J. Am. Chem. Soc. 1988, 110, 5345–5349

# Interaction of Iron with Boron in Metal-Rich Metallaboranes Resulting in Large Deshielding and Rapid Relaxation Processes of the Boron-11 Nucleus

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**Abstract:** A first-order, parameterized model for calculating $^{11}B$ chemical shifts in metal-rich ferraboranes and a correlation of chemical shift with boron Mulliken populations from Fenske–Hall calculations are presented. These correlations are qualitatively different from those reported earlier for boranes and suggest that direct iron–boron interactions lead to large deshielding due to substantial increases in multiple-bond contributions to the shielding tensor. Relaxation rates have been measured for $[Fe_4(CO)_{12}BH_{3-n}]^{n-}$ ($n$ = 0–2) and correlated with electric field gradients at the boron nucleus estimated from Fenske–Hall calculations. These results demonstrate that formation of the boride, $[Fe_4(CO)_{12}B]^{3-}$, by deprotonation is accompanied by the development of large asymmetries in the electronic charge distribution around the boron nucleus. Finally, $^7Li$ NMR is used to probe the nature of the anions $[Fe_4(CO)_{12}BH_{3-n}]^{n-}$ ($n$ = 1–3), and observed line shapes suggest close association of $Li^+$ with the trianion.

Although classified as a non-metal, the element boron exhibits some characteristics of a metal in its varied compounds.[1] This is not unexpected as boron is an electropositive element with intrinsic valence unsaturation (fewer valence electrons than valence orbitals). Hence, like transitions metals, it shows a pronounced tendency to form hydridic compounds with hydrogen, to accept electron pairs provided by Lewis bases, and to form three-dimensional, delocalized cluster bonding networks. Indeed, more and more mixed metal–boron frameworks, metallaboranes, have been characterized in recent years.[2] These metallaboranes provide a setting in which the behavior of boron can be contrasted with that of a transition metal.

In the course of our continuing characterization of metal-rich metallaboranes with boron atoms, we have noted large downfield shifts associated with direct (unbridged) metal–boron interactions. While this observation is hardly unique,[3] the ferraboranes constitute a sufficiently large sample of monoboron metallaboranes to allow the source of these shifts and, hence, the metal–boron interaction, to be examined. In the following we demonstrate a simple empirical correlation and present a rationale. In addition, we show that an examination of the effects of direct metal–boron bonding on the relaxation time of the $^{11}B$ nucleus also provides insight into the nature of the interaction. Finally, $^7Li$ NMR is used to probe the nature of a set of related ferraborane anions.

**Table I.** Observed and Calculated $^{11}B$ Chemical Shifts and Selected Mulliken Populations for Monoboron Ferraboranes

| | shift[a] | | | | |
|---|---|---|---|---|---|
| compd | obsd | calcd[b] | $q_B$(total) | $q_B$(2p) | ref |
| $(\mu\text{-H})Fe_3(CO)_9H_3BH$[c] | 2 | [2] | 3.400 | 2.304 | *f* |
| $[(\mu\text{-H})Fe_3(CO)_9H_2BH]^-$ | 6 | 36 | 3.669 | 2.492 | *f* |
| $(\mu\text{-H})Fe_3(CO)_9H_3BCH_3$ | 22 | [22] | 3.220 | 2.171 | *f* |
| $[(\mu\text{-H})Fe_3(CO)_9H_2BCH_3]^-$ | 29 | 58 | 3.444 | 2.323 | *f* |
| $(\mu\text{-H})Fe_3(CO)_{10}HBH$ | 56 | 70 | 3.733 | 2.486 | *g* |
| $[Fe_3(CO)_9(PMe_2Ph)HBH]^-$ | 57 | 70 | | | *h* |
| $[Fe_3(CO)_{10}HBH]^-$ | 58 | 70 | 3.776 | 2.521 | *g* |
| $[Fe_3(CO)_{10}HBCH_3]^-$ | 74 | 94 | 3.658 | 2.411 | *h* |
| $(\mu\text{-H})Fe_3(CO)_{10}HBCH_3$ | 76 | 94 | 3.521 | 2.333 | *h* |
| $(\mu\text{-H})Fe_4(CO)_{12}BH_2$[c] | 116 | [116] | 3.797 | 2.530 | *i* |
| $[Fe_4(CO)_{10}(PMe_2Ph)_2BH_2]^-$ | 118 | 116 | | | *i* |
| $[(\mu\text{-H})Fe_4(CO)_{12}BCH_3]^-$ | 122 | 128 | | | *j* |
| $(\mu\text{-H})_2Fe_4(CO)_{12}BCH_3$ | 126 | 128 | | | *j* |
| $(\mu\text{-H})Fe_4(CO)_{12}(AuPPh_3)BH$ | 138 | | | | *k* |
| $Fe_4(CO)_{12}(AuPPh_3)_2BH$ | 141 | | 4.037[d] | 2.654[d] | *l* |
| $[(\mu\text{-H})Fe_4(CO)_{11}(PMe_2Ph)BH]^-$ | 143 | 150 | | | *i* |
| $[(\mu\text{-H})Fe_4(CO)_{12}BH]^-$ | 150 | [150] | 3.958 | 2.611 | *i* |
| $[Fe_4(CO)_{12}BH]^{2-}$ | 153 | 150 | 3.934 | 2.594 | *j* |
| $[Fe_4(CO)_{12}B]^{3-}$ | *e* | 184 | 4.090 | 2.619 | *j* |
| $[Fe_4(CO)_{12}(AuPPh_3)_2B]^-$ | 192 | | | | *k* |

