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Contribution from the Department of Chemistry,
McMaster University, Hamilton, Ontario, Canada L8S 4M1

Bonding in Transition-Metal Tetrahydroborates: A Multinuclear Magnetic Resonance Study of $(C_5H_5)_2Sc(BH_4)$ and $Sc(BH_4)_3$ and Some Comments on the Isolobality of BH_4^-, Halide, and η^5-$C_5H_5^-$ Groups

MARY MANCINI, PETER BOUGEARD, ROBERT C. BURNS, MICHAEL MLEKUZ, BRIAN G. SAYER,
J. IAN A. THOMPSON, and MICHAEL J. McGLINCHEY*

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$(C_5H_5)_2Sc(BH_4)$ has been synthesized and shown to contain a triply bridged tetrahydroborate moiety. Multinuclear magnetic resonance data (^1H, ^{11}B, and ^{45}Sc) are reported for $(C_5H_5)_2Sc(BH_4)$ and for $Sc(BH_4)_3$; double- and triple-resonance experiments have allowed the evaluation of all the coupling constants. It is shown that there is no exchange of ring and borohydride protons in $(C_5H_5)_2Sc(BH_4)$ in toluene-d_8 at elevated temperature as has been claimed for $(C_2H_5)_2Zr(BH_4)_2$. In this light, the proposed exchange process has been reinvestigated for $(C_5D_5)_2Zr(BH_4)_2$ with use of ^2H NMR. The structures of the known main-group and transition-metal borohydrides are rationalized in terms of a correlation between the number of bridging hydrogens and the number of vacant metal orbitals of suitable energy and symmetry. Finally, the similarities in bonding patterns of chloride, tetrahydroborate, and cyclopentadienide groups are analyzed with use of the concept of isolobality.

Introduction

In recent years interest has focused on tetrahydroborate derivatives of early transition metals,[1] not only because they provide routes to the synthetically useful hydrides[2] but also because the structure, bonding, and conformational variability may also be relevant to the chemistry of the isoelectronic CH_4 molecule. To our knowledge, the only such derivatives of scandium are the complexes $Sc(BH_4)_3$ and $[C_5H_3(SiMe_3)_2]_2Sc(BH_4)$.[3] We now report multinuclear magnetic resonance data on the former compound and on the new molecule $(C_5H_5)_2Sc(BH_4)$. These results, together with our earlier data on $Zr(BH_4)_4$,[4] allow comparisons to be made of the M–H and B–H interactions in a series of $M(BH_4)_n$ complexes via their NMR coupling constants. Finally, we address the question of the number of bridging hydrogens used by the tetrahydroborate ligand when bonding to transition metals of differing electronic requirements. It has been suggested that tetrahydroborates might display different reducing capabilities to organic functional groups depending upon their mode of complexation,[5] and so an understanding of the factors governing such complexation may prove valuable.

Experimental Section

^1H, ^{11}B, and ^{45}Sc NMR spectra were obtained on a Bruker WM250 spectrometer operating at 250, 80.21, and 60.735 MHz, respectively. The $^{45}Sc\{^{11}B\}$ data were obtained with a Bruker WH90 spectrometer operating in the FT mode at 21.964 MHz; ^{11}B decoupling was achieved with a General Radio 1164-A frequency synthesizer, locked to a 5-MHz source from the spectrometer, and an RF Communications Inc. Type 805 amplifier. ^2H spectra were also obtained on the WH90 operating at 13.815 MHz. Mass spectrometry was performed on a VG Micromass 7070 spectrometer equipped with a VG 2035 data system; the electron energy was 70 eV and the ion source temperature was 200 °C. Infrared spectra were obtained with a Perkin-Elmer Model 283 spectrometer.

$(C_5H_5)_2Sc(BH_4)$. Anhydrous scandium trichloride was prepared by heating Sc_2O_3 (Nucor, Phoenix, AZ) with NH_4Cl in a furnace at 200 °C for 6 h. The excess NH_4Cl was removed by vacuum sublimation at 300 °C.[6] Following the method of Manzer,[7] we heated anhydrous scandium trichloride (1.00 g, 6.61 mmol) and freshly sublimed cyclopentadienylthallium (4.00 g, 14.85 mmol) under reflux in dry tetrahydrofuran (50 mL) for 2 h under a nitrogen atmosphere. The precipitated thallium chloride was filtered off, the colorless solution was treated with lithium tetrahydroborate (0.151 g, 6.86 mmol), and the suspension was stirred for 4 h at room temperature. The solvent was removed at room temperature under vacuum and the residual solid sublimed at 120–130 °C (10^{-3} mmHg) to give white crystals of $(C_5H_5)_2Sc(BH_4)$ (0.49 g, 2.58 mmol; 39% overall yield based on $ScCl_3$), showing strong infrared bands at 2490, 2180, and 2130 cm^{-1} (in C_6H_6) and major mass spectral peaks at the following m/z values (%): 190, 191, $C_{10}H_{14}BSc^+$ (3); 175, $C_{10}H_{10}Sc^+$ (36); 125, 126, $C_5H_9BSc^+$ (40); 110, $C_5H_5Sc^+$ (100). NMR data are as follows: ^1H (toluene-d_8, relative to Me_4Si) $\delta(C_5H_5) = 6.4$, $\delta(BH_4) = 0.65$, $J(^{11}B,^1H) = 86$ Hz (note the coupling was only observed on heating to ~100 °C); ^{11}B (benzene-d_6, relative to $Et_2O\cdot BF_3$) $\delta = -17.7$, $J(^{11}B,^{45}Sc) = 15.5$ Hz; ^{45}Sc (benzene-d_6, relative to saturated $ScCl_3$ in D_2O) $\delta = 67.5$, $J(^{45}Sc,^1H) = 28 \pm 2$ Hz.

$Sc(BH_4)_3\cdot 2THF$ was prepared by the method of Morris and Smith[3a] and purified by sublimation at 100 °C (10^{-3} mmHg).

