also corresponds to an asymmetric arrangement of one-electron holes in the high-energy d orbitals, both Jahn–Teller requirements and the forces of eq 1 demand a distorted structure. However eq 1 holds for *all* transition metal complexes irrespective of the nature of the electronic state and in fact, subject to the restrictions of the Pauli principle, is independent of the total spin multiplicity of the system (*i.e.*, the *orbital* energy of a complex with electronic configuration (⋯11) is independent of whether these electrons are spin paired or not). However, in addition to arriving at distorted structures for Jahn–Teller unstable systems, the present approach is able to consider the stereochemistry of species which cannot use the theorem as an excuse to distort. In our previous work on the angular geometry of transition metal complexes[1] using eq 1 we found that Fe(CO)$_3$ ($^3A_2$) was predicted and observed to be a pyramidal molecule whereas there was no reason under the Jahn–Teller scheme for the geometry to distort from planar. Similarly in our quantitative molecular orbital calculations (using the Wolfsberg–Helmholtz approximation, closely related to the overlap integral determined stabilization energy of eq 1) on binary transition metal carbonyls[2] it was found that orbital energy changes on distortion, in addition to Jahn–Teller considerations, were required to rationalize the computed equilibrium geometries. Although we do not deny the existence of marked vibronic effects which have been well documented in some metal hexafluorides for example (dynamic Jahn–Teller effect), there are considerable misgivings about the utility of Jahn–Teller arguments to rationalize transition metal structures.

The angular overlap model on the other hand is a relatively crude simplistic approach. We have deliberately ignored interactions with s and p orbitals on the metal which are of course responsible for holding d^{10} complexes together and have left out any dependence of overlap integral on metal–ligand bond length. With regard to the latter comment, our arguments therefore strictly hold only for an idealized arrangement where all M–L bond lengths are equal. The model therefore may only faithfully represent gross structural effects. At its present stage of development we do not look to it for the finer details of molecular geometry. Its overwhelming advantage is that it is a simple, easy-to-use way (and at present the only method of universal applicability) of looking at the salient structural features of transition metal complexes.

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(15) The situation is of course not quite as simple as this since in the d^{10} complex CdCl$_5^{3-}$ the axial bond lengths are slightly shorter (2.527 (5) Å) than the equatorial ones (2.564 (5) Å: T. V. Long, A. W. Herlinger, E. F. Epstein, and I. Bernal, *Inorg. Chem.*, **9**, 459 (1970)). However these authors pointed out that the axial "compression" in CuCl$_5^{3-}$ compared to CdCl$_5^{3-}$ is of electronic origin (as we claim here) and not due to crystal effects.

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Photoelectron Spectroscopy of *closo*-Carboranes. Observation of Exo-Polyhedral Molecular Orbitals

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The He(I) photoelectron spectra of 1,5-dicarba-*closo*-pentaborane(5), 1,6-dicarba-*closo*-hexaborane(6), 2,4-dicarba-*closo*-heptaborane(7), and 1,7-dicarba-*closo*-icosaborane(12) are reported. It is shown that the spectra of these molecules provide experimental justification for a theoretically predicted separation of the molecular orbitals of these species into exo- and endo-polyhedral types. In addition, it is pointed out that ionization from certain exo-polyhedral orbitals results in bands with empirically recognizable characteristics. Finally, the photoelectron spectrum of pentaborane(9) indicates that the exo–endo separation is valid for the boranes as well.

There have been a number of successful approaches to a systemization of the chemistry of the boranes and heteroboranes. These range from empirical approaches based on reaction chemistry[1] or synthesis[2] to theoretical approaches based on topological rules.[3] On the theoretical side, a valence-bond treatment with localized three-center and two-center bonds gives a generally adequate and conceptually useful description of the bonding for nido or arachno (open) structures. However, the highly interconnected structures and delocalized bonding of the *closo*-boranes and heteroboranes are only fruitfully treated with molecular orbital methods.[3] These approaches, although conceptually more complex, have been used to rationalize sites of substitution *via* various calculations of charge distributions.[4] In addition, calculations of this type have given insight into rearrangement pathways[5] while localization routines applied to SCF calculations have been used to test the idea of a localized three-center bond.[6]

