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Notes

Molecular Orbital Analysis of the Trend in ^{11}B NMR Chemical Shifts for $(Cp^*M)_2B_5H_9$ (M = Cr, Mo, W; Cp* = η^5-C_5Me_5)

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Summary: The ^{11}B NMR shifts of the two types of boron atoms directly bonded to the metal atoms in $(Cp^*M)_2B_5H_9$ (M = Cr, Mo, W) experience a large systematic shift to higher field in going from Cr to Mo to W, whereas the shifts for the boron atoms connected to the metal atoms via M−H−B bridge bonds are invariant. The origin of this behavior is traced to two high-lying filled MO's and two low-lying unfilled MO's, both of which have metal and boron character. The energy differences of these sets of MO's correlate well with the observed chemical shifts, and the properties of these MO's provide an explanation of the observations and a comment on the nature of the boron−metal cluster bonding.

One consequence of the Born−Oppenheimer approximation is that problems in structure and bonding are addressed by constructing a description of the distribution of the available electrons over a fixed nuclear skeleton.[1] The language of approximate molecular orbital (MO) theory permeates these descriptions, and its pictorial representations of crucial orbital interactions delineate concepts of useful generality.[2] In many instances there is a simple, indeed beautiful, connection between MO ideas and observables, e.g., the eclipsed ligands in a metal dimer with a metal−metal quadruple bond,[3,4] the comparison of the photoelectron spectra (PES) of Ne, HF, H_2O, NH_3, and CH_4,[5] the structural perturbation caused by varying the valence electron population of cubane clusters,[6] and more.

The use of ESR spectroscopy to trace out the distribution of spin over the nuclei of a radical species and, hence, the properties of the MO in which the odd electron resides, is well-known,[7] e.g., the metal atom d-orbital character from all three metals of the MO containing the odd electron of $(CO)_9Co_3S$.[8] Less well appreciated is the fact that the ubiquitous use of multinuclear NMR spectroscopy has generated a wealth of data that contain equally important experimental information on electronic structure. Unfortunately, the connection between NMR parameters and useful bonding concepts is far from transparent mostly because, in contrast to PES and ESR, there is no simple connection between the observations and the properties of a single MO.[9] It is only recently that quantitative connections between observed chemical shifts (δ) and those calculated from first principles have proved useful in resolving long-standing structural problems.[10−13] This has created an important new tool for the experimental chemist interested in species not amenable to conventional X-ray diffraction techniques, e.g., reaction intermediates.

However, in a focus on an exploration of the change in chemical shift with geometric structure, the connection between electronic structure and δ is bypassed. Thus, since exploring the use of approximate MO descriptions of the effects of transition metals on ^{11}B chemical shifts in metallaboranes,[14,15] we have sought situations that might allow a connection to be drawn between δ and the properties of a highly restricted set of MO's in the tradition of the classic experiments noted above. This note reports one such situation.

Our ability to synthesize dimetallaboranes from the reaction of monocyclopentadienylmetal halides and monoboranes for a variety of metals creates the possibility of directed syntheses of closely related molecules. Thus, we have prepared and characterized the series $(Cp^*M)_2B_5H_9$ (Cp* = η^5-C_5Me_5; M = Cr,[16] Mo,[16,17] W[18])

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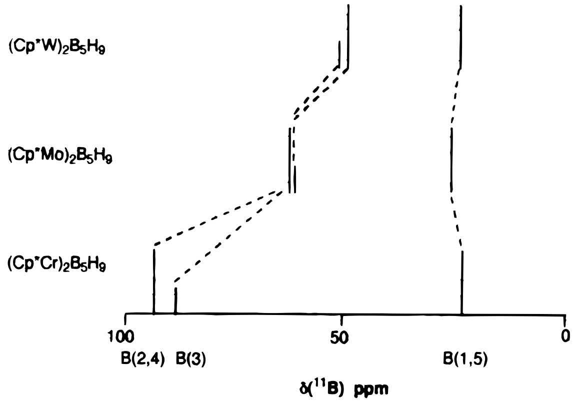
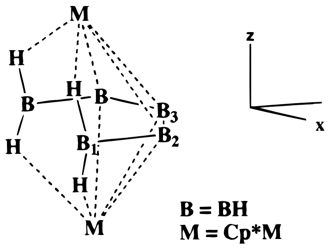


