CONNECTIONS BETWEEN ^{11}B NMR CHEMICAL SHIFTS AND ELECTRONIC STRUCTURE IN METALLABORANES. A PRÉCIS

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Dedicated to Dr Stanislav Heřmánek on the occasion of his 70th birthday in recognition of his outstanding contributions to the areas of borane chemistry and NMR spectroscopy and in rememberance of his stimulating first visit to the University of Notre Dame in 1970.

An analysis of selected sets of metallaboranes in terms of a molecular orbital (MO) model of ^{11}B chemical shift change is used to demonstrate the origin of transition metal effects on boron shifts for: (i) M–B edge protonation; (ii) replacement of direct B–B by M–B interactions; (iii) encapsulation of B in a metal cluster; (iv) change in metal identity; and (v) change in vertex coordination number. Metal effects on both filled and unfilled MO's are important but changes in the latter appear to dominate. Consequently, models based solely on filled orbital properties, *e.g.*, electronic charge, are inadequate. A short review with 56 references.

Key words: Boranes; Metallaboranes; NMR spectroscopy, ^{11}B; Clusters; Molecular orbitals; Review.

The effective use of ^{11}B NMR spectroscopy in the characterization of compounds containing boron has a long history[1–5]. Beyond structural considerations, the empirical analysis of trends in chemical shifts permits the recognition of connections between certain compositional or geometric features and nuclear shielding, *i.e.*, connections to electronic structure. Stan Heřmánek is a master at this and his efforts have lead to the development of a number of rules, *e.g.*, the antipodal effect, that facilitate the interpretation of ^{11}B spectra by the experimental chemist[6,7].

In recent years, quantum chemical methods of treating the NMR shift problem have advanced sufficiently to provide usefully precise, calculated chemical shifts as a function of geometric structure[8–10]. The application of these methods have resolved some longstanding structural problems in borane and heteroborane chemistry[11,12]. Importantly, they also provide the experimental chemist with another structural tool to apply in situations where solid state X-ray diffraction structure data are unavailable, *i.e.*, metastable species that cannot be isolated are now amenable to structural analysis and the mechanistic implications are beginning to be exploited[13].

This being the case, the reader may well wonder at any further attempts at empirical analyses or the application of low-level molecular orbital (MO) methods to ^{11}B chemical shift problems. There are two basic reasons why the older, non-quantitative approaches continue. First, even calculated chemical shifts need interpretation. The chemist is used to the interpretation of the metrics of geometry in terms of bonding (discovering "where the electrons are" based on "where the nuclei are") and, in fact, chemical shifts also depend on "where the electrons are", albeit in a complex way. Beyond information on bonding, these analyses provide generalizations useful to the experimental chemist in the sense that the ability to unravel the spectra of compounds with complex cluster bonding moves the chemistry forward more rapidly. Again, this is where Stan Heřmánek has been a prime contributor[14].

Second, although metallaboranes will ultimately be treated by quantum chemical methods with sufficient precision to yield useful calculated chemical shifts, they presently present a large calculational problem[15,16]. Thus, an empirical approach offers an opportunity of using the large and growing accumulation of chemical shift data to tease out some of the more prominent connections between structure and shift.

In this short essay I focus on comparisons of sets of selected compounds related in such a fashion that the effects of a single, or at most a few, structural features can be identified with observed changes in ^{11}B chemical shift. Of course, the effects of a given structural feature are never completely separable from its molecular context but the examples have been chosen so that each dominates the shift change. This process is aided by two facts. First, in contrast to pure boranes and substituted boranes, the effect of a metal fragment on chemical shift can be an order of magnitude larger than the effect of a main group heteroatom or a simple exo-cage substituent. Consequently, in this paper I deal with large chemical shift changes (tens of ppm). Second, for some time now we have been interested in the synthesis of sets of closely related metallaboranes that can, for example, be compared with isoelectronic organometallic clusters[17,18]. These compounds are particularly suitable for the empirical approach described. However, even though most of the comparisons are drawn from our own work, a similar approach could be extended to the host of metallaboranes described in the literature[19–21].