Of more pertinence to this work is the conclusion of a molecular orbital study of Hoffmann and Lipscomb.[7] In order to obtain better insight into the nature of the structure and bonding of *closo*-boranes, they investigated simplifications of the complete molecular orbital picture. In fact, they examined various ways of factoring the secular equation and, by comparison of factored and unfactored results, it was concluded that orbitals that point out from the polyhedral framework and which are involved in heavy-atom hydrogen interactions are separable from those involved in bonding the framework atoms. This factorization, which is formally analogous to the σ–π separation in organic systems, predicts that in a polyhedral borane or heteroborane with N heavy atoms there will be N molecular orbitals that are exo-polyhedral bonding and endo-polyhedral nonbonding in character. This idea has been generally accepted as exemplified in a recent proposal for the systemization of borane and heteroborane chemistry in terms of "magic" numbers of electrons which explicitly excludes the electrons involved in exo-polyhedral bonds.[8]

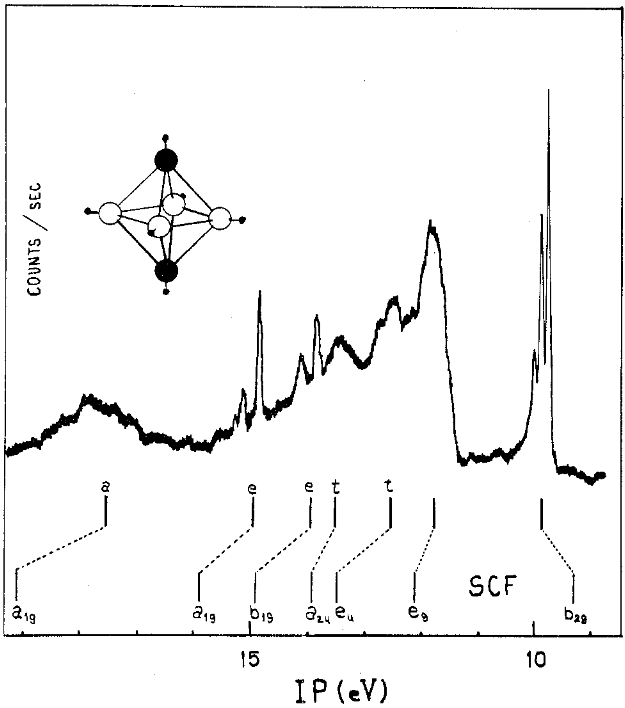


Figure 1. Photoelectron spectrum of 1,6-$C_2B_4H_6$. The structure is shown in the upper left-hand corner. The vertical lines immediately below the spectrum are the empirical vertical ionization potentials while the lines with symmetry designations are the vertical ionization potentials derived from the SCF calculations of ref 13.

Photoelectron spectroscopy yields direct information on the electronic structure of ions and yields a representation of the molecular orbital structure of molecules.[9] The shape and fine structure associated with a photoelectron band characterize the nature of the molecular orbital from which ionization takes place and in favorable circumstances allow assignment of the band.[9,10] For this reason we undertook an investigation of the photoelectron spectra of some *closo*-carboranes in the hope of experimentally verifying the concept of exo- and endopolyhedral molecular orbitals in these species. The photoelectron spectra presented below clearly demonstrate the validity of this concept.

Experimental Section

The photoelectron spectrometer used in these studies was constructed using information published by other workers.[11] Spectra were obtained using He(I) radiation only. The resolution of the instrument was 25 mV (full width at half-height) at 5-eV electron energy. Calibration was carried out using an internal standard consisting of a mixture of argon and xenon.

The small *closo*-carboranes were purchased from Chemical Systems Inc., Irvine, Calif. They were purified by trap to trap fractionation before use and the purity was established by mass spectrometry. After purification the purity was estimated, assuming equal mass spectrometric sensitivities, to be better than 95%. The 1,7-$C_2B_{10}H_{12}$ was purchased from Alfa Inorganics, Beverly, Mass. The pentaborane(9) was purchased from the Callery Chemical Co., Callery, Pa., and was also fractionated before use.

