Covalent Transition Metal, Lanthanide, and Actinide Tetrahydroborate Complexes

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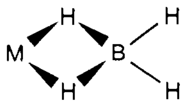
I. Introduction

The tetrahydroborate[1,2] ion, BH_4^-, is the simplest known anionic boron hydride. Among its diverse chemical properties is the tendency to form unusual covalent (i.e., volatile, soluble in nonpolar solvents) complexes with transition metals, lanthanides, and actinides. The ligation is invariably through bridging hydrogen atoms, as exemplified below.



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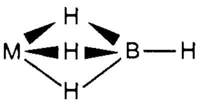


tridentate coordination

The chemical and physical nature of such compounds has been of current interest to inorganic and organometallic chemists both within the general context of studying how metals activate small, electron-rich ligands, and also because the unique configuration of the ligand-metal bond may be related to important species in catalytic transformations. How the chemical and electronic properties of the hydride bridging system respond to variation of metal and accompanying ligands may provide some insight into metal-to-substrate and reductant-to-metal hydride transfer processes. Since BH_4^- and CH_4 are isoelectronic, prototype structures for saturated hydrocarbon activation are also presented. In a more technical vein, several metal tetrahydroborates have been shown to be hydrogenation and polymerization catalysts.

It is the purpose of this article to review and analyze recent developments in the field of covalent transition metal, lanthanide, and actinide BH_4^- complexes. The approach will be both chemical and physicochemical, so that recent developments in the chemistry can be presented in the light of new results in spectroscopy, molecular dynamics, and bonding theory. Our choice of topics is not intended to demean the relative importance of salt-like ionic tetrahydroborates, which are of great utility as selective reducing agents. That area along with earlier work on metal complexes was discussed in detail in a previous (1970) review.[8] Other treatises on ionic tetrahydroborates are also available,[9,10] as are earlier reviews on metal complexes.[10] By restricting the scope to d and f transition metals, we have chosen to focus upon main group tetrahydroborates (e.g., $Be(BH_4)_2$) only to the extent that they provide models and points of reference for the various characteristics of the complexes under discussion. The chemical scope of this review is indicated by Figure 1, which summarizes the metals for which covalent BH_4^- complexes have been prepared and characterized.

This review begins with a discussion of synthetic methods and the chemical properties of known tetrahydroborates. Structural characterization by vibrational spectroscopy and nuclear magnetic resonance are next presented, along with discussion of bonding trends as deduced from the spectral features, and of the marked propensity for stereochemical nonrigidity in these systems. The section on structural studies further quantifies the geometric parameters associated with the metal-ligand interaction. Finally, a discussion of the bonding in covalant metal tetrahydroborates is presented with the goal being the qualitative correlation of chemical and physical properties with bonding theory. It is hoped that the methods and ideas put forth in this article will serve both as a guide and as an impetus to further research in the field.

II. Syntheses and Chemical Properties of Metal Tetrahydroborate Complexes

By far the greatest number of covalent metal tetrahydroborate complexes has been prepared by the simple substitution of a BH_4^- group for, in most cases, a halide ion. Quite often it is necessary to use an excess of the ionic alkali tetrahydroborate or other hydroboration agent to effect complete substitution. In a number of cases substitution by a tetrahydroborate ligand for a halide has been accompanied by a corresponding reduction in the oxidation state of the metal ion, most frequently from a state of $+n$ to $+n - 1$.

This section will detail the synthesis of covalent metal (transition, lanthanide, and actinide) tetrahydroborate complexes. Where the authors consider it to be of import, chemical and physical properties of the complexes will be described. Each

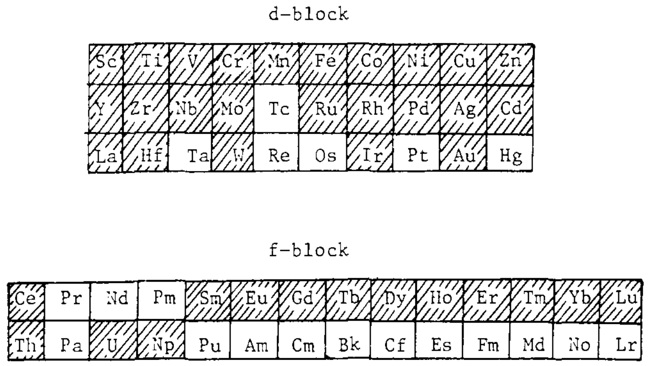


Figure 1. Transition metals and lanthanide and actinide metals for which tetrahydroborate complexes exist (cross-hatching).

triad of the transition elements will be considered in order. Lanthanide and actinide tetrahydroborates will be grouped together at the end of this section.

A. Scandium, Yttrium, Lanthanum

The only tetrahydroborate complex of scandium was obtained by the treatment of anhydrous $ScCl_3$ with a slight excess of $LiBH_4$ in tetrahydrofuran (THF) at room temperature. The volatile white solid was readily sublimable at 80 °C. Mass spectrometric studies confirmed the formulation as $Sc(BH_4)_3 \cdot THF$.[11] Although not a homoleptic tetrahydroborate complex due to the Lewis acidity of the scandium(III) ion[12] and its subsequent ability to coordinate to the oxygen atom of THF, this is nonetheless a covalent compound.