[a] $\delta$ ($BF_3{\cdot}Et_2O$) = 0. [b] Values used to determine parameters in brackets. [c] Structure in solid state by X-ray diffraction. [d] Calculated with $CuPH_3$ to model $AuPPh_3$. [e] The $^{11}B$ signal was not observed. [f] Vites, J.; Housecroft, C. E.; Eigenbrot, C.; Buhl, M. L.; Long, G. J.; Fehlner, T. P. *J. Am. Chem. Soc.* **1986**, *108*, 3304. [g] Vites, J. C.; Housecroft, C. E.; Jacobsen, G. B.; Fehlner, T. P. *Organometallics* **1984**, *3*, 1591. [h] Housecroft, C. E.; Fehlner, T. P. *J. Am. Chem. Soc.* **1986**, *108*, 4867. [i] Wong, K. S.; Scheidt, W. R.; Fehlner, T. P. *J. Am. Chem. Soc.* **1982**, *104*, 1111. Housecroft, C. E.; Fehlner, T. P.; Buhl, M. L.; Long, G. J. *J. Am. Chem. Soc.* **1987**, *109*, 3323. [j] Rath, N. P.; Fehlner, T. P. *J. Am. Chem. Soc.* **1987**, *109*, 5273. [k] Housecroft, C. E. *Polyhedron* **1987**, *6*, 1935. [l] Housecroft, C. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 6420.

**Chemical Shifts.** Although the $^{11}B$ NMR chemical shift of the boron atom is a sensitive measure of the boron atom's environment, the connection between the chemical shift and the electronic structure of the boron atom in a borane is poorly understood. Unfortunately, the relationship between the chemical shift of any NMR-active nucleus and its electronic environment is not a simple one.[4] An empirical method of approaching the problem is to seek parameterizations of chemical shifts based on some description of the nuclear environment. These parameterized models are of interest not only because they provide a phenomenological description of electronic structure but also because they provide experimental information useful in the characterization of unknown systems. However, even for closely related substituted boron compounds, simple parameterizations of $^{11}B$ NMR shifts based on first-order substituent constant models are not found to be satisfactory. More complicated, and less useful, approaches are required to obtain reasonable agreement with experiment.[5] On the other hand, a number of correlations between boron chemical shifts and calculated or empirical parameters have been published.[6] For example, good correlations with $^{13}C$ NMR shifts

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(3) For example, see: Miller, V. R.; Weiss, R.; Grimes, R. N. *J. Am. Chem. Soc.* **1977**, *99*, 5646.

(4) Eaton, G. R.; Lipscomb, W. N. *NMR Studies of Boron Hydrides and Related Compounds*; Benjamin, New York, 1969.

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(6) Teixidor, F.; Vinas, C.; Rudolph, R. W. *Inorg. Chem.* **1986**, *25*, 3339. Hermánek, S., Ed. *Boron Chemistry*; World Scientific: Teaneck, NJ, 1987; p 26.

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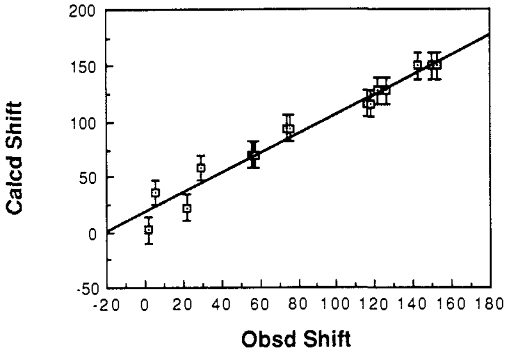

**Figure 1.** Plot of calculated $^{11}B$ shift vs observed for ferraboranes containing a single boron. The straight line corresponds to the equation $\delta(\text{calcd}) = 18.45 + 0.886\delta(\text{obsd})$, $R = 0.98$, and the error bars give the standard error of the data.