Figure 1. Bar graph of the ^{11}B NMR chemical shifts for $(Cp^*M)_2B_5H_9$ (M = Cr, Mo, W).[16,18]

Chart 1



(Chart 1), the Mo derivative having been described earlier as the η^5-C_5H_4Me derivative.[19]

Given the plane of symmetry, three ^{11}B NMR resonances in the ratio of 2:2:1 are observed. Consistent with empirical observations,[20] the chemical shifts of the two types of borons directly bonded to the metals (B_2, B_3) are found at low field, whereas the other (B_1) is found within the range typical of boranes. Unexpected was the large change in the chemical shifts of B_2 and B_3, but not B_1, in going from Cr to Mo to W (Figure 1). Reports of metallaborane compounds of all three metals in a triad in which the metal−ligand set is the same are scarce,[21] and crystallographically characterized examples are even more so. Although differences in ^{11}B chemical shifts between metallaborane congeners have been noted previously,[21] to our knowledge such a large difference on moving from first- to third-row metal has not been reported. Thus, the present set of metallaboranes provides a rare chance to investigate the connection between electronic structure and chemical shift for compounds not easily addressed by high-level calculations.

As the compounds $(Cp^*M)_2B_5H_9$ are isostructural, the observed change in chemical shift can only arise from the perturbation of the electronic environment of the boron atoms by the metal. In fact, there is an excellent correlation of chemical shift with the sum of ionization potential and electron affinity of the metal, i.e., Mulliken electronegativity (Figure 2). As the compounds are also valence isoelectronic with qualitatively identical MO descriptions, we expect many of the complex factors connecting δ with MO properties, which are poorly described by approximate MO treatments, to disappear in a comparison of chemical shift changes within the series.

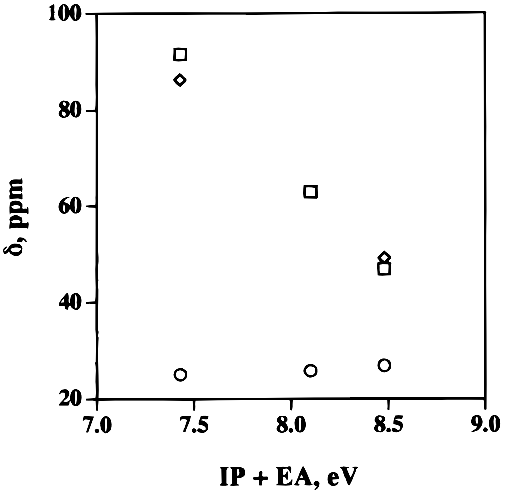


Figure 2. Correlation between ^{11}B NMR chemical shifts for $(Cp^*M)_2B_5H_9$ (M = Cr, Mo, W) and the sum of ionization potential and electron affinity of the metal: (circles) B_1; (squares) B_2; (diamonds) B_3.

The question addressed is as follows: can the selective, large changes in chemical shift observed in this highly correlated set of molecules be explained by the properties of a small number of MO's? It is the treatment of Ramsey that provides the framework for the analysis,[22] and extensive discussions of various approximate applications are available.[9] Briefly, the shielding is expressed in a diamagnetic and a paramagnetic term and large low-field shifts, and the changes therein, are ascribed to the paramagnetic term. This term is considered to arise from a charge circulation effect in that the complex orbital angular momentum matrix elements found in the expression for the paramagnetic term are nonzero only when they correspond to the rotation of a high-lying occupied B 2p orbital into the space previously held by a low-lying unoccupied B 2p orbital.[14]

