Substituent Effects in Cluster Species. 2. Photoelectron Spectra of 2- and 2,4-Substituted 1,6-Dicarba-*closo*-hexaborane(6)

G. A. Beltram and T. P. Fehlner*

Contribution from the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556. *Received December 14, 1978*

Abstract: The He(I) photoelectron spectra of 2-X-1,6-$C_2B_4H_5$ and 2,4-X_2-1,6-$C_2B_4H_4$ where X = Cl, Br, and I are reported. The syntheses and characterizations of the new disubstituted derivatives are described. A simple three-parameter model is used to describe the effects of halogen substitution on the photoelectron spectrum of the closo carborane. A π-type interaction between the surface orbitals of the cage and the filled halogen p orbitals constitutes the major effect. The parameters generated permit the relative electronic charge at the 2 position of 1,6-$C_2B_4H_6$ to be compared to that at the 1 and 2 positions of B_5H_9. In addition the relative extent of interaction of X with the six-atom cage is compared to that for a six-atom aromatic ring system. This work demonstrates that the surface (π endo) orbitals of a cluster play an important role in determining the effect of substitution on cluster properties.

There is a growing interest in the structure and reactivity of discrete clusters, particularly those composed of metal atoms.[1] It is natural that the emphasis of much of this work is on developing a relationship between cluster structure, reactivity, and cluster bonding. For clusters or cages containing first-row atoms, e.g., the boranes, there has been much progress in that useful models now exist and permit much of the observed chemistry to be organized in a systematic fashion.[2] For metal clusters the situation is much less clear and a variety of approaches are pursued. Many seek to compare aspects of mono-, di-, tri-, etc., metallic compounds;[3] however, we have adopted the approach in which a cluster containing metal atoms is compared with a related cluster containing only first-row atoms.[4] In such a comparison the unique aspects of the metal are highlighted. The experimental technique we choose to use in this comparison is UV photoelectron spectroscopy in which a direct comparison of the properties of the corresponding radical cation states in a series of related molecules is made.[5] Essentially then, we empirically compare systems with electronic structures that are formally related by the electron counting rules developed for boranes[6] in order to reveal and understand situations in which the rules "fail".[7] With this philosophy we are investigating three aspects of cluster bonding, namely, the effects of composition,[4,8] size, and nonhydrogenetic exo-cluster ligands[9] on the nature of cluster bonding.

This work constitutes a contribution to the last-named area. In many considerations of cluster bonding a separation of the problem into exo- and endo-cluster bonding is assumed.[10,11] Situations exist in which interaction between ligands and the cluster bonding system is allowed by symmetry and, if such exo-endo interaction is significant, it will perturb the cluster bonding. Consequently, the interaction between cage and substituents is important in predicting and understanding reactivities. In certain cases the perturbation can be large enough so that the simple rules relating electron count to structure can breakdown.[12] In previous work we have explored some aspects of exo substitution on a nido cage[9] and herein extend this work to a closo system. In doing so it was necessary to prepare some of the disubstituted cages and we report the preparation and characterization of these new derivatives as well.

Results

Dihalogenated Carboranes. The boron-substituted monochloro, monobromo, and monoiodo derivatives have been previously prepared and characterized.[13-15] The general approach was to react the carborane directly with halogen in the presence of AlX_3. The resulting compounds were characterized spectroscopically and the pertinent ^{11}B NMR data, including that for the parent compound,[16a] are compiled in Table I. In no case, however, was the formation of a disubstituted compound reported.[16b] We have found that a small change in the reaction conditions results in disubstitution at boron. As these compounds facilitate the interpretation of the photoelectron spectra they have been isolated and characterized. In addition, the position of substitution was determined by an analysis of the ^{11}B spectra, also gathered in Table I.

It has been stated that for carboranes substitution on a boron by chlorine or bromine results in a downfield shift of the ^{11}B resonance.[17] More important for our purposes is the fact that such shifts are accompanied by significant shifts elsewhere in the molecule. Examples are known in 6-,[18] 7-,[19] and 12-atom[20] closo carborane cages as well as in the nido pentaborane(9) cage.[21] Recently, the systematic nature of such shifts was demonstrated by two groups.[22,23] It was shown that for 1,12-$C_2B_{10}H_{12}$ replacement of H by a halogen gives rise to measurable shielding of the antipodal boron and deshielding of the vicinal boron.[24] These observations allow us to distinguish disubstitution leading to 2,3-X_2-1,6-$C_2B_4H_4$ from that leading to 2,4-X_2-1,6-$C_2B_4H_4$.

The data in Table I demonstrate that monohalogen substitution does not always lead to a downfield shift of the associated ^{11}B resonance but that in all cases it leads to deshielding at the 3,5 positions (vicinal). In two cases shielding at the position (antipodal) is observed while in one case there is no net effect at the 4 position. Thus, for 2,3 substitution where each BH is vicinal to one substituted boron and antipodal to the other we expect to see for the single BH resonance observed either cancellation of the two shielding effects or, in the case of the dibromo compound, a chemical shift about equal to that of B(3,5) in the monobromo derivative. On the other hand, for 2,4 substitution each BH is vicinal to both substituted borons; thus they should be deshielded to a greater extent than the 3,5 borons in the monohalogenated compounds. In all cases the ^{11}B doublet in the disubstituted compound is shifted downfield with respect to the B(3,5) doublet in the monosubstituted compound. Thus, we assign these compounds as the 2,4-disubstituted derivatives.

An attempt was made to thermally rearrange the 2,4-chloro and bromo disubstituted derivatives in solution.[25] On heating, the ^{11}B NMR resonances associated with the 2,4 derivatives rapidly disappeared and new resonances appeared (see Experimental Section). However, the new signals had an intensity

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Table I. ^{11}B Chemical Shifts of 1,6-$C_2B_4H_6$, 2-X-1,6-$C_2B_4H_5$, and 2,4-X_2-1,6-$C_2B_4H_4$[a]

compd	chemical shift[b] [coupling constant][c]			ref
	B(2)	B(3,5)	B(4)	
1,6-$C_2B_4H_6$	−18.9 [184]			16
2-Cl-1,6-$C_2B_4H_5$	−8.8	−16.4 [192]	−28 [194]	13
2-Br-1,6-$C_2B_4H_5$	−27.7	−16.3 [193]	−18.2 [205]	14
2-I-1,6-$C_2B_4H_5$	−32.7	−15.9 [189]	−20.1 [196]	15
	−31.8	−15.2 [200]	−19.4 [211]	this work
2,4-Cl_2-1,6-$C_2B_4H_4$	−15.7	−15.1 [190]		this work
2,4-Br_2-1,6-$C_2B_4H_4$	−19.0	−14.8 [212]		this work
2,4-I_2-1,6-$C_2B_4H_4$	−33.8	−13.0 [190]		this work

[a] Values obtained at 25.2 MHz in this work in CD_2Cl_2 as solvent. [b] With respect to $(C_2H_5)_2O\cdot BF_3$ as reference. Downfield shifts are positive: *J. Organomet. Chem.*, **131**, C43 (1977). [c] In hertz.