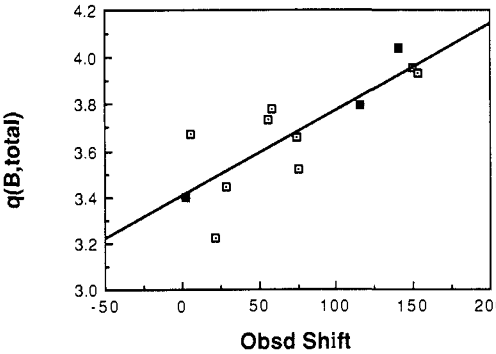

**Figure 2.** Plot of total boron Mulliken population vs observed chemical shift for selected ferraboranes. The straight line corresponds to the equation $q_B = 3.40 + 0.00376\delta(\text{obsd})$, $R = 0.82$. The filled squares correspond to compounds with known solid-state structures.

**Table II.** Observed $^{11}B$ Chemical Shifts and Mulliken Populations for $Fe_2(CO)_6B_3H_7$ and $[Fe_2(CO)_6B_3H_6]^-$

| compd | shift, ppm | $q_B$(total) | $q_B$(2p) |
|---|---|---|---|
| $Fe_2(CO)_6B_3H_7$ | | | |
| B(1,3) | 4.2 | 3.389 | 2.373 |
| B(2) | 12.4 | 3.118 | 2.291 |
| $[Fe_2(CO)_6B_3H_6]^-$ | | | |
| B(1) | 2.4 | 3.377 | 2.357 |
| B(2) | 8.6 | 3.080 | 2.173 |
| B(3) | 33.9 | 3.591 | 2.514 |

have been reported,[7] but this provides only marginal help in understanding the interaction between boron and other atoms as there are problems with rationalizing the observed $^{13}C$ NMR data in terms of bonding models. Correlations with calculated Mulliken populations on boron, however, do yield insight into the bonding interactions.[8] Against this background, the following simple parameterization of the chemical shifts of metal-rich metallaboranes and their correlation with calculated Mulliken populations is particularly significant.

The observed chemical shift data are given in Table I. A first-order approach consists in considering boron being perturbed by only its nearest neighbors. The chemical shift is taken to be $\delta = \sum\delta(A_i)$ where $\delta(A_i)$ is the parameter for the $i$th atom and $i$ runs from 1 to $n$, where $n$ is the number of nearest neighbors. For the iron–boron clusters only four parameters are required. The "substituent" parameters ($\delta(H_{\text{term}}) = -34$, $\delta(CH_3) = -10$, $\delta(H_{\text{bridgeFe}}) = 12$, and $\delta(Fe) = 46$) were defined by the chemical shifts of the four compounds indicated in Table I. Two of these compounds have been structurally characterized in the solid state, and the other two are related to the first two by either methyl substitution or proton loss. The calculated shifts are given in Table I, and a correlation between calculated and observed shifts is shown in Figure 1. Note that this correlation is over a chemical shift range of about 150 ppm and that no attempt has been made to optimize the parameters. The largest deviation is for $[HFe_3(CO)_9BH_3]^-$, a compound in which the boron is coupled to four protons. However, the spectroscopic data (Mössbauer and IR) show that the most stable static structure has two Fe–H–B bridges and one Fe–H–Fe bridge.[9] The substantial deviation of the observed shift from the calculated one may indicate a significantly different Fe–B interaction from those found in the other compounds.

Several points are worthy of note. First, the replacement of a B–H–Fe with a B–Fe interaction results in a more positive shift of 34 ppm. The B–H–Fe three-center bond may well involve some direct Fe–B interaction, but the deshielding is attributed to an increase in the direct metal–boron interaction on removal of the bridging proton. Second, the data in Table I show that either electronically perturbing the metal by $PR_3$ substitution for CO or increasing the net cluster charge by deprotonation at a M–H–M site causes only relatively small changes in the chemical shift. That is, the gross chemical shift for these compounds depends only on the atoms directly attached to B apparently because the large deshielding resulting from the metal interaction swamps the expected, but smaller, changes due to substituents and charge. Therefore, for $B_1$ systems at least, the $^{11}B$ chemical shift clearly defines boron nearest neighbors independently of the particular details of the molecule itself. Of course the simplicity of the correlation has a drawback in that substantial changes in a given system do not result in appreciable changes in the boron chemical shift. Finally, this correlation would predict a chemical shift for $[Fe_4(CO)_{12}B]^{3-}$ of $\delta$ 184 ppm, but, as noted below, the boron resonance for this anion has not been observed.[10]