MODEL

The complexity of the connection between chemical shift and electronic structure is well known and many simple concepts, such as charge and ring current, have been used to guide the interpretation of shifts in, *e.g.*, organic molecules. In terms of MO descriptions, there is no way of connecting chemical shift to the properties or energy of a single MO. This can be contrasted with the simple and elegant descriptions of, *e.g.*, multiple bonds and the ionization of closed shell molecules. Likewise, correlations of shift with single parameters like Mulliken populations (charge) are problematic. On the other hand, the perturbation treatment of Ramsey[22] provides a language based on MO concepts that can be used to describe the origins of large chemical shift changes in a set of closely related molecules in terms of MO concepts[23].

An analogy is pertinent. The reaction chemist uses the language of absolute rate theory (transition state theory) to describe the origin of large differences in relative reaction rates even though the theory provides a poor measure of absolute rate. Years of effective use generate confidence that in the comparison of closely related species, many of the parameters required by the theory will disappear thereby permitting a chemically understandable, and useful, description. Likewise, the approach used herein to describe the electronic origins of chemical shift is based on the assumption that all but a few of the orbital parameters necessary for defining the absolute chemical shift will disappear in the comparison of the shifts of closely related species. This “chemists’ approach” will never provide quantitative shift information but has the potential of providing chemically sensible explanations of shift changes that can be identified with characteristic structural features.

Specifically, in the Ramsey model the shielding is expressed in a diamagnetic and a paramagnetic term (the term names have no physical meaning). Large low-field shifts, which are characteristic of the effects of transition metals on ^{11}B resonances, 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 non zero only when they correspond to the rotation of a high-lying occupied B2p orbital into the space previously held by a low-lying unoccupied B2p orbital[23]. In terms of a one-electron MO model of the electronic structure, this analysis limits contributions to the paramagnetic term to pairs of filled and unfilled molecular orbitals that satisfy three criteria simultaneously: a small energy difference, ΔE, between the filled and unfilled MO's; large B2p orbital coefficients, α, of the specified boron atom in both filled and unfilled MO's; and the proper B2p symmetries such that the B2p contributions of the filled MO and unfilled MO are coupled by the angular momentum operator.

For any given complex molecule the remaining number of orbital pairs are still formitable; however, consideration of a set of closely related molecules adds yet another component to the grid of criteria – the MO's must be affected by the molecular feature that varies across the series. These ideas are summarized in the diagram in Fig. 1 in which the parameters leading to a significant contribution to the Ramsey paramagnetic term (and a downfield shift) are defined. In this example, the fourth variable in the series is the identity of the transition metal fragment, M, in the metallaborane and, hence, the fourth criterion is substantial metal character in one or both of the members of the MO pair.

The objective is to apply this model to series of metallaboranes that are related in a manner such that for any given series of compounds the set of four criteria, that must be simultaneously satisfied, allow the observed changes in chemical shift to be associated with a small number of MO pairs. Keeping in mind that the energy of a MO and its composition (atomic orbitals from the constituent atoms) are interdependent, the explanation may be couched in terms of the magnitude of ΔE or orbital coefficients or both. In this way features of the electronic structure, expressed in the language of molecular orbital theory, will be connected with chemical shift changes. In most of the examples described a complete description will be found in the references; however, in other cases the results are based on unpublished Fenske–Hall MO calculations[24,25] carried out in like manner. Finally, the physical ideas are not new and, indeed, chemical shifts

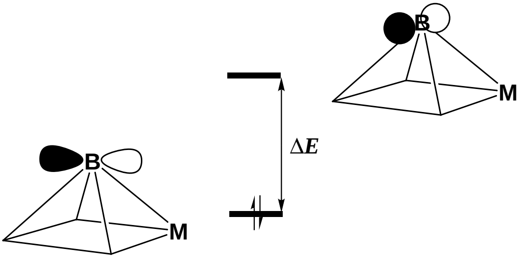

FIG. 1

Factors that increase the magnitude of the paramagnetic term in the Ramsey expression of shielding leading to downfield shifts. 1. ΔE small, 2. αB2p and αB′2p large, 3. B2p and B′2p orthogonal, 4. αM and/or αM′ large characteristic of metallaboranes have been discussed along similar, albeit more general, lines previously[26].