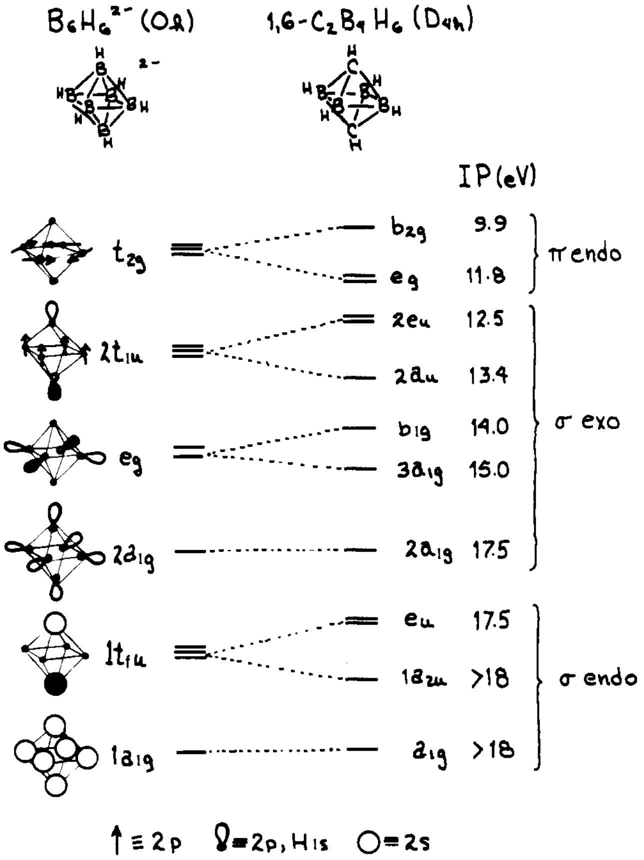


Figure 1. Schematic description of the filled molecular obtitals for $B_6H_6^{2-}$ and 1,6-$C_2B_4H_6$. Only one component of each degenerate group is shown. The ionization potentials are taken from ref 8.

distribution that could not be attributed to a disubstituted derivative. Fractionation of the heated material yielded only trace amounts of a disubstituted compound. It must be concluded that, under the conditions employed, the original compound decomposed either with or without rearrangement into a nonvolatile material of unknown composition.

Model Considerations. Before we can consider the effect of substituents on the cage it is necessary to review the molecular orbital structure of the cage itself. On the left-hand side of Figure 1 is shown a representation of the filled orbitals for $B_6H_6^{2-}$. These correlate with the indicated orbitals of 1,6-$C_2B_4H_6$ for which the ionization potentials are known. The assignment of orbitals with ionization potentials is discussed in previous publications[8,26] but it should be noted that the b_{2g}, e_g, b_{1g}, and $3a_{1g}$ ionizations are unambiguously assigned on the basis of observed vibrational fine structure. Also as noted on the figure, we have found it useful in our work to classify the cage orbitals according to their symmetry with respect to a radial direction of a sphere that contains the heavy atoms of the cage as π endo (surface), σ exo, and σ endo where endo and exo refer to cage and ligand (H) bonding, respectively.[8]

In replacing an exo hydrogen by a substituent X the cage molecular orbital structure will be perturbed in a number of ways. First, one BH ionization (σ exo) will be lost and one BX ionization will be gained. Second, if the electronegativity of X is different from that of H, all the orbitals will be shifted to higher or lower ionization potential. Finally, if the substituent has orbitals of π symmetry with respect to the cage, there can be an interaction with the cage surface orbitals. As this last interaction is expected to have a more noticeable effect on the properties of a carborane,[27] we choose to use halogens as substituents as they have filled p orbitals of π symmetry with respect to the cage. The extent to which such an interaction is visible depends on the symmetry of cage and halogen orbitals, the relative energies of cage and halogen orbitals, the cage orbital coefficient at the position of attachment, and the intrinsic magnitude of the perturbation. We can parametrize the interaction of a single cage orbital with a halogen p orbital using a three-parameter filled orbital model. This model is schematically drawn in Figure 2a and discussed elsewhere.[28] Trial values of the two parameters, α_c and α_x, are obtained from model compounds and the parameter β from an ionization potential of the substituted compound. The three parameters allow the other ionization potential to be predicted. Note also that α_x can be varied by changing the substituent.

With this model it is possible to make qualitative predictions of the changes expected by replacement of H by a halogen. In this preliminary discussion we ignore the shift due to the change in electronegativity in going from H to X[29] and the BX ionization.[30] We consider only the interaction of the "lone pair" halogen p orbitals with the cage orbitals. In terms of the symmetry and energy criteria only interactions with the b_{2g}, e_g, $2e_u$, and $2a_u$ orbitals have to be considered. However, the orbitals derived from the $2t_{1u}$ set of $B_6H_6^{2-}$ are expected to have much smaller orbital coefficients at the position of attachment than are those derived from the t_{2g} set, an expectation supported by published calculations.[31] Thus, only interactions with the b_{2g} and e_g orbitals need be considered. The net result is shown in Figure 2b,c for monochlorination and dichlorination. In the former case one filled p orbital of the halogen interacts with the b_{2g} cage orbital and the other splits the degeneracy of the e_g pair. In the latter case only two of the four possible sets of p orbitals can interact with the cage. Again one interacts with the b_{2g} orbital and the other splits the degeneracy of the e_g orbital.