Results and Discussion

The ideal species[7] for this investigation is $B_6H_6^{2-}$; it has high symmetry (O_h) and relatively few atoms. Although it is not possible to study $B_6H_6^{2-}$, we were able to examine the photoelectron spectrum of the isoelectronic species 1,6-dicarba-*closo*-hexaborane(6), $C_2B_4H_6$, which has D_{4h} symmetry.[12] For $B_6H_6^{2-}$ we expect six exo-polyhedral molecular orbitals of symmetries a_{1g}, e_g, and t_{1u}.[7] Under D_{4h} symmetry the e_g orbitals split into orbitals of b_{1g} and a_{1g} symmetry and the t_{1u} orbitals split into orbitals of e_u and a_{2u} symmetry. The photoelectron spectrum of 1,6-$C_2B_4H_6$ is presented in Figure 1 and the data are tabulated in Table I. In this figure the empirical vertical ionization potentials are compared with those predicted on the basis of an SCF calculation[13] using Koopmans theorem.[14] It will be noted that there is a one to one correspondence between calculated and measured ionization potentials. In addition the quantitative discrepancies are about 10% which is typical for such a comparison.[15] Thus, the SCF results provide one way of assigning the spectrum with some confidence. Using the criteria of proper symmetry and largest H(1s) orbital coefficients one concludes that ionization from what should be exo-polyhedral molecular orbitals yields the bands marked (t), (e), and (a) in the Figure 1. Of these bands, the (e) bands have well-resolved fine structure, the (a) band has poorly resolved structure, and the (t) bands are broad and featureless. The bands with fine structure are amenable to the following empirical interpretation.

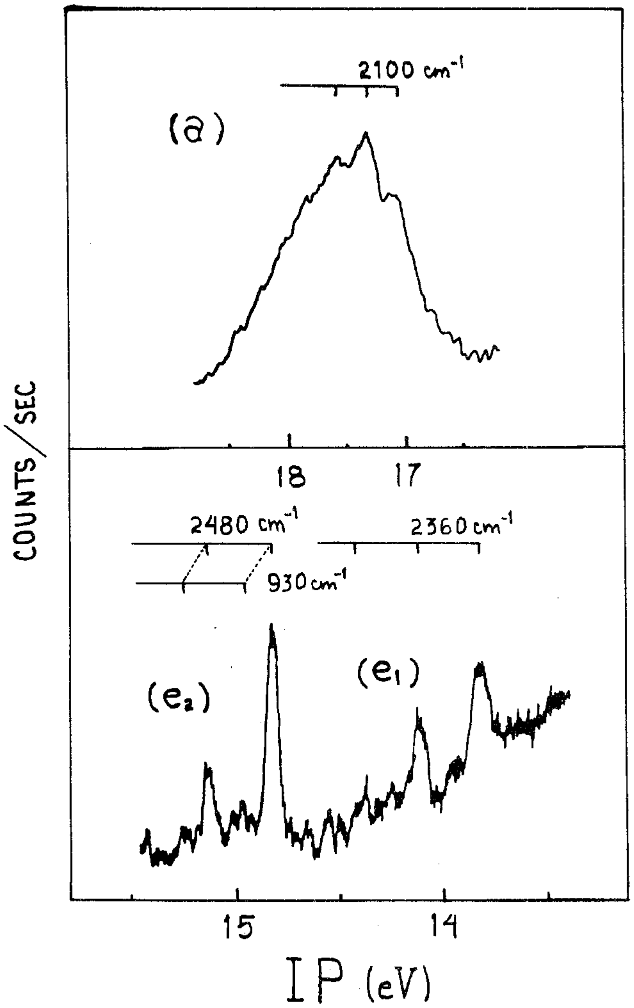


Figure 2. Photoelectron bands from 1,6-$C_2B_4H_6$ showing analysis of the associated fine structure.

In Figure 2 the (e) and (a) bands are shown in expanded scale. In the (e_1) and (e_2) bands short progressions with frequencies of 2360 and 2480 cm^{-1}, respectively, are observed. In addition the (e_2) band exhibits the weak excitation of a mode with frequency of 930 cm^{-1}. The vibrational spectrum of 1,6-$C_2B_4H_6$ has been analyzed.[16] This allows the modes at $\sim$2400 cm^{-1} in the ion to be assigned to the B–H symmetric stretch which has a frequency of 2667 cm^{-1} in the molecule. This assignment is unambiguous for the following reason. From the difference between the vertical and adiabatic ionization potentials (ΔE) for bands (e_1) and (e_2) and the frequencies observed in the ion, one calculates frequencies of 2670