$Y(BH_4)_3$ was prepared analogously from $LiBH_4$ and YCl_3 in dry tetrahydrofuran.[8]

$(C_5D_5)_2Zr(BH_4)_2$. C_5D_5Tl[9] and $ZrCl_4$ yielded $(C_5D_5)_2ZrCl_2$, which in turn was converted into the final product with use of $LiBH_4$, following the procedure of Nanda and Wallbridge.[10]

Discussion

The burgeoning use of the early-transition-metal hydrides in organic and organometallic synthesis[2,11,12] has prompted studies of the corresponding tetrahydroborates which are their precursors. Scandium offers a unique opportunity in this regard since we can exuperate the conventional spectroscopic approaches by using ^{45}Sc NMR as a direct probe for the interaction of the borohydride with the central metal. Scandium-45 is an excellent NMR nucleus. It is 100% abundant and has a relative sensitivity 1709 times that of ^{13}C; it is the sixth most favorable nucleus, with only ^1H, ^{19}F, ^{51}V, ^{93}Nb, and ^{115}In being better.[13,14] The quadrupole moment of -0.22×10^{-28} M^2 is to some extent alleviated by the large nuclear spin

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Table I. NMR Chemical Shifts (ppm) and Coupling Constants (Hz) for $M(BH_4)_n$ Systems

	$NaBH_4$[a]	$Al(BH_4)_3$[b]	$Sc(BH_4)_3$[c]	$Y(BH_4)_3$[c]	$Zr(BH_4)_4$[d]
^1H[e]	−2.0	−1.27	0.5	1.35	1.65
$J(B,H)$	82	89	80	84	90
$J(M,H)$	0	44	30	<2	28
^{11}B[f]	−40	−37	−18.7	−23.2	−8.0
$J(M,B)$	0	9	15.5	<2	18
M		71.1[g]	113.3[h]		40.7[i]

[a] Reference 13, p 89. [b] Lauterbur, P. C.; Hopkins, R. C.; King, R. W.; Ziebarth, D. V.; Heitsch, C. W. *Inorg. Chem.* **1968**, *7*, 1025. [c] This work; solvent benzene-d_6. [d] Reference 4. [e] Relative to Me_4Si. [f] Relative to $Et_2O{\cdot}BF_3$. [g] Relative to saturated $AlCl_3{\cdot}6H_2O$. [h] Relative to saturated $ScCl_3$ in D_2O. [i] Relative to $(C_5H_5)_2ZrBr_2$ in C_6D_6.

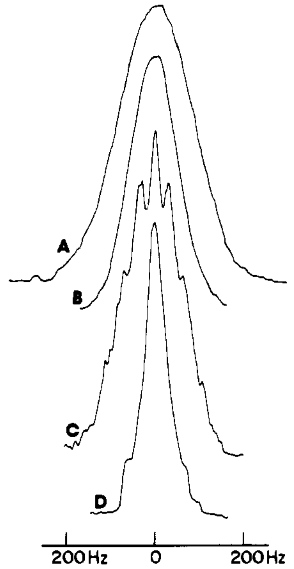

Figure 1. ^{45}Sc NMR spectrum of $Sc(BH_4)_3$: (A) normal spectrum; (B) ^1H decoupled spectrum; (C) ^{11}B decoupled spectrum; (D) ^1H and ^{11}B decoupled spectrum.

value ($I = {}^7/_2$), so, even for systems of less than cubic symmetry, line widths are not a particular problem.

We now report some multinuclear magnetic resonance data on $Sc(BH_4)_3$ together with those of related molecules (see Table I), which allow one to draw comparisons with other homoleptic tetrahydroborates. It should be noted, however, that the coupling constants to scandium are only obtained with considerable effort. Figure 1 shows the ^{45}Sc spectrum of $Sc(BH_4)_3$ under various decoupling conditions. At first, one obtains only a broad featureless peak (Figure 1A, $W_{1/2} \approx 180$ Hz), which narrows to ~120 Hz on proton decoupling (Figure 1B). Figure 1C shows the effect of ^{11}B decoupling to reveal a multiplet ($J = 30$ Hz) of relative intensities appropriate for a 13-line spectrum attributable to coupling to 12 equivalent protons. A subsequent triple-resonance experiment (Figure 1D) yielded a single line ($W_{1/2} \approx 20$ Hz) superimposed on a broad multiplet derived from residual ^{10}B coupling; as with the analogous experiment on $^{91}Zr(BH_4)_4$,[4] we observe a small ^{10}B isotope shift (6 Hz) to high frequency. The $^{11}B\{^1H\}$ spectrum of $Sc(BH_4)_3$ exhibits a typically partially quadrupolar collapsed signal[15] with the separation of the outer lines of the octet (^{45}Sc has $I = {}^7/_2$), allowing evaluation of $J(^{45}Sc,^{11}B)$ as 15.5 Hz. The ^1H spectrum exhibits a 1:1:1:1 quartet typical of the highly fluxional tetrahydroborates showing coupling to a ^{11}B nucleus ($I = {}^3/_2$) in an effectively tetrahedral environment. Analogous experiments on the previously unknown $(C_5H_5)_2Sc(BH_4)$ gave similar results except that in this case the room-temperature ^1H spectrum is quadrupolar broadened and only reveals a distinct quartet at 100 °C. The data for the congeneric $Y(BH_4)_3$ are included in Table I; we have thus far been unable to observe the ^{89}Y spectrum, but efforts are continuing in this area.

Table II. Reduced Coupling Constants for $M(BH_4)_n$ Systems

	$Al(BH_4)_3$	$Sc(BH_4)_3$	$Zr(BH_4)_4$
$J(M,B)$[a]	9	15	18
$K(M,B)$[b]	0.90	1.61	5.02
$J(M,H)$[a]	44	30	28
$K(M,H)$[b]	1.41	1.03	2.51
$^1K(M,H)$[b,c]	2.82	1.37	3.35

[a] Observed coupling constants (in Hz). [b] Reduced coupling constants (in N A^{-2} m^{-3}), all values must be multiplied by 10^{20}. [c] Reduced coupling constants for the metal-bridging-hydrogen interaction; see text.