Before considering the spectra a comment on our use of orbital discussions of photoelectron spectra is in order. A connection between orbital energies and ionization potentials was established by Koopmans.[32] Quantitatively equating observed ionization potentials to the negative of calculated orbital energies had led to considerable discussion of the validity of Koopmans' theorem as there are well-established examples in

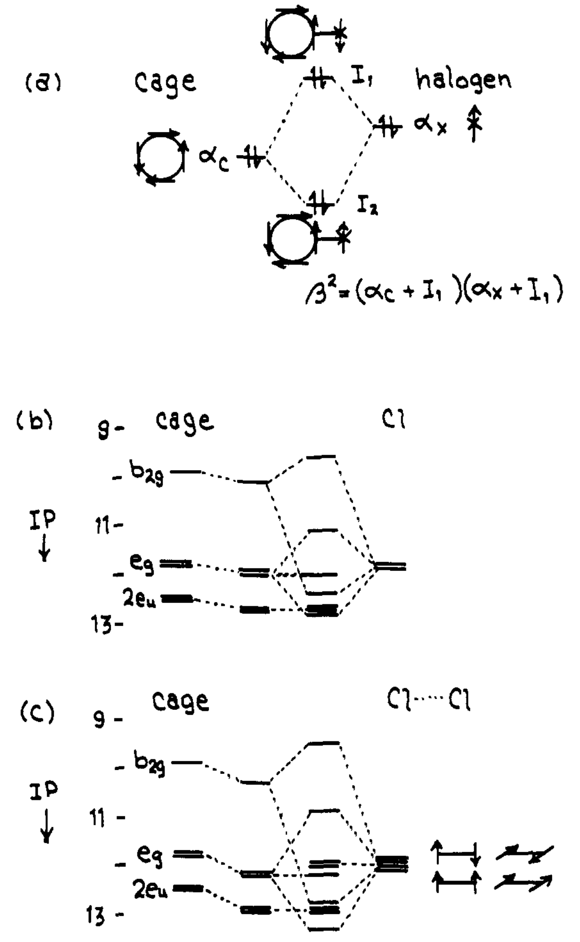


Figure 2. (a) The parametrization scheme for the interaction of a single surface orbital with a substituent π orbital. I_1 and I_2 are measured ionization potentials and α_c, α_x, and β are parameters. (b and c) Parametrization of the effects of the replacement of the 2 and 2,4 hydrogens by chlorine on the photoelectron spectrum of 1,6-$C_2B_4H_6$. Both drawings are to scale with the ionization potential in eV.

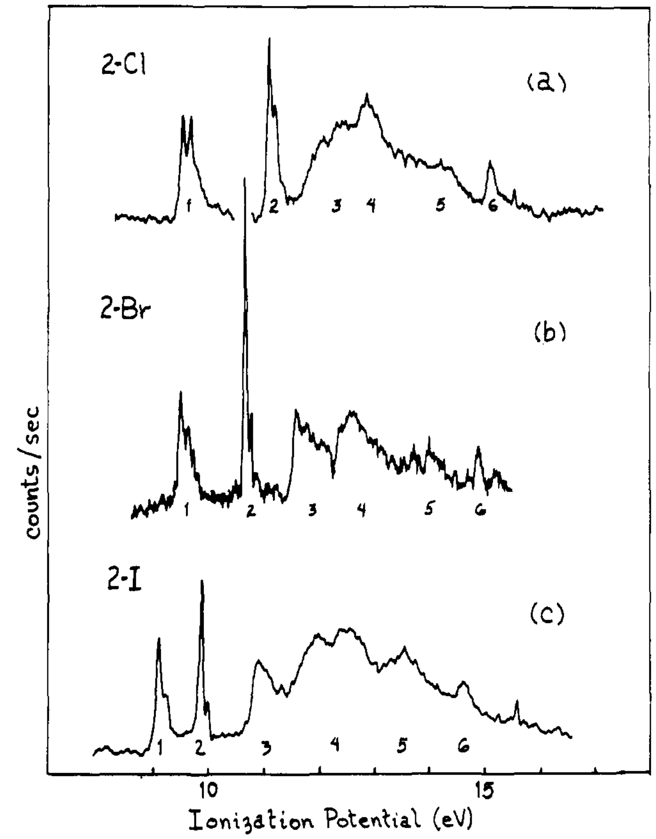


Figure 3. Photoelectron spectra of (a) 2-Cl-1,6-$C_2B_4H_5$, (b) 2-Br-1,6-$C_2B_4H_5$, and (c) 2-I-1,6-$C_2B_4H_5$.

which it fails. In our work, however, we use Koopmans' theorem in a *qualitative* sense, i.e., we use orbitals as a language to discuss the nature of empirically characterized cation states in a series of structurally and chemically related compounds. Thus, although we speak in molecular orbital terms, any numbers that we use refer to the states of the radical cations. On the other hand, we do expect the trends in numbers observed for the radical cation states of a related series of molecules to be chemically relevant to the molecules themselves; i.e., any Koopmans' defect cancels out in such a comparison.

Photoelectron Spectra. The He(I) photoelectron spectra of 2-X-1,6-$C_2B_4H_5$ and 2,4-X_2-1,6-$C_2B_4H_4$ for X = Cl, Br, and I are shown in Figures 3-5 and the data are gathered in Table II.[33] In all cases the spectra consist of a number of sharp bands with vibrational fine structure at the lowest ionization potentials followed by broad bands at higher ionization potentials. In the following we give a complete analysis of the chloro and dichloro derivatives followed by a summary of the results for the bromo and iodo derivatives.

The first two bands of 2-Cl-1,6-$C_2B_4H_5$ are shown in expanded scale in Figure 5a. Both bands exhibit narrow Franck-Condon envelopes which strongly suggests significant halogen character. The first band shows clear excitation of an ionic vibrational mode at 1060 cm^{-1} while the unusual intensity distribution of the lines and the presence of shoulders suggest the excitation of a second mode at about 700 cm^{-1}. The second band shows three lines having an uneven spacing. Again the shoulder on the second line along with the uneven spacing suggests the excitation of at least two vibrational modes. One is clearly 740 cm^{-1} and the other is thought to be about 1100 cm^{-1}. In both cases the excitation of the mode at 1100 cm^{-1} is attributed to one of the symmetric cage vibrations (1096 and 986 cm^{-1} in the unsubstituted molecule and 940 cm^{-1} in the band assigned to the ionization of the b_{2g} orbital in the unsubstituted molecule).[26,34] The information available does not allow the assignment of the 700-cm^{-1} mode. It is possibly due to excitation of the B-Cl stretch (471 cm^{-1} in $^{11}BCl_3$) and, if so, would imply that both ionizations result from orbitals strongly antibonding with respect to cage and halogen. Taken together the band shapes and fine structure indicate that the two bands result from ionization of orbitals with both cage and halogen character.

