity of the model to changes in the ring and polar fragment compositions. Thus, both the Koopmans' theorem SCF results on the 2,4 isomer and the model estimates for the 1,7 isomer (ring orbital energies are $\alpha - 1.6\beta$, $\alpha - 1.6\beta$, $\alpha + 0.6\beta$, $\alpha + 0.6\beta$, $\alpha + 2\beta$ ³⁴) are shown in Figure 4. By intercomparing observed band features, calculated orbital coefficients, and orbital diagrams, a correlation between the three sets of levels can be carried out. This is also indicated in Figure 4. As expected, the introduction of carbon into the ring splits the degeneracy of the ring fragment orbitals. Although this splitting cannot be ignored, it appears to be overestimated in the calculations. In a crude sense, in going from the 1,7 isomer to the 2,4 isomer those orbitals that lose carbon character are shifted to higher energy (dotted lines) while those with greater carbon character go to lower energy (solid lines). Despite the different locations of the carbon atoms in the two isomers both have an orbital structure consisting of four π -endo-polyhedral orbitals above seven σ -exo-polyhedral orbitals which in turn are above four σ -endo-polyhedral orbitals. At this level of partitioning, the model is independent of isomer type.

Pyramidal (Nido) Structures. B_5H_9 . The He(I) and Ne(I) spectra of this molecule are presented in Figure 5 and the data are gathered in Table I. This species has been the subject of several previous experimental studies as well as numerous calculations.^{15,17,36,37} All agree that the first four bands result from the ionization of 2, 3, 3, and 1 molecular orbitals, respectively. The fine structure on band 3 that largely disappears in switching to Ne(I) indicates that at least some of the three ionizations are from exo-polyhedral orbitals.

Beginning with the B_4H_4 ring fragment and a single BH polar fragment the relative orbital energies of the closed shell $B_5H_5^{4-}$ species may be generated in the manner indicated in the previous section with but one change. As suggested by the analysis of the $C_2B_5H_7$ spectrum, the effect of decreasing the nuclear charge in going from a CH polar fragment to a BH polar fragment can be compensated for by increasing the energies of the orbitals associated with the polar fragment and polar ring interactions by about 1 eV. The relative orbital energies and compositions for $B_5H_5^{4-}$ estimated in this fashion are indicated at the bottom of Figure 5.

To generate B_5H_9 four protons must be added to the ring. Protonation yields a net stabilization of all orbitals but some will be much more strongly affected than others. This is demonstrated very clearly by comparing the photoelectron spectra of CS and HBS for which band assignments are unambiguous.^{38,39} We can consider the change from CS to HBS as involving the removal of a proton from the carbon nucleus to a position on the BS axis near boron. The net result is a large stabilization of the former σ_c orbital (the highest lying orbital on CS) owing to a more effective Coulombic interaction. On the other hand both the σ_s and π orbitals are destabilized owing to the lower nuclear charge of boron compared to carbon. A stabilization of ~ 4 eV on protonation and a destabilization of ~ 1 eV upon reduction of nuclear charge by 1 unit carries over into larger systems as well. Comparison of the photoelectron spectra of C_2H_4 with B_2H_6 demonstrates that removing a proton from each carbon in ethylene and protonating the double bond results in about 4 eV stabilization of the equivalent orbital in B_2H_6 .⁴⁰ The other orbitals rise 1–2 eV on changing the nuclei from carbon to boron.

In $B_5H_5^{4-}$ there is one ring orbital that will be very strongly affected by the addition of four protons, i.e., the highest filled surface orbital. It is not surprising then that protonation results in about a 4–5 eV stabilization of the orbital with respect to the others. Finally, the other ring orbitals are directly transferred from $C_2B_4H_6$ yielding the estimated orbital scheme in