HYDROGEN BRIDGED *versus* UNBRIDGED M–B INTERACTIONS

One of the fascinating features of polyhedral boranes is the fact that these "electron defficient" cages can function as Broensted acids[27–29]. The hydrogen atom involved in a three-center two-electron B–H–B bridge bond is distinctly protonic and can be removed by a base. Relative acidity depends on the cage size as well as on other parameters[30]. In removing a proton from a B–H–B bond, a Lewis basic, two-center $[B–B]^–$ bond is created. It is generally accepted that in a B–H–B bond there is little direct B–B bonding. By analogy, the removal of a bridging hydrogen atom from a M–H–B edge is expected to enhance the effect of the metal atom on the boron shift. A clear example is provided by the conjugate acid–base pair $HFe_4(CO)_{12}BH_2$ and $[HFe_4(CO)_{12}BH]^–$ in which the boron resonance moves 34 ppm down field on removal of one Fe–H–B bridging hydrogen atoms to create a direct Fe–B bonding interaction[31–33] (Fig. 2a).

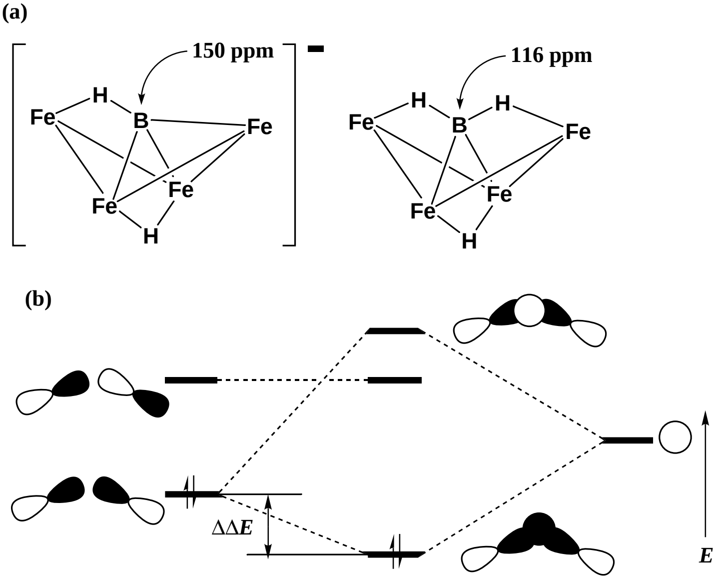

FIG. 2

a Protonation/deprotonation of $[HFe_4(CO)_{12}BH]^–/HFe_4(CO)_{12}BH_2$. b Main group atom orbital model for the formation of a three-center two-electron bonding interaction from a two-center bond and a proton

The Ramsey model, in the form described above, is particularly apt for comparison of conjugate base pairs as the two species are isostructural and isoelectronic. Thus, it is the perturbation of the proton on the MO structure that generates the fourth criterion[34]. The addition of a proton, a 1s orbital, to a two center two-electron bond consisting of a filled bonding and empty antibonding set of two orbitals causes the bonding orbital to be split into a lower-lying three-center bonding orbital and a higher-lying three-center antibonding orbital[35] (Fig. 2b). This is a large effect, *i.e.*, in the comparison of the photoelectron spectra of isoelectronic C_2H_4 and B_2H_6 moving protons from the carbon nuclei to bridging positions results in a stabilization of 3–4 eV (ref.[36]). Consequently, deprotonation of $HFe_4(CO)_{12}BH_2$ causes a filled orbital of Fe and B character to rise to higher energy. Hence, the ΔE for all terms in the Ramsey expression containing the affected B2p functions from this boron atom is reduced by a $\delta\delta E$ (Fig. 2b) generating a low-field shift in the resonance. In fact, the perturbation of the bridging proton is sufficiently large that the effect of a metal on an adjacent boron atom to which it is bonded is effectively turned off. This is confirmed by noting that the boron atom in $HFe_3(CO)_9H_3BH$, which is bound to three Fe atoms *via* three Fe–H–B bonds, resonates at 2 ppm, within the normal range for tetracoordinate boron atoms[37].

DIRECT B–B *versus* M–B INTERACTIONS

Since the pioneering work of Grimes and coworkers on the syntheses of metal-rich metallaboranes[38,39], it has been recognized that the association of a given boron atom with several transition metals leads to large low-field ^{11}B chemical shifts[40]. Indeed, for a given metal type there is a good correlation between the number of direct metal–boron bonding interactions and the magnitude of the low-field shift[33]. The most striking example is provided by a boron atom in the center of a six-metal octahedral cluster[41] (see below). The six M–B interactions generate the largest low-field ^{11}B shift observed for a diamagnetic compound.