The only tetrahydroborate complex of yttrium was formed by the reaction of lithium tetrahydroborate with YCl_3 in THF.[13] This leads to the formation of $YCl(BH_4)_2$. At 100–200 °C, the chlorobis(tetrahydroborate) decomposes and disproportionates to $Y(BH_4)_3$ and $YCl_2(BH_4)$ as in the reaction[13b]

$$2YCl(BH_4)_2 \xrightarrow{>100\ ^\circ C} YCl_2(BH_4) + Y(BH_4)_3 \qquad (1)$$

Thus, three tetrahydroborates are formed ultimately from a single reaction. Reaction of the $YCl(BH_4)_2$ species with sodium methoxide yields the compound $(CH_3O)_2Y(BH_4)$.[13c]

A different route to the preparation of a lanthanum tetrahydroborate complex was taken by Klejnot.[14] He reacted diborane with lanthanum(III) alkoxides in tetrahydrofuran to yield lanthanium(III) tris(tetrahydroborate). Physical and chemical data for this species are sparse.

B. Titanium, Zirconium, Hafnium

More tetrahydroborate complexes exist for this triad than for any other grouping of transition metals, lanthanides, or actinides. Homoleptic tetrahydroborates exist for all three metals, i.e., $M(BH_4)_n$, where n may be 3 when M = Ti, and $n = 4$ when M = Zr or Hf. The first of these, tris(tetrahydroborato)titanium(III), $Ti(BH_4)_3$, was prepared by the reaction of a twofold excess of $LiBH_4$ with $TiCl_4$ vapor.[15a] Parallel reduction of Ti(IV) to Ti(III) accompanies substitution and $Ti(BH_4)_3$ is formed. Three independent research groups have published reports indicating that the synthesis is not as straightforward as ref 15a indicates.[10a,16,17] In addition, yields of this compound are minimal with $ClTi(BH_4)_2$ formed as a by-product. $Ti(BH_4)_3$ is reported to be a volatile green solid which is highly air sensitive and which decomposes autocatalytically at 25 °C to form a metallic mirror as well as hydrogen.

James and Wallbridge have treated titanium(IV) tetrabutoxide with diborane in tetrahydrofuran solution to form the complex $Ti(BH_4)_2(OC_4H_9) \cdot (OC_4H_8)$.[16] In this case, just as when simple substitution of $TiCl_4$ by BH_4^- was attempted, substitution is accompanied by corresponding reduction of the metal to yield a formal titanium(III) complex.

The reaction of tris(tetrahydroborato)aluminum(III) with titanium tetrachloride yields the compound bis(tetrahydroborato)titanium chloride[15a] (eq 2). $Ti(BH_4)_2Cl$ is a deep-blue solid which was reported to be moderately volatile at 25 °C.

$$2TiCl_4 + 3Al(BH_4)_3 \rightarrow 2TiCl(BH_4)_2 + 3AlCl_2(BH_4) + B_2H_6 + H_2 \qquad (2)$$

Nöth has noted[15c] that the reaction of titanium tetrahalides (where the halide may be chloride, bromide, or iodide) with $LiBH_4$ in pentane yields a dimeric, blue $[(BH_4)_2TiX]_2$ (eq 3) species where the mononuclear subunits are joined by two bridging halide ions. These dimeric species may be cleaved by ether yielding the compounds $(BH_4)_2TiX(O(C_2H_5)_2)$. The use of tetrahydrofuran (THF) as a solvent, however, results in the dissociation of the dimer into $Ti(BH_4)_3 \cdot 2(THF)$ and $TiX_3 \cdot n(THF)$, where n is an integral number.

$$TiX_4 + \text{excess } LiBH_4 \rightarrow [(BH_4)_2TiX]_2 \qquad (3)$$

Zirconium and hafnium tetrakis(tetrahydroborate) are very similar chemically and structurally (see section V). The initial synthesis of these complexes was a solid-phase reaction between $ZrCl_4$ or $HfCl_4$ and an excess of lithium tetrahydroborate (eq 4).[17,18]

$$MCl_4 + 4LiBH_4 \rightarrow M(BH_4)_4 + 4LiCl \quad (M = Zr, Hf) \qquad (4)$$

An alternative, but less convenient synthesis of these compounds is the reaction of the pentafluorometalate anion with excess $Al(BH_4)_3$[15a] as in eq 5.

$$NaMF_5 + 2Al(BH_4)_3 \rightarrow M(BH_4)_4 + 2AlF_2(BH_4) + NaF \qquad (5)$$

Factors influencing relative yields in both (4) and (5) are unclear. Recently a more facile and higher yield synthesis of $Zr(BH_4)_4$ was published.[19] This was a variation of reaction 4 with enough diethyl ether being added to form a slurry. The final purification step of the reaction was carried out on a vacuum line and yields were consistently 80% or greater. A similar variation has been applied to the preparation of $Hf(BH_4)_4$ utilizing an almost catalytic amount of diethyl ether.[20]

$Zr(BH_4)_4$ and $Hf(BH_4)_4$ are extremely similar in chemical properties. Both are highly volatile colorless solids, melting around room temperature, inflaming in air, and hydrolyzing with explosive rapidity. When allowed to stand at 25 °C they slowly decompose, liberating hydrogen gas.