We have already described[16] important features of a MO analysis of the Cr and Mo derivatives based on the Fenske−Hall method,[23] and the W compound has been treated similarly. Thus, we were in a position to search for pairs of filled and unfilled molecular orbitals that satisfied four criteria simultaneously: a small energy difference, ΔE, between the filled and unfilled MO's, large metal character, large B 2p contributions of the specified boron atom in both filled and unfilled MO's, and the proper B 2p symmetries such that the B 2p contribution of the filled MO and unfilled MO are coupled by the angular momentum operator. This highly restrictive grid of criteria easily generated the four contributors shown in Chart 2 (only B 2p contributions are shown). On the basis of composition, the 40−45 pair contributes to the deshielding of B_3, whereas 40−44 and

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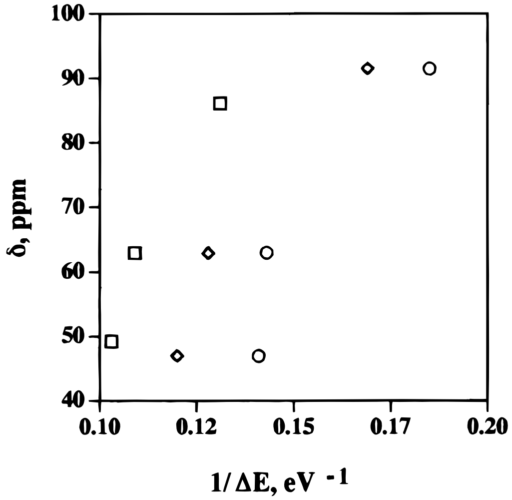
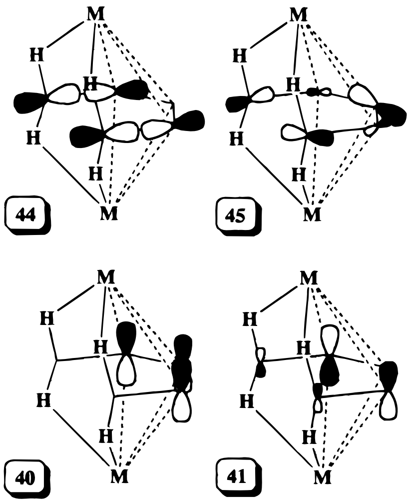


Figure 3. Correlation between ^{11}B NMR chemical shifts for $(Cp^*M)_2B_5H_9$ (M = Cr, Mo, W) and the inverse of orbital energy differences: (squares) B_3 MO's 40−45; (diamonds) B_2 MO's 40−44; (circles) B_2 MO's 41−44.

Chart 2



41−44 contribute to the deshielding of B_2. As the MO compositions are approximately independent of metal identity, δ should depend most strongly on the difference in energies between the pair of MO's. In fact, considering the approximate nature of the MO treatment, an excellent correlation between δ and $1/\Delta E$ exists (Figure 3).

Table 1. Pertinent MO Parameters for $(Cp^*M)_2B_5H_9$ (M = Cr, Mo, W)

MO		E (eV)	character	% M	AO coefficients			type
					$B_{1,5}$	$B_{2,4}$	B_3	
45	Cr	−6.3	MB ab[a]	58	0.36	0.18	0.39	$2p_x$
	Mo	−4.8	MM b[a]	56	0.38	0.28	0.41	$+2p_y$[b,c]
	W	−4.7		50	0.30	0.25	0.45	
44	Cr	−8.0	MB ab	60	0.39	0.42	0.15	$2p_x$
	Mo	−6.2	MM b	52	0.39	0.41	0.08	$+2p_y$[b,c]
	W	−6.1		50	0.38	0.31	0.14	
41	Cr	−13.4	MB b	49	0.13	0.38	0.03	$2p_z$[b,d]
	Mo	−13.2	MM ab	39	0.15	0.43	0.00	
	W	−13.2		33	0.10	0.38	0.01	
40	Cr	−13.9	MB b	31	0.07	0.30	0.44	$2p_z$[b,d]
	Mo	−14.0	MM b	24	0.07	0.29	0.49	
	W[e]	−14.4		17	0.05	0.30	0.46	

[a] Legend: ab = antibonding; b = bonding. [b]Coordinate system shown in Chart 1. [c]Less than 0.1% p_z. [d]Less than 0.2% $p_x + p_y$. [e]Corresponds to MO 39.