The specific comparison to be discussed in this section is the series B_5H_9, 2-$Cp^*CoB_4H_8$ (refs[42,43]), 2,4-$\{Cp^*Co\}_2B_3H_7$ (ref.[44]), and 2,3-$\{Cp^*Rh\}_2B_3H_7$ (refs[45,46]) ($Cp^* = \eta^5\text{-}C_5Me_5$) with a focus on the chemical shift of the apical boron atom (Fig. 3). The effect of the metal is dramatic. In going from 0 to 1 to 2 Co–B interactions there is a downfield shift of 56 and 119 ppm, respectively. For the Rh derivative, for which no monometal analog presently exists, the overall shift is 97 ppm. The difference between Co and Rh is attributed to different metals rather than different isomeric structures (see below). Some time ago we generated an empirical correlation between the ^{11}B chemical shifts in a number of ferraboranes involving $Fe(CO)_3$ fragments by associating a parameter with each of the boron atoms nearest neighbor interactions[33]. Consistent with these CpM compounds, a downfield shift of 46 ppm for each Fe–B interaction was used. Clearly the metal effect is a large one. But how is it to be explained in terms of the MO structure of a square pyramidal, *nido* borane?

A focus on the apical boron atom is appropriate as the basal boron atoms are largely (but not completely) "isolated" from the effects of the metals by the bridging hydrogen atoms completely in accord with the conclusions of the last section. In addition, the connection between the apical and basal atoms in the square pyramid contains an essential feature of cluster bonding – a boron atom bonded to five nearest neighbors by four bonding orbitals (3 B–B bonding and 1 B–H bonding). Note that the high-field shift of the apical atom in B_5H_9, so familiar to the pentaborane chemist, is not found for the metallaboranes: indeed the opposite is true for the dimetallapentaboranes in spite of constant coordination number.

For the hypothetical $[B_5H_5]^{4-}$ ion the MO description of apical–basal bonding is generated by allowing the three orbitals of a capping BH fragment to interact with three of the four symmetry combinations of the out

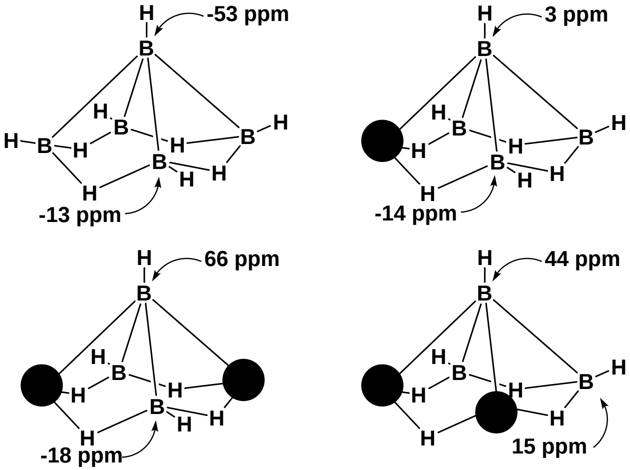

FIG. 3
Schematic structures and ^{11}B chemical shifts for B_5H_9, 2-$Cp^*CoB_4H_8$, 2,4-$\{Cp^*Co\}_2B_3H_7$, and 2,3-$\{Cp^*Rh\}_2B_3H_7$, where the filled circles represent the metal fragments

of plane B2p orbitals of a planar square B_4H_4 ring (Fig. 4). In this well known description[35], the doubly degenerate HOMO results from the π symmetry bonding interaction whereas the LUMO is the nonbonding δ ring orbital which, by symmetry, contains no apical boron character. These orbitals also constitute the frontier orbitals for B_5H_9.

Although there are low-lying unfilled and high-lying filled MO's containing apical B2p_x and B2p_y character, there are none containing significant B2p_z character. Thus, the small paramagnetic term of the apical boron (larger shielding, high field resonance) relative to the basal borons is attributed in part to a large ΔE_1, *i.e.*, the pair of orbitals defined by ΔE_2 in Fig. 4 contributes nothing to the paramagnetic term as the empty δ orbital contains zero apical B2p character. Again, as the emphasis is on describing a change in relative shielding rather than the total shielding in a single molecule, many terms can be ignored.