An interesting addendum to the work on homoleptic group 4A metal tetrahydroborates is the fact that monoanionic species, i.e., $M(BH_4)_n^-$, may be formed for all three metals.[21] In the case of titanium, it appears that the reason for consistently poor yields of the compound $Ti(BH_4)_3$ which ensue when $LiBH_4$ and $TiCl_4$ are reacted in diethyl ether is the formation of the ionic compound $Li[Ti(BH_4)_4] \cdot O(C_2H_5)_2$.[10a] Presumably the coordination geometry about titanium is, as it is in $Zr(BH_4)_4$ and $Hf(BH_4)_4$ (see section V), dodecacoordinate. Four tridentate tetrahydroborate groups would account for this. In addition, $Zr(BH_4)_4$ and $Hf(BH_4)_4$ yield the ionic species $Li[Hf(BH_4)_5]$ and $Li[Zr(BH_4)_5]$[21] when treated with $LiBH_4$ in ether (eq 6).

$$LiBH_4 + M(BH_4)_4 \rightarrow Li[M(BH_4)_5] \quad M = Zr, Hf \qquad (6)$$

It is interesting to speculate on the geometry which would be adopted by the complex anions in these species. Will each of the tetrahydroborate units remain tridentate or will this sterically inhibited environment force some or all of the BH_4 units to function as bidentate ligands? Hopefully crystals suitable for diffractometric investigations will be available in order to answer this particularly fascinating question. Infrared spectra (see section III) seem to indicate the adaptation of bidentate modes of bonding for the tetrahydroborate ligands in the complex anions.[21] The hafnium complex forms more readily than does the zirconium complex. Increased Lewis acidity of hafnium toward the base BH_4^- was the explanation given for this behavior.[21] Both complexes are thermally unstable decomposing above ca. −20 °C. Another similar method of preparation is the treatment of the tetrakistetrahydroborates with either tetrabutylammonium tetrahydroborate or trioctylpropylammonium tetrahydroborate in ether to form, in turn, the corresponding tetraalkylammonium pentakis(tetrahydroborato) metalates. The properties of these complex ionic species are quite similar to the simpler $Li[M(BH_4)_5]$ species.[21]

Another interesting reaction which $Zr(BH_4)_4$ undergoes is given by the equation:

$$Zr(BH_4)_4 + 4LiAlH_4 \rightarrow Zr(AlH_4)_4 + 4LiBH_4 \qquad (7)$$

The metathetic reaction amounts to a simple replacement of the tetrahydroborate units by tetrahydroaluminate ligands. This complex exhibits thermal instability, decomposing in a few hours when allowed to remain at room temperature.[17]

The treatment of $Zr(BH_4)_4$ with tetraalkylammonium salts of $B_2H_7^-$ (eq 8) results once again in the formation of the complex anion $[Zr(BH_4)_5^-]$.[21] The facet of greatest interest is the observation that Zr^{4+} is functioning as a Lewis acid with an acidity in excess of that exhibited by BH_3.

$$(R_4N^+)(B_2H_7^-) + Zr(BH_4)_4 \rightarrow [R_4N^+][Zr(BH_4)_5^-] + \tfrac{1}{2}BH_3 \qquad (8)$$

The reaction of the organometallic complex bis(cyclopentadienyl)titanium(IV) dichloride with a twofold excess of lithium tetrahydroborate yields bis(cyclopentadienyl)titanium(III) tetrahydroborate:[22]

$$2(\eta^5\text{-}C_5H_5)_2TiCl_2 + 4LiBH_4 \rightarrow 2(\eta^5\text{-}C_5H_5)_2Ti(BH_4) + 4LiCl + B_2H_6 + H_2 \qquad (9)$$

The product is purified by sublimation and is isolated as a highly air-sensitive, paramagnetic, violet solid. It has been fully characterized spectroscopically and crystallographically (see section V), and the tetrahydroborate group is bidentate.

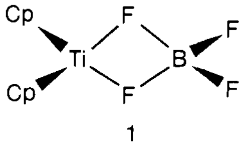
$(C_5H_5)_2TiBH_4$ undergoes a number of interesting substitution reactions whereby the BH_4^- ligand may be replaced. The first of these is given by

$$(C_5H_5)_2TiBH_4 + BX_3 \rightarrow (C_5H_5)_2TiX \qquad (10)$$

In this case the BX_3 may be either BCl_3 or BBr_3.[22] When $(C_5H_5)_2TiBH_4$ is treated with boron trifluoride etherate (eq 11),

$$3(C_5H_5)_2TiBH_4 + 4BF_3 \cdot O(C_2H_5)_2 \rightarrow 3(C_5H_5)_2TiBF_4 \qquad (11)$$

the tetrahydroborate ligand is in essence replaced by a tetrafluoroborate ligand. This light blue complex is extremely sensitive to atmospheric oxidation and moisture. The compound is monomeric in dioxane. Nöth and Hartwimmer proposed a bidentate BF_4 ligand but, other than analytical results, no further data were presented.[22] The proposed structure is given as 1.