Apart from some recent cases,[1,16] the exchange between bridging and terminal hydrogens of covalently bonded tetrahydroborates has too low an activation energy to be made slow on the NMR time scale. However, the number of protons bridging the boron and the central metal is, in most cases, readily ascertained from vibrational data.[1] The strong infrared absorptions at 2490, 2180, and 2130 cm^{-1} for $(C_5H_5)_2Sc(BH_4)$ are clearly characteristic of a triply bridged borohydride moiety. Likewise, $Sc(BH_4)_3$ has peaks at 2520, 2235, and 2150 cm^{-1}, indicative of a predominantly triple-bridged conformation in solution; the crystal structure of $Sc(BH_4)_3{\cdot}2THF$ is known to adopt a trigonal-bipyramidal geometry with two of the BH_4 units triply bridged while the third is bonded via only two hydrogens.[17] With these data in mind, we can now examine more closely the metal–hydrogen and metal–boron NMR coupling constants collected in Table I.

At the outset it is important to realise that direct comparison of observed coupling constants ($^nJ_{AB}$ values) between different pairs of nuclei is generally a meaningless exercise. This is so because such a comparison takes no account of the different nuclear properties of the atoms involved. One must instead compare the much more fundamental and significant *reduced* coupling constants ($^nK_{AB}$), which are related to the experimentally observed J_{AB} values via the equation[18]

$$J_{AB} = K_{AB}\gamma_A\gamma_B\frac{h}{4\pi^2}$$

where γ_A and γ_B are the magnetogyric ratios of the nuclei involved. That is, if $J(^1H,^1H)$ and a $J(^{13}C,^1H)$ are numerically equal, the C–H coupling constant is actually about fourfold

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[15] For a superb example of partial quadrupolar collapse, see: Franklin, K. J.; Lock, C. J. L.; Sayer, B. G.; Schrobilgen, G. J. *J. Am. Chem. Soc.* **1982**, *104*, 5303.

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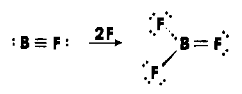
greater but this is masked by the larger magnetogyric ratio of ^{1}H relative to ^{13}C. Indeed, it has been shown that for internuclear couplings dominated by the contact term the square root of the K values for a related series of molecules, e.g., CH_4, SiH_4, GeH_4, and SnH_4, increases linearly with the atomic number of the central atom.[19] The use of K values to make meaningful periodic correlations has been described recently,[20] and conversion factors for all useful pairs of nuclei are also tabulated.

Turning now to the borohydride complexes, we present in Table II the J and K values for the metal–boron and metal–hydrogen interactions. However, it is necessary to take account of one more factor, viz., the number of hydrogens directly bonded to the metal. Thus, in $Zr(BH_4)_4$, the observed $J(^{91}Zr,^1H)$ coupling constant is 28 Hz,[4] but this is merely the average of the bridging and terminal couplings such that $J_{\rm obsd} = {}^1/_4(3J_{\rm bridging} + J_{\rm terminal})$. For simplicity, assuming that $^3J(^{91}Zr,^1H)$ is very small, then $^1J(^{91}Zr,^1H) \approx 37$ Hz. Table II also lists the reduced coupling constant, ^1K(M,H) for the protons directly bonded to the metal. We see that the ^1K(Al,H) value of 2.82 is rather less than ^1K(Zr,H), and this result is in keeping with our expectation since in the former there is a double bridge to the trivalent central metal (Z = 13) while in the latter there exists a triple bridge to a formally tetrapositive zirconium (Z = 40). In contrast, ^1K(Sc,H) is rather low, reflecting the less covalent nature of the bond. This trend toward weaker metal–BH_4 interactions culminates in $Y(BH_4)_3$, for which the yttrium–boron and yttrium–hydrogen coupling constants are zero. Yttrium-89 is a spin $^1/_2$ nucleus of 100% abundance and gives rise to readily observable coupling constants under appropriate conditions.[21] Since K values for closely analogous molecules generally increase with atomic number, one might anticipate that K(Y,H) in $Y(BH_4)_3$ should at least equal that in $Sc(BH_4)_3$. Such considerations would lead to a $J(^{89}Y,^1H)$ value of at least 6 Hz and would thus result in a doubling of the peaks in the ^{1}H and ^{11}B spectra. However, no coupling to ^{89}Y is observed, reflecting the increasing tendency to ionic bonding in yttrium compounds relative to their scandium analogues.[22]

Having isolated $(C_5H_5)_2Sc(BH_4)$ and completed a multinuclear magnetic resonance study, we were interested to see whether this molecule showed any evidence of exchange between the cyclopentadienyl protons and those of the tetrahydroborate moiety as has been previously reported for the $(C_5H_5)_2Zr(BH_4)_2$ system in toluene-d_8 solution.[23] However, we could obtain no evidence of such an exchange process for $(C_5H_5)_2Sc(BH_4)$ in the same solvent over the range 30–110 °C, at which temperature extensive decomposition was evident. This result prompted us to reexamine the $(C_5H_5)_2Zr(BH_4)_2$ data since it was reported that this molecule too decomposed at elevated temperature. The strongest evidence supporting the exchange of ring and borohydride protons was in fact the solid-state thermolysis of $(C_5H_5)_2Zr(BD_4)_2$, which showed extensive formation of (BD_nH_{4-n}) groups, and it was suggested that the protons originated from the C_5H_5 rings.[23] We note that this occurs in the solid state and no direct evidence for protium–deuterium exchange was found in solution. To clarify the results in solution, a variable-temperature ^{2}H NMR study was performed on $(C_5D_5)_2Zr(BH_4)_2$ in benzene. However, no detectable incorporation of deuterium into the BH_4 groups, nor of protium into the C_5D_5 rings was observed; again, after several hours at elevated temperature, decomposition of the starting material became apparent. On the basis of these results it seems, therefore, that exchange between tetrahydroborate and π-C_5H_5 protons in solution in both the scandium and zirconium complexes is not detectable on the NMR time scale. This contrasts with the situation in $(C_5Me_5)_2ZrH_2$, where the evidence of exchange seems to be more firmly substantiated.[24] We will report data on $(C_5Me_5)_2Sc(BH_4)$ at a future time.

Tetrahydroborate as a Model for Chloride Bonding to Metals. A number of papers have addressed the problem of rationalizing whether a borohydride group would be singly, doubly, or triply bridged in a given situation. Much emphasis has been placed on steric requirements, and attempts have been made to correlate the numbers of bridging hydrogens with the metal–boron distances.[25] We have noted previously[26] that for a borohydride moiety to function as a two-, four-, or six-electron donor one must have available on the central metal, respectively, one, two, or three vacant orbitals of the correct symmetry, energy, and spatial extension. Let us clarify this point by considering first of all the bonding of a halide to a central metal and then discussing the isolobal relationship between halide and borohydride moieties.