Table I. Experimental and Theoretical Ionization Potentials

Molecule	Band assignment	Adiabatic IP, eV	Vertical IP, eV	Band character[a]	Vibrational modes excited, cm^{-1}	KT, eV
$1,5\text{-}C_2B_3H_5$		10.54	10.88	b	470	
			11.72	b		
			12.12	b		
			13.46	b		
		14.26	14.46	s	2170, 500	
		15.85	15.99	b	490?	
			16.92	b		
			17.51	b		
$1,6\text{-}C_2B_4H_6$	$1b_{2g}$	9.77	9.87	s	940	9.25[b]
	$1e_g$		11.79	b	940?	12.02
	$3e_u$		12.51	b		13.38
	$3a_{2u}$		13.44	b		13.84
	$2b_{1g}$	13.83	14.04	s	2360	14.80
	$5a_{1g}$	14.84	14.99	s	2480, 930	15.81
	$4a_{1g}$	17.11?	17.53	b	2100?	18.93
	$2e_u$		19.77	b		19.78
$2,4\text{-}C_2B_5H_7$	$12a_1$	10.54	10.94	b	400?	10.12[c]
	$1a_2$		11.23	b		11.13
	$6b_2$, $3b_1$, $11a_1$		11.66	b		12.35, 12.43, 12.92
	$5b_2$		12.86	b		13.85
	$10a_1$		13.73	b		14.96
	$9a_1$	14.05	14.18	s	1800, 840?	15.32
	$4b_2$	15.02	15.07	s	930	16.13
	$8a_1$		15.20	b		16.81
	$2b_1$, $7a_1$		17.28	b		19.49, 19.53
$1,7\text{-}C_2B_{10}H_{12}$		10.19	11.41 (?)[d]			
		13.23	13.67		2300, 720	
			14.81			
		16.02	16.32		750	
			17.72			
			18.42			
B_5H_9	4e	9.94	10.53	b		10.31[e]
	$6a_1$		12.23	b		12.54
	3e		12.66	b		13.87
	$2b_1$	13.78	14.3	b	1900	15.21
	$1b_2$					15.53
	$5a_1$	14.33	14.6	b	2100	15.79
	$4a_1$		16.41	b		18.50
	2e		18.65	b		21.12

[a] b = broad, s = sharp. [b] Reference 13. [c] Reference 18. [d] Probably more than one band; see Figure 4. [e] Reference 20.

and 2660 cm^{-1} for the corresponding mode in the molecule.[17] Thus, the observed band envelope is not compatible with excitation of either the C–H stretch (3118 cm^{-1} in the molecule) or framework modes ($\sim$1000 cm^{-1} in the molecule). The weak lines at 930 cm^{-1} in band (e_2) are most reasonably assigned to excitation of a framework mode, probably the symmetric B–B stretch (986 cm^{-1} in the molecule). It is quite clear that these ionizations can be empirically assigned to molecular orbitals that are boron–hydrogen bonding (albeit weakly) and essentially nonbonding with respect to the framework atoms. This is exactly the predicted behavior for an exo-polyhedral molecular orbital.[7] The SCF molecular orbitals to which bands (e_1) and (e_2) are assigned have as major component atomic orbitals B(2s), B(2p), and H(1s), the hydrogens being those attached to the boron atoms.[13]

Band (a), which according to the SCF calculation should result from ionization from an exo-polyhedral orbital, is also shown in more detail at the top of Figure 2. Members of a progression of 2100 cm^{-1} are visible but the band is quite broad and several other modes must be excited as well. The ΔE of this band suggests that the observed progression corresponds to a heavy-atom–hydrogen stretch and it is noted that the SCF orbital to which the band is assigned is in large part C(2s), C(2p), and H(1s), the hydrogens being attached to carbon. The character of this band suggests that a number of other modes are excited. This may indicate that the orbital involved mixes with an endo-polyhedral (framework) orbital of proper symmetry. A similar mixing could account for the broad featureless character of the bands marked (t). As there are other possible reasons for the loss of structure in a photoelectron band,[9,10] one cannot use such evidence to conclude that such mixing takes place. However the SCF calculations indicate that orbitals assigned as endo-polyhedral do have some H(1s) character. Thus, it would appear that the prediction of separability is not rigorously correct. However, one would not expect it to be so except in highly symmetric species, *e.g.*, $B_6H_6^{2-}$. Therefore, the fact that clear evidence of exo-polyhedral character is observed in two bands is all that is necessary to establish the physical reality of exo–endo factorization.