1

A compound similar to $(C_5H_5)_2TiBH_4$ has been prepared by the reaction of cyclopentadienyltitanium(IV) trichloride with a threefold excess of lithium tetrahydroborate to yield cyclopentadienyltitanium(III) bis(tetrahydroborate):[23]

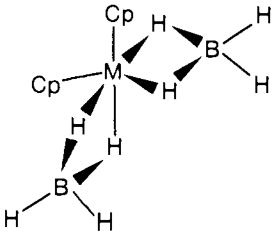
$$2(\eta^5\text{-}C_5H_5)TiCl_3 + 6LiBH_4 \rightarrow 2(\eta^5\text{-}C_5H_5)Ti(BH_4)_2 + 6LiCl + B_2H_6 + H_2 \qquad (12)$$

This compound is a volatile green solid which melts below room temperature and has moderate thermal stability.

Unlike the corresponding titanium(IV) compounds, zirconium and hafnium compounds do not undergo reduction when reacted with excess $LiBH_4$. For example, when the compound $(\eta^5\text{-}C_5H_5)_2MCl_2$, where M = Zr or Hf, is reacted with a twofold excess of lithium tetrahydroborate (eq 13),[24] the bis(tetrahydroborate) compounds are formed[18] in contrast to the mono(tetrahydroborate) formed where M = Ti.[13] In addition to these products a volatile chlorotetrahydroborate, $(C_5H_5)_2ZrCl(BH_4)$, is formed when stoichiometric amounts of the reactants are used.[24] Each

$$(C_5H_5)_2MCl_2 + 4LiBH_4 \rightarrow (C_5H_5)_2M(BH_4)_2 \qquad (13)$$

of these three compounds is purified by vacuum sublimation above 110 °C, which results in some loss of product. Circumvention of this difficulty has recently been achieved[19] by precipitation of the pure product from a filtered benzene solution of the reactants upon addition of petroleum ether. Yields by this method are typically in excess of 70%. A plausible structure for these complexes is illustrated as **2**.



2

The reaction of $(C_5H_5)_2M(BH_4)_2$ with a twofold excess of trimethylamine in benzene yields a white polymeric solid formulated as $[(C_5H_5)_2ZrH_2]_n$ and, when equimolar amounts of reactants are employed, yields a volatile colorless solid, $(C_5H_5)_2Zr(H)BH_4$, purified by vacuum sublimation at 50 °C.[25] This abstraction of BH_3 by $(CH_3)_3N$ is in contrast to the behavior of $(C_5H_5)_2Ti(BH_4)$ which does not react with trialkylamines to form the corresponding hydrides.[25] Facinetti et al.[204] have recently reported that the reaction of $(C_5H_5)_2TiBH_4$ or $(C_5H_5)_2Zr(BH_4)_2$ with carbon monoxide and triethylamine in benzene yields $(C_5H_5)_2Ti(CO)_2$ or $(C_5H_5)_2Zr(CO)_2$, respectively. The mechanism of this highly interesting reductive process is unknown.

A number of borodeuterides of titanium, zirconium, and hafnium, e.g., $Zr(BD_4)_4$,[26] $(C_5H_5)_2Ti(BD_4)$,[27] $(C_5H_5)_2Zr(BD_4)_2$,[27] and $(C_5H_5)_2Hf(BD_4)_2$,[27] were prepared in identical manners to the undeuterated compounds. For the most part, these complexes were prepared in order to compare the spectroscopic properties of the deuterated complexes with the undeuterated complexes.[26,27]

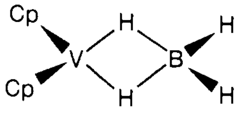
C. Vanadium, Niobium, Tantalum

There are relatively few tetrahydroborate complexes of vanadium and niobium and none of tantalum known at present. The first and, as yet, still unconfirmed synthesis of a vanadium tetrahydroborate was the treatment of vanadium alkoxides with diborane to give the molecular species $V(BH_4)_3$.[10a] Properties of the compound are unreported.

Quite recently the preparation of an organometallic species, $(\eta^5\text{-}C_5H_5)_2V(BH_4)$, was reported.[28] The synthesis was quite similar to that of the corresponding titanium compound, $(\eta^5\text{-}C_5H_5)_2Ti(BH_4)$. The reaction of bis(cyclopentadienyl)vanadium(IV) dichloride with a threefold excess of lithium tetrahydroborate in 1,2-dimethoxyethane at −10 °C reduces the vanadium(IV) to vanadium(III) in forming bis(*pentahapto*cyclopentadienyl)vanadium(III) tetrahydroborate:

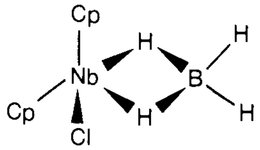
$$(\eta^5\text{-}C_5H_5)_2VCl_2 + 3LiBH_4 \rightarrow (\eta^5\text{-}C_5H_5)_2V(BH_4) \qquad (14)$$

The compound is a pyrophoric, dark violet crystalline solid which is purified by vacuum sublimation at 55 °C. The authors proposed a structure analogous to $(C_5H_5)_2Ti(BH_4)$ (**3**). It appears from the volatility as well as the vibrational spectrum (section III) that the covalency of the compound $(\eta^5\text{-}C_5H_5)_2V(BH_4)$ is greater than $(\eta^5\text{-}C_5H_5)_2Ti(BH_4)$.[28,23] The vanadium complex decomposes slowly under N_2 at room temperature. The fluxional behavior of this molecule is discussed in section IV.