As seen in Fig. 5, the situation changes dramatically in going to 2-$CpCoB_4H_8$. The presence of the metal breaks the four-fold symmetry of B_5H_9 and the LUMO of the metallaborane, which is a metal analog of the δ nonbonding MO of B_5H_9, now contains significant (11%) apical B2p character. Effectively the orbital pair defined by ΔE_2 in Fig. 4, which makes a contribution to the paramagnetic term for the basal boron atom in B_5H_9, is now turned on for the apical boron atom in the metallaborane as well.

In the more complex dimetallapentaboranes, additional orbital pairs must be considered and the filled MO's make contributions. Examination

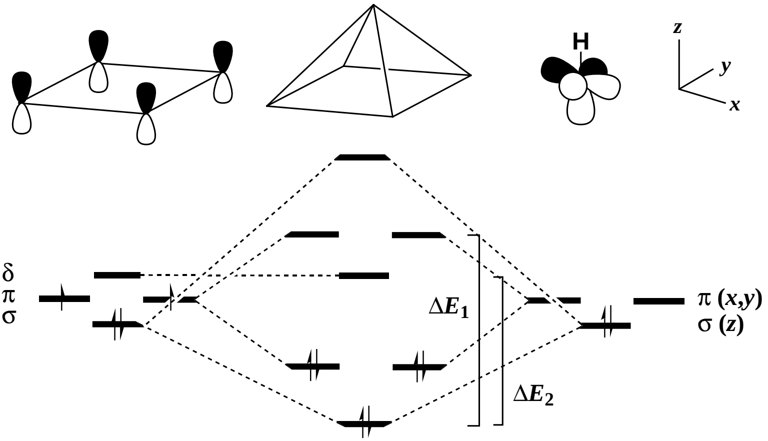

FIG. 4
MO model for the formation of the apical-basal five-center six-electron cluster bonding interaction in the *nido* square pyramidal $[B_5H_5]^{4-}$ ion

of the HOMO in the monometallaborane is instructive. This MO contains a large Co3d lone pair component but also contains boron character which is seen to be related to the π bonding MO's of B_5H_9. Because of the large Co3d character, this filled MO with significant (17%) apical B2p character lies at higher energy relative to the π bonding MO's of B_5H_9 thereby enhancing the downfield shift. Thus, the essence of the explanation of the large down field shifts experienced by boron atoms directly bonded to transition metal atoms is that the replacement of a BH fragment by a transition metal fragment introduces both higher-lying filled MO's containing B2p character and lower-lying unfilled MO's containing B2p character[34]. Both effects result in deshielding. Note that calculated Mulliken charge on a given boron atom increases with the number of metal–boron interactions leading to the counter-intutitive correlation with electronic charge mentioned in earlier work[33]. Consequently, filled orbital properties alone are insufficient to explain the observations.

INTERSTITIAL BORON ATOMS

The situation with interstitial boron atoms, such as that found in [*trans*-$Rh_2Fe_4(CO)_{16}B]^-$ (Fig. 6, ref.[41]) and other borides[47], is directly related to that discussed in the previous section; however, because of high symmetry the MO explanation of the very low field ^{11}B resonance observed is particularly straightforward[48]. The electronic structure of octahedral metal clusters containing interstitial atoms has been well studied both for molecular species

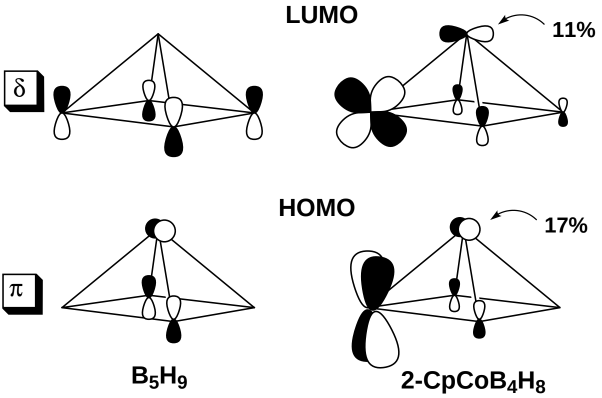

FIG. 5
Comparison of the atomic orbital compositions of the HOMO and LUMO of B_5H_9 and 2-$CpCoB_4H_8$

as well as solid state Zintl cluster phases[49]. For a main group interstitial atom the four valence functions interact strongly with metal orbitals of the appropriate symmetry leading to very low energy filled MO's with main group atom character. Clearly the low-field shifts cannot be explained by only considering the filled orbitals containing B2p character.