There is one other sharp band in the spectrum of $1,6\text{-}C_2B_4H_4$ that deserves comment. This band, representing ionization from the highest filled orbital of the carborane, is clearly seen in Figure 1. The 0 ← 0 transition is the most intense and there is a short progression of a vibrational mode with frequency of 940 cm^{-1}. This is probably due to excitation of the symmetric B–B stretch (986 cm^{-1} in the molecule). Both the small change in vibrational frequency and the short progression indicate that the molecular orbital involved must be essentially nonbonding. It is interesting to note, then, that the orbital to which this band is assigned *via* the SCF calculations is an endo-polyhedral orbital involving only B(2p) atomic orbitals (structure I). The characteristics of this band should be compared with those of the next higher band. The latter results from an ionization of a doubly degenerate orbital similar to I but with two borons replaced with carbons, *i.e.*, structure II. (In O_h symmetry these three orbitals are degenerate and of t_{2g} symmetry.) The latter band has no fine structure and

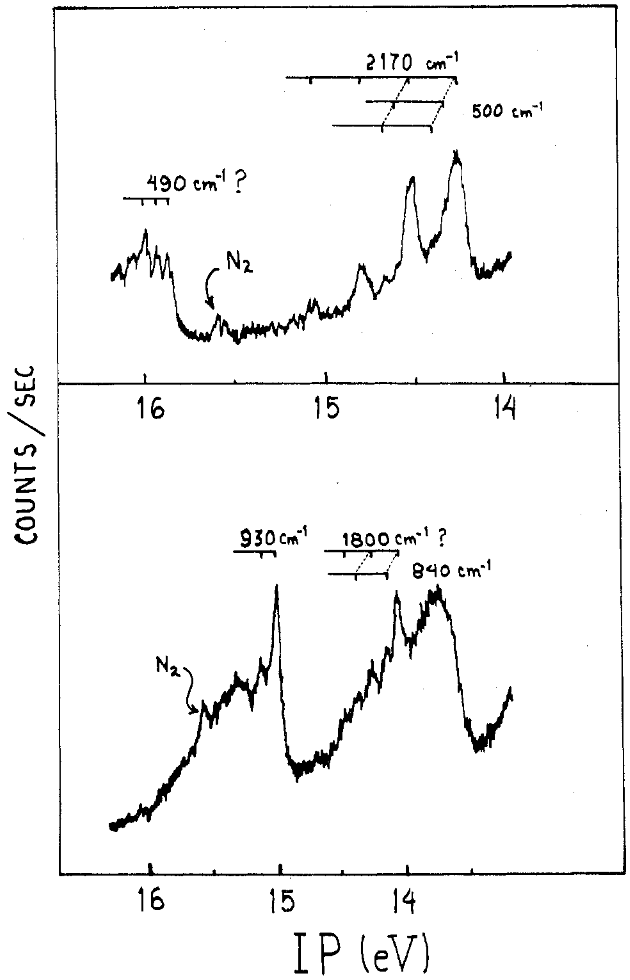
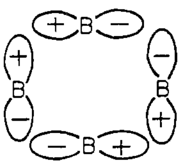


Figure 3. Partial photoelectron spectra of 1,5-$C_2B_3H_5$ (top) and 2,4-$C_2B_5H_7$ (bottom) showing analysis of the fine structure.

appears more bonding in character. It seems that the appearance of a band is directly related to the carbon character of the orbital. This provides an empirical explanation for the featureless character of the (à) and (t) bands discussed above, in that the orbitals to which these bands are assigned all contain significant carbon character.



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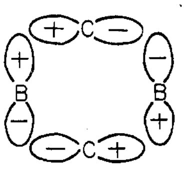

II

Obviously, it is of interest to see whether exo-polyhedral orbitals may be identified in other carboranes. In Figure 3 and Table I the data on 2,4-$C_2B_5H_7$ are presented. The photoelectron spectrum of this molecule exhibits sharp bands in the 14–15-V region very similar to those observed for 1,6-$C_2B_4H_6$. Unfortunately, the bands are somewhat obscured by being superimposed on other broad bands and the fine structure is not easily analyzed. However, SCF calculations have been carried out for this molecule as well[18] and both of these bands may be assigned to molecular orbitals made up of mainly B(2s), B(2p), and H(1s). The observations support the previous conclusions. Certain bands, assigned to ionization from exo-polyhedral orbitals, appear to be nonbonding with respect to the framework.