3

There are two covalent niobium tetrahydroborates known. The first reported compound was bis(cyclopentadienyl)chloroniobium(IV) tetrahydroborate,[29] $(C_5H_5)_2Nb(Cl)BH_4$, synthesized by reaction of niobium pentachloride, sodium cyclopentadienide and lithium tetrahydroborate under a pressure of hydrogen. The compound is soluble in benzene and methylene chloride. No characterization of the bridging mode of the tetrahydroborate ligand was attempted. Structure **4** seems likely.



4

A quite similar compound is $(C_5H_5)_2Nb(BH_4)$[28,30] which is synthesized by the reaction of $(\eta^5\text{-}C_5H_5)_2NbCl_2$ with a large excess of either sodium or lithium tetrahydroborate in THF or diethyl ether, respectively, at 0 °C. The green, microcrystalline solid is purified by vacuum sublimation at 55 °C. Although it is air and moisture sensitive, it is not as extreme in this regard as its vanadium homolog. This compound, like $(C_5H_5)_2V(BH_4)$, appears to be quite covalent, more so than $(C_5H_5)_2Ti(BH_4)$;[28] it most likely has structure **3**.

D. Chromium, Molybdenum, Tungsten

The chromium tetrahydroborate complex, $[Cr(NH_3)_6](BH_4)_3 \cdot 0.5NH_3$,[31] is apparently an ionic compound where the tetrahydroborate is present as a counteranion to the complex cation.

Hein and Schroer have isolated, from aqueous solution, a complex formulated as bis(biphenyl)chromium tetrahydroborate, $(C_{12}H_{10})_2CrBH_4$.[32] This appears to be an ionic species with two biphenyl ligands π-bonded to a chromium(I) ion. The tetrahydroborate group then would serve as a counteranion to the cationic organometallic. No definitive experimental work has been performed to date in conclusively establishing the covalency or ionicity of this compound.

The first reported example of a molybdenum tetrahydroborate complex was $(\eta^5\text{-}C_5H_5)_2MoO(BH_4)_2$[33] which was synthesized in THF under nitrogen according to the equation:

$$(\eta^5\text{-}C_5H_5)_2MoOCl_2 + 2.5LiBH_4 \longrightarrow (\eta^5\text{-}C_5H_5)_2MoO(BH_4)_2 + 2LiCl \quad (15)$$

The authors claim that the tetrahydroborate ligands are bidentate on the basis of some similarity between their infrared spectrum and that of $(Ph_3P)_2Cu(BH_4)$.[34]

The only tungsten tetrahydroborate known was prepared in an identical fashion to eq 15 starting with the compound $(\eta^5\text{-}C_5H_5)_2WOCl_2$ and yielding ultimately $(\eta^5\text{-}C_5H_5)_2WO(BH_4)_2$.[33]

A result yet to appear in print but of which the authors are aware is the synthesis and single-crystal x-ray diffraction study of $([(C_6H_5)_3P]_2N)^+[Mo(CO)_4(BH_4)]^-$ formed by the reaction of $([(C_6H_5)_3P]_2N)^+Mo(CO)_5I^-$ with $([(C_6H_5)_3P]_2N)^+BH_4^-$ in refluxing THF:[35]

$$Mo(CO)_5I^- + BH_4^- \longrightarrow Mo(CO)_4BH_4^- + CO + I^- \quad (16)$$

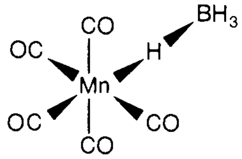
The fluxional behavior of this molecule is discussed in section IV and the structural data in section V.

E. Manganese, Technetium, Rhenium

There are no known tetrahydroborate complexes of technetium or rhenium, covalent or ionic. There are three complexes of manganese, however. The first is tris(tetrahydroborato)manganese, formed by the action of diborane on manganese(III) alkoxides. Details of the behavior of this complex are sparse.[10] The reaction of Li_2MnBr_4 and $LiBH_4$ in anhydrous ether at −80 °C yields $Mn(BH_4)_2$.[36] This species was reported to be soluble in anhydrous ether but relatively little data were presented as to its chemical and physical properties. A third volatile, unstable, covalent manganese tetrahydroborate is formed by the reaction of manganese pentacarbonylbromide and aluminum tris(tetrahydroborate) in mesitylene:[37]

$$3Mn(CO)_5Br + Al(BH_4)_3 \longrightarrow 3Mn(CO)_5(BH_4) + AlBr_3 \quad (17)$$

The compound decomposes at 25 °C to yield other carbonyl borane species such as $Mn_3(CO)_{10}(BH_3)_2H$, a compound prepared in another fashion and reported in the same communication. It is unfortunate that instability impairs the study of $Mn(CO)_5(BH_4)$. A structure determination to ascertain the effect on the bridge bonding in the tetrahydroborate ligand of the bulky $Mn(CO)_5$ fragment should prove worthwhile and interesting. A structure such as **5** seems plausible for this metal carbonyl derivative.