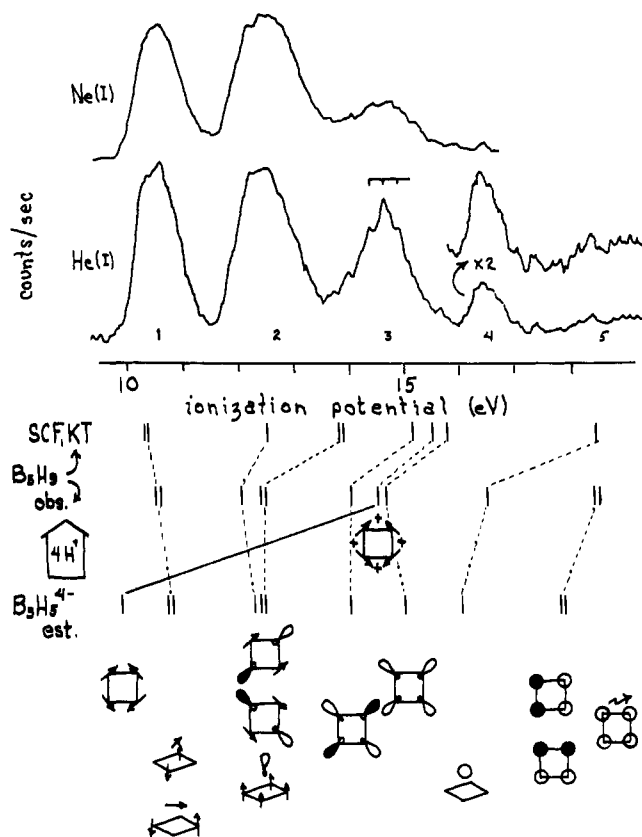


Figure 5. The photoelectron spectra of B_5H_9 and the modification of the ring-polar model for a protonated, pyramidal structure.

Figure 4. Orbital types agree well with the SCF results and energies correspond well with both experimental and SCF results. Thus, with the empirically sound adjustments for the change in nuclear charge of the polar atom and one adjustment for protonation, a good representation of the electronic structure of B_5H_9 is generated. As in the case of the bipyramid, the highest occupied molecular orbital is a π -endo-polyhedral orbital. In the case of B_5H_9 this is the doubly degenerate ring-polar interaction orbital.

B_6H_{10} , 2- CB_5H_9 , and 2,3- $C_2B_4H_8$. The photoelectron spectra of these species have not been previously reported; however, both B_6H_{10} and 2,3- $C_2B_4H_8$ have been examined via quantum chemical methods.^{41,42} The three molecules are isoelectronic and have pentagonal pyramidal cage structures. The molecules differ in number of carbon atoms and bridging hydrogens in the ring fragment.

The spectra are shown in Figures 6 and 7 and the data are gathered in Table I. The lower symmetry of these molecules results in more overlapping bands in the 11–14 eV region. Still, some empirical observations are possible. Comparison of relative band areas suggest that band 1 in CB_5H_9 results from the ionization of twice as many orbitals as band 1 in either B_6H_{10} or $C_2B_4H_8$. In the case of CB_5H_9 this is confirmed by a comparison of He(I) and Ne(I) band shapes (see the inset of Figure 6) which indicates that the ionization of at least two orbitals produce this band. Taking two as the most reasonable number, band areas and contours suggest that five to seven ionizations are involved in band 2 of all three species. The sharp nature of band 3 (and the reduced intensity with Ne(I)) suggests ionization of exo-polyhedral orbitals.

A description of the electronic structure of the six-atom pyramidal cage can be generated via $B_6H_6^{4-}$ by using the B_5H_5 ring and a BH polar fragment. Orbital types and relative energies are shown at the bottom of Figure 6 using the parameters developed in the previous sections. By reference to