Correlations of the chemical shift of polyboranes and carboranes with both the total Mulliken populations and the B 2p populations on boron have been reported previously.[11] They are of the form $-\delta(^{11}B) \propto q_B$, i.e., the greater the boron population, the more negative the chemical shift. The most complete correlation was obtained when only the B 2p populations [$q_B(2p)$] were considered, and this was taken as evidence that boron charge density and coordination number affect $\sigma_d$, the diamagnetic contribution to the net shielding. These authors indicated that the correlation observed with $q_B(2p)$ was due to changes in the local paramagnetic contribution to the shielding, which is given by the approximate equation[12]

$$\sigma_p(B) \propto -[1/\Delta E][\langle r^{-3}\rangle_{PB}][\textstyle\sum Q_{BX}] \quad (1)$$

where $\Delta E$ is the "excitation energy", $\langle r^{-3}\rangle_{PB}$ is the mean inverse cube of the radius of the p orbitals on the boron atom, and $\sum Q_{BX}$ is the "bond order" term between boron and atom X. The last two terms were thought to lead to the observed correlation.

The calculated populations for the ferraboranes (Table I) also correlate with the chemical shifts, and the fit is about the same for either $q_B$ or $q_B(2p)$ populations (Figure 2). However, the slopes of the correlations, although similar in magnitude, have the opposite sign of those previously published; i.e., $\delta(^{11}B) \propto q_B$. There is no reason to believe that the previous correlation depends on the method of calculation as, for example, the Fenske–Hall method yields a higher boron population [$q_B$(total) or $q_B(2p)$] on the apical boron of $B_5H_9$ than the basal boron and the chemical shift of the former is more negative. Additional evidence that the opposite trends exhibited by these two correlations are not artifacts of the approximate calculational methods results from an examination of the boron shifts and populations of the different

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(10) Rath, N. P.; Fehlner, T. P. *J. Am. Chem. Soc.* **1987**, *109*, 5273.

(11) See ref 8. Note that the pre-1976 sign convention for the $^{11}B$ chemical shift is used in this paper.

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**Table III.** $^{11}$B Line Widths, Relaxation Times, Calculated $q_{zz}$'s, and Asymmetry Parameters for I ($[Fe_4(CO)_{12}BH_{3-n}]^{n-}$, $n$ = 0–2) and $^{11}$B Line Widths, Calculated $q_{zz}$'s, and Asymmetry Parameters for I ($[Fe_4(CO)_{12}BH_{3-n}]^{n-}$, $n$ = 3) and II ($[Fe_4(CO)_{12}(AuPPh)_2BH]$)

| compd | line width (fwhm),[a] Hz | $T_1$,[a] ms | Mulliken populations[b] | | | $(q_{zz}/q_p)^2 \times 10^4$ [c] | $(1 + 1/3\eta^2)$ |
|---|---|---|---|---|---|---|---|
| | | | $n_x$ | $n_y$ | $n_z$ | | |
| I, $n = 0$ | 100 | 4.2 | 0.850 | 0.823 | 0.857 | 9 | 1.039 |
| I, $n = 1$ | 120 | 2.6 | 0.795 | 0.927 | 0.889 | 127 | 1.085 |
| I, $n = 2$ | 240 | 0.2 | 0.790 | 0.922 | 0.882 | 125 | 1.095 |
| I, $n = 3$ | ∞ | | 0.747 | 0.960 | 0.912 | 357 | 1.048 |
| II,[d] | 110 | | 0.856 | 0.898 | 0.900 | 18 | 1.002 |

[a] Measurements were made on the neutral compound or Li$^+$ salts of the anions in THF at 20 °C except where noted. [b] The geometry of the $Fe_4(CO)_{12}B$ cluster is the same for all calculations. The axes are given in Chart I. [c] The $z$ axis is defined by the largest component of the electric field gradient. [d] In acetone at 20 °C. Populations calculated with $CuPH_3$ as a model for $AuPPh_3$.[16]

borons in $Fe_2(CO)_6B_3H_7$ and $[Fe_2(CO)_6B_3H_6]^-$.[13,14] The pertinent data are given in Table II where it is seen that for the central boron of $Fe_2(CO)_6B_3H_7$ a low boron population is associated with a more positive shift; i.e., in agreement with the Wrackmeyer correlation, a borane-like boron in a metallaborane follows the borane correlation. However, on deprotonation to form $[Fe_2(CO)_6B_3H_6]^-$ a direct Fe–B interaction is formed, and the boron affected becomes less shielded even though the calculated boron population increases; i.e., the change is in the direction predicted by the correlation observed for the monoboron metal-rich ferraboranes. These observations imply that the large deshielding exhibited by the compounds with direct Fe–B interactions has an essentially different origin from that in boranes with no direct metal interactions.