This is exactly what is expected on the basis of the predicted qualitative behavior outlined in Figure 2b; i.e., the first two bands result from the ionization of orbitals arising from the antibonding combination of surface orbitals and halogen p orbitals with the one at lower ionization potential having the higher cage character. With the empirical identification of the first two bands, it is now possible to generate the model parameters and complete the assignment.

According to the procedure outlined above one needs five parameters to model the effect of the substituent: $\alpha_{b_{2g}}$, α_{e_g}, α_{Cl}, $\beta_{b_{2g}}$, and β_{e_g}. Trial values of $\alpha_{b_{2g}}$ and α_{e_g} may be obtained from unsubstituted $C_2B_4H_6$.[36] The magnitude of the shift due to the change in electronegativity of the substituent may be estimated from the behavior of the e_g orbital upon substitution. One component will experience a two-center interaction with a halogen p orbital whereas the other will only be shifted due to the difference in electronegativities between hydrogen and the halogen (inductive effect). The ionization energy of the e_g orbital in the unsubstituted compound is 11.8 eV and the

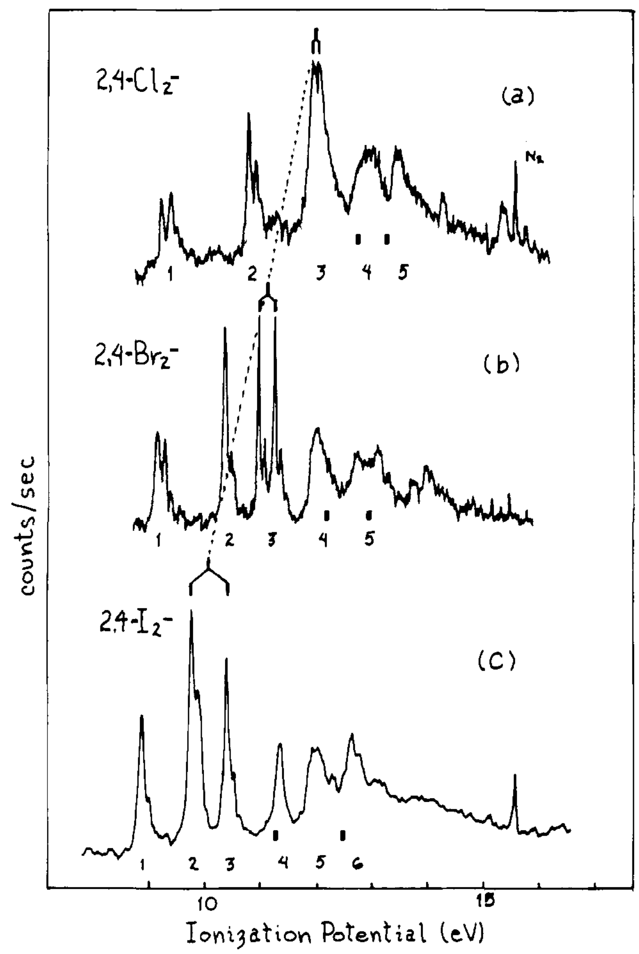


Figure 4. Photoelectron spectra of (a) 2,4-Cl_2-1,6-$C_2B_4H_4$, (b) 2,4-Br_2-1,6-$C_2B_4H_4$, and (c) 2,4-I_2-1,6-$C_2B_4H_4$. The correlation between the lone-pair bands with characteristic spin-orbit splitting is indicated by the dashed line. The small solid rectangles indicate predicted band positions based on the fit of the first three bands (see text).

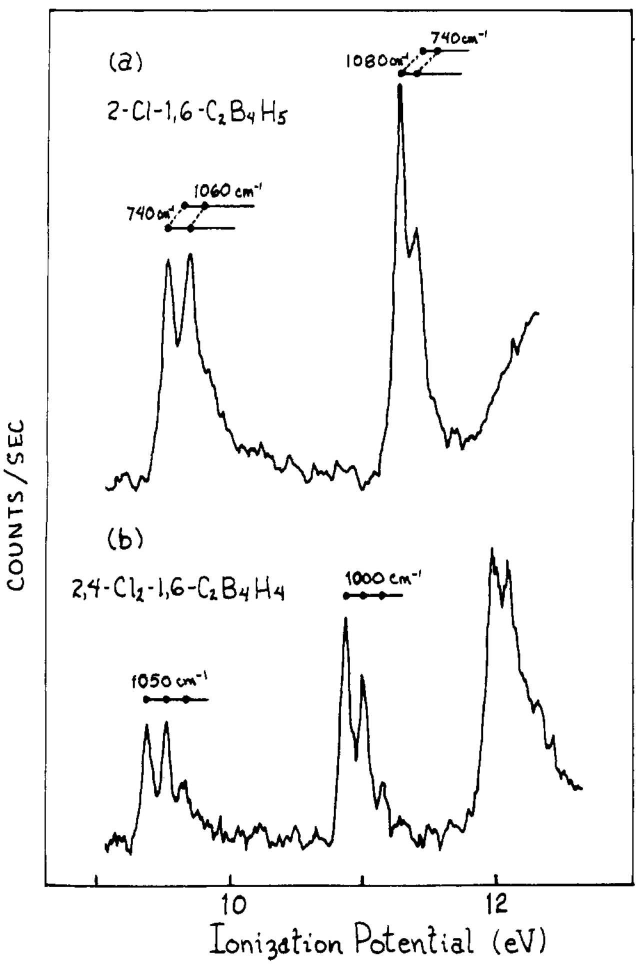


Figure 5. The photoelectron spectra of (a) 2-Cl-1,6-$C_2B_4H_5$ and (b) 2,4-Cl_2-1,6-$C_2B_4H_4$ with expanded scale showing the vibrational fine structure of the first two bands.

closest match in Figure 3a is the band at 12.0 eV. Thus, the electronegativity shift produces a stabilization of 0.2 eV on the c_g orbitals. This inductive shift is assumed to apply to all of the cage orbitals[37] as indicated in Figure 2b.