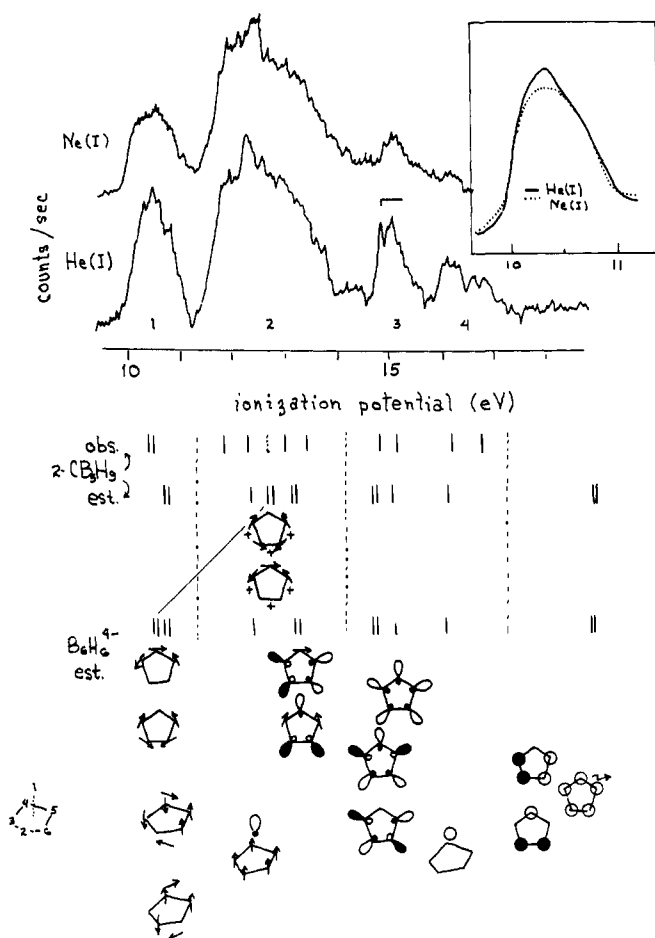


Figure 6. The photoelectron spectra of 2-CB₅H₉ and the band assignments using the ring-polar model.

B₅H₉ it is expected that protonation will stabilize the highest lying surface orbitals most strongly. As in the case of 1,7-C₂B₅H₇ and 2,4-C₂B₅H₇ substitution of carbon and unsymmetrical protonation of the ring will remove the degeneracies in the various classes of orbitals. The splitting cannot be estimated here either. However, comparison of the spectra and model predictions should reveal the magnitude of the splitting for various combinations of ring carbons and borons and degrees of ring protonation.

We consider CB₅H₉ first in Figure 6. The energy levels estimated on the basis of the ring-polar model assuming zero splitting due to asymmetrical carbon distribution and ring protonation are compared with the observed levels in Figure 6. This representation is consistent with the observed band positions and areas. A rationalization of the apparently small splitting in this molecule can be suggested for the highest occupied molecular orbitals. These ring-polar interaction orbitals involve ring p_z combinations with polar p_x and p_y orbitals (see Figure 8). The relative stabilization of the Bp_x interaction by two bridging protons is apparently about equal to the relative stabilization of the Bp_y interaction with Cp_z and one bridging proton.

In the cases of B₆H₁₀ and C₂B₄H₈ both the experimental observations and the calculations indicate that the highest occupied molecular orbital is a single orbital well separated from the orbital of next lower energy. In the case of B₆H₁₀ the splitting is 2.2 eV while for C₂B₄H₈ it is 1.7 eV. A qualitative rationale for this observation is given in Figure 8 where it is suggested that for B₆H₁₀ the Bp_x is stabilized over Bp_y by ring protonation. In the case of C₂B₄H₈ the opposite is true. The position of the carbons and ring protonation stabilize Bp_y over Bp_x. These explanations are rather speculative even though