Two questions remain. (a) Why is the shielding of B_2 and B_3 strongly affected by metal atom identity whereas that of B_1 is not? (b) What property of M causes ΔE to increase in going from Cr to W? The first question is easily answered. It does not lie in the unfilled orbitals, as both unfilled MO's 44 and 45 have substantial B $2p_{x,y}$ character (but little B $2p_z$ character) from all three boron types (Table 1). The situation is different for the filled MO's. Only B_2 has large B $2p_z$ character (and little B $2p_{x,y}$) in filled MO 41 (Table 1) and only B_2 and B_3 have B$2p_z$ character (and little B $2p_{x,y}$) in MO 40. MO's 40 and 41 are M−B bonding but, as they contain substantial metal d character, lie at high energy. B_1 is largely absent from the high-lying filled orbitals because the B_1−M interaction is highly stabilized due to the presence of B_1−H−M bridging hydrogens. Consequently, these MO's have reduced metal character. This aspect of the MO structure is consistent with earlier studies of the effects of bridging hydrogens on electronic structure[24] and is corroborated by the substantial ^{11}B downfield shift associated with the removal of a B−H−M bridge proton by a base.[25] The classic example is the PES study of isoelectronic diborane and ethylene, in which ionization potential associated with the B−H−B MO's of B_2H_6 is found to be several electronvolts higher than that of the π ionization of C_2H_4.[26]

This MO analysis also provides a chemically reasonable answer to the second question. The energy of the filled MO's 40 and 41 decrease somewhat in going from Cr to W, whereas the unfilled orbitals 44 and 45 increase in energy. The former correlates with intrinsic metal AO energies, as the first ionization potentials increase in going from Cr to W, whereas the opposite trend of the latter requires an explanation based on metal−boron orbital interactions. The trend in the energy of the unfilled orbitals is reminiscent of the increase in the spectrochemical splitting parameter Δ as one goes from a first-row transition metal to the third-row congener, keeping the ligand geometry and identity constant. In an octahedral complex, for example, this is attributed to a larger gap between the t_{2g} and e_g* orbitals due to increasing strength in covalent bonding in going from Cr to W. As MO's 44 and 45 are M−B antibonding, an increased strength of M−B bonding in going from Cr to W would likewise account for the observations described here.

To establish that the metal wave functions employed give chemically reasonable results, calculations on the hypothetical $[MH_6]^{6-}$ octahedral ions were carried out. These show an increasing HOMO (M t_{2g})−LUMO (M−H e_g*) gap in going from Cr to Mo to W (6.3, 7.7, 9.2 eV; d_{MH} = 1.6, 1.8, 1.8 Å), as expected. Further, the energies of the purely metal-based t_{2g} orbitals show a relatively large decrease (11.5 eV) in going from Cr to Mo and a small increase (1.0 eV) in going from Mo to W. The experimental metal band ionization energies of $M(CO)_6$

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(8.14, 8.23, 8.24 eV) and M(η-$C_6H_3Me_3$)$(CO)_3$ (7.20, 7.35, 7.32 eV) complexes (M = Cr, Mo, W) exhibit similar trends.[27,28]

This analysis of the ^{11}B chemical shift variation in the series $(Cp^*M)_2B_5H_9$ (M = Cr, Mo, W) supports the existence of strong, direct M−B bonding in metallaborane clusters. As argued previously in analyzing the photoelectron spectra of isoelectronic $(CO)_3FeB_4H_8$ and $(CO)_3Fe(\eta^4$-$C_4H_4)$,[29] the good match of boron and metal properties promotes covalent character and the borane fragment acts less like a ligand. It is interesting to note that the ^{11}B shifts for the metallacarborane series 3-(η-C_6H_6)-3,1,2-$MC_2B_9H_{11}$ (M = Fe,[30,31] Ru,[31] Os[32]) do not differ significantly. This is consistent with viewing these compounds as essentially metal−ligand complexes, in contrast to the metallaboranes discussed here, in which the metal partakes in a more intimate covalent cluster bonding interaction with boron.[33] The analysis also supports the basic validity of the MO bonding model for these compounds and indirectly adds support to its use in describing the unique aspects of the electronic structure associated with unsaturated metallaborane clusters.[34]

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