The explanation in terms of the Ramsey MO model is really very simple. In Fig. 6 the interactions of the interstitial B2p functions with the t_{1u} symmetry manifold of an octahedral O_h symmetry metal cluster are delineated (only the t_{1u} manifold needs to be considered because of the symmetry requirements of the angular momentum operator). Indeed, the bonding interaction leads to low energy filled orbitals with high B2p character but the empty antibonding partners, necessarily generated, also lie at very low energy. It is this set of three, low-lying unfilled orbitals with large B2p character generates the low-field shifts observed for the boride clusters.

METAL IDENTITY

Comparison of metallaboranes containing light *versus* heavy metals suggests that the heavier metals generate modestly higher-field shifts. Re-

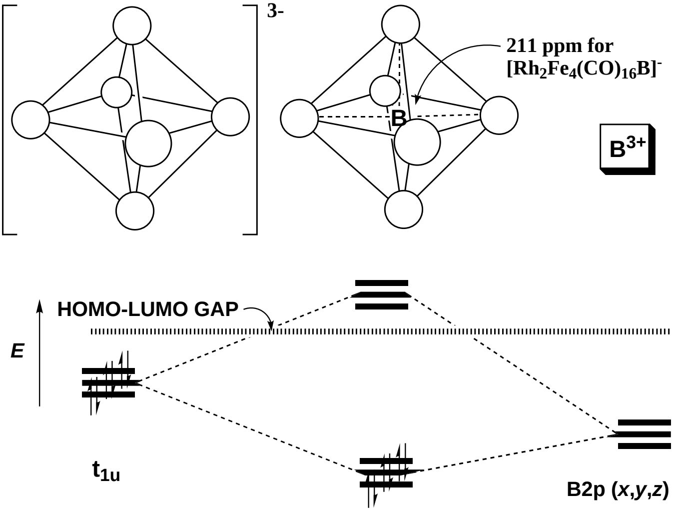

FIG. 6

The interaction of the B2p (t_{1u} symmetry) with the filled t_{1u} high metal character cluster orbitals for an octahedral (O_h symmetry), 86 electron homonuclear M_6 trianion to yield a neutral borido cluster. Note that none of the other 40 filled cluster bonding, nonbonding or metal ligand orbitals are shown in this simplified diagram cently, we prepared a set of isoelectronic and isostructural compounds containing group 6 metals exhibiting surprisingly large shifts as a function of metal. Hence, these compounds provided an opportunity to probe another aspect of the role of the metal atom on boron shift in the context of the MO model.

The set of compounds is $(Cp^*M)_2B_5H_9$, M = Cr (ref.[50]), Mo (refs[50,51]), W (ref.[52]), with a structure based on a bicapped trigonal bipyramid (Fig. 7). As shown in the figure, the ^{11}B shifts of the boron atoms directly bonded to the metals depends strongly on metal identity whereas that of the type connected *via* M–H–B bridges is essentially invarient and serves as an internal standard. The latter observation is again consistent with the discussion given in the first section and the former clearly reveals a metal dependence.

In view of the examples discussed already it will not be a surprise to learn that the explanation of the metal dependence lies in pairs of filled–unfilled orbitals with both large metal and boron character[53]. Thus, for example, the pair shown in Fig. 8 (metal character not shown) is responsible for the low-field shift of the unique boron in $(Cp^*M)_2B_5H_9$. For this pair of MO's, it is found that ΔE increases as M goes from Cr to W. This correlates nicely

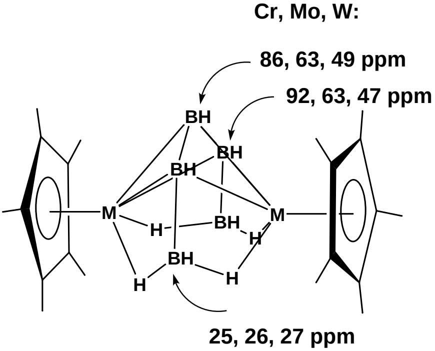

FIG. 7
Structure and ^{11}B shifts for the three boron environments in $Cp^*_2M_2B_5H_9$, M = Cr, Mo, and W