The data on 1,5-$C_2B_3H_5$ are presented in Table I and Figure 3. In this case the 14–15-V region exhibits a clearly resolved

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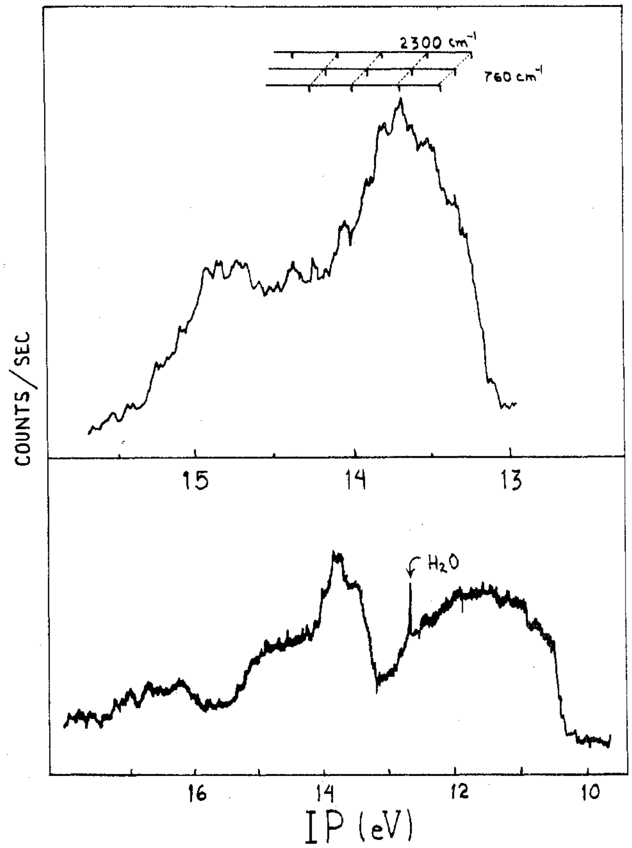

Figure 4. Photoelectron spectrum of 1,7-$C_2B_{10}H_{12}$ (bottom) showing vibrational analysis of one band (top).

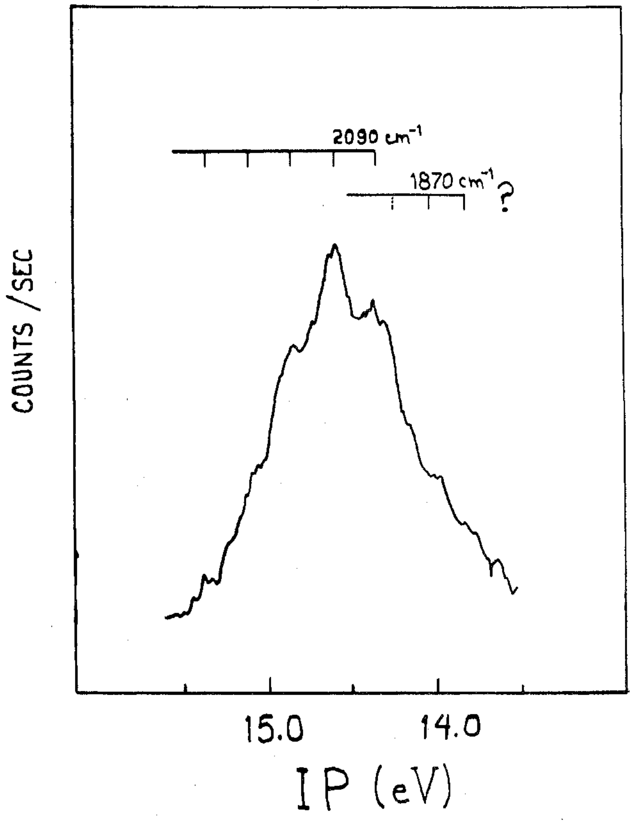

Figure 5. Partial photoelectron spectrum of B_5H_9 with vibrational analysis.

band with a progression in the B–H stretching frequency (calculated[17] frequency in molecule 2580 cm^{-1}, observed[16] 2631 cm^{-1}). The SCF calculations have not been done for this molecule but we confidently assign this ionization to that from an exo-polyhedral molecular orbital.