We show in the following that the large downfield shifts in the metal-rich metallaboranes can be attributed to large paramagnetic contributions to the shielding resulting from the nature of the direct metal–boron interaction. To do so we utilize eq 1, which is the most commonly used approach to the calculation of chemical shifts. However, it has limited theoretical value as $\Delta E$ is essentially an adjustible parameter.[12] Despite this, eq 1 is sufficient to provide a framework for discussing the essentially empirical observations that follow.

The diamagnetic contribution to the net shielding accounts for a relatively small chemical shift range and is proportional to the electronic charge on boron;[12] i.e., $-\delta(^{11}B) \propto q_B$. This is clearly not the situation for the compounds in Table I. The paramagnetic contribution contains three terms as indicated above. The first term predicts a correlation between the chemical shift and $1/\Delta E$, but there is no reasonable way for estimating $\Delta E$, and, like earlier workers, we assume it is constant. The second term, $\langle r^{-3}\rangle_{PB}$, is proportional to the net charge on boron[12] and predicts a correlation with calculated boron populations as found for the metallaboranes, $\delta(^{11}B) \propto q_B$. The last term, $\sum Q_{BX}$, contains three parts. The first corresponds to the p-electron charge density on boron while the second, which has a negative sign, represents the multiple-bond contributions to the shielding tensor between boron and other atoms, X, in the molecule. The third part is said to be small.[12] Again, the first part predicts a correlation $\delta(^{11}B) \propto q_B$. For the multiple-bond term we can obtain a qualitative estimate of its contribution to the shielding by considering terms derived from Fe 4p and B 2p orbitals for bridged and unbridged interactions in $[Fe_4(CO)_{12}BH]^{2-}$. These multiple-bond terms are of similar magnitudes but negative for the unbridged Fe–B interaction and positive for the H-bridged Fe–B interaction. Hence, removal of a bridging proton, thereby creating a direct Fe–B interaction, leads to a change in the multiple-bond term that leads to an increased positive chemical shift. We conclude that the large deshielding associated with introducing a direct metal–boron interaction is due to a large paramagnetic contribution to the shielding with a substantial amount coming from the multiple-bond contributions to the shielding tensor. Note that because the latter contains $\sigma$ and $\pi$p orbital bond order terms, unless atom X has valence electrons besides s electrons, there will be no contribution to $\sigma_p$; i.e., a hydrogen atom bonded to boron yields zero contribution.

Because atoms adjacent to boron must have p valence electrons to contribute to the multiple-bond term, the behavior of the gold derivatives is interesting simply because the $[AuPPh_3]^+$ fragment is often viewed as a pseudoproton.[15] The addition of $[AuPPh_3]^+$ to $[HFe_4(CO)_{12}BH]^-$ to produce $(\mu\text{-H})Fe_4(CO)_{12}(AuPPh_3)BH$ results in a 12 ppm shift to more negative $\delta$.[16] That is, replacement of a Fe–H–B interaction in $HFe_4(CO)_{12}BH_2$ with a Fe–Au–B interaction results in $^2/_3$ of the shift expected for a direct Fe–B interaction. Addition of a second gold at the same distance from the boron as the first gold atom in $Fe_4(CO)_{12}(AuPPh_3)_2BH$ results in only a 3 ppm more positive shift, suggesting that there is no large deshielding to be associated with the B–Au interaction. This strongly suggests that the shift associated with the Fe–B interaction is, in fact, due to multiple–bond contributions to the shielding tensor. This is confirmed by the shift observed for $[Fe_4(CO)_{12}(AuPPh_3)_2B]^-$, which is only 8 ppm larger than that predicted for four direct Fe–B interactions.[3]

**Relaxation Times.** Parallels have been pointed out between $^{11}$B line widths and chemical shifts.[17] Hence, in conjunction with the large downfield shifts observed for metal-rich metallaboranes, it is of interest to point out our recent observation of the change in line widths of the $^{11}$B signals in the series $[Fe_4(CO)_{12}BH_{3-n}]^{n-}$, $n$ = 0–3, in which the boron signal from the trianion is so broad as to be unobservable.[10] Measurement of the relaxation times of the first three compounds (Table III) shows that the line broadening can be attributed to an increase in the relaxation rate on successive proton losses. On the other hand, the compound, $Fe_4(CO)_{12}(AuPPh_3)_2BH$, which has a chemical shift close to that of the dianion, exhibits a $^{11}$B signal with a width similar to that of the neutral compound. The pertinent data are gathered in Table III, and the following explanation is proposed.