Conventionally, we are accustomed to think of a halide ion as donating an electron pair to a central ion while the other three electron pairs in the valence shell are nonbonding. However, when the central atom clearly has a vacant orbital of the appropriate energy and symmetry, we invoke π bonding; a classic example of this type would be BF_3.[27] The opposite approach would require that a halide *always* involve three bonding electron pairs *unless* there is some factor that prevents such an interaction. That is, one tries to maximize the bonding between the metal and the halogen by placing the greatest possible amount of electron density between the two nuclei. Thus, the molecule BF is well represented by the simple Lewis diagram **1**; the charge density plots of Bader are in excellent accord with such a view.[28] Now, the approach of two more fluorines must perforce distort the electron cloud between the nuclei in BF to allow electron density to be positioned so as to bond the other two fluorines to boron. Thus, in **2** we see that the original fluorine can now donate *only* two electron pairs to the boron since no more vacant orbitals are available. Since all fluorines are actually equivalent, BF_3 is usually written in terms of three valence bond structures of this type. Of course, the more realistic MO approach would lead to a picture as in **3** whereby a boron p orbital overlaps with a linear combination of fluorine p orbitals spanning the a_2'' irreducible representation in D_{3h} symmetry.[29]



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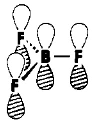

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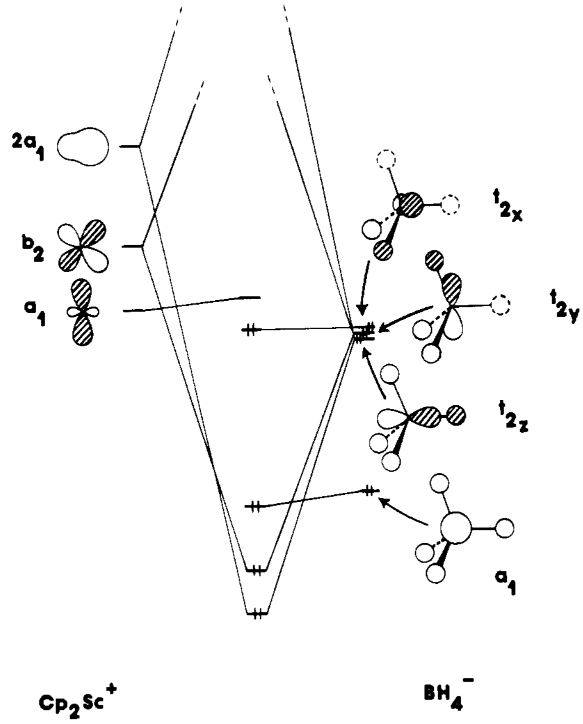
We now consider two extreme examples, viz., $TiCl_4$ and CCl_4. The former has been analyzed as a classical tetrahedral d^0 complex,[30,31] in which the bonding is described by interactions between the metal d orbitals (augmented by s and p orbitals) and symmetrized linear combinations of the s, p_x, p_y, and p_z orbitals on the ligands. The symmetry-adapted linear combinations of atomic orbitals spanning the a_1, e, t_1, and t_2 representations of the T_d point group have been depicted previously.[26] Initially, it might appear that one can construct a molecule in which the titanium has 24 electrons in its valence shell since all four chlorides are each allowed to donate 6 electrons. However, while the group orbitals derived from the 12 p orbitals of the chlorides span $a_1 + e + t_1 + 2t_2$, in fact only 9 of these group orbitals will find a symmetry match among the titanium valence orbitals (no metal orbitals transform as t_1); that is, $TiCl_4$ has a formal 18-electron configuration around titanium with the remaining 6 electrons occupying 3 nonbonding group orbitals of t_1 symmetry. Thus on average, each Cl^- ligand donates 4.5 electrons to the central titanium atom.[32] (We shall return to this point later when discussing the tetrakis(π-cyclopentadienyl) derivatives of thorium and uranium, where f-orbital participation in the bonding has been proposed.)[33]

We contrast the above situation with that of CCl_4, in which the central carbon atom is completely saturated when the ligands function purely as two-electron donors so that the ligands must of necessity each bear three nonbonding electron pairs. The gradual transition of the chloride ligand from a two- through six-electron donor is nicely reflected in the markedly decreasing quadrupole coupling constants obtained from ^{35}Cl NQR measurements for CCl_4, BCl_3, $SiCl_4$, and $TiCl_4$ of 81, 43, 41, and 12 MHz, respectively.[34-36] The involvement in the bonding of one, two, or three p orbitals leads to increasing axial symmetry along the M–Cl bond and a consequent decrease in the value of e^2qQ/h, the quadrupole coupling constant.[37]

Let us now, somewhat naively, regard the borohydride ligand as being closely analogous to the isoelectronic F^- (or O^{2-}) species except that each lone pair is now readily located since it bears a "flag" (i.e., the proton). Thus, while we can only infer when a halide ligand donates one, two, or three electron pairs, with borohydride we can actually "see" how many atoms (and hence orbitals) are involved in the bonding. We have previously reported[26] the close correspondence in the photoelectron spectra of $M(BH_4)_4$ (where M is Zr or Hf and the borohydride is triply bridged) and of $TiCl_4$, which we have already described in terms of the chlorides as six-electron donors. The PES data were also supported by EHMO–DVXα calculations following the methods of Baerends, Ellis, and Ros.[38] In a similar vein, $Al(BH_4)_3$ adopts the doubly bridged conformation[39] in accordance with the idea of Al–Cl π bonding in monomeric $AlCl_3$, as previously outlined for BF_3. We note parenthetically that the description of B_2H_6 as arising formally from the interaction of BH_2^+ and BH_4^- moieties via a double bond (i.e., BH_4^- as a four-electron donor) is an idea of some considerable vintage![40]

The correlation of the number of bridging hydrogens with orbital vacancies on the central metal is beautifully exemplified by the series of $M\cdots BH_4^-$ systems where M = Cp_2Sc^+, Cp_2Nb^+, $(OC)_4Mo$, $(OC)_5Mn^+$, $(R_3P)_3Cu^+$, $(R_3P)_2Cu^+$, and $(R_3P)Cu^+$, which we now describe.