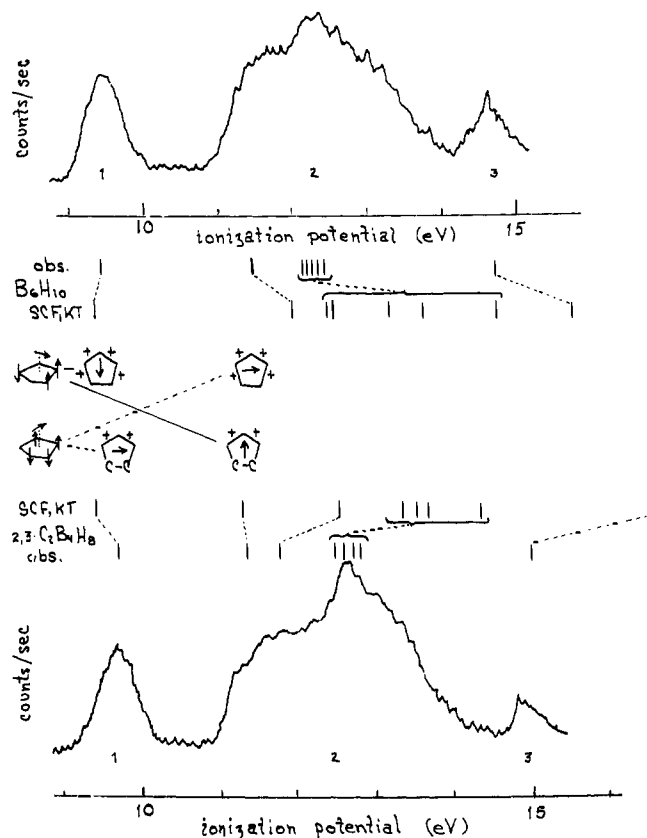


Figure 7. The photoelectron spectra of B₆H₁₀ and 2,3-C₂B₄H₈ and the assignment of the ring-polar interaction orbitals. The SCF orbital energies are taken from ref 41 and 42.

the relative ordering agrees with the results of the calculations. Nevertheless, in an empirical sense, the splitting between the highest ring-polar interaction orbitals is a rather sensitive function of the ring composition. Thus, in related compounds the magnitude of this splitting can serve as a probe of the nature of the ring structure.

For the lower lying orbitals the ring-polar model does not yield the detailed picture of previous examples. However, in terms of orbital density as a function of energy it gives a good representation of the observations. In considerations of reactivity and substituent effects, the filled orbital of primary interest is the orbital of highest energy. Here the model does predict the basic nature of the HOMO. Again it is a π -endo-polyhedral orbital of the ring-polar interaction type.

Conclusions

We have demonstrated that conceptually simple ideas may be used to provide a reasonable explanation of the electronic structures of clusters of boron and carbon as revealed by their photoelectron spectra. The electronic structure of the cluster may be considered to be made up of π -endo-, σ -exo-, and σ -endo-polyhedral orbitals. In all cases the ordering of cluster orbitals is $E \pi$ -endo $> E \sigma$ -exo $> E \sigma$ -endo. For molecules of high symmetry the ring-polar model yields a more detailed picture of the orbital compositions and energies. In going from closed clusters to more open systems there is a reduction in the number of high-lying π -endo-polyhedral orbitals due to protonation. The π -endo-polyhedral or surface orbitals are of particular interest as they lie at high energy and have π symmetry with respect to exo substituents. Therefore they should be strongly perturbed by substituent orbitals of π symmetry in the same manner as the π system in benzene. This has already been demonstrated for the B₅H₉ system¹⁶ and recent work substantiates the conclusion for the C₂B₄H₆ system.⁴²

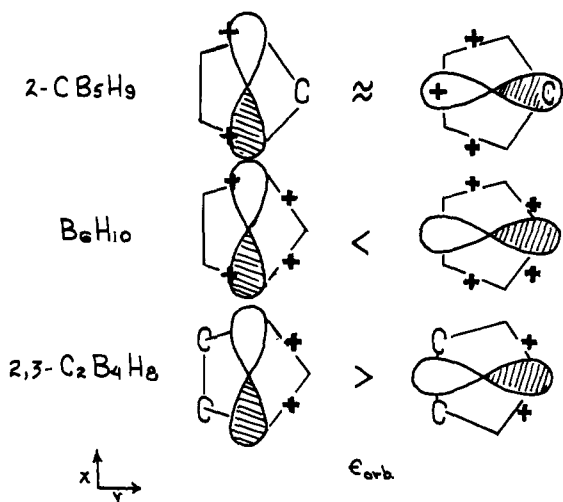


Figure 8. Schematic representation of the ring-polar interaction orbitals for 2-CB₅H₉, B₆H₁₀, and 2,3-C₂B₄H₈.