If one assumes electric quadrupolar relaxation is dominant in these systems, then the relaxation time in a series of related compounds will be given by[12] eq 2 where $eq_{zz}$ is the largest component of the electric field gradient at the $^{11}$B nucleus, $\tau_c$ is the correlation time, which is assumed to be constant for these closely related ions, and $\eta$ is the asymmetry parameter given by eq 3.

$$1/T_1 \propto (eq_{zz})^2(1 + {}^1\!/_3\eta^2)\tau_c \qquad (2)$$

$$\eta = (q_{xx} - q_{yy})/q_{zz} \qquad (3)$$

When the approximate approach of Townes and Dailey[18] is used, molecular orbital calculations can be used to seek the cause of the line broadening; i.e., $q_{ii}$ can be expressed in terms of the 2p orbital populations, $n_i$, of boron as eq 4 where $eq_p$ is the electric field gradient due to a single electron. The necessary parameters are obtained from Fenske–Hall calculations and are tabulated in Table III. One notes immediately a qualitative trend between

$$q_{zz} = [n_z - {}^1\!/_2(n_x + n_y)]q_p \qquad (4)$$

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**Chart I**

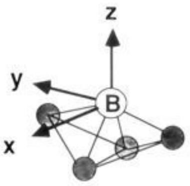
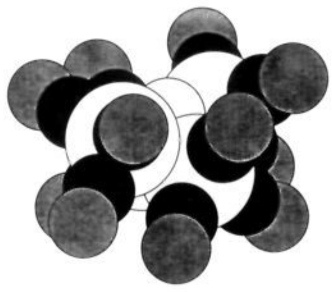


**Chart II**



values of line widths and the calculated ratios of $(q_{zz}/q_p)^2$ for the $[Fe_4(CO)_{12}BH_{3-n}]^{n-}$ series. There is also a correlation with measured $T_1$'s which is reasonable as for this system $T_2 \approx T_1$. Significantly, the calculated $(q_{zz}/q_p)^2$ for $Fe_4(CO)_{12}(AuPPh_3)_2BH$ also correlates well with the observed line width.

Two conclusions are evident. The "boron-silent" boride almost certaily results from very rapid quadrupolar relaxation caused by the generation of large asymmetries in the electronic charge distribution around the boron as protons are removed. The calculations show this in detail. As the two B–H–Fe protons are removed from $HFe_4(CO)_{12}BH_2$, electron density is localized in the resulting B–Fe edges in the $p_y$ direction mainly at the expense of the existing B–Fe interactions in the $p_x$ directions (see Chart I and Table III). These sites of electron density on the B–Fe-(wind-tip) edges generate the charge asymmetry.[19] Adding a $[AuPPh_3]^+$ fragment to a BFe edge produces a more symmetrical charge distribution around boron; i.e., the gold atom behaves like a proton. While the observed chemical shift appears to depend only on the number of direct M–B interactions, the line width depends on the extent to which the boron in the $Fe_4B$ cluster is "exposed", and adding either $H^+$ or $[AuPPh_3]^+$ to the open Fe–B edges reduces the line width.

**$^7$Li NMR.** It occurred to us that the cation, if interacting with the boron–metal site of the anion, provides an additional source of information with which to corroborate our explanation of the "silent" borido cluster anion. The alkali metals also have quadrupolar nuclei and will be very sensitive to the symmetry of the charge distribution around the observed nucleus.[20] Hence, if tight ion pairs are formed and if the ion pair has a structure such that the charge asymmetry of the exposed boron of the cluster (Chart II) is sensed by the alkali metal cation, the quadrupolar relaxation of the cation should be promoted and the line width of the resonance increased. This assumes that the lifetime of the ion pair will be long with respect to the reorientation correlation time of the complex and that the quadrupolar mechanism constitutes a significant pathway for relaxation of the lithium nucleus. Evidence for the formation of tight ion pairs for the trianion results from the fact that the dianion, but not the trianion, forms when $HFe_4(CO)_{12}BH_2$ is treated with BuLi-12-crown-4. Thus, we have examined the $^7$Li NMR of the Li salts of the anions.