$Cp_2Sc(BH_4)$. The three frontier orbitals of the bent Cp_2M fragment are well-known from the work of Lauher and Hoffmann,[41] and in the Cp_2Sc^+ case all three of them are vacant. We have already demonstrated above that the tetrahydroborate group is triply bridged; the six electrons donated by the BH_4^- moiety thus brings the electron count around scandium to 18. However, in this triple-bridged system we can readily identify only two strong interactions, viz., the overlaps of the b_2 and $2a_1$ metal orbitals with the appropriate borohydride orbitals derived from the t_2 orbitals quantized along the metal–boron axis, as shown by **4**.[42] The third interaction must be very weak since the only remaining BH_4^- orbital of a_1 symmetry is the low-lying totally symmetrical one. Not only is the energy match poor but also the coefficients of the hydrogen wave functions are small; i.e., the electron density is primarily in the boron 2s orbital.[43] Nevertheless, the third interaction is *not destabilizing* (it is merely nonbonding) and so a triply bridging conformation can result with the BH_4^- ligand effectively donating 4 electrons to the central metal atom; i.e., it is a 16-electron system. The weaker nature of this triply bridging interaction relative to that found in $Zr(BH_4)_4$ is reflected in the infrared frequencies associated with the B–H vibrations. Thus we note that for $Zr(BH_4)_4$ in Nujol[44] the boron–bridging-hydrogen stretches occur at 2179 and 2117 cm^{-1} while in $(C_5H_5)_2Sc(BH_4)$ in benzene solution



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[30] Ziegler, T.; Rauk, A.; Baerends, E. J. *Chem. Phys.* **1976**, *16*, 209.

[31] Foti, A. E.; Smith, V. H., Jr.; Whitehead, M. A. *Mol. Phys.* **1982**, *45*, 385.

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[33] Burns, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 3815.

[34] Livingston, R. *J. Phys. Chem.* **1953**, *57*, 496.

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[36] Hamlen, R.; Koski, W. S. *J. Chem. Phys.* **1956**, *25*, 360.

[37] Lucken, E. A. C. "Nuclear Quadrupole Coupling Constants"; Academic Press: London, 1969; pp 250–251.

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[39] Almenningen, A.; Gundersen, G.; Haaland, A. *Acta Chem. Scand.* **1968**, *22*, 328.

[40] For a summary of the early approaches to this problem, see: Wade, K. "Electron Deficient Compounds"; Nelson: London, 1971; pp 14–21.

[41] Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

[42] It should be noted that in this diagram, and those following, the symmetries of the frontier MO's of the interacting fragments are those pertaining to the isolated fragments so that the symmetries of the MO's of the resulting moieties are generally lower and may be obtained from correlation tables.

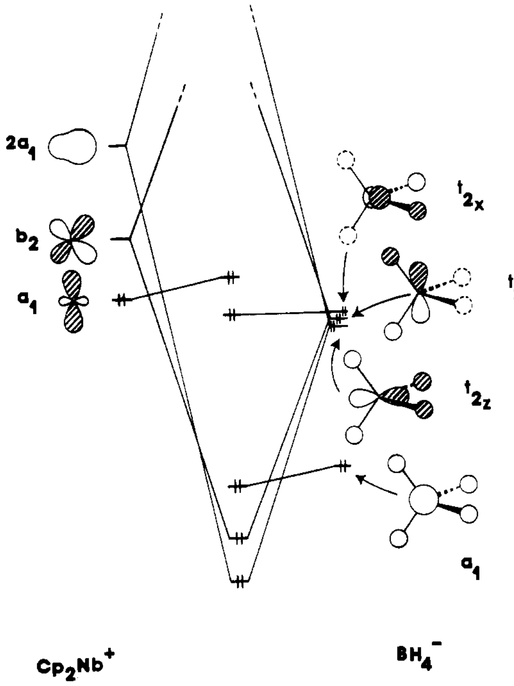
[43] Hegstrom, R. A.; Palke, W. E. Lipscomb, W. N. *J. Chem. Phys.* **1967**, *46*, 920.

[44] Marks, T. J.; Kennelly, W. J.; Kolb, J. R.; Shimp, L. A. *Inorg. Chem.* **1972**, *11*, 2540.

they are found at 2180 and 2130 cm^{-1}, i.e., to marginally higher frequencies. This reflects somewhat stronger boron–hydrogen bonding in $(C_5H_5)_2Sc(BH_4)$ than in $Zr(BH_4)_4$ because of greater donation to the complement of bonding electrons in the latter (4.0 vs. 4.5 electrons/BH_4^-, respectively).[32] More convincingly, perhaps, it is clear that the terminal hydrogens are then held more strongly to the boron in $Zr(BH_4)_4$ than in $(C_5H_5)_2Sc(BH_4)$, as shown by frequencies of 2560 and 2490 cm^{-1}, respectively.

Very recently Lappert et al. have reported[3b] that substitution of two trimethylsilyl groups into each cyclopentadienyl ring leads to a doubly bridged structure; undoubtedly the large steric effects of the Me_3Si groups play an important role here. This is analogous to the occurrence of $(C_5Me_5)_2ZrH_2$ as a monomer[24] while $(C_5H_5)_2ZrH_2$ is dimeric.[12] Lappert et al. also claim that in their molecule the BH_4^- moiety is not fluxional at low temperature on the NMR time scale since the ^{11}B spectrum is broad at room temperature but sharpens to give a 1:4:6:4:1 quintet at high temperature. Their interpretation is questionable, and the broadness may well be due to quadrupolar effects.