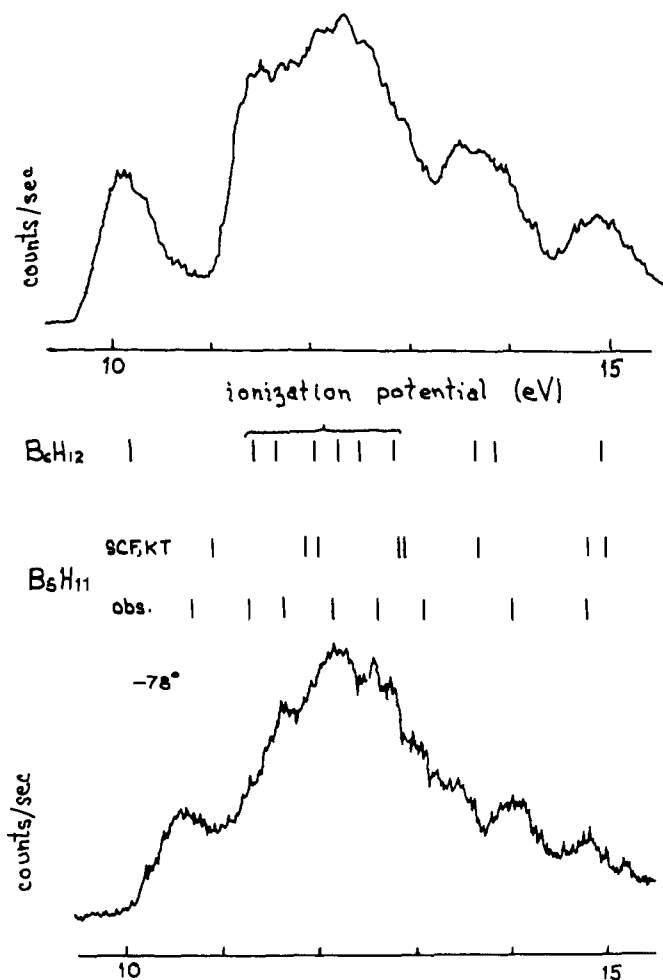


Figure 9. Photoelectron spectra of B₅H₁₁ and B₆H₁₂. The SCF orbital energies for B₅H₁₁ are taken from ref 37.

The ring-polar model can now be applied to a more interesting class of cluster systems, those containing transition metals.⁴⁴

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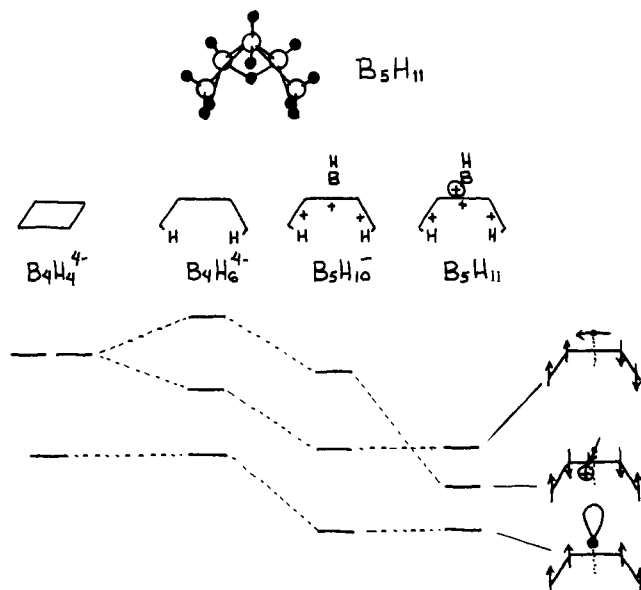


Figure 10. Schematic representation of the generation of the highest occupied molecular orbitals of B₅H₁₁ from the (BH)₄ ring-(BH) polar interaction orbitals.

Appendix

Open (Arachno) Structures. B₅H₁₁ and B₆H₁₂. For completeness the photoelectron spectra of five- and six-atom examples of the third well-established structural class of boranes are presented in Figure 9. The spectra, as expected, are even more diffuse; however, both molecules exhibit a band at low ionization potential that is quite distinct and which, on the basis of area, is probably due to the ionization of a single orbital. SCF calculations have been carried out on B₅H₁₁ and for comparative purposes the energy levels are represented in the figure.