The assignment proceeds as follows. As indicated above, bands 1 and 2 in the spectrum (Figure 3a) result from the interaction of cage orbitals with chlorine lone pairs. The band at lowest ionization potential has major cage character and is derived from the former b_{2g} cage orbital. As a destabilization of 0.5 eV results from the interaction, this assignment implies the presence of a band at $(-\alpha_{Cl} + 0.5)$ eV. Band 2, on the other hand, appears to have major chlorine character which implies that $-\alpha_{Cl}$ is closer to 11.1 eV than is $-\alpha_{e_g}$. This requires a destabilization of the halogen lone pair of $(-\alpha_{Cl} - 11.1)$ eV and another ionization at $(12.0 - \alpha_{Cl} - 11{,}1)$ eV. From the relative areas of bands 1-4 it appears that bands 3 and 4 contain five ionizations. The shoulder on 3 has already been assigned to the former e_g component that does not interact with the chlorine p orbitals. Two of the remaining four ionizations may be assigned to ionization of the former e_u orbitals which is expected at about 12.7 eV. The maxima at 12.3 and 12.8 eV are assigned to the expected cage-halogen interaction bands at $(-\alpha_{Cl} + 0.5)$ and $(-\alpha_{Cl} + 0.9)$ eV, respectively. This yields two determinations of $-\alpha_{Cl}$, 11.8 and 11.9 eV, respectively. Finally, $\beta_{b_{2g}}$ and β_{e_g} are calculated and all the parameters are gathered in Table III. The parameters are of the expected magnitudes but, without the data on the dichloro derivative (see below), cannot be considered a unique fit.

The dichloro derivative can be assigned in the same fashion but now α_{Cl} can be unambiguously obtained from the spectrum. By symmetry, two of the four combinations of chlorine p orbitals shown in Figure 2c cannot interact with either the b_{2g} or e_g orbitals of the cage and thus serve as a direct measure of α_{Cl}. It is not surprising then that, in contrast to the monohalogenated spectra, the dihalogenated spectra exhibit an intense, relatively sharp band with a splitting characteristic of the spin-orbit splitting of the halogen and lying about 0.6 eV lower in ionization potential than the corresponding halogen acid (Figure 4).[38] These bands result from the strictly localized p ionizations of the halogens and the mean of the split band is taken to be $-\alpha_X$. For X = Cl this band corresponds to band 3 in Figure 4 which lies at 12.0 eV. As the shoulder on band 3 and the relative area suggests the presence of another ionization at 12.2 eV we take $-\alpha_{e_g} = 12.2$ and, thus, $-\alpha_{b_{2g}} = 10.3$ eV for the dihalogenated derivatives.

The interaction scheme in Figure 2c suggests that with the exception of the noninteracting lone pairs the spectrum of the dichloro derivative should be very similar to that of the monochloro derivative. In conformance with these expectations, the first two bands have vibrational fine structure (Figure 5b); however, in both cases the major mode excited in the ion corresponds most closely to a cage frequency. Both bands are assigned to cage-halogen interaction bands, the one at lower ionization potential being assigned to that derived from the b_{2g} orbital. These two assignments along with the α values above allow $\beta_{b_{2g}}$ and β_{e_g} to be calculated. This fit of bands 1, 2, and 3 in the spectrum yields a prediction of the positions of the two

Table II. Vertical Ionization Potentials, Relative Band Areas, and Vibtational Fine Structure

molecule	band[a]	IP,[b] eV	*A* (rel)	vibrational structure, cm^{-1}
2-Cl-1,6-$C_2B_4H_5$	1	(9.53)[c]	1.0	1060, 700
		9.6		
	2	11.1	1.1	740, 1080
	3	12.0 sh	4.9	
		12.3		
	4	12.8		
	5	14.3		
	6	15.1		
2-Br-1,6-$C_2B_4H_5$	1	(9.43)	1.0	1080
		9.5		
	2	10.6	1.0	880
	3	11.7	4.6	
	4	12.6		
	5	14.0		
	6	14.9		
2-I-1,6-$C_2B_4H_5$	1	(9.16)	1.0	1070
		9.2		
	2	9.9	1.0	900
	3	10.9	1.0	
	4	12.0 sh		
		12.6		
	5	13.6		
	6	14.9		
2,4-Cl_2-1,6-$C_2B_4H_4$	1	(9.38)	1.0	1050
		9.5		
	2	10.9	1.3	1000
	3	12.0	3.2	840[d]
		12.2 sh		
	4	13.0	1.9	
	5	13.5	1.6	
2,4-Br_2-1,6-$C_2B_4H_4$	1	(9.17)	1.0	1020
		9.3		
	2	10.4	1.2	870
		11.03[d]		
	3	11.33	2.1	860
	4	12.1	1.8	
	5	13.0	2.3	
2,4-I_2-1,6-$C_2B_4H_4$	1	(8.86)	1.0	1090
		8.9		
	2	9.8	2.3	980
	3	10.4	1.2	860
	4	11.3	0.7	
	5	12.0		
	6	12.7		

[a] See figures for numbering. [b] Energies refer to band centers. Shoulders on bands are indicated by sh following the energy. [c] The number in parentheses refers to the adiabatic ionization potential. [d] Splitting due to spin-orbit interactions rather than vibrational excitation.

Table III. Parameters (eV) Characterizing the Effects of Halogen Substituents on the b_{2g} and e_g Molecular Orbitals of 1,6-$C_2B_4H_6$

		2-X-1,6-$C_2B_4H_5$			
X	$-\alpha_{b_{2g}}$	$-\alpha_x$	$-\beta_{b_{2g}}$	$-\alpha_{e_g}$	$-\beta_{e_g}$
Cl	10.1	11.9	1.06	12.0	0.82
Br	10.1	11.2	0.99	12.0	0.88
I	10.1	10.1	0.90	12.0	0.65
		2,4-X_2-1,6-$C_2B_4H_4$			
X_2	$-\alpha_{b_{2g}}$	$-\alpha_x$	$-\beta_{b_{2g}}$	$-\alpha_{e_g}$	$-\beta_{e_g}$
Cl	10.3	12.0	1.41	12.2	1.20
Br	10.3	11.2	1.38	12.2	1.20
I	10.3	10.1	1.30	12.2	0.85

Table IV. A Comparison of α_x Values (eV) for Two Cages and B(1s) Binding Energies and Two Calculations of Charge

cage		B_5H_9[a]	B_5H_9[a]	1,6-$C_2B_4H_6$[b]
position		1-	2-	2-
$-\alpha_x$, eV	Cl	11.5	11.7	11.9
	Br	10.6	11.1	11.2
	I	9.6	9.8	10.1
CNDO[c,d]		−0.15	0.01	−0.02
SCF[e]		0.00	0.06	0.10
BE B(1s)[c]		194.2	196.1	194.5

[a] Reference 9. [b] This work. [c] Reference 44. [d] Reference 39. [e] References 31 and 40.

other cage-chlorine interaction bands at 12.8 and 13.3 eV (Figure 4a). The former lies in band 4 along with the former e_u ionizations and the latter in band 5. With the exception of the relative area of band 4 the overall fit is good. The consistency in the values of parameters used in the two molecules (Table III) and the good fit of the spectra lend confidence to the assignment.