Normal $^7$Li signals from $Li^+$ salts exhibit chemical shifts over a rather small range with values that depend strongly on conditions.[21] The relaxation mechanism of the $^7$Li nucleus has been characterized as "nonpurely quadrupolar", and line widths of 1 Hz are usually observed.[20] For LiCl in $D_2O$ we observe a line width of 2 Hz under conditions employed in this study. The results on the lithium salts of the anions of I are shown in Table IV. Clearly, the $[HFe_4(CO)_{12}BH]^-$ ion does not significantly increase the relaxation rate of the lithium ion, thereby suggesting a fully solvated cation. For $[Fe_4(CO)_{12}BH]^{2-}$ the $^7$Li spectrum consists of a single resonance with an increased peak width of 23 Hz and a Lorentzian shape ($\nu_{1/8}/\nu_{1/2} = 2.62$).[22] The increased relaxation rate is undoubtedly due to interaction with the dianion (tight ion pair) and also suggests that a quadrupolar relaxation mechanism is operative. For $[Fe_4(CO)_{12}B]^{3-}$ a single resonance is again observed, but now the peak width has increased to a value of 85 Hz and the peak shape is distinctly non-Lorentzian ($\nu_{1/8}/\nu_{1/2} = 4.25$; Figure 3). This means that the relaxation of the transverse magnetization is nonexponential.[22,23] Similar behavior for $^{23}$Na NMR has been interpreted in terms of exchange between free and bound states.[22] To observe such relaxation behavior, the extreme narrowing condition must not be satisfied at one site, and relaxation times and exchange times at one site must be much smaller than at the other. If a $Li^+$ is bound to the boron on the open face of $[Fe_4(CO)_{12}B]^{3-}$ (Chart II), it would experience an asymmetric environment and its relaxation rate would be enhanced relative to that in a simple ion pair like that proposed for the dianion. This would satisfy one of the required criteria. Hence, we suggest that for the trianion there are three types of binding. One $Li^+$ is tightly bound to the exposed boron of the butterfly, one $Li^+$ is in the first coordination sphere of the trianion, and one $Li^+$ is fully solvated.

**Table IV.** $^7$Li Chemical Shifts and Line Widths for I ($[Fe_4(CO)_{12}BH_{3-n}]Li_n$, $n$ = 1–3)

| $n^a$ | shift,$^b$ ppm | line width (fwhm), Hz |
|---|---|---|
| 1 | −0.4 | 5 |
| 2 | 0.4 | 23 |
| 3 | 0.8 | 85$^c$ |

$^a$ In THF at 20 °C. $^b$ With respect to the same solution of 1 M LiCl in $D_2O$ as external reference. Negative shifts to higher field. $^c$ Non-Lorentzian; see Figure 3.

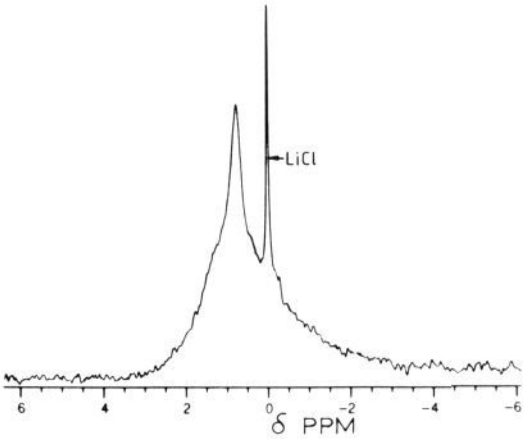


**Figure 3.** $^7$Li 116.6-MHz NMR spectrum of $[Fe_4(CO)_{12}B]Li_3$ in THF with an external reference of LiCl.

**Summary.** The metal-rich ferraboranes provide a clear example of a boron–metal interaction that can dominate observed $^{11}$B chemical shifts. The large positive chemical shifts are caused by the paramagnetic contributions to the shielding, most likely by large multiple-bond terms, and are characteristic of direct iron–boron interactions. It seems clear from the chemical shifts reported for the few other metal-rich systems known[3] that this effect is not

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[19] See Figure 11 in: Fehlner, T. P.; Housecroft, C. E.; Scheidt, W. R.; Wong, K. S. *Organometallics* **1983**, *2*, 825.

[20] Detellier, C. *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic: New York, 1983; Vol. 2, p 105.

[21] For example, see: Scherr, P. A.; Hogan, R. J.; Oliver, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 6055.

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restricted to iron.[24] These chemical shifts are modulated by bridging protons but only slightly by pseudoprotons such as $[AuPPh_3]^+$. On the other hand, the direct Au–B interaction does not lead to large downfield shifts. Partial encapsulation of the boron by metal can lead to large asymmetries in the electric field gradient at the boron nucleus. The resulting rapid quadrupolar relaxation leads to line broadening to such an extent that boron signals are easily lost in the background noise of a spectrum. Bridging the exposed B–M edges with either protons or pseudoprotons such as $[AuPPh_3]^+$ results in a large reduction in the electric field gradient at the boron nucleus.

### Experimental Section

Fenske–Hall calculations[25] were carried out by using geometries derived from solid-state structures or by using reasonable geometries based on model compounds. The calculations employed single-$\zeta$ Slater basis functions for the 1s and 2s functions of B, C, and O. The exponents were obtained by curve fitting the double-$\zeta$ functions of Clementi[26] while orthogonal functions were maintained; the double-$\zeta$ functions were used directly for the 2p orbitals. For hydrogen, an exponent of 1.16 was used. The iron 1s–3d functions were taken from the results of Richardson et al.[27] and were all single-$\zeta$ except the 3d function, which is double-$\zeta$ and was chosen for the +1 oxidation state. Both the 4s and the 4p exponents were chosen to be 2.0.

The spin-lattice relaxation times ($T_1$'s) for $^{11}B$ were determined for the series of ferraboranes $[Fe_4(CO)_{12}BH_{3-n}]^{n-}$ by the optimized inversion recovery technique,[28] and the standard software package (T1IRCA) supplied with the Nicolet NT-300 spectrometer was utilized. $BH_3{\cdot}THF$ was used to obtain proper pulse widths. Parameters used were the following: 180° pulse width, 78 μs; 90° pulse width, 39 μs; delay, 5× the longest $\tau$ value. $T_1$ values were determined from plots of the equation $\ln (A_\infty - A) = \ln 2(A_\infty) - \tau/T_1$, where $A_\infty$ is the limiting value of $A$ at large $\tau$ and $A$ is the amplitude following the 90° pulse at time $\tau$.

The $^7Li$ NMR spectra were acquired on a Nicolet NT-300 spectrometer with a sweep frequency of 116.6 MHz. Solutions were made in THF by freshly prepared lithium salts of the anions. The lithium salts were washed with hexane to remove any excess BuLi. An external reference of 1 M LiCl in $D_2O$ was used, and the same reference was used for each measurement: pulse width, 15 μs; delay, 1 s.

**Acknowledgment.** The support of the National Science Foundation is gratefully acknowledged. We thank Dr. C. E. Housecroft for communicating results prior to publication.

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# Infrared Spectroscopy of Half-Methemocyanin Cyanide: Evidence for Two Nonequivalently Bound Cyanides

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**Abstract:** The cyanide vibrational modes of half-methemocyanin cyanide were studied by infrared spectroscopy to further understand the structure of the binuclear copper hemocyanin active site. Half-methemocyanin (one copper in the +2 oxidation state and the other in the +1 oxidation state) was found to bind one or two cyanide ligands, each having separate infrared vibrational frequencies. The first cyanide had a $\nu(CN)$ at 2112 $cm^{-1}$, consistent with a $\mu$-1,2 bridging geometry. The second cyanide had a $\nu(CN)$ at 2092 $cm^{-1}$, consistent with a carbon end-on-bonded geometry. These assignments were confirmed using $^{13}CN^-$ and $C^{15}N^-$ isotopes. The bridging cyanide binds with $K > 10^3$ $M^{-1}$, whereas the second, end-on-bonded cyanide binds with $K = 7.1$ $M^{-1}$. The model that emerged for half-methemocyanin cyanide is completely consistent with the model developed by Solomon and co-workers using EPR and UV-visible spectroscopies. A smaller than expected $^{13}C$ shift in the end-on-bonded cyanide may be an indication of nonlinearity in the metal cyanide bond, and a 2-$cm^{-1}$ shift upward in the bridging cyanide band in $D_2O$ may indicate that this cyanide forms a weak hydrogen bond with an imidazole.

The binuclear copper active site in hemocyanin, the oxygen-transport protein in molluscs and arthropods, has been the subject of intense investigation over the past 10 years. Many of these investigations have involved spectroscopic studies of oxyhemocyanin and chemically prepared derivatives that contain exogenous ligands bound to either one or both of the copper atoms.[1] The active site in oxyhemocyanin is best described as two antiferromagnetically coupled Cu(II)'s bridged by peroxide dioxygen; each copper has up to three imidazole ligands from histidine amino acid residues, and the coppers may be bridged by an additional endogenous ligand.[2-4] Methemocyanin has two Cu(II)'s with no dioxygen bridge, but the coppers are still antiferromagnetically coupled, implying an endogenous ligand bridge.[5] Methemocyanin binds exogenous ligands such as halogen anions, azide, and thiocyanate.[5] Half-methemocyanin, which has a Cu(II)–Cu(I) site, can bind exogeneous ligands such as halogens, cyanide, azide, and thiocyanate and may have an endogenous ligand bridge.[4]

Solomon and co-workers[4,5] have extensively studied the hemocyanin derivatives using EPR, UV-visible, and CD spectroscopies deriving a "spectroscopically effective" active site structure for oxy-, met-, and half-methemocyanins, which involves an en-

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