There is no direct way that the ring-polar model can be applied to these compounds; however, in the case of B₅H₁₁ something can be said concerning the nature of the HOMO. Assuming that the HOMO correlates with the ring-polar interaction orbitals of B₅H₉, one may begin by opening the B₄H₄⁴⁻ ring to give B₄H₆⁴⁻ (i.e., the analogy would be cyclobutadiene to butadiene). As indicated in Figure 10 the originally degenerate out-of-plane p combinations would then be split. Interaction with a polar BH would yield the HOMOs for B₅H₇⁴⁻ as indicated. Addition of four protons would yield B₅H₁₁; however, only three can be placed on the former ring. The fourth is placed on the polar BH thereby stabilizing the HOMO of B₅H₇⁴⁻ as indicated. The result is a good representation of the three highest filled orbitals resulting from the SCF calculations.³⁷ More importantly, these rationalizations provide an explanation for the increase in ionization potential in going from B₅H₉ to B₅H₁₁. Finally, B₅H₁₁ has only a single orbital that can be classified as a surface orbital.

There is no straightforward way of getting to the proposed structure of B₆H₁₂ by opening the five-atom ring in B₆H₆⁴⁻ with H₂. On the other hand, it seems reasonable to assume that the band at lowest ionization potential is due to a surface type orbital and that the higher ionization potential of B₆H₁₂ compared to that of B₆H₁₀ results from the protonation of the orbital that correlates with the HOMO in B₆H₁₀. Even so, one is forced to conclude that in open clusters of low symmetry this qualitative model is of marginal utility.

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Characterization of Ferraboranes by Ultraviolet Photoelectron Spectroscopy

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Abstract: The He(I) and Ne(I) photoelectron spectra of C₂B₃H₅Fe(CO)₃, C₂B₃H₇Fe(CO)₃, B₄H₈Fe(CO)₃, B₅H₉Fe(CO)₃, and B₅H₃Fe(CO)₅ are reported. Spectra are assigned utilizing observed band characteristics and an empirical model based on an analysis of the spectra of boranes and carboranes of similar size and structure. Comparison of B₄H₈Fe(CO)₃ with B₅H₉ and C₄H₄Fe(CO)₃ reveals that the electronic structure of the borane is a good model for the ferraborane. Characteristic features of the spectra of B₅H₉Fe(CO)₃ suggest a close relationship to B₆H₁₀ while observations on B₅H₃Fe(CO)₅ are consistent with a structure involving 2CO molecules bound to the cage in exo-polyhedral positions. The nature of the perturbation of the iron atom by the cage and the cage by the iron atom is also revealed in the analysis of the spectra.

Recently a number of compounds containing a borane framework and one iron tricarbonyl group have been discovered and characterized.¹⁻³ These ferraboranes and related ferracarboranes have small enough structures and sufficient volatility such that they can be conveniently investigated with the technique of valence level photoelectron spectroscopy. As the photoelectron spectrum is directly related to the electronic structure of the molecule cast in a one-electron molecular orbital description,⁴ this technique provides a means of probing the nature of the metal-cage interaction. The usual means of analyzing photoelectron spectra involves the utilization of quantum chemical calculations. With metals this presents some difficulties. First, quantitative calculations involving metals require more than a casual, semiempirical approach, and, second, comparison of good calculated energy levels with photoelectron spectra has provided evidence for exceedingly large Koopmans' defects for orbitals having large metal d character.⁵ In the preceding paper⁶ in which the electronic

structure of small pyramidal and bipyramidal boranes and carboranes was considered, we presented an alternative to calculations. In this approach the photoelectron spectra of model compounds are used as sources of parameters for a qualitative description of related compounds. This method is adopted here to describe the spectra of ferracarboranes and ferraboranes and also to reveal the behavior of an iron atom in the environment generated by the borane cage.

The interaction of transition metals with borane and carborane cages has been and still is of great interest.⁷ In terms of a valence bond description, there are at least three distinct ways known by which a metal is coupled to a cage. In one a single atom of the cage is bonded to the metal by a two-electron, two-center bond and the metal functions as any other exo-polyhedral ligand. In the second the metal is in a bridging position of the cage and the interaction is considered to take place through a three-center, two-electron bond. In the third, the metal may be considered as interacting with the cage by