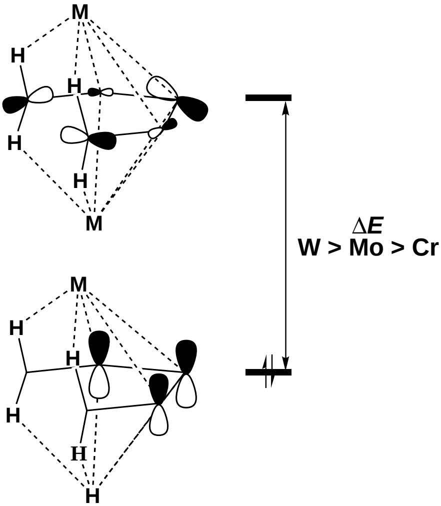

FIG. 8
The pair of occupied and unoccupied MO's of $Cp^*_2M_2B_5H_9$, M = Cr, Mo, and W, that give rise to the large downfield shift of the unique boron atom (metal character is not shown)

with the shift to high field observed for the unique boron in going from Cr to W. Note that although the empty orbital contains B2p character for the M–H–B bridged boron atoms, its filled partner does not. Because of the bridging protons, filled MO's with the appropriate B2p character are only found at much lower energy and, consequently, contain low metal character.

The MO analysis permits the identification of the properties of M that cause ΔE to increase in going from Cr to W. Although the energy of the filled MO decreases somewhat in going from Cr to W, the unfilled orbital rises 2 to 3 times more in going from Cr to W. Again it is the empty orbitals which dominate. The former stabilization is understandable in terms of effective nuclear charge but this cannot be the explanation of the increasing energy of the unfilled MO. However, the unfilled MO is M–B antibonding which suggests that it is stronger M–B bonding in going from Cr to Mo to W that lies behind the observations. In fact, the trend in the energy of the unfilled orbitals is reminiscent of the increase in the spectrochemical splitting parameter Δ in going from a first-row transition metal to a third-row metal. In coordination chemistry, this is attributed to a larger gap between the t_{2g} and e_g* orbitals due to increased strength in covalent bonding. Thus, the MO explanation of the effect of metal on ^{11}B shift is fully consonant with classical transition metal coordination chemistry – an increase in metal–ligand bonding strength in going from Cr to W.

COORDINATION NUMBER

One of the empirical principles of ^{11}B NMR is that high coordination number leads to higher shielding[54]. We have recently come across an example of a metallaborane that constitutes a spectacular example of the interplay of metal effects and coordination number. As shown in Fig. 9, a direct comparison of the shifts of the boron atoms capping the square pyramids in B_5H_9 and $Cp*_2Ru_2B_4H_8$ (ref.[46]) might lead one to conclude incorrectly that these boron atoms are in similar environments.

It is much more useful to compare $Cp*_2Ru_2B_4H_8$ with $Cp*_2Rh_2B_3H_7$ (ref.[46]) in that one can use the 44 ppm chemical shift of the apical boron atom of the latter as a reference point for a four coordinate boron atom bound to two metal and two boron atoms. Now one sees that the boron capping the square pyramid and adjacent to two metal atoms is shifted upfield by 77 ppm in going from a coordination number of 4 to 5 (coordination number defined by the connectivity of the cage vertex). Contrarywise, the shift of the boron at capping the M_2B face (also adjacent to two metal atoms) is shifted 78 ppm downfield in going from a coordination number of 4 to 3. Thus, one finds the extraordinary situation of the boron atoms of two adjacent, bonded BH vertices differing by 155 ppm. Note that once more the nearly constant basal boron atom shift serves as a control. A similar situation was observed in a closed tungstaborane cluster where a correlation with coordination number for borons with nearly equivalent metal environments was useful in corroborating the assignment[55].