$Cp_2Nb(BH_4)$. The difference between this molecule and the $Cp_2Sc(BH_4)$ just discussed is the presence of two extra metal electrons, which are accommodated in the lowest of the three Cp_2M frontier orbitals (a_1). There are now *only two* vacant orbitals into which the tetrahydroborate ligand can donate, and consequently the double bridged structure results (**5**).[45]



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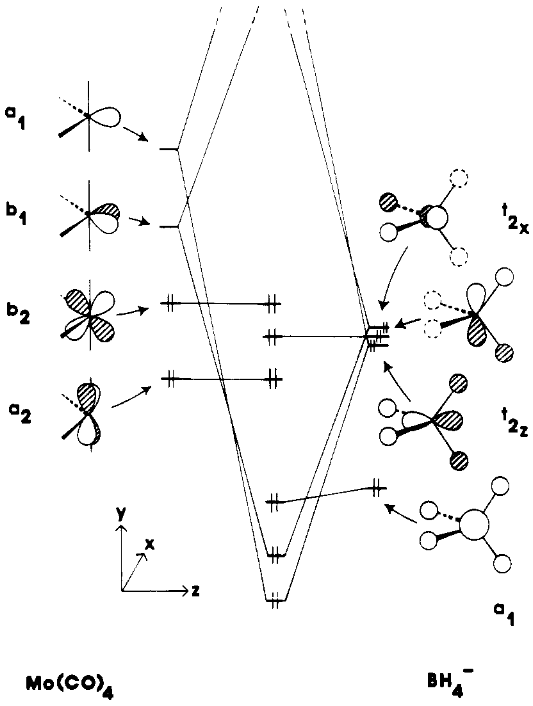
$(OC)_4Mo(BH_4)^-$. The electronic structure of ML_4 fragments with C_{2v} symmetry has been extensively studied;[46] for the d^6 $Mo(CO)_4$ moiety the two vacant frontier orbitals (a_1, b_1) are depicted below together with the two highest occupied MO's and provide a rationale not only for the dibridged nature of the linkage but also for its orientation in the *xz* plane (**6**). Furthermore, it is in these d^6 cases that the fluxional process, which interchanges bridging and terminal hydrogens, can be made slow on the NMR time scale.[16c] Presumably, the destabilizing interaction encountered when the BH_4^- moiety is rotated through 90° about the *z* axis (which brings two filled orbitals into close proximity) increases the activation energy for the exchange process. Similar arguments can be made for the isoelectronic $(Me_3P)_4MoH(BH_4)$.[47]



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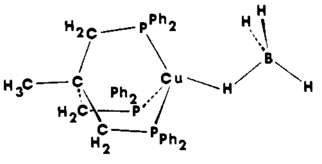
$(OC)_5Mn(BH_4)$. The d^6 $Mn(CO)_5^+$ fragment has only a single vacant frontier orbital[48] and would thus be expected to give rise to a monobridged borohydride complex. The available data[49,50] on $(OC)_5Mn(BH_4)$ and on $[(C_6H_{11})_3P]_2Ru(H)(CO)_2BH_4$ are in accord with this picture.

$(R_3P)_nCu(BH_4)$. The d^{10} Cu^+ system predominantly adopts the tetrahedral geometry as typified by $CH_3C(CH_2PPh_2)_3CuCl$. Replacement of chloride by tetrahydroborate (**7**) would be expected to lead to the monobridged isomer and indeed it does![51] It is gratifying to note that the analogous cobalt complex, viz., $CH_3C(CH_2PPh_2)_3Co(BH_4)$ (**8**), is isomorphous with **7** and has almost identical unit cell parameters yet the tetrahydroborate is double bridged to cobalt.[52] We can see clearly now that this is not a steric effect causing differing bonding modes of the the BH_4^- ligand, but rather a reflection of the versatility of the borohydride ligand in maximizing its bonding interactions with the d^8 cobalt atom



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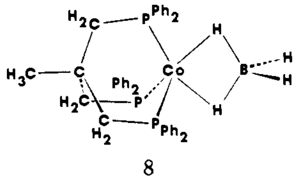

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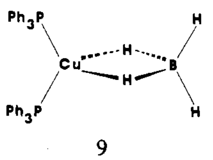

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(46) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.

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(48) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

(49) Bird, P. H.; Wallbridge, M. G. H. *Chem. Commun.* **1968**, 687.

(50) Holah, D. G.; Hughes, A. N.; Hui, B. C. *Can. J. Chem.* **1976**, *54*, 320.

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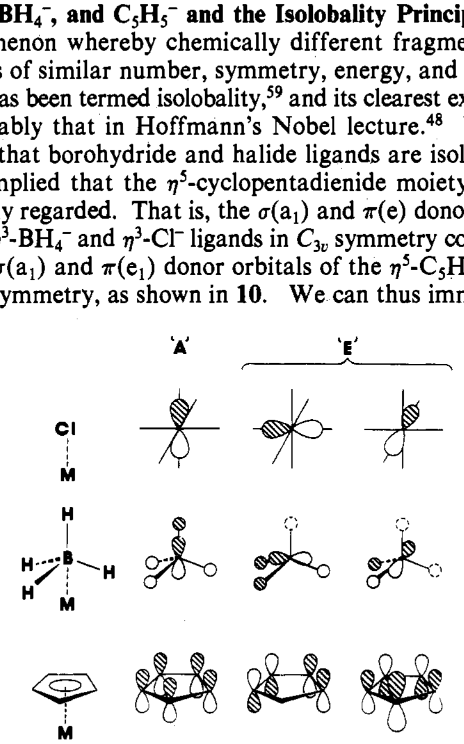
while being limited to the formation of only a single bond to the d^{10} copper center. In keeping with this trend, the 14-electron $(Ph_3P)_2Cu^+$ moiety can accept two electron pairs from the tetrahydroborate as in **9**.[53] One might thus venture a prediction that a 12-electron fragment bearing a single positive charge would triply bridge to a borohydride moiety; an obvious candidate here is $(Ph_3P)Cu^+$, and we will report experimental data on this system at a future time.