The spectrum of a large *closo*-carborane, 1,7-$C_2B_{10}H_{12}$, is presented in Figure 4 and the data are shown in Table I. At the top of the figure a band showing obscure, but reproducible, structure is shown in more detail. One possible assignment of this structure, indicated in the figure, is in terms of progressions in a frequency of 2300 cm^{-1}. Although SCF calculations have not been done for this species, we again suggest that this band, or part of it, may be assigned to ionization from an exo-polyhedral orbital.

Finally, we wish to point out that exo-polyhedral orbitals present evidence for themselves in the photoelectron spectra of boranes as well. We have measured the spectrum of pentaborane(9) and the results are reported in Table I. Our results agree with those reported previously[19] with the exception of the band at highest ionization potential. In the previous study,[19] the real band at 18.65 eV is obscured by a large tail which is probably caused by scattered electrons. The point of interest to this study is the band between 14 and 15 eV which is presented in Figure 5. There is reproducible structure which can only be reasonably assigned to a boron–hydrogen stretch. The SCF calculations[20] (Table I) indicate that this band may result from ionization from three molecular orbitals, two of which involve boron and terminal hydrogens and which would be defined as exo-polyhedral molecular orbitals. The third involves bridge hydrogens and is endo-polyhedral. This is the only band in the spectrum that shows fine structure, and even though it is indistinct, we feel that the structure would suffice to identify the band as exo-polyhedral.

In summary, it has been shown that the validity of the exo–endo separation of the molecular orbitals of boranes and heteroboranes is substantiated by the photoelectron spectra of these species. In particular, certain exo orbitals exhibit characteristic empirical features that should enable them to be identified even in the absence of good calculations. This appears particularly true of those orbitals that may be crudely considered as the in phase combination of terminal boron–hydrogen interactions. It is possible that an examination of these bands as a function of chemical environment may well lead to a better understanding of the electronic structure of these species.

Acknowledgment. The aid of Mr. Harold Zielinski in constructing the photoelectron spectrometer is gratefully acknowledged.

Registry No. 1,5-$C_2B_3H_5$, 20693-66-7; 1,6-$C_2B_4H_6$, 20693-67-8; 2,4-$C_2B_5H_7$, 20693-69-0; 1,7-$C_2B_{10}H_{12}$, 16986-24-6; B_5H_9, 19624-22-7.

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Notes

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Fixation of Molecular Nitrogen in Aqueous Solution. Catalysis by Platinum Group Metal Ions

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Nitrogen fixation is a subject of very active research interest in many laboratories in recent years. Much of the work on nitrogen fixation is centered on the use of titanium catalysts, in the presence of strong reducing agents like metallic aluminum,[1] metallic potassium,[2] or sodium naphthalide,[3,4] or electrolytic reduction in the presence of aluminum isopropoxide.[5] In all these cases the yield of ammonia varies from a fraction of 1 mol of ammonia/mol of the catalyst to a stoichiometric yield. While many stable dinitrogen complexes of various platinum group metal ions are known, none of them were previously used as catalysts in nitrogen fixation studies. We report in this note the fixation of nitrogen at atmospheric temperature and pressure in aqueous solution catalyzed by Ru(II)–, Ru(III)–, Rh(III)–, Ir(III)–, Os(II)–, and Os(III)–chloro complexes.

Experimental Section

Materials. Commercial samples of ruthenium(III) chloride, rhodium(III) chloride, iridium(III) chloride, osmium(III) chloride, titanium(III) chloride, and dimethyltin dichloride were obtained from Alfa Inorganics. Stannous chloride, triphenylphosphine, and hydrazine were Fischer AR grade reagents. $^{15}N_2$ (25% enrichment) was obtained from Volk Radiochemicals, Inc.

Procedure. A mixture of 1 vol. of nitrogen and 3 vol. of hydrogen at room temperature (25°) and 1 atm pressure was passed through a catalyst solution of the above-mentioned metal ions (10^{-3}–10^{-4} *M*) in 3 *M* hydrochloric acid. The catalytic solutions were obtained by adding a suitable reducing agent ($TiCl_3$, $SnCl_2$, $(CH_3)_2SnCl_2$) to the requisite transition metal ion in a 10:1 molar ratio. The resulting solution has the characteristic absorption spectrum of the transition metal ion. After circulation of nitrogen and hydrogen for about 24 hr, a sample of the solution was withdrawn from the reaction mixture and the amount of ammonia formed estimated with a micro-Kjeldahl apparatus.