It is a simple matter to extend this procedure to the bromo and iodo derivatives. The only significant difference is that α_x changes by about 2 eV in going from Cl to I, thus introducing more and more halogen character into the first two bands. This is evident in the sharpening of the two bands as one goes from Cl to I (Figures 3 and 4). Again a fit of the monohalogenated compound yields a value of α_x while a fit of the bands at low ionization potential for the dihalogenated compound allows the prediction of two other band positions. The predicted band positions are shown in Figure 4 and the parameters are listed in Table III. In all six molecules the fits and predicted positions are good and the qualitative assignment developed in Figure 2 is verified. Thus, for all six molecules the highest occupied molecular orbital is that derived from the antibonding combination of the b_{2g} orbital of $C_2B_4H_6$ with one or two halogen p orbitals. As one proceeds down the series Cl, Br, I, the percentage halogen character in this orbital increases, becoming dominant in $I_2C_2B_4H_4$.

Discussion

The parameters, α_x, are useful in that they provide information on the electronic charge distribution in the cages. As it is used here, α_x is the energy of an electron in a p orbital in the field of a shielded halogen nucleus. The difference in effective electronegativity of the halogen and the cage atom to which it is bound can either increase or decrease the shielding of X with respect to some reference state, e.g., HX. Thus, in a series of compounds with X in different positions, α_x measures the relative shielding experienced by a halogen p electron at the position of substitution. Alternatively, α_x can be viewed as the energy necessary to create a hole in a p orbital localized on a halogen atom bound to a specific cage position. In both views α_x reflects the electronic charge at the position of substitution.

We have previously measured α_x for 1- and 2-substituted pentaborane(9)[9] and the values obtained are compared in Table IV with those for the carborane. There are two significant points. First, α_x depends on the cage and the position of substitution. Second, the trends observed are independent of the halogen used as probe. Going from right to left across the table corresponds to an increase in shielding of the halogen p electrons which is presumably due to increased electron density at the position of substitution. Alternatively, proceeding from right to left corresponds to a decrease in the energy necessary to create the hole in the halogen substituent. Ignoring any differential stabilization of the hole in the final state, the numbers in Table IV reflect the relative electron density at the position of substitution. It should be noted especially that these

Table V. Parameters (eV) Characterizing the Effects of Halogen Substituents on the π e_g Molecular Orbitals of Benzene[a]

	C_6H_5X		
X	$-\alpha_x$	$-\alpha_{e_g}$	$-\beta_{e_g}$
Cl	11.3	9.7	1.16
Br	10.6	9.7	.98
I	9.4	9.6	.83
	$1,4\text{-}C_6H_4X_2$		
X	$-\alpha_x$	$-\alpha_{e_g}$	$-\beta_{e_g}$
Cl	11.6	9.9	1.47
Br	10.8	10.0	1.33

[a] IPs obtained from D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley-Interscience, New York, 1970.

numbers are "absolute" in the sense that they do not depend on a method of partitioning charge.

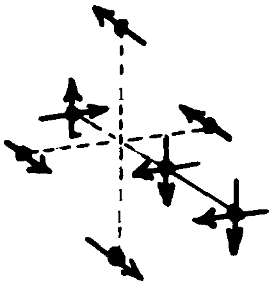
It is of interest then to compare this empirical measure of charge to typical theoretical measures. Table IV also contains the results of CNDO/2[39] and SCF[30,40] calculations. In terms of relative charge along the series, the SCF calculation appears to reproduce the observed behavior better than the CNDO/2 calculations. One of the significant uses of calculated charges is to predict the relative ease of electrophilic substitution as a function of position.[41] Although the calculations consider only the reactant molecule charge distributions, rather good agreement is reported between theory and experiment.[42] The parameters α_x reported here should be a much better measure of relative reactivity with respect to electrophilic attack on the cage. Insofar as electron density is removed by the attacking reagent α_x should be a measure of the barrier to attack. Because α_x is a measured "ionization potential" final state effects are included. In addition, α_x should be of predictive value in relative rate of electrophilic attack on positions of different cages.

Another technique that has been used to probe the charge on atoms in molecules is that of X-ray photoelectron spectroscopy in which binding energies of core electrons are measured. These energies are found in general to depend on two quantities: the charge on the atom in question and the potential generated at the atom by neighboring atoms.[43] The B(1s) binding energies for the compounds in Table IV have been measured along with many others.[44] Although for many types of atoms a calculation of charge is sufficient to obtain a reasonable correlation of binding energies, in the case of B(1s) binding energies no correlation with CNDO charge exists.[44] Thus, the fact that the B(1s) binding energies for the B-1 boron of B_5H_9 and the B-2 boron of $1,6\text{-}C_2B_4H_6$ are similar cannot be taken to imply similar charges. For charge measurements, we suggest that a probe connected to, but outside, the cage is better than one inside the cage itself.

The replacement of hydrogen by chlorine in the 2 position of $1,6\text{-}C_2B_4H_6$ was examined in the CNDO/2 study.[39] By calculating the net change in charge densities upon substitution, it was concluded that there is little net transfer of charge around the cage network and, therefore, little "aromaticity" As this conclusion is in marked contrast to the implications of some recent observations,[45] it is of interest to compare the substituent effects of halogens on a six-atom cage to those on a six-atom aromatic ring, i.e., benzene. Spectra of both mono-halogenated and 1,4-dihalogenated benzenes have been published[5] and can be parametrized by application of the scheme shown in Figure 2a. The out-of-plane p orbital of the halogen interacts with one component of the π e_g orbital thereby splitting it. The value of α_x is obtained from the noninteracting in-plane p orbital of X and the value of α_{e_g} is obtained from the noninteracting component of the π e_g orbital. The disubstituted case is similar except that there are three halogen lone pair combinations that by symmetry cannot interact with the ring π orbitals. The parameters generated by this analysis are gathered in Table V.

In comparing the parameters for benzene with those for the carborane in Table III a number of interesting points arise. First, for the monohalogenated compounds $|\alpha_x|$ is about 0.6 eV higher for the carborane than for benzene. The cage appears to have a significantly higher effective electronegativity than the benzene ring with respect to a halogen. This is the same general conclusion reached in a study of $B_4H_8Fe(CO)_3$ and $C_4H_4Fe(CO)_3$[4] in which it was found that with respect to iron d ionizations the B_4H_8 ring has a higher electronegativity than the C_4H_4 ring. Secondly, the inductive stabilization of the π e_g orbital in benzene on adding one halogen is about 0.4 eV while the stabilization of the e_g orbital in the carborane is only 0.2 eV. This also suggests that the difference in electronegativities is less in the case of the carborane than in the case of benzene; i.e., the carborane is more electronegative. On adding a second halogen to benzene there is a further inductive stabilization of the halogen lone pair (0.3 eV) and further inductive stabilization of the π e_g (0.3 eV). On the other hand, addition of a second halogen to the carborane has only a small effect on α_x and α_{e_g}. The C_6H_4X unit is expected to have a higher net electronegativity than the C_6H_5 unit. Thus $|\alpha_x|$ for $X\text{-}C_6H_4X$ is expected to be higher than $|\alpha_x|$ for $X\text{-}C_6H_5$ as observed. The same reasoning applies to $X\text{-}C_2B_4H_4X$ compared to $X\text{-}C_2B_4H_5$; however, here the electronegativity of $C_2B_4H_5$ starts out closer to that of X and therefore the net effect is smaller.

A more pertinent comparison with respect to possible delocalization in the cage is that between the values of β in the two systems. In both cases the values of β are in the vicinity of -1 eV, are larger for disubstitution than for monosubstitution, and decrease in the order Cl > Br > I. The same observation is true for 1- and 2-substituted pentaboranes as well. Insofar as the β values reflect relative electron donation into the π system of benzene,[46] they should reflect electron donation into the π endo orbitals or π system of the cage. In this regard it is of significant interest to note that a correlation has been demonstrated between ^{13}C chemical shifts of the para-position of monosubstituted benzenes and ^{11}B chemical shifts of the antipodal atom of substituted cages for electron-donating substituents.[45] The high-lying π endo (surface) orbitals of the cage provide a possible mechanism for coupling of the antipodal atoms, i.e., the 2,4 positions. As shown in the sketch below,



the 2,4 positions are coupled to a π substituent by twice as many surface orbitals as the 2,3 positions. In any closed cage the antipodal positions will be similarly coupled. The similarities between halogen substituent effects on the benzene system and the carborane surface orbitals must at least be taken as circumstantial evidence for extensive delocalization in the cages.[47]

Finally, the photoelectron spectra of the mono- and dihalogenated carboranes and the analysis presented above empirically establish the π endo (surface) character of the highest occupied molecular orbitals of $C_2B_4H_6$. This point is important for two reasons. First, the electron counting rules strongly imply that the highest occupied molecular orbital in a cluster is associated with the cluster bonding.[48] Second recent theoretical papers have stressed the importance of surface orbitals in metal clusters.[49,50] As the qualitative behavior of cluster surface orbitals should be independent of cluster composition, similar inductive and conjugative effects should be observed in more complex systems as well.

Experimental Section

The photoelectron spectrometer used in these studies was the same as that described previously.[26] Spectra were obtained using He(I) radiation, the instrument was operated at a resolution of 25 meV (full width at half-height) at 5 eV electron energy, and scanning was accomplished by variation of the analyzer voltage. Calibration was carried out using an internal standard consisting of a mixture of argon and xenon.

The carborane, 1,6-$C_2B_4H_6$, was purchased from Chemical Systems, Inc., Irvine, Calif., the chlorine (research purity) from Matheson, and the bromine and iodine (analytical reagent) from Mallinckrodt. Manipulations were carried out in a standard high-vacuum apparatus.[51] Mass spectra were measured on an Associated Electrical Industries MS 902 mass spectrometer. Gas-phase infrared spectra were recorded on a Perkin-Elmer 475 spectrometer. The ^{11}B NMR spectra were recorded on a Varian XL-100 spectrometer at 25.2 MHz with $(C_2H_5)_2O{\cdot}BF_3$ as an internal standard.

2,4-Cl_2-1,6-$C_2B_4H_4$. About 3 mmol of $AlCl_3$ was introduced into a 200-mL bulb provided with a 12-mm Teflon stopcock. After the $AlCl_3$ was sublimed onto the walls, about 2 mmol each of $C_2B_4H_6$ and Cl_2 were condensed into the bulb at −196 °C. The chlorine color disappeared rapidly and after 2 h the mixture was fractionated in the vacuum line with −45, −95, and −196°C traps. The contents of the −45°C trap was a pure compound having a mass spectrum with a high mass cutoff of *m/e* 146 corresponding to $^{37}Cl_2{}^{12}C_2{}^{11}B_4{}^1H_4$, infrared bands at (cm^{-1}) 3130 w, 2680 s, 1382 m, 1335 s, 1309 vs, 1289 vs, 1238 s, 1200 m, 1149 m, 1130 mw, 982 m, 958 m, and 778 m, and the ^{11}B resonances shown in Table I. As discussed above, this compound is identified as 2,4-Cl_2-1,6-$C_2B_4H_4$. The 2-Cl-1,6-$C_2B_4H_5$ contained in the −95°C trap exhibited mass and IR spectra in accord with published spectra.[13]