The above series of molecules exemplifies clearly the capacity of the tetrahydroborate ligand to donate two through six electrons to a central metal depending on the number of vacant metal orbitals of suitable energy and symmetry. There are, however, two caveats to bear in mind when drawing analogies between BH_4^- and halide ligands. First, the steric requirements of the BH_4^- fragment[54] are obviously more stringent than those of chloride, so, for a mono(tetrahydroborate) complex, one can only predict a maximum possible number of bridging hydrogens in a given case and the experimentally observed number may occasionally be less but should never be more. In compounds in which two or more tetrahydroborates are bonded to the same metal, the situation can be complicated since a compromise of maximum orbital overlap and minimum stereochemical crowding must be achieved. This is nicely exemplified in the molecule $(C_5H_4CH_3)_2Hf(BH_4)_2$, for which a neutron diffraction study has been reported.[55] The frontier orbitals of $(C_5H_4CH_3)_2Hf^{2+}$ are the same as are given above, in **4**, for Cp_2Sc^+; now if each borohydride were to donate just two electrons via a single hydrogen bridge, a 16-electron system would result. This would leave an unfilled frontier orbital, which, in principle, could accept electrons via a π-type interaction if one tetrahydroborate becomes doubly bridged. However, given the propensity of borohydrides to be bonded equivalently, if possible, the problem is solved in this case by both borohydrides adopting double bridged conformations but showing considerable distortion. In each BH_4^- unit there is a bridging hydrogen in the plane that bisects the methylcyclopentadienyl rings and contains the hafnium and boron atoms. The other bridging hydrogen atom of each borohydride ligand lies at a greater distance from the metal and out of this plane so that the local symmetry is C_2 rather than C_{2v}. In essence, a compromise is reached such that each BH_4^- ligand forms a σ bond to the metal and each contributes partially to the π-type interaction. The overall effect is to fill the three frontier orbitals of the Cp_2Hf^{2+} unit yet minimize the steric problems that would arise from having two coplanar doubly bridging tetrahydroborates. Indeed, such a twisted conformation had been proposed by Lauher and Hoffmann some years previously.[41] One can only speculate on the bonding in Cp_2HfCl_2, where the orientation of the bonding orbitals cannot be directly observed. The second caveat recognizes that structures of chlorides and borohydrides are not always comparable because of the proclivity of chloride to occur in bridging sites between metal centers.[56] Thus, although $Cp_2Sc(BH_4)$ is monomeric with a triple hydrogen bridge, crystallographic data for bis(cyclopentadienyl)scandium chloride show it to be dimeric;[57] a similar situation occurs for $Al(BH_4)_3$[39] and Al_2Cl_6.[58] One might rather tentatively propose that in the monomeric chloro compounds the supposed lone pairs used in π bonding to the metal are less firmly held than are the electrons in the B–H σ bonds. Hence the π bonds in the chloro compounds are more basic and are better able to donate to a second metal center than are electrons that even while bonding a metal to a boron are still closely associated with a proton. In any event, PES data show the "π-bonding electrons" in $TiCl_4$ to have slightly lower binding energies than do the corresponding ones in $Zr(BH_4)_4$.[26]

Cl^-, BH_4^-, and $C_5H_5^-$ and the Isolobality Principle. The phenomenon whereby chemically different fragments have orbitals of similar number, symmetry, energy, and extent in space has been termed isolobality,[59] and its clearest explication is probably that in Hoffmann's Nobel lecture.[48] We have shown that borohydride and halide ligands are isolobal and have implied that the η^5-cyclopentadienide moiety may be similarly regarded. That is, the $\sigma(a_1)$ and $\pi(e)$ donor orbitals of the η^3-BH_4^- and η^3-Cl^- ligands in C_{3v} symmetry correspond to the $\sigma(a_1)$ and $\pi(e_1)$ donor orbitals of the η^5-$C_5H_5^-$ ligand in C_{5v} symmetry, as shown in **10**. We can thus immediately transfer the results for $TiCl_4$ to the pseudotetrahedral Cp_4Th[60] (or Cp_4U,[61] if the extra two electrons reside in the 5f shell). In these molecules, the central actinide need not have 24 electrons in its valence shell since only 9 of the group orbitals derived from the $C_5H_5^-$ ligands will find a symmetry match among the metal s, p, and d orbitals. It is now apparent that the bonding modes in UCl_4, $(\eta^3\text{-}BH_4)_4U$,[62] and $(\eta^5\text{-}C_5H_5)_4U$ are not as different as one might at first sight envisage. However, as we decrease the size of the central metal, the steric bulk of the η^5-C_5H_5 group becomes an important factor. Thus, although MCl_4 and $(\eta^3\text{-}BH_4)_4M$, where M is Zr or Hf, have T_d symmetry,[63,64] the Cp_4M complexes do not. It is clear that there is only a small η^1–η^5 interconversion barrier in these Cp_4M systems since (a) the X-ray crystallographically determined structures are $(\eta^5\text{-}C_5H_5)_2Hf(\eta^1\text{-}C_5H_5)_2$[65] and $(\eta^5\text{-}C_5H_5)_3Zr(\eta^1\text{-}C_5H_5)$[66] and (b) the molecules are highly flux-



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(53) Lippard, S. J.; Melmed, K. M. *Inorg. Chem.* **1967**, *6*, 2223.

(54) Typically, in $Sc(BH_4)_3 \cdot 2THF$, only two of the tetrahydroborates triple bridge while the third is double bridged.[17]

(55) Johnson, P. L.; Cohen, S. A.; Marks, T. J.; Williams, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 2709.

(56) An example of a bridging tetrahydroborate ligand has very recently been crystallographically characterized: Holah, D. G.; Hughes, A. N.; Maciaszek, S.; Magnuson, V. R. *J. Chem. Soc., Chem. Commun.* **1983**, 1308.

(57) Smith, K. D.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1972**, 593.

(58) Wade, K.; Banister, A. J. In "Comprehensive Inorganic Chemistry"; Bailar, J. C., Jr., Emeléus, H. J., Nyholm, R. S., Trotman-Dickenson, A. F., Eds.; Pergamon Press: Oxford, 1973; Vol. 1, p 1013.

(59) (a) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058. (b) Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Ibid.* **1976**, *15*, 1148. (c) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585.

(60) Fischer, E. O.; Triebner, A. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1962**, *17B*, 276.

(61) Fischer, E. O.; Hristidu, Y. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1962**, *17B*, 275.

(62) $(\eta^3\text{-}BH_4)_4U$ is tetrahedral in the vapor phase but not in the solid state: Bernstein, E. R.; Hamilton, W. C.; Keiderling, T. A.; LaPlaca, S. J.; Lippard, S. J.; Mayerle, J. J. *Inorg. Chem.* **1972**, *11*, 3009.

(63) (a) Bird, P. H.; Churchill, M. R. *Chem. Commun.* **1967**, 403. (b) Plato, V.; Hedberg, K. *Inorg. Chem.* **1971**, *10*, 590.

(64) Broach, R. W.; Chuang, I.-S.; Marks, T. J.; Williams, J. M. *Inorg. Chem.* **1983**, *22*, 1081.