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F. Iron, Ruthenium, Osmium

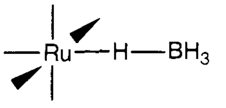
Osmium is the only member of this triad for which there is no covalent tetrahydroborate complex. Ferrous tetrahydroborate, $Fe(BH_4)_2$, has been prepared by the reaction of $FeCl_3$ and $LiBH_4$ in diethyl ether at −45 °C.[38] The compound is a colorless solid, only sparingly soluble in diethyl ether and very temperature sensitive, suffering total decomposition above −10 °C to yield a number of pyrophoric products. Monnier also reported this compound, although it was synthesized in his preparation by the action of Li_2FeBr_4 on $LiBH_4$ at −80 °C.[36]

Stone and co-workers prepared the complex $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(BH_4)$ in THF under a nitrogen atmosphere.[39] Unfortunately their interest in the compound lay only in the $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2$ moiety so that no further characterization to elucidate the bonding of the BH_4 group was carried out.

$$(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl + \text{excess } NaBH_4 \longrightarrow (\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(BH_4) \quad (18)$$

Holah and co-workers, in a series of papers[40] encompassing several metal ions, have synthesized a number of tetrahydroborate complexes which incorporate phosphine ligands, hydrides, and, in some cases, carbonyls as well as BH_4^-. The reactions were carried out by mixing free phosphines, metal chlorides, and a massive excess of sodium tetrahydroborate. In this manner the complex $RuH(BH_4)(P(C_6H_5)_3)_3$ was formed.[40a,b] When the initial metal containing reactant was an ethanolic solution of ruthenium carbonyl, the complexes $Ru(H)(BH_4)$-

$(CO)(P(C_6H_5)_3)_3$ and $Ru(H)(BH_4)(CO)_2(P(C_6H_{11})_3)_2$ were formed after combination with a tenfold excess of $NaBH_4$ and the respective phosphine.[40b] On steric grounds and on the basis of some infrared spectral evidence the authors propose, in this series of ruthenium tetrahydroborates, that the BH_4^- ligand is monodentate (**6**). It would appear that further experimental work to clarify the mode of bonding may be warranted for these complexes.



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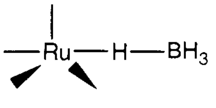


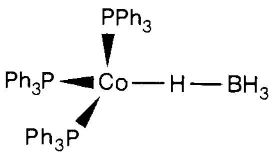
6b

G. Cobalt, Rhodium, Iridium

The treatment of cobalt dibromide with lithium tetrahydroborate in diethyl ether was purported to yield $Co(BH_4)_2$ although the off-white solid was not fully characterized.[41] In another article also lacking in chemical and physical data, the compound was synthesized by treating Li_2CoBr_4 with $LiBH_4$ in anhydrous ether at -80 °C. Monnier further reported that the compound was unstable, decomposing to cobalt metal and hydrogen when allowed to warm.[36]

Recently the compound hydridotetrahydroboratobis(tricyclohexylphosphine)cobalt(II) was prepared and fully characterized.[42] The crystal structure determination is presented elsewhere in this review (see section V). The synthesis was carried out by treating a solution of cobalt dichloride hexahydrate and tricyclohexylphosphine in toluene/ethanol with excess sodium tetrahydroborate. The product was purified by crystallization from methanol in the presence of free $P(cyclohexyl)_3$. The compound is an air sensitive paramagnetic brown-yellow solid. The BH_4 ligand is bound to the cobalt in a bidentate fashion.

Holah has reported[40c] that the reaction of $CoX_2{\cdot}6H_2O$ (X = Cl, Br, I) with $P(C_6H_5)_3$ and a tenfold excess of $NaBH_4$ in ethanol yields the compound $Co(BH_4)(P(C_6H_5)_3)_3$. The authors suggest that the electronic spectrum of this complex is typical of a tetrahedral d^8 system and, as such, militates in favor of a monodentate tetrahydroborate ligand (**7**).



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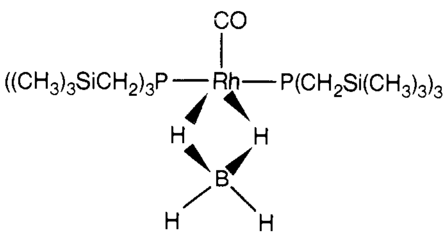
Treatment of $Co(BH_4)(P(C_6H_5)_3)_3$ with nitrogen-saturated benzene or *n*-hexane produces a yellow-brown complex of formulation $Co(N_2)(BH_4)(P(C_6H_5)_3)_3$.[40a] Infrared and analytical results are insufficient to clarify fully the bonding in this interesting molecule. The authors propose[40a] that the tetrahydroborate is bonded in a bidentate fashion.

There have been a number of tetrahydroborate complexes of rhodium and iridium reported in the past several years. Treatment of the compound *trans*-$[P(CH_2Si(CH_3)_3)_3]_2Rh(CO)Cl$ with an excess of sodium tetrahydroborate in ethanol under a nitrogen atmosphere gives *trans*-$[P(CH_2Si(CH_3)_3)_3]_2Rh(CO)(BH_4)$.[43]

$$Rh[P(CH_2Si(CH_3)_3)_3]_2(CO)Cl + \text{excess } NaBH_4 \rightarrow Rh[P(CH_2Si(CH_3)_3)_3]_2(CO)(BH_4) \quad (19)$$

There are strong infrared bands at 2370 and 2385 cm^{-1} indicating that the tetrahydroborate is most likely bonded in a bidentate manner to the rhodium (see section III) as in structure **8**. The compound is mildly air sensitive. When *trans*-$[P(CH_2Si(CH_3)_3)_3]_2Ir(CO)Cl$ is subjected to the same conditions, a compound, $Ir[P(CH_2Si(CH_3)_3)_3]_2(CO)(BH_4)$, exactly analogous to the rhodium complex is formed.[43] Presumably, physical and chemical properties are very similar.



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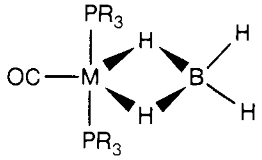
A number of analogous rhodium and iridium tetrahydroborate complexes were synthesized by Vaska and co-workers.[44] In this work the starting materials were perchlorate compounds and the hydroboration agent was sodium tetrahydroborate. Equation 20 indicates the general reaction scheme.

$$trans\text{-}[M(OClO_3)(CO)L_2] + NaBH_4 \rightarrow trans\text{-}[M(BH_4)(CO)L_2] + NaClO_4 \quad (20)$$

$$M = Rh, Ir;\ L = PPh_3, P(C_6H_{11})_3$$

The compounds formed all presumably have structure **9**. Three of the possible permutations of the variable parameters, M and L, were reported while the only compound not synthesized was the compound with iridium and triphenylphosphine. All three complexes formed are air stable in the crystalline state but decompose rapidly in solution. The stability of the tricyclohexylphosphine complexes is greater than the triphenylphosphine complex. No extended attempt was made to analyze the infrared spectrum, but the authors assumed bidentate geometry for the tetrahydroborate ligand by a comparison of their spectra with the spectrum of $(Ph_3P)_2Cu(BH_4)$.[34]

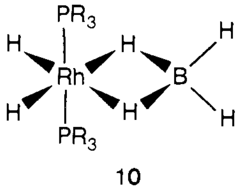


9

Empsall et al. have recently reported the preparation of a number of interesting iridium complexes each containing a single covalently bonded tetrahydroborate ligand.[45] The generalized reaction is

$$IrHCl_2(PR_3)_2 + NaBH_4 \rightarrow IrH_2(BH_4)(PR_3)_2 \quad (21)$$

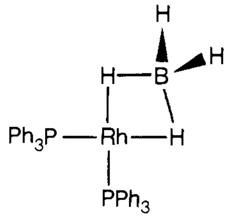
The reactions are carried out at 0 °C in ethanol. The phosphines used here are $PBu^t{}_2Me$, $PBu^t{}_2Bu^n$, and $PBu^t{}_2Ph$. The proposed structures are illustrated as **10**. When $IrH_2Cl(PR_3)_2$ is used as a starting material and $NaBH_4$ or $NaBD_4$ used as reductants the complexes $IrH_2(BH_4)(PBu^t{}_3)_2$ and $IrH_2(BD_4)(PBu^t{}_3)_2$ are formed. These compounds are all relatively stable in solution and in the solid state. All the complexes with the exception of those including $PBu^t{}_3$ ligands decompose slowly to the pentahydrides, $IrH_5(PR_3)_2$. There is evidence here that the inclusion of the bulky phosphine ligands in the coordination sphere of the iridium ion stabilizes tetrahydroborate ligation. This will be more in evidence with the softer transition elements (vide infra). An analogous rhodium complex, $RhH_2(BH_4)(PBu^t{}_2Me)_2$, was prepared in a manner identical with reaction 21. Physical and chemical



10

properties are presumed to be quite similar to its iridium homolog. All of the above complexes are unusual in that bridge-terminal hydrogen interchange within the tetrahydroborate ligand (section IV) is rather slow on the NMR timescale (Rh) or apparently nonexistent (Ir) at room temperature.

Holah and co-workers have synthesized $Rh(BH_4)(PPh_3)_2$ by the reaction of sodium tetrahydroborate with $RhCl(PPh_3)_3$ in a benzene/ethanol solvent system.[40d] This complex is very air sensitive and decomposes rapidly in solution. Infrared data are in accord with structure **11** containing a bidentate tetrahydroborate ligand. In the same work the synthesis of $Rh(H)(BH_4)((o\text{-tolyl})_3P)$ was reported according to the equation



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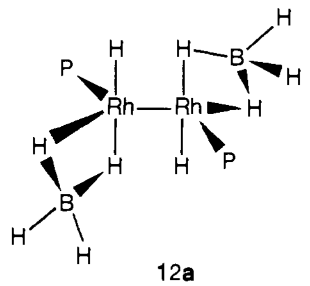
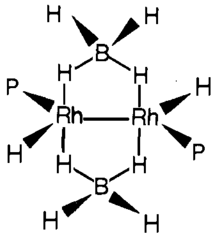
$$RhCl_2(P(o\text{-tolyl})_3)_2 + NaBH_4 \rightarrow Rh(H)(BH_4)(P(o\text{-tolyl})_3) + P(o\text{-tolyl})_3 \quad (22)$$

The compound is moderately oxygen sensitive but has some air stability over short periods. The structure of this complex is uncertain. Magnetic measurements indicate a diamagnetic ground state, most probably indicative of a dimeric compound. The authors propose on the basis of magnetic and infrared measurements structure **12a** or **12b.**



12a

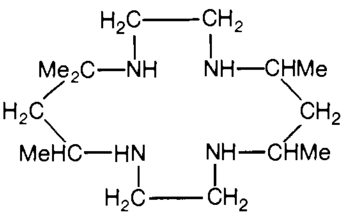


12b

H. Nickel, Palladium, Platinum

Until 1971 the only examples of covalent tetrahydroborate complexes of any of the three metals of this triad were of nickel. There were also a number of complex ionic species of nickel known, but the tetrahydroborate group was considered to be a counteranion for various complexed nickel cations.[46–48] An example is $Ni(NH_3)_6(BH_4)_2$.[46]

Several mononuclear molecular complexes of nickel containing the tetrahydroborate ligand have been synthesized.[49] The complexes are of the general formulation $NiA(BH_4)_2$ and $NiA(BH_4)(ClO_4)$, where A is a cyclic tetramine or noncyclic tetradentate Schiff base amine (**13, 14**). A may exist as a mixture of isomers. Thus there are in total six tetrahydroborate complexes of nickel(II) here. The synthesis of these complexes was effected by the addition of varying amounts of sodium borohydride to the perchlorate salts of the nickel–amine complexes.



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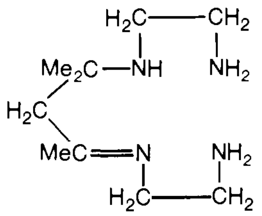

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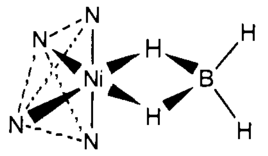
The mixed tetrahydroborate-perchlorate compounds are only sparingly soluble, even in strong donor solvents, while the bis(tetrahydroborates) are more soluble than the starting perchlorate salts. The complexes are not hygroscopic or susceptible to decomposition even after prolonged exposure to atmospheric oxidation or moisture. They are, in fact, soluble in aqueous solutions with no detectable decomposition. The solubility appears to be limited, however, to strongly basic donor solvents. The mixed tetrahydroborate–perchlorate salts explode violently when heated, a fact not unexpected in light of the presence of both a strong oxidant (ClO_4^-) and a strong reductant (BH_4^-) in the coordination sphere of the nickel atom. The bis(tetrahydroborates) are thermally stable to temperatures in excess of 120 °C. Solutions of these complexes are less stable, however, as evidenced by a color change from orange to blue-violet as the complex decomposes even when air is rigorously excluded. Infrared spectra of these complexes indicate either a covalent, bidentate tetrahydroborate ligand or a tightly ion-paired anionic BH_4^- group. Steric congestion would most likely disallow any tendency toward tridentate ligation on the part of the tetrahydroborate group. In the case of the mixed tetrahydroborate–perchlorates, Curtis[49] proposed a bidentate BH_4 group as most plausible. The bridging hydride ligands occupy two sites on the octahedron surrounding nickel, the remaining four being utilized by donor nitrogen atoms, and the steric difficulties are overcome (**15**).



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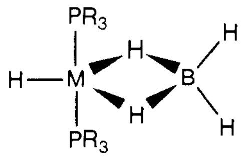
In addition to these complexes a homoleptic species, $Ni(BH_4)_2$, has been reported,[10a,14] but details concerning its preparation, properties, and reactivity are sparse.

Green and co-workers in 1971 reported several nickel and palladium complexes containing covalently bonded tetrahydroborate ligands.[50] The starting materials for these complexes were the compounds *trans*-$(R_3P)_2M(H)Cl$ where the metal was either nickel or palladium and the phosphine was triisopropyl- or tricyclohexylphosphine. The solvent system was a variable mixture of acetone and ethanol, and reaction temperatures ranged from room temperature to −5 °C. The generalized reaction is given in eq 23.

$$trans\text{-}(R_3P)_2M(H)Cl + NaBH_4 \rightarrow trans\text{-}(R_3P)_2M(H)BH_4 + NaCl \quad (23)$$

$$M = Ni, Pd;\ R = \text{isopropyl, cyclohexