Electron Delocalization in Paramagnetic Metallocarboranes

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Abstract: The isotropic shifts of the ^{11}B and ^{13}C nuclear resonances in paramagnetic metallocarboranes of the type $(C_5H_5)M(C_2B_nH_{n+2})$ and $M(C_2B_nH_{n+2})_2$, where M = Cr^{III}, Fe^{III}, Ni^{III}, and Co^{II} and n = 9, 8, 7, and 6, have been evaluated. The mode of electron delocalization is primarily ligand to metal charge transfer, except for icosahedral Co^{II} where it is metal to ligand. The extent of delocalization in metallocarboranes is minimal and is primarily localized on the metal bonding face. The results of this study are compared to available data and theories related to paramagnetic metallocenes.

Since the initial report of the preparation of carborane analogs of the metallocenes in 1965,[1,2] the area of metallocarboranes has expanded in scope and diversity so as to exceed the structural and chemical variations which are possible in the parent metallocene systems. The most comprehensive review of metallocarboranes and closo heteroboranes has recently appeared.[3] The recognition of the similarity of the bonding capabilities of $C_2B_9H_{11}{}^{2-}$ and $C_5H_5{}^-$, *i.e.*, each moiety containing six electrons in five molecular orbitals for "π-bonding" to various transition metals, served as the impetus for the synthesis of metallocarboranes. This similarity of the bonding allows an analogy to be made between the electron delocalization in paramagnetic metallocenes and metallocarboranes. The extensive work in the area of spin distribution in the metallocenes has recently been reviewed.[4] The methodology which has been used to evaluate the mode of electron delocalization in metallocenes has been to examine the shift in the ^1H nuclear magnetic resonance caused by the presence of electron spin density at various nuclear sites. For the case of the metallocarboranes, it was the purpose of this study to evaluate the mode and extent of electron delocalization, by observing the isotropic shifts of the ^{11}B and ^{13}C resonances. In addition it was anticipated that by comparison of the nmr line widths of the various resonances it would be possible to determine experimentally the type and number of atoms which are directly involved in bonding to the transition metal. The initial report of contact shift of the ^{11}B resonance in several Fe^{III} carborane complexes was in 1965.[5] These spectra were obtained at 19.1 MHz and, owing to the experimental difficulties associated with low field ^{11}B nmr, were incorrectly assigned.

Theoretical Considerations

Isotropic shifts in paramagnetic transition metal complexes have been used to study the spin densities at various magnetic nuclei within the complex. The observed shift of the nuclear resonance is the sum of the

contributions from the scalar (or Fermi) isotropic hyperfine contact interaction, which arises from electron spin delocalization or spin polarization $(\Delta\nu/\nu_0)_{contact}$, and the nuclear–electron dipolar interaction or pseudo-contact shift $(\Delta\nu/\nu_0)_{dipolar}$.[4] The contact shift is related

$$(\Delta\nu/\nu_0)_{obsd} = (\Delta\nu/\nu_0)_{contact} + (\Delta\nu/\nu_0)_{dipolar}$$

to the nuclear electron coupling constant A_n (in gauss) by the equation

$$(\Delta\nu/\nu_0)_{contact} = -A_n \frac{g_{av}{}^2\beta_e{}^2}{g_n\beta_n} \frac{S(S+1)}{3kT} \qquad (1)$$

where g_n = 1.792 (^{11}B), 1.405 (^{13}C), and 5.585 (^1H) and the remaining notations are standard. For the evaluation of the dipolar contribution to the observed shift, Jesson[6] has described four limiting cases depending on the values of the Zeeman anisotropy energy, $|g_{\parallel} - g_{\perp}|\beta H/\hbar$, the correlation time for the tumbling of the molecule, τ_c, and the electron spin–lattice relaxation time, $T_1{}^e$. The equation for evaluating dipolar shifts is of the form

$$(\Delta\nu/\nu_0)_{dipolar} = -\left(\frac{\beta_e{}^2 S(S+1)}{3kT}\right)\left(\frac{3\cos^2\theta - 1}{R^3}\right)F(g) \qquad (2)$$

where $F(g)$ is an algebraic function of the g tensor. Kurland and McGarvey[7] have pointed out that this method may not be strictly applicable since eq 2 (a) assumes only one thermally populated energy level, (b) ignores zero-field splittings, and (c) assumes that the orbital contribution to the isotropic nmr shift can be accounted for indirectly by use of g tensor components. The evaluation of the dipolar contribution using all thermally accessible spin states in the complex can be accomplished by using the single-crystal magnetic susceptibility anisotropy data.[8] The factors affecting the nmr line width by paramagnetic ions having isotropic g factors have been evaluated by La Mar.[9] Sternlicht has calculated the expressions for nuclear relaxation when the relaxation is due to a paramagnetic ion having an axially anisotropic

(1) D. C. Young, P. A. Wegner, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **87**, 1818 (1965).

(2) T. D. Andrews and M. F. Hawthorne, *Chem. Commun.*, 19 (1965).

(3) G. B. Dunks and M. F. Hawthorne in "Chemistry of Hydrogen and its Compounds," Vol. II, E. L. Muetterties, Ed., Marcel Dekker, New York, N. Y., 1973, Chapter 11.

(4) M. F. Rettig in "Chemical Applications of NMR in Paramagnetic Molecules," G. N. LaMar, W. D. Horrocks, Jr., and R. H. Holm, Ed., Academic Press, New York, N. Y., 1973.

(5) M. F. Hawthorne and R. L. Pilling, *J. Amer. Chem. Soc.*, **87**, 3987 (1965).

(6) J. P. Jesson, *J. Chem. Phys.*, **47**, 579 (1967).

(7) R. J. Kurland and B. R. McGarvey, *J. Magn. Resonance*, **2**, 286 (1970).

(8) D. D. Hall and W. D. Horrocks, Jr., *Inorg. Chem.*, **10**, 2368 (1971).

(9) G. N. La Mar and G. R. Van Hecke, *J. Chem. Phys.*, **52**, 5676 (1970), and references therein.
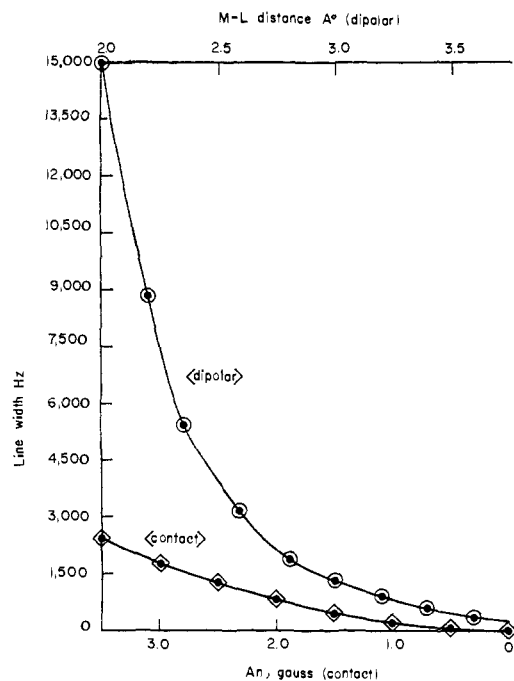
Figure 1. Theoretical line width variation for ^{11}B nuclei when attached to a paramagnetic center with $S = \frac{1}{2}$ and an isotropic g tensor. Curves calculated for ^{11}B resonance at 59 kG, and $T_1^e \approx \tau_c = 10^{-10}$ sec.

g tensor.[10] The appropriate equations relating the correlation time and line width are

$$\Delta H_{1/2} = B\left[4\tau_c + \frac{3\tau_c}{1 + \omega_n^2\tau_c^2} + \frac{13\tau_c}{1 + \omega_s^2\tau_c^2}\right] +$$
$$C\left[T_1^e + \frac{T_1^e}{1 + \omega_s^2(T_1^e)^2}\right] \quad (3)$$

where

$$B = \frac{S(S + 1)g_e^2\beta_e^2g_n^2\beta_n^2}{15r^6\hbar^2}$$

$$C = \frac{S(S + 1)}{3}(A/h)^2$$

$$\tau_c^{-1} = \tau_r^{-1} + (T_1^e)^{-1}$$

The rotational tumbling time in solution can be estimated by the Debye equation (eq 4).

$$\tau_r = 4\pi\eta r^3/ekT \quad (4)$$

The electron spin relaxation times can be evaluated by the equations outlined previously.[11] The estimates of the electron relaxation time for metallocenes place them in the range of $T_1^e \leq 10^{-11}$ sec.[5] The rotational correlation time for metallocarboranes using an effective radius $r = 8 \times 10^{-8}$ cm in acetone is estimated to be $\tau_r = 2 \times 10^{-10}$ sec. Therefore the correlation time is probably predominated by the electron spin relaxation time such that $\tau_c^{-1} \approx (T_1^e)^{-1}$.

Under the experimental conditions in a magnetic field of 58.95 kG, $\omega_s = 1.04 \times 10^{12}$ and $\omega_n = 5.06 \times 10^8$ radians/sec. Therefore $\omega_s^2(T_1^e)^2 \gg 1 \gg \omega_n^2\tau_c^2$

(10) H. Sternlicht, *J. Chem. Phys.*, **42**, 2250 (1965).
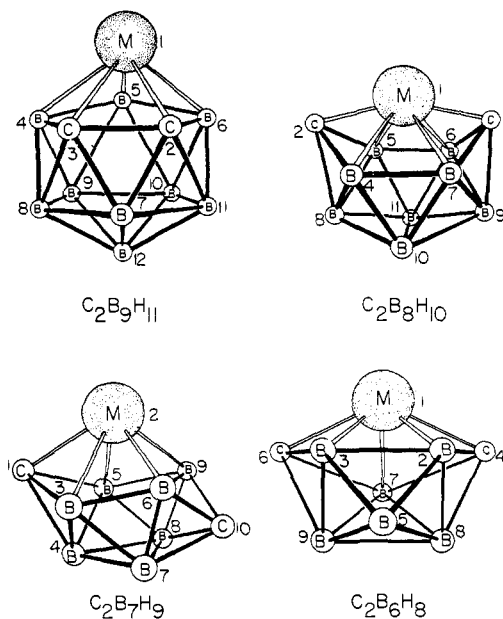(11) B. R. McGarvey, *J. Phys. Chem.*, **61**, 1232 (1957).

Figure 2. Ligand geometries and numbering for various heteroboranes.

and eq 3 can then be simplified to

$$\Delta H_{1/2} = \left(\frac{7S(S + 1)g_e^2\beta_e^2g_n^2\beta_n^2}{15r^6\hbar^2}\right)\tau_c +$$
$$\frac{S(S + 1)}{3}(A/h)^2T_1^e \quad (5)$$

The first term in eq 5 represents the increase in the nmr line width caused by a dipolar relaxation process and is proportional to $1/r^6$. The second part of the equation reflects the contact broadening of the nuclear resonance and is proportional to $(A/h)^2$. Figure 1 shows the variation of the dipolar and contact broadening for a ^{11}B nmr peak when attached to a $S = \frac{1}{2}$ paramagnetic metal with $\tau_c \approx T_1^e = 10^{-10}$ sec for various values of the internuclear distance and nuclear–electron hyperfine coupling constant which are found in metallocarboranes (*vide infra*). Figure 1 clearly reveals that the various magnetic nuclei which are directly attached to the paramagnetic metal center will be appreciably broader than nonadjacent nuclei, under the limits imposed by rapid electron spin relaxation. Equation 5 and Figure 1 also indicate that if the electron relaxation time decreases to $T_1^e = 10^{-9}$ sec, the magnetic resonance peak of the adjacent atoms will be broadened to the point of being unobservable, while the nonadjacent atoms will still be relatively narrow.

Results

Cr^{III} **Complexes.** The preparation of $Cs\{Cr^{III}-[2,3-(CH_3)_2-2,3-C_2B_9H_9]_2\}$ has been previously reported[12] and the crystal structure determined.[13] The ligand geometry and numbering are shown in Figure 2.[14] The 80-MHz ^{11}B nmr spectrum of the Cr^{III} complex is shown in Figure 3.

The assignment of the resonances is based primarily

(12) H. W. Ruhle and M. F. Hawthorne, *Inorg. Chem.*, **7**, 2279 (1968).
(13) D. St. Clair, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **10**, 2587 (1971).
(14) The ligand geometries and numbering are based on heteroboranes with the various metals as the heteroatoms.
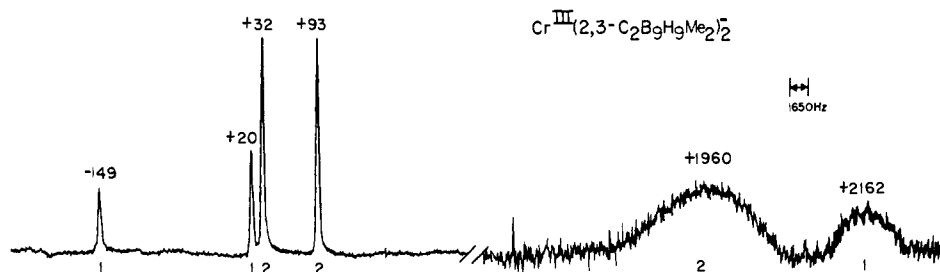
Figure 3. An 80-MHz ^{11}B nmr spectrum of $(CH_3)_4N\{Cr^{III}[2,3-(CH_3)_2-2,3-C_2B_9H_9]_2\}$ in acetone.

on the results of Fe^{III} complexes to be discussed in the next section. The ground-state electronic configuration for $Cr^{III}(d^3)$ is $(a_{1g})^1(e_{2g})^2$ or ^4A (assuming C_{5v} symmetry). The room-temperature magnetic susceptibility is $\mu_{eff} = 3.88$ BM $vs.$ the spin-only value of 3.84 BM. The esr spectra of polycrystalline $(CH_3)_3N^+[Cr^{III}-(C_2B_9H_9Me_2)_2]$ in $CHCl_3$–DMF at 80°K were obtained at both X and Q band.[15] The results were analyzed according to the method of Geusic, et $al.$[16] The experimental data are $g_{||} = 1.97$, $g_\perp = 2.02$, and $|D| = 1.47$ cm^{-1}. The almost isotropic g components indicated very little dipolar shift should be present. The rapid electron relaxation time is most probably dominated by the zero-field splitting, resulting in relatively narrow nmr lines. The nuclear–electron coupling constants are tabulated in Table I and were calculated using eq 1.

Table I. Coupling Constants for $[Cr^{III}(2,3-C_2B_9H_9(Me_2)_2]^-$

B atom	Obsd shift,^{a} ppm	Line width, Hz	A_n, G
4,6	+1960	6500	−1.66
5	+2160	6500	−1.84
8,11 (9,10)	+93	200	−0.07
9,10 (8,11)	+32	200	−0.02
7	−150	200	+0.14
12	+20	200	±0.00

^{a} The average ligand diamagnetic shift was assumed to be $ca.$ +15 ppm.

Fe^{III} **Complexes.** The controversy concerning the ground-state electronic configuration of d^5 metallocenes, $(a_{1g})^2(e_{2g})^3$, $^2E_{2g}$ $vs.$ $(e_{2g})^4(a_{1g})^1$, $^2A_{1g}$, has been resolved on the basis of the low-temperature esr work of Maki[17] and variable temperature (40–300°K) magnetic susceptibility by Gray.[18] The esr data clearly indicated that the ground state is $^2E_{2g}$ and, in conjunction with the magnetic susceptibility data, that the temperature independence of the effective magnetic moments is explicable in terms of either a temperature-dependent, low symmetry crystal field distortion (external and/or internal) or thermal population of the $^2A_{1g}$ state. An estimate of the separation between the $^2E_{2g}$ and $^2A_{1g}$ state is about 380–540 cm^{-1}. The esr data for various Fe^{III} metallocarboranes are listed in Table II.

(15) The authors are indebted to Professor August H. Maki and his coworkers at the University of California, Riverside, for obtaining the data at Q band.

(16) J. E. Geusic, M. Peter, and E. O. Schulz-DuBois, $Bell$ $Syst.$ $Tech.$ $J.$, **38**, 291 (1959).

(17) A. H. Maki and T. E. Berry, $J.$ $Amer.$ $Chem.$ $Soc.$, **87**, 4437 (1965).

(18) D. N. Hendrickson, Y. S. Sohn, and H. B. Gray, $Inorg.$ $Chem.$, **10**, 1559 (1971).

Table II

Compound	$g_{||}$	$g_\perp$	μ_{eff} (300°K)
(1) $(CH_3)_4N[Fe(2,3-C_2B_9H_{11})_2]^a$	3.94	1.53	2.42
(2) $(C_5H_5)Fe(2,3-C_2B_9H_{11})^a$	3.58	1.78	2.30
(3) $(C_5H_5)Fe(2,4-C_2B_9H_{11})^b$	4.17	2.04	2.62
(4) $(C_2H_5)_4N[Fe^{III}(2,9-C_2B_9H_{11})_2]^b$	4.17	1.93	
(5) $(2,3-C_2B_9H_{11})Fe^{III}(5-Et_2S-2,3-C_2B_9H_{10})$			2.44
(6) $(C_5H_5)Fe(2,3-C_2B_9H_{10})^c$	2.08	1.58	
(7) $(C_5H_5)Fe(4,6-C_2B_8H_8)^c$	2.06	1.62	
(8) $(C_5H_5)Fe(1,8-C_2B_8H_8)^c$	2.06		

^{a} Polycrystalline in $CHCl_3$–DMF at ~85°K, ref 17. ^{b} Polycrystalline in CH_2Cl_2–DMF at ~4°K. ^{c} Polycrystalline in CH_2Cl_2 at ~80°K.

While formally the $C_2B_9H_{11}^{2-}$ ligand possesses only C_s symmetry, the esr data are consistent with a system which exhibits axial symmetry, in which, at least in the case of a planar C_2B_3 bonding face, the atoms are essentially equivalent such that $g_{zz} = g_{||}$ and $g_{xx} \approx g_{yy} = g_\perp$. The presence, in the Fe^{III} metallocarboranes, of low-lying orbital states, which result from a spin-orbit coupling in these ions, which have orbitally degenerate ground states leads to a very rapid electron relaxation time. In addition, the very small energy difference between the ground states and excited states is evident by comparing the esr g tensors at low temperature and the room-temperature magnetic susceptibility. The 80-MHz ^{11}B spectra of $(C_5H_5)Fe^{III}(2,3-C_2B_9H_{11})$, $(C_5H_5)Fe^{III}(2,4-C_2B_9H_{11})$, $(C_2H_5)_4N[Fe^{III}(2,9-C_2B_9H_{11})_2]$, $(5-Et_2S-2,3-C_2B_9H_{10})Fe^{III}(2,3-C_2B_9H_{11})$, and $(CH_3)_4N[Fe(2,3-C_2B_9H_{11})_2]$ are shown in Figure 4. By comparing the observed shifts within the series it is possible to assign the various resonances. The high field portion of the spectrum (300–700) is assigned to the boron atoms adjacent to the metal on the basis of their line width. In the 2,3 or 2,4 isomers there are three unique boron environments (2,3-$C_2B_9H_{11}$, positions 5, 7, and 12; 2,4-$C_2B_9H_{11}$, positions 3, 10, and 12). The presence of a resonance of area 1 in the 30–80 region is assigned to the boron 12 since it remains unchanged within the isomeric series. The remaining unique boron appears at −105 to −114 in the 2,3 series and at −2 in the 2,4 series. The remaining four boron atoms in the −20 to +5 ppm range are assigned to the two pairs of B atoms in the second belt. It is interesting that in the case of an asymmetrically substituted metallocarborane, $[5-Et_2S-2,3-C_2B_9H_{10}]Fe^{III}[2,3-C_2B_9-H_{11}]$, separate resonances are observed for each cage. This type of behavior may be extremely useful in assigning positions of substitution of exopolyhedral derivatives of metallocarboranes.

Owing to the anisotropic g values in the $Fe^{III}C_2B_9H_{11}$

Table III. ^{1}H, ^{13}C, and ^{11}B Shifts for $(C_5H_5)Fe^{III}(2,3\text{-}C_2B_9H_{11})$

Atom	Obsd shift	Diamagnetic shift	Net shift	Dipolar shift	Contact shift	A_n, G
C_5H_5 ^{1}H[a]	-27.8	-4.5	-23.3	$+19.4$	-42.7	$+0.41$
C_5H_5 ^{13}C[b]	-68.6	$+99.7$	-168	-202	$+34$	-0.08
$C_2B_9H_{11}$ ^{13}C[b]	$+754$	$+139.9$	$+614$	-63	$+677$	-1.62
B-5	$+502$	c	$+487$	-81	$+568$	-1.73
B-4, -6	$+457$	c	$+442$	-89	$+531$	-1.62
B-7	-112	c	-127	-65	-62	$+0.19$
B-8, -11	$+4.1$	c	-11	-65	$+54$	-0.16
B-9, -10	-10.2	c	-25	-65	$+40$	-0.12
B-12	$+84$	c	$+69$	-57	$+126$	-0.38

[a] Data obtained at 251 MHz. [b] Data obtained at 63.1 MHz, using Fourier transform spectra, normally 10,000 transients. [c] Average diamagnetic shift of $+15$ ppm.
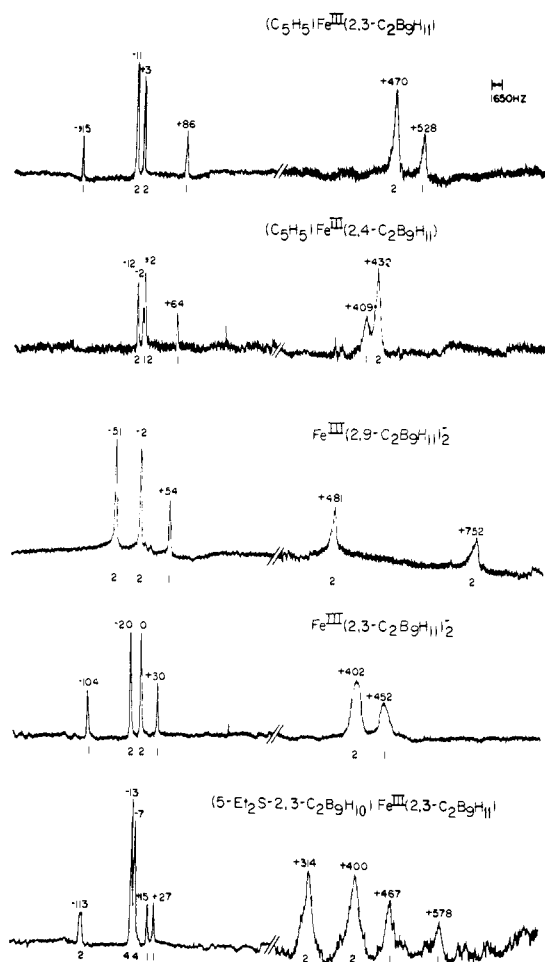

Figure 4. The 80-MHz ^{11}B nmr spectra of various Fe^{III}–$C_2B_9H_{11}{}^{2-}$ complexes.

complexes, there would be anticipated to be a sizable dipolar shift in these complexes. Under the experimental conditions, the dipolar shift takes the form[6]

$$(\Delta\nu/\nu_0) = -\left[\frac{\beta^2 S(S+1)}{3kT}\right] \times$$

$$\left(\frac{3\cos^2\theta - 1}{R^3}\right)\frac{(g_{||} + g_\perp)(g_{||} - g_\perp)}{3}$$

when $1/\tau_r \ll |g_{||} - g_\perp|\beta H/\hbar$ and $T_1^e \ll \tau_r$. The geometrical factors were calculated from the crystal structure data on $(C_5H_5)Fe^{III}(2,3\text{-}C_2B_9H_{11})$.[19]

(19) A. Zalkin, D. H. Templeton, and T. E. Hopkins, J. Amer. Chem. Soc., 87, 3988 (1965).

The dipolar shift for each atom was calculated from the structural data. For the cyclopentadienyl ligand the C–H bond length was assumed to be 1.07 Å. The dipolar shifts were not averaged, assuming free ligand rotation, but were evaluated for a locked configuration. Actually the changes which would result from a rotational averaging, to yield an exactly planar five-atom equivalent bonding face, are minimal when compared to the calculated values.

The ^{1}H, ^{13}C, and ^{11}B shifts for $(C_5H_5)Fe^{III}(2,3\text{-}C_2B_9H_{11})$ are listed in Table III. The associated dipolar shifts and hyperfine coupling constants are also listed.

The dipolar contribution to the shift has been calculated only for the ground state, $^2E_2$, with the anisotropy averaged using the ground-state g values, i.e., $g_{||} = 3.58$, $g_\perp = 1.78$, and $g_{av} = 2.30$.

For the case of $(C_5H_5)Fe^{III}(2,3\text{-}C_2B_9H_{11})$ it has been shown (vide supra) that there is probably appreciable population of a $^2A_1$ state at room temperature, which would lead to an almost isotropic g tensor and very little dipolar shift. As a consequence of the thermal population of an ^2A state with no dipolar shift, the coupling constants calculated to arise primarily from dipolar shift correction should be relatively suspect in an absolute sense, i.e., B-8, -9, -10, and -11 in Table IV. Additionally, the ^{13}C contact shift for $C_5H_5{}^-$ may actually be of opposite sign, when the corrections for population of a ^2A state are included. However, the five atoms (three B, two C) in the bonding face of $C_2B_9H_{11}{}^{2-}$ yield a large negative coupling constant which will be essentially unaffected by decreasing the dipolar contribution.

The hyperfine coupling constants for the remaining isomers of $Fe^{III}C_2B_9H_{11}{}^{2-}$ are listed in Table IV. The dipolar shifts in these cases were calculated from the crystal structure of $(C_5H_5)Fe^{III}(2,3\text{-}C_2B_9H_{11})$ with the g tensor averaged using the appropriate values obtained from the esr data (Table II).

The complexes of Cr^{III} and Fe^{III} with various isomers of the $C_2B_9H_{11}{}^{2-}$ ligand were prepared from the nido ligand $C_2B_9H_{12}{}^-$. Using this method of preparation, and assuming no carbon atom migration had occurred in the preparation, the bonding face of the ligand (B_3C_2 or B_4C) is reasonably well established. However, with the development of the "polyhedral expansion" reaction[20] the bonding face of the ligand is totally unknown. The reason for this ambiguity is that the polyhedral expansion reaction is based on the reduction of closo car-

(20) W. J. Evans, G. B. Dunks, and M. F. Hawthorne, J. Amer. Chem. Soc., 95, 4565 (1973).

Table IV. Coupling Constants for Various $Fe^{III}-B_9C_2H_{11}{}^{2-}$ Complexes

	Obsd shift	Contact shift[a]	A_n, G
	$(CH_3)_4N[Fe^{III}(2,3-C_2B_9H_{11})_2]$		
$2,3-^{13}C$	+630	+543	−1.30
B-4, -6	+402	+476	−1.53
B-5	+452	+518	−1.66
B-7	−104	−54	+0.17
B-8, -11	+0.5	+51	−0.16
B-9, -10	−21	+29	−0.09
B-12	+30	+71	−0.23
	$(C_5H_5)Fe^{III}(2,4-C_2B_9H_{11})$		
$C_5H_5-^{13}C$	−92	+85	−0.15
$2,4-^{13}C$	+677	+659	−1.19
B-3	+409	+505	−1.16
B-5, -6	+432	+539	−1.24
B-9, -11	+2.5	+76	−0.17
B-7, -8	−12	+62	−0.14
B-10	−2.0	+71	−0.16
B-12	+64	+126	−0.29
	$(C_2H_5)_4N[Fe^{III}(2,9-C_2B_9H_{11})_2]$		
B-3, -6	+481	+592	−1.44
B-7, -8	+752	+863	−2.10
B-5, -6	−2.3	+75	−0.18
B-8. -10	−51	+26	−0.06
B-12	+54	+119	−0.29

[a] Corrected for diamagnetic and dipolar shifts.

boranes or metallocarboranes, followed by the complexation with various transition metals. The structure of the reduced carborane is unknown at the present time and, as a consequence, the bonding face of the transition metal complexes has heretofore been established by the symmetry exhibited in the ^{11}B nmr of the diamagnetic complexes.[3]

The complex of $(C_5H_5)Fe^{III}(C_2B_8H_{10})$ serves as a good example of the ambiguity which can result by structural assignments based on only diamagnetic ^{11}B nmr spectra. The ^{11}B nmr of the diamagnetic $(C_5H_5)Fe^{II}(C_2B_8H_{10})^-$ exhibits doublets in the ratio of 2:4:2 at −1.5, +19, and +25 ppm, with equivalent carborane C-H resonances at τ 7.1. Assuming a closo octadecahedral structure, there are three sets of possible positions for the carbon atoms consistent with the ^{11}B and ^1H nmr data. The structure of the $C_2B_8H_{10}{}^{2-}$ ligand is shown in Figure 2 with the carbon atoms on a mirror plane at positions 2,3; 8,9; or 10,11. By using the ^{11}B nmr of the paramagnetic $(C_5H_5)Fe^{III}(C_2B_8H_{10})$, the atom arrangement in the bonding face is clearly established as $(C_5H_5)Fe^{III}(2,3-C_2B_8H_{10})$. The 80-MHz ^{11}B spectrum of $(C_5H_5)Fe^{III}(C_2B_8H_{10})$ is shown in Figure 5 and exhibits two resonances of equal area (4:4) at +241 ($\Delta H_{1/2}$ = 11,000 Hz) and −57 ($\Delta H_{1/2}$ = 800 Hz) ppm. The two other ligand geometries, 8,9 or 10,11, would exhibit resonances in the ratio of 6:2. From the earlier discussion of the broadening of nuclear resonance lines (see Figure 1), the $2,3-C_2B_8H_{10}{}^{2-}$ ligand should exhibit resonances of area 4 (broad due to proximity of the paramagnetic metal center) and 4 (relatively sharp due to the $1/r^6$ dependence of the dipolar broadening).

The esr spectrum of $(C_5H_5)Fe^{III}(2,3-C_2B_8H_{10})$ at liquid N_2 temperature exhibits an isotropic g tensor with g = 2.06 (Table II). This indicates that the ground state for the Fe^{III} complex is orbitally nondegenerate and exhibits no spin–orbit coupling. This can result from a
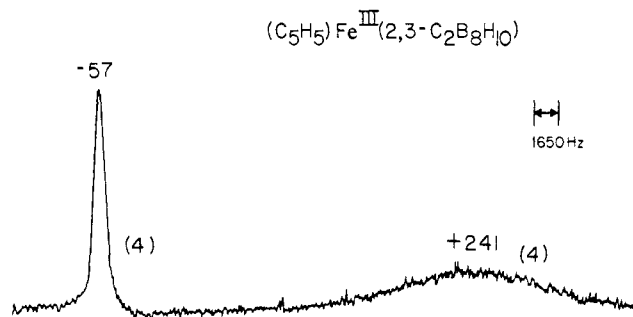
$(C_5H_5) Fe^{III}(2,3-C_2B_8H_{10})$

Figure 5. The 80-MHz ^{11}B nmr spectrum of $(C_5H_5)Fe^{III}(2,3-C_2B_8H_{10})$ in acetone.

change in the ground state from ^2E to ^2A in going from pseudo-C_5 to pseudo-C_6 symmetry, since the energies of these two ground-state configurations are very close in energy for various Fe^{III} metallocene complexes.[4] Alternatively, the ligand field symmetry around the metal may be only C_2 which would again lead to orbitally nondegenerate ground states. However, the room temperature magnetic susceptibility with μ_{eff} = 1.60 ± 0.05 BM, g_{av} = 1.78, indicates that there is thermal population of an excited state similar in energy to the ground state with some orbital angular momentum which implies an effective ligand field of greater than C_2 symmetry.

Consequently, even though the ground state is orbitally nondegenerate (no dipolar shift) based on the esr data (80°K), the presence of a thermally populated orbitally degenerate state (with a dipolar contribution) from the magnetic susceptibility (300°K) implies that there is dipolar shift of unknown magnitude and direction in the paramagnetic ^{11}B nmr spectrum of $(C_5H_5)-Fe^{III}(2,3-C_2B_8H_{10})$. However, it is highly unlikely that the dipolar shifts are equal to or greater than those in the $Fe^{III}-C_2B_9H_{11}{}^{2-}$ systems. The resulting hyperfine coupling constants for $(C_5H_5)Fe^{III}(C_2B_8H_{10})$, based on the observed shifts (diamagnetic shifts), are B(4,5,6,7) at +222 ppm = −0.90 G; B(8,9,10,11) at −72 ppm = (+0.29 G).

The polyhedral expansion of $1,7-C_2B_6H_8{}^{20}$ yields at least two monometallic complexes of the formula $(C_5H_5)Fe^{III}(C_2B_6H_8)$. The first isomer $(C_5H_5)Fe^{III}(4,6-C_2B_6H_8)$ exhibits doublets in the ^{11}B nmr of the diamagnetic Fe^{II} complex at −17.0, +5.8, +16.0, and +31.0 in the ratio of 1:2:2:1 with equivalent carborane CH's at τ 4.42. The spectrum (Figure 6) of the Fe^{III} complex exhibits resonances in the ratio of 3:3 at +92 ppm ($W_{1/2}$ = 2300 Hz) and +6.0 ppm ($W_{1/2}$ = 150 Hz). Again the magnetic properties (Table III) indicate an orbitally nondegenerate ground but a thermally accessible state with orbital angular momentum. The hyperfine coupling based on the observed (corrected for the diamagnetic) shifts indicates values of −0.41 G for the boron atoms adjacent to the metal (2, 3, 7) and A_{11B} = 0.00 for the nonadjacent boron atoms (5, 8, 9).

The second complex of $(C_5H_5)Fe^{III}(C_2B_6H_8){}^{20}$ exhibits doublets in the ^{11}B nmr spectrum of the diamagnetic Fe^{II} complex in the ratio of 2:2:2 at −1.2, +10.4, and +13.5 ppm, with equivalent carborane CH's at τ 7.1 (250-MHz ^1H nmr).

The ^{11}B nmr spectrum of the paramagnetic Fe^{III} complex exhibits resonances at +82.1 ppm ($W_{1/2}$ = 1600 Hz), area 2, and a sharper resonance of area 4 at +11
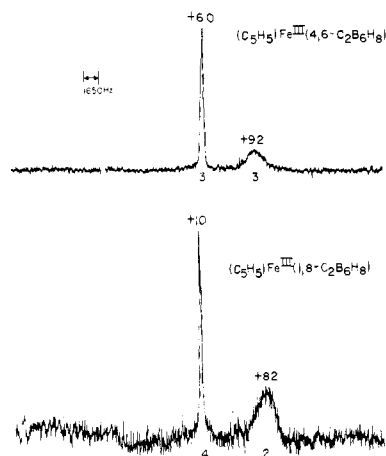
Figure 6. The 80-MHz ^{11}B nmr spectra of $(C_5H_5)Fe^{III}(C_2B_6H_8)$.

ppm $(W_{1/2} = 300$ Hz). These data indicated that the structure should have two boron atoms adjacent to the metal. Such a structure, which is consistent with both the paramagnetic and diamagnetic ^{11}B nmr and diamagnetic ^{1}H nmr data, is based on the tricapped trigonal prism geometry with the caps being the Fe^{III} and two boron atoms and the two carbon atoms adjacent to the metal and symmetrically placed in the trigonal prism. Such an unusual geometry, i.e., low-coordinate metal and high-coordinate carbon, is unique in closo metallocarboranes. In this case, the only possible geometry consistent with the diamagnetic data is the proposed unique geometry, and the data obtained from the paramagnetic ^{11}B nmr spectrum support the original proposal.[20] The hyperfine coupling constants based on the observed shift (diamagnetic shift) being purely contact shift are -0.35 G for B-3 and -5 and 0.00 G for B-2, -6, -7, and -8.

Ni^{III} and Co^{II} Complexes. The ground state for Co$^{II}(C_5H_5)_2$, d^7, has been shown to be $(a_{1g})^2(e_{2g})^4(e_{1g}*)^1$, $^2E_{1g}$, based on esr data and molecular orbital calculations.[4] The esr at 4°K exhibits axial symmetry with an almost isotropic g tensor $(g_1 = 1.67, g_2 = 1.74)$.[21] As a consequence there is expected to be very little dipolar contribution to the observed shift in the d^7 metallocenes. The crystal structure of $(CH_3)_4N[Ni^{III}(2,3-C_2B_9H_{11})_2]$ has recently been reported[22] and again exhibits the symmetrical π-sandwich-type bonding with the average Ni-B(C) distance of 2.13 ± 0.02 Å. The low temperature esr spectrum (77°K, polycrystalline in CH$_2$Cl$_2$-DMF) exhibits an axially symmetric g tensor with $g_\parallel = 2.06$ and $g_\perp = 2.01$. As a consequence there should be only a small dipolar contribution. The ground state for a d^7 metallocarborane is a low-spin, $S = 1/2$, ^2E state which could undergo a Jahn-Teller type distortion giving rise to low-lying excited states which would effectively decrease the T_1^e and the ^{11}B nmr should be observable. The room-temperature magnetic susceptibility has $\mu_{eff} = 1.74$ BM.[23] The magnetic susceptibility data indicate that the thermally populated low-lying excited states do not possess any orbital angular momentum.

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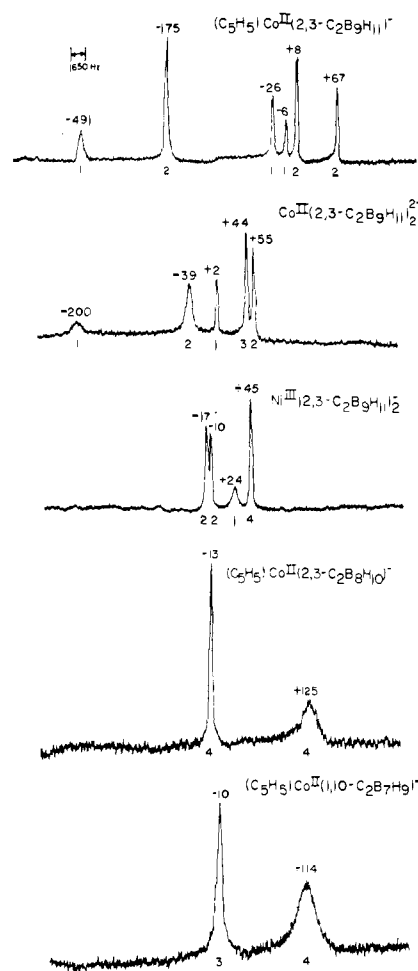
Figure 7. The 80-MHz ^{11}B nmr spectra of various Co^{II} and Ni^{III} (d^7) metallocarboranes.

The 80-MHz ^{11}B nmr spectrum of $(CH_3)_4N^+Ni^{III}$-$(2,3-C_2B_9H_{11})_2$ in acetone is shown in Figure 7. In this case the total spectrum width is only about 60 ppm. As a result, since the corresponding diamagnetic Ni^{IV} (d^6) complex is not isostructural and the Ni^{II} (d^8) is paramagnetic, no diamagnetic reference is available.[3] Because the shifts are so small, no coupling constants were calculated, owing to the large inherent error.

The cobalt complexes of carboranes have been the most widely studied series.[3] This predominance of complexes of Co^{III} (d^6) is a consequence of the unique nature of Co^{III} to behave as a "pseudo"-boron atom in most all reactions of the metallocarboranes.[24] In addition the diamagnetic Co^{III} complexes allow structural characterization, based on the symmetry which is observed in the ^{11}B nmr spectra. As a consequence of the redox stability of Co^{III} complexes, to study the contact shifts of the Co^{II} (d^7) complexes (Table V) it was necessary to reduce the Co^{III} to Co^{II} using either Na-(Hg) or controlled potential electrolysis. In general, the $E_{p/2}$ for the reduction of various monometallic carboranes lies in the region of -0.7 to -1.5 V vs. sce.

The X-ray crystal structure of $Cs[Co^{III}(2,3-C_2B_9H_{11})_2]$ · H$_2$O[25] and $(C_2H_5)_4N[Co^{III}(1,6-C_2B_7H_9)_2]$[26] have been

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Table V. Hyperfine Coupling Constants for Co^{II} Metallocarboranes

	Contact shift,[a] ppm	A_n, G
Co^{II}(2,3-C$_2$B$_9$H$_{11}$)$_2$$^{2-}$		
B-4, -6	-43	+0.13
B-5	-190	+0.58
B-8, -11	+30	-0.09
B-9, -10	+51	-0.16
B-7	-18	+0.06
B-12	+46	-0.14
(C$_5$H$_5$)Co^{II}(2,3-C$_2$B$_9$H$_{11}$)$^-$		
B-4, -6	-181	+0.55
B-5	-485	+1.48
B-8, -11	-8	+0.02
B-9, -10	+61	-0.19
B-7	-49	+0.15
B-12	-4	+0.01
(C$_5$H$_5$)Co^{II}(2,3-C$_2$B$_8$H$_{10}$)$^-$		
B-4, -5, -6, -7	+112	-0.34
B-8, -9, -10, -11	-22	+0.07
(C$_5$H$_5$)Co^{II}(1,10-C$_2$B$_7$H$_9$)$^-$		
B-3, -5, -6, -9	+98	-0.30
B-4, -7, -8	0	±0.00

[a] Corrected for diamagnetic ligand.

reported. In the case of the Co^{III}(C$_2$B$_9$H$_{11}$)$_2$$^-$ complex, which is a symmetrically bonded complex, the average Co–B(C) distance is 2.07 ± 0.01 Å. For the Co^{III}-(C$_2$B$_7$H$_9$)$_2$$^-$ complex, which has a distinctly nonplanar bonding face, the average Co–B(C) distance is 2.06 ± 0.07 Å.

Attempts to obtain esr data on the Co^{II} complexes prepared chemically or electrochemically have, in general, been unsuccessful. The only data obtained from the complexes which will be discussed are for (C$_5$H$_5$)-Co^{II}(C$_2$B$_8$H$_{10}$)$^-$ in acetonitrile at 77°K. The esr spectrum is a broad (550 G) line centered at g = 2.10 with some evidence for ^{59}Co hyperfine splitting. The ground state for the Co^{II} metallocarboranes is presumed to be a ^{2}E state which distorts in such a manner to yield low-lying excited states which account for rapid electron relaxation.

In the case of Cr^{III} and Fe^{III} complexes nmr spectra were obtained in each case, though there was a large variation in line width. For the Co^{II} metallocarboranes, in a large number of cases, no spectra were observable upon reduction of the diamagnetic Co^{III} complexes. Since each of Co^{III} complexes exhibits very similar electrochemical redox behavior, i.e., reversible one-electron reduction of Co^{III} to Co^{II}, the inability to observe any ^{11}B nmr spectra of the reduced complexes must be associated with an increase in the electron relaxation time (T_1^{e}). This conclusion is based on the following observations. The 80-MHz ^{11}B nmr spectrum of (C$_5$H$_5$)Co^{II}(2,3-C$_2$B$_9$H$_{11}$)$^-$ in acetone is shown in Figure 7. This spectrum of the Co^{II} species can be obtained by controlled potential electrolysis or reduction with excess Na(Hg) (vide infra) of the (C$_5$H$_5$)Co^{III}(2,3-C$_2$B$_9$H$_{11}$). In this case the line width of the -500 ppm resonance is about 500 Hz. Reduction of (C$_5$H$_5$)Co^{III}-(2,4-C$_2$B$_9$H$_{11}$) under similar conditions causes the spectrum to broaden, so that in the fully reduced Co^{II} complex only a single broad (800 Hz) resonance is observed at about +10 ppm. This observation can be interpreted

as indicating that when the ligand field is changed, i.e., going from 2,3-C$_2$B$_9$H$_{11}$ to 2,4-C$_2$B$_9$H$_{11}$, the energy of the excited states, which lead to rapid electron relaxation in the 2,3 isomer, is increased in the 2,4 isomer with a concomitant increase in the electron relaxation time. Since the line widths are primarily determined by dipolar relaxation of the nucleus by the electron spin fluctuations, an increase in the electron spin relaxation time would broaden the nuclear resonance to the point that it cannot be observed. The possibility of ligand reduction can be discounted, since the ^{11}B nmr of the atoms non-adjacent to the metal are observable, which would not be the case for a Co^{III}–carborane radical complex.

The 80-MHz ^{11}B nmr spectra of (C$_5$H$_5$)Co^{II}(2,3-C$_2$B$_9$H$_{11}$)$^-$, Co^{II}(2,3-C$_2$B$_9$H$_{11}$)$_2$$^{2-}$, (C$_5H_5$)Co^{II}(2,3-C$_2B_8$-H$_{10}$)$^-$, and (C$_5H_5$)Co^{II}(1,10-C$_2B_7H_9$)$^-$ are shown in Figure 7. The hyperfine couplings are listed in Table V. The diamagnetic shifts for the 2,3-C$_2$B$_9$H$_{11}$$^{2-}$ complexes were taken from the spectra which have been assigned in the literature.[27]

In the case of the Co^{II} complexes, as in the Fe^{III} and Cr^{III} (vide supra), the resonances of the atoms adjacent to the metal are appreciably broader than those non-adjacent. The line width variation of resonances within a closo metallocarborane (due to the $1/r^6$ dependence of the dipolar relaxation mechanism) can be used as an additional feature which aids in the assignment of the atom arrangement in the bonding face.

Discussion

The metallocenes have served as the model precursors for the extensive chemistry which has developed in the area of metallocarboranes. Consequently the available data for metallocenes with respect to the mode of electron delocalization will be discussed and compared to the results for metallocarboranes. The ^{1}H nmr isotropic shifts for the metallocene compounds of the type M(C$_5$H$_5$)$_2$ where M = V, Cr, Mn, Co, and Ni have been interpreted by Rettig and Drago[28] as follows, based on experimental and theoretical results. In V(C$_5$H$_5$), d^3, (e$_{2g}$)^2(a$_{1g}$)^1, the observed ^{1}H hyperfine coupling constant is predominated by a "σ-delocalization" mechanism. The "σ-delocalization" mechanism is consistent with delocalization involving an a$_{1g}$ molecular orbital which is composed of the metal d$_{z^2}$ orbital and the in-plane part of the ligand (carbon 2p$_x$, 2p$_y$, and 2s and hydrogen 1s). This mechanism can be viewed as metal to ligand electron transfer. The mode of delocalization in Cr(C$_5$H$_5$)$_2$, d^4, (e$_{2g}$)^3(a$_{1g}$)^1, is believed to be essentially the same as for the vanadium species. For the cobalt metallocenes, Co(C$_5$H$_5$)$_2$, d^7, (e$_{2g}$)^4(a$_{1g}$)^2-(e$_{1g}$*)^1, the ring hydrogen shifts are dominated by (e$_{1g}$*) π-delocalization, arising from overlap of the metal d$_{xz}$ and d$_{yz}$ orbitals with carbon p$_z$ orbitals, and electron transfer from metal to ligand. The results for Ni(C$_5$H$_5$)$_2$, d^8, (e$_{1g}$)^4(a$_{1g}$)^2(e$_{1g}$*)^2, can again be explained by allowing the π-delocalization mechanism to be the dominant factor.

It must be pointed out that in the area of the interpretation of ^{1}H contact shifts there are a number of alternate proposals which have been suggested. The first attempt to account for the signs of the ^{1}H contact

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Table VI. Paramagnetic Metallocenes

Compound	Ground-state electron configuration	Magnetic data (μ_{eff})	^{1}H shift,[a] ppm	^{13}C shift,[b] ppm
V(C$_5$H$_5$)$_2$	(e$_{2g}$)^2(a$_{1g}$)^1	$S = {}^3/_2$, (3.84 ± 0.04)	−307	+660
Cr(C$_5$H$_5$)$_2$	(e$_{2g}$)^3(a$_{1g}$)^1	$S = 1$, (3.20 ± 0.16)	−314	+440
Fe(C$_5$H$_5$)$_2^+$	(e$_{2g}$)^3(a$_{1g}$)^2	$S = {}^1/_2$,[c] $g = 1.87$ $g = 3.28$		
Co(C$_5$H$_5$)$_2$	(e$_{2g}$)^4(a$_{1g}$)^2(e$^*_{1g}$)^1	$S = {}^1/_2$ (1.76 ± 0.07)	+54	−440
Ni(C$_5$H$_5$)$_2$	(e$_{2g}$)^4(a$_{1g}$)^2(e$^*_{1g}$)^2	$S = 1$ (2.86 ± 0.11)	+255	−1300

[a] Shifts *vs.* Fe(C$_5$H$_5$)$_2$ in toluene or benzene solution, ref 4. [b] Shifts *vs.* ^{13}C$_6$H$_6$ for the solid metallocenes, see ref 32. [c] A. Hansfield and A. Wasserman, *J. Chem. Soc. A*, 3202 (1970).

shifts was offered by Levy and Orgel[29] in 1961. The mode of electron delocalization in the d^7 and d^8 metallocenes is essentially the same as Drago's later work, *i.e.*, electron transfer from metal to ligand, the spin density reaching the hydrogens by the McConnell-type[30] π–σ exchange mechanism and leads to upfield shifts, as observed.

However, the interpretation of the downfield ^{1}H shifts in the d^3 through d^5 metallocenes is different from the "σ-delocalization mechanism" (*vide supra*). According to the Levy–Orgel mechanism the unpaired electron density on the metal in a$_{1g}$ and e$_{2g}$ molecular orbitals, having little ligand character, and the essentially nonbonding metal unpaired electrons could polarize the strongly bonding, predominantly ligand e$_{1g}$ electrons such that negative spin density would predominate at the ligand carbon atoms. In a valence bond sense, this mechanism amounts to parallel spin transfer from ligand to metal, resulting in a downfield ^{1}H shift as observed. Clearly the two mechanisms differ in the prediction of the spin density and direction of the shift at the carbon atoms. The "σ-delocalization" mechanism would predict a downfield shift of the ^{13}C resonance, while the "π-polarization" mechanism would predict the upfield shift of the ^{13}C resonance. The upfield shift of the ^{13}C resonance in the V(C$_5$H$_5$)$_2$ and Cr(C$_5$H$_5$)$_2$[31,32] would be more consistent with the "π-polarization" mechanism, as being the predominant mechanism in understanding the shift in the ^{13}C resonance.

One additional mechanism has also been advanced to explain the ^{1}H isotropic shifts, particularly for vanadium and chromium species. This mechanism is based on the concept of allowing certain ligand hydrogen atoms, if they are appropriately sterically situated, to directly overlap with metal d orbitals to account for the observed shift.[33] The available data on paramagnetic metallocenes are summarized in Table VI.

The nuclear–electron coupling constants for metallocarboranes can be used to evaluate the mode and extent of electron delocalization. However, a number of points must be discussed prior to an evaluation and comparison of the delocalization mechanism.

First, the effect of dipolar ligand contributions to the observed shifts will be discussed. The evaluation of

ligand-centered dipolar shifts has been discussed by McGarvey[34] and Kurland.[7] The ligand-centered dipolar shifts can arise when there is appreciable electron density in nonhydrogen ligand orbitals. If the hybridization of the atoms is noncubic, *i.e.*, distorted tetrahedron, a dipolar shift of various magnetic nuclei is possible. The equation for estimating the ligand-centered dipolar shift for an A ground state is[32]

$$\left(\frac{\Delta H}{H}\right)^{ligand}_{dipolar} = -(2/45)\left[\frac{S(S+1)\beta^2}{kT}\right](g_{\parallel} - g_{\perp})\langle r^{-3}\rangle_{2p}f_{2p}$$

where f_{2p} = fraction of unpaired electron spin in the p orbital, and $\langle r^{-3}\rangle_{2p}$ = average value of r^{-3} for the p orbital ($= 5.41 \times 10^{24}$ cm^{-3} for ^{11}B and 6.68×10^{24} cm^{-3} for ^{13}C). Substitution of appropriate values and letting $S = {}^1/_2$, $|g_{\parallel} - g_{\perp}| = \pm1$, and $f_{2p} = 0.1$ electron lead to a calculated ligand-centered dipolar contribution of ±38 ppm for ^{11}B and ±47 ppm for ^{13}C. Clearly the ligand-centered dipolar shifts can only contribute a minor fraction of the observed shifts (~500 ppm).

Secondly, in the case of the metallocenes, the hybridization of the carbon atoms in the cyclopentadienyl moiety is "sp^2 + p," meaning that the ligand π system (p orbitals) can be separated from the sp^2 σ-bonding orbitals, in a very formal manner. However, as has previously been pointed out, there is actually no separation of σ- and π-orbitals permissible under the symmetry observed in the metallocenes. In fact the "σ-delocalization" (*vide supra*) mechanism uses the in-plane "σ-type" molecular orbitals to explain the mode of electron delocalization in the d^3–d^5 metallocene complexes.

In the carborane ligand systems, the actual hybridization of the boron atoms is unknown. In a valence bond type of discussion, the bonding in boron hydrides, polyhedral boranes, and carboranes assumes that the hybridization is sp^3.[35,36] In fact the more recent calculations of boron hydrides have shown that the boron hybridization is around sp$^{2.8}$.[37] While the exact hybridization is unknown, the most appropriate discussion is that the boron atoms are more likely to be an "sp^3-type" of hybrid (or cubic environment) than the carbon atoms in a planar C$_5$H$_5^-$ ring. It must be pointed out that as the hybrid exhibits more p character then the possible polarization of the B (1s) by B (2p)

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must also be considered. Such a polarization has been discussed by Karplus and Fraenkel[38] for explaining ^{13}C hyperfine interactions. The theoretical calculations of the ^{13}C hyperfine coupling constants for planar aromatic systems (sp^2 + p) show that the C (1s) orbital spin polarization contributes a term of negative sign with a magnitude comparable to that from the C (2s) orbital. For the purposes of discussion the effective hybridization of B and C in polyhedral metallocarboranes is sp^3.

The nuclear–electron coupling constant is related to the electron density at the ligand nucleus by the familiar equation

$$A_n = \frac{8\pi}{6s} g_e\beta_e g_{^{11}B}\beta_n |\psi_0(2s)|^2$$

which for ^{11}B is $A_{^{11}B}$ = 2020 MHz (804 G).[39] Therefore for one electron in an sp^3 boron orbital, the predicted coupling constant would be 201 G. A crude estimate can then be made, with the hybridization restrictions, that approximately (2.0 G/201 G) 0.01 electron is the average unpaired spin density at each of the boron (carbon) atoms in the bonding face of the $C_2B_9H_{11}^{2-}$ ligand system.

In the Cr^{III} and various Fe^{III} (d^3 and d^5) complexes of $C_2B_9H_{11}^{2-}$ the large (−1.0 to −2.0 G) negative coupling constants for the atoms (B and C) adjacent to the metal implies a net negative (the average electron spin moment is aligned antiparallel to the field) spin density at the nucleus. This result is a very good indication that the mode of delocalization is by the "π-polarization"[29] or ligand to metal electron transfer mechanism. For the Co^{II} (d^7) complexes the positive coupling constants can be interpreted as indicative of direct delocalization of unpaired metal electrons into appropriate ligand orbitals or metal to ligand electron transfer. For the Fe^{III} and Co^{II} complexes of the $C_2B_8H_{10}^{2-}$ ligand, Co$^{II}(C_2B_7H_9)^-$, and Fe$^{III}(C_2B_6H_8)$, all exhibit negative couplings of varying magnitudes (generally decreasing with a decrease in the size of the carborane ligand) which implies that in these cases again the mode of delocalization is by ligand to metal charge transfer.

The extent of the delocalization process, whether ligand to metal or metal to ligand, is extremely limited in metallocarboranes. In "π-type" delocalization, the magnitude of the coupling constant is relatively invariant although alternating in sign in odd-alternate hydrocarbons, i.e., Ni^{II} aminotroponiminates.[40] For σ-type delocalization, the magnitude of the coupling constants falls off rapidly with metal–nuclear distance, i.e., in Ni^{II} propylamine, where the observed $\alpha{:}\beta{:}\gamma$ coupling is −1.0:−0.3:−0.07.[41] Therefore, since the metallocarborane complexes show a great reduction in the hyperfine coupling constant for atoms nonadjacent to the metal (2.0–0.2 G), the extent of delocalization can be treated as qualitatively "σ-type" in character. However, it must be pointed out that the appreciable coupling constant observed for B-12 in Fe^{III}–(C$_2$B$_9$H$_{11}$)$^{2-}$ complexes implies some degree of "π-type" delocalization. It is obvious that both types of mechanisms are

plausible in polyhedral structures. This delocalization behavior may be qualitatively analyzed as indicating that indeed the hybridization of the boron atoms is effectively sp^3, which would account for the limited ability of the carborane cage to extensively delocalize the spin density to all portions of cage. However, it must be emphasized that these studies are only measuring the effect of *one* nonbonding unpaired metal electron on the various ligand nuclei. These data cannot in any way be applied to any arguments which emphasize the bonding of the cage in itself or even metal to ligand bonding. These data can only be used to evaluate the type of ligand molecular orbital which is of proper symmetry and energy to overlap with metal orbitals containing unpaired spin density and how it accommodates the donation or acceptance of electron density from the metal.

Conclusions

The isotropic shifts of the ^{11}B and ^{13}C nuclear resonances in a wide variety of paramagnetic metallocarboranes of the type M(C$_2$B$_n$H$_{n+2}$) where M = Cr^{III}, Fe^{III}, Ni^{III}, and Co^{II}, and n = 9, 8, 7, and 6 have been evaluated. The isotropic shifts which reflect large negative nuclear–electron hyperfine coupling constants for Cr^{III} and Fe^{III} can be interpreted as being consistent with parallel spin transfer from ligand to metal. The positive isotropic coupling constants for the Co^{II}-(C$_2$B$_9$H$_{11}$) complex may be interpreted as arising from direct delocalization of metal-centered electron density into ligand orbitals. In the nonicosahedral Co^{II} metallocarboranes, the observed negative coupling constants again reflect the mode of electron delocalization as arising from ligand to metal charge transfer.

The isotropic coupling constants for all of the paramagnetic metallocarboranes show a rapid reduction to atoms which are not directly bonded to the metal. This behavior is reminiscent of a σ-type of delocalization mechanism, in that only those atoms which are directly bound to the paramagnetic metal center exhibit large shifts in their nuclear resonance. This type of behavior cannot be taken as evidence of the ability of polyhedral boranes to transmit electronic effects through the cage bonding molecular orbitals but can only be used as evidence for the ability to delocalize unpaired electron density which is primarily centered in nonbonding metal-centered orbitals.

The diminution of the isotropic coupling constants in metallocarboranes to atoms which are not directly bound to the metal center can, in a large number of cases, be used for evaluation of the atomic make-up of the ligand bonding face. In all cases the nuclear resonances of the atoms which are bound to the metal are appreciably broader than the nonbonded nuclear resonances.

And finally, the magnitude and direction of the isotropic shifts of the metallocarboranes and metallocenes (^{13}C shifts but not ^{1}H shifts) are very similar. This result implies that the energetics of the metal–ligand interaction are similar, i.e., that the highest filled molecular orbital is primarily metal centered and non-bonding in nature.

Experimental Section

The methods of preparation and purification of the various compounds used in this study have previously been reported.[4,20]

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All spectra were obtained on a superconducting spectrometer built by Professor F. A. L. Anet of this department (59 kG) with 251 MHz ^{1}H, 63.1 MHz ^{13}C, and 80.5 MHz ^{11}B. The ^{1}H and ^{11}B spectra were obtained using continous wave techniques, while the ^{13}C spectra were obtained using Fourier transform techniques, normally with the accumulation of 10,000 transients.

The use of eq 1 implies that the magnetic properties vary linearly with temperature. The normal method used to evaluate A_n is from linear plots of $(\Delta\nu/\nu_0)$ vs. $1/T$. In the majority of the paramagnetic metallocarboranes, such a method of evaluation has proved impossible. The minimal temperature range imposed by the solubility of the complexes in appropriate solvents (ca. -30 to $+30°$), coupled with the large uncertainty in accurate chemical shift measurements

on very broad peaks, precluded any meaningful temperature dependence data to be obtained. However, within the experimental limitations, the plots of $(\Delta\nu/\nu_0)$ vs. $1/T$ were approximately linear. Rather the magnetic behavior of the ground state and excited state was estimated from the available esr and magnetic susceptbility data.

Self-Consistent Field Wave Functions of Boron Hydrides and Ions: B_8H_{12}, B_9H_{15}, $B_6H_6^{2-}$, $B_{10}H_{10}^{2-}$, and $B_{10}H_{14}^{2-}$

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Abstract: A minimum basis set of Slater orbitals has been used for *ab initio* self-consistent field wave functions for B_8H_{12}, B_9H_{15}, $B_6H_6^{2-}$, $B_{10}H_{10}^{2-}$, and $B_{10}H_{14}^{2-}$. From these wave functions we give bond midpoint densities, overlap populations, atomic charges, molecular dipole moments, diamagnetic susceptibilities, and diamagnetic shielding constants. Some analysis is also given relating probable sites of nucleophilic and electrophilic attack to the charge distributions, and some discussion is included relating to the few positive (unbound) occupied eigenvalues of the negative ions. A comparison is also made of these accurately computed SCF results with approximate SCF wave functions obtained by the method of partial retention of diatomic differential overlap (PRDDO). Excellent charge distributions and eigenvalues are obtained by the PRDDO method in computing times less than those of the SCF method by about a factor of 50.

Boron hydrides, carboranes, and their derivatives have been studied extensively by theoretical and experimental methods in recent years. Synthetic methods have yielded a large number of new interesting compounds. Closely related theoretical studies have indicated new features of electronic structures, rearrangements, and reactivities of electron deficient species. Recent theoretical studies have included *ab initio* self-consistent field (SCF) studies,[1] from which localized molecular orbitals (LMO) have been obtained[2,3] supporting three-center bond theory.[4] New insight has also been obtained in terms of percentages of delocalization of bonds and, most notably, a new theory in which transferable fractional bonds occur.[5] Simplification of the topological theory[4,6] of localized

bonds in electron-deficient molecules has also occurred, allowing a conceptually simple but powerful method for understanding of valence structures and chemical reactivities and providing a systematization of boron chemistry.

Partly as a result of substantial progress in computer capabilities and effective programs, *ab initio* SCF wave functions have recently become available for a number of small boron hydrides and their ions, including BH_3,[7] BH_4^-,[8] B_2H_6,[3a] $B_2H_7^-$,[9] $B_3H_8^-$,[10] B_4H_4,[11] B_4H_{10},[12] B_5H_9,[12] and B_6H_{10}.[3c] Among the larger boranes, only $B_{10}H_{14}$[13] has previously been studied by SCF methods. Here, we extend these theoretical methods to B_8H_{12}, B_9H_{15}, $B_6H_6^{2-}$, $B_{10}H_{10}^{2-}$, and $B_{10}H_{14}^{2-}$. Some of the ground-state properties studied are charge distributions, overlap populations, midpoint densities in bonds, ionization potentials, atomization energies, diamagnetic susceptibilities, and diamagnetic contributions to chemical shifts.

In a separate section we compare *ab initio* SCF results

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