(65) Rogers, R. D.; Bynum, R. V.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 692.

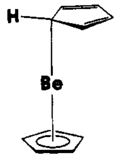
ional.[67,68] It has previously been noted that $(\eta^5\text{-}C_5H_5)_3Zr(\eta^1\text{-}C_5H_5)$ is an 18-electron system;[41] similar reasoning applies to the $(C_5H_5)_3MoNO$ system studied by Cotton[69] in the hope of freezing out the C_5H_5 rings in the η^1, η^3, and η^5 bonding modes. Now as we continue to decrease the size of the group 4 metal, we see that $(C_5H_5)_4Ti$ can be frozen out on the NMR time scale.[70] Presumably, the formation of $(\eta^5\text{-}C_5H_5)_3Ti(\eta^1\text{-}C_5H_5)$ is sterically disfavored and so raises the activation energy into the NMR-accessible region. We note also that the tetrakis(tetrahydroborate) of Ti is not synthesizable and $TiCl_4$ and $LiBH_4$ yield $Ti(BH_4)_3$;[71] of course, the tetrachloride has no steric problems and $TiCl_4$ adopts the expected T_d geometry.

If the frontier orbitals of the η^5-cyclopentadienyl group and a halogen are indeed as similar as is proposed above, then there should be some electronic properties in which they closely resemble each other. It is interesting to note that, viewed from the perspective of the zirconium nucleus, the C_5H_5 and Br fragments in $(C_5H_5)_2ZrBr_2$ are virtually indistinguishable.[68] Thus, the ^{91}Zr NMR spectrum of this molecule yields a surprisingly sharp resonance more typical of the line widths encountered in molecules such as $Zr(BH_4)_4$, where the quadrupolar zirconium nucleus is in a cubic point group.[4]

The isolobality of Cl^- and Cp^- fragments is also clearly seen in the structures of Cp_2M and MCl_2, where M is Ge, Sn, and Pb, and all these molecules have similar bent geometries (**11**).[72]

11

Other nice examples are seen in beryllium chemistry; at −120 °C,[73] $(C_5H_5)_2Be$ is not D_{5h} or D_{5d} like a conventional metallocene but instead has one regular η^5 ring while the other parallel ring is variously described as σ bonded, "slipped", or ionically bonded (**12**). Since the maximum number of available acceptor orbitals on beryllium is four,[74] one might formally assign the molecule as $(\eta^5\text{-}C_5H_5)Be(\eta^1\text{-}C_5H_5)$. At room temperature[75] the two C_5H_5 rings are still parallel, but less "slipped", while an electron diffraction study of the vapor (~70 °C) shows that the molecule has parallel but staggered C_5H_5 rings, with the beryllium somewhat closer to one of them (giving C_{5v} symmetry).[76,77] The molecule appears to be heading toward a D_{5d} structure where each of the (formal) $C_5H_5^-$ rings donates four electrons to the (formal) Be^{2+}, with the other four electrons in a nonbonding e_{1g} group orbital. This behavior is somewhat reminiscent of the $(C_5H_5)_4M$ species discussed above and has been the subject of a number of theoretical treatments.[78-80] Other examples (**13**) include $BeCl_2$,[81] $(C_5H_5)BeCl$,[82] and $(C_5H_5)Be(BH_4)$,[83] the last having a dibridged tetrahydroborate moiety.[84] Formally, gaseous, monomeric $BeCl_2$ could be written $(\eta^2\text{-}Cl)_2Be$, while the BH_4^- fragment in $(C_5H_5)Be(BH_4)$ would appear to be a four-electron donor, as would then be the $C_5H_5^-$ group. The $(C_5H_5)Be$ fragment is indeed indistinguishable from the related fragment in $(C_5H_5)_2Be$, as is that in $(C_5H_5)BeCl$; this suggests that, like BH_4^- above, chloride is also a four-electron donor here. A less ambiguous case in which the chloride and tetrahydroborate ligands are closely analogous in structure, and presumably in bonding, is the trimetallic system **14** with bridging *tert*-butoxy groups.[85] Furthermore, we note that the doubly bridging BH_4^- moiety in $(Et_2O)_2Li(BH_4)$[86] again satisfies the tetrahedral requirement for the central metal (**15**).



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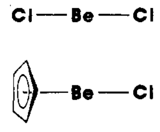

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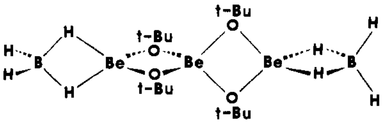

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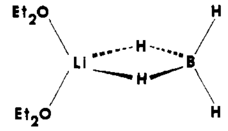

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One should perhaps finish with a prediction.[87] The molecule $Fe(BH_4)_2$ was synthesized some years ago, but its thermal stability is low.[88] By analogy with ferrocene, it should contain two triply bridging tetrahydroborate moieties. One might even visualize such a molecule as being based on octahedral FeH_6^{4-} with two opposed triangular faces capped by BH^{2+} units, giving a molecule of D_{3d} symmetry. We hope to report some new data on this molecule at a future time.

Concluding Remarks

It has been shown that the number of bridging hydrogens through which a tetrahydroborate moiety can bond to a metal correlates with the number of vacant metal orbitals of suitable energy and symmetry. This electronic factor can predominate over steric effects as in $L_3Co(BH_4)$ and $L_3Cu(BH_4)$, which have almost identical gross structures yet have different numbers of bridging hydrogens. For systems in which several BH_4 units are bonded to a single metal center, one must consider the group orbitals that allow the tetrahydroborate moieties to maximize their bonding to the central metal.

It had previously been noted[44] that doubly bridging BH_4^- groups resemble the allyl ligand in their bonding capabilities; we show here that triply bridging BH_4^- groups are closely analogous to the $\eta^5\text{-}C_5H_5^-$ functionality.

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Registry No. $Cp_2Sc(BH_4)$, 88968-66-5; $Sc(BH_4)_3\cdot 2THF$, 63312-92-5; $Y(BH_4)_3$, 72033-96-6; $(C_5D_5)_2Zr(BH_4)_2$, 88968-67-6; $ScCl_3$, 10361-84-9; $LiBH_4$, 16949-15-8; cyclopentadienylthallium, 34822-90-7.

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