2,4-Br_2-1,6-$C_2B_4H_4$. About 1 mmol of Br_2 was introduced into a 100-mL bulb containing about 1 mmol of aluminum metal and provided with a teflon stopcock. After degassing, the mixture was allowed to react for 4 h at room temperature to give $AlBr_3$. $C_2B_4H_6$ (1 mmol) was then condensed in the bulb at −196°C and the bulb warmed to room temperature. The bromine color gradually disappeared and after 4 h the mixture was fractionated in the vacuum line with −45, −78, and −196°C traps. The contents of the −45°C trap was a pure compound having a mass spectrum with a high mass cutoff of *m/e* 234 corresponding to $^{81}Br_2{}^{12}C_2{}^{11}B_4{}^1H_4$, infrared bands at (cm^{-1}) 2678 m, 1368 vw, 1290 m, 1270 s, 1250 sh, 1230 m, 1209 m, 1140 mw, 970 mw, 763 mw, and the ^{11}B resonances shown in Table I. The compound is identified as 2,4-Br_2-1,6-$C_2B_4H_4$. The 2-Br-1,6-$C_2B_4H_5$ contained in the −78 °C trap exhibited mass and IR spectra in accord with published spectra.[14]

2,4-I_2-1,6-$C_2B_4H_4$. About 4 mmol of I_2 and 1 mmol of aluminum metal were placed in an evacuated break-seal bulb and heated at 180°C for 24 h to prepare the aluminum halide. About 2.5 mmol of the carborane was introduced, the bulb resealed, and the mixture heated at 75°C for 24 h, during which time the iodine color disappeared. The mixture was then fractionated in the vacuum line with −23, −78, and −196°C traps. The material in the −23°C fraction was a pure compound whose mass spectrum exhibited a high mass cutoff of *m/e* 326 corresponding to $^{127}I_2{}^{12}C_2{}^{11}B_4{}^1H_4$ (325.879 amu, exptl; 325.878 amu, calcd), infrared bands at (cm^{-1}) 2670 s, 1388 s, 1325 sh, 1255 w, 1190 m, 1158 mw, 1020 mw, 938 w, 870 mw, and the ^{11}B resonances listed in Table I. The 2-I-1,6-$C_2B_4H_5$ contained in the −78°C trap exhibited mass, IR, and ^{11}B NMR spectra in accord with published spectra.[15]

Rearrangement of 2,4-Cl_2-1,6-$C_2B_4H_4$ and 2,4-Br_2-1,6-$C_2B_4H_4$. Samples of the two derivatives in hexane were sealed in heavy-walled NMR tubes and heated at a temperature of about 180 °C. Based on the ^{11}B NMR spectra, in a period of about 50 min 90% of the starting material had disappeared. During this period new resonances appeared at 31.8, 6.6, and −1.3 ppm in the case of the chloro compound and −13.7, −19.0, and −27.3 ppm in the case of the bromo compound. The two higher field resonances had equal relative intensities throughout but in both cases the intensity of the low-field resonance decreased with respect to the two higher field resonances as the extent of decomposition increased. At 90% decomposition the relative intensities were about 1:1:1. Fractionation of the chloro sample after the experiment yielded a very small amount of a volatile material that was identified as $Cl_2C_2B_4H_4$ by mass spectrometry. The product NMR signals are attributed to the soluble but nonvolatile material left in the NMR tube after fractionation.

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Strong Metal-to-Metal Quadruple Bonds in a Series of Five Isostructural Compounds as Indicated by Photoelectron Spectroscopy

Bruce E. Bursten,[1a] F. Albert Cotton,*[1a] Alan H. Cowley,*[1b] Brian E. Hanson,[1a] Michael Lattman,[1b] and George G. Stanley[1a]

Contribution from the Departments of Chemistry, Texas A&M University, College Station, Texas 77843, and the University of Texas, Austin, Texas 78712.

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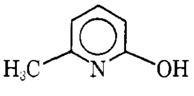
Abstract: The He(I) photoelectron spectra of five homologous compounds, MM′(mhp)$_4$, where mhp is the 2-oxo-6-methylpyridine ion and MM′ = Cr_2, CrMo, Mo_2, MoW, and W_2, have been measured; the spectra of the gaseous Hmhp and Hhp (2-hydroxypyridine) molecules are also reported. The oxidation potentials of the complexes have been recorded by cyclic voltammetry and the Raman spectra of all five compounds are also tabulated (ν_{Cr-Mo} 504 ± 3 cm^{-1}). On the basis of all of this information, with guidance from MO calculations (not given in detail here), we are able to suggest consistent assignments of the PE spectra leading to the conclusion that the M–M δ bonding electrons have ionization energies of 6.8–5.3 eV (through the series from Cr_2 to W_2) and that these energies correlate well with the voltammetrically measured $E_{1/2}$ values. The ionization energies for the molecular orbitals principally responsible for M–M π bonding are fairly constant at about 7.7 eV and the principal σ-bonding orbitals have ionization energies in the range 10.2–10.6 eV. We do not believe that an assignment that places the π and σ ionizations very close together, as suggested by others, is tenable on the basis of all of the evidence available from our experimental studies.

Introduction

Photoelectron (PE) spectroscopy has proven to be a powerful source of data on the electronic structures of both organic and inorganic[2] compounds. It has already been employed in connection with compounds containing triple and quadruple bonds between metal atoms.[3-5] The interpretation of the spectra for compounds containing Mo≡Mo bonds[5] has not provoked controversy, but the bonding details and, hence, the interpretation of PE spectra for compounds containing quadruple bonds have aroused considerable differences of opinion.[6-8]

The recent discovery[9,10] and characterization of a series of five homologous, quadruply bonded compounds of the type MM′(mhp)$_4$, where mhp is the anion of 2-hydroxy-6-methylpyridine, **1**, and MM′ represents Cr_2, CrMo, Mo_2, MoW, and W_2, presents us with an unusually good opportunity for a study of the PE spectra by a procedure based on comparisons between similar, homologous molecules in which only the metal atoms are changed. The structures of all these molecules are as shown schematically in **2**, and the idealized point symmetry (which presumably is the actual symmetry when the molecules are in the gas phase or in nonpolar solvents) is D_{2d}.



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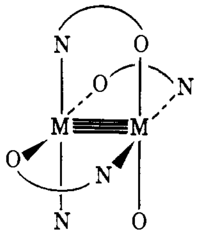

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We report here the photoelectron spectra of these five molecules and of the free protonated ligand, Hmhp, as well as various other data which bear on the interpretation of the PE spectra and an understanding of the metal-to-metal bonds in these molecules. The compounds studied are listed in Table 1.

0002-7863/79/1501-6244$01.00/0