A good idea of the MO origin of these differences can be gleaned from an examination of the changes in the frontier orbital structure of $[B_5H_5]^{4-}$ (see also Fig. 4) as it is capped with a $[BH]^{2+}$ fragment to produce $[B_6H_6]^{2-}$ (Fig. 10). As described by Mingos and Wales[56], the orbitals of a capping

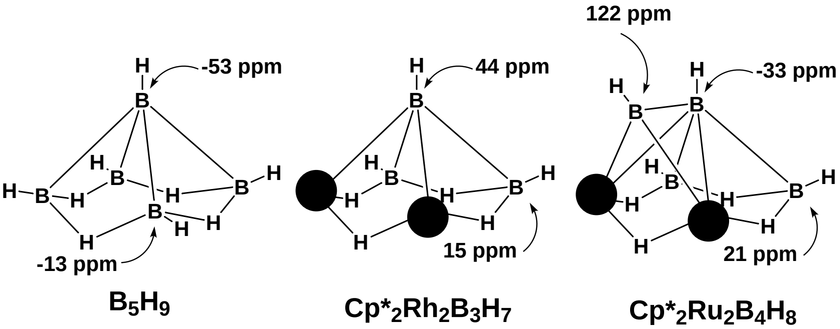

FIG. 9

The schematic structures and ^{11}B shifts of B_5H_9, $Cp^*_2Rh_2B_3H_7$, and $Cp^*_2Ru_2B_4H_8$ illustrating the effects of changing coordination number in a single cluster type

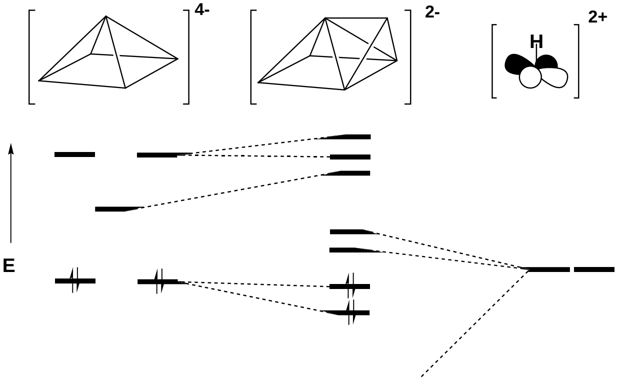

FIG. 10

Generation of low-lying empty MO's of high B2p character in the formation of a capped $[B_6H_6]^{2-}$ cluster by addition of a BH^{2+} fragment to a *nido* square pyramidal $[B_5H_5]^{4-}$ ion (see also Figs 4 and 6) fragment interact with the primary cluster orbitals to yield a set of more strongly bonding cluster orbitals but no more of them. In this sense it is like adding a proton to a cluster edge – there is selective stabilization of filled orbitals but no increase in their number. However, an important consequence flows from the fact that the number of unoccupied MO's increases.

Thus, as can be seen from Fig. 10, the tangential orbitals of the capping fragment introduce a pair of low-lying empty orbitals into the manifold of the capped square pyramid. Just as for metal clusters with an interstitial boron atom, this correlates with the large downfield shift observed for the three coordinate, capping vertex. The five coordinate boron is similar to that in $[B_5H_5]^{4-}$ (the high-lying filled and low-lying unfilled orbitals lack significant contributions from the radial B2p orbital of this boron atom) and this metal-free model gives no direct information on the five coordinate boron shift in the metallaborane. However, note that the empty δ orbital of $[B_5H_5]^{4-}$, which contains no apical B2p character at all but which picks up such character on replacing a basal BH with a metal fragment (see above), has now risen to considerably higher energy. Thus, the downfield shift expected on replacing basal BH fragments with metal fragments should be considerably moderated as, in fact, observed in the metallaborane (+20 rather than +97 ppm).

CONCLUSIONS

The effects of transition metals on ^{11}B chemical shifts can be very large even if the boron atoms are adjacent. Although the interpretation of absolute shifts of single compounds using approximate MO methods is of doubtful value, the sets of closely related compounds described reveal several factors that are important in determining relative observed shifts. The presence or absence of bridging hydrogens (and capping fragments), the number of direct M–B interactions, metal identity, and coordination number are all major contributors. Although filled orbitals cannot be ignored, the perturbation of unfilled orbitals seems to be much more important in explaining the large observed chemical shift changes. The use of transition metals to tune borane properties, in the manner of the organometallic chemist, is one of our objectives and ^{11}B chemical shift constitutes a measure that reflects, indeed magnifies, the perturbation in electronic structure caused by the metal. Additional connections with structure and, ultimately, reactivity are sought as newly characterized metallaboranes supply additional series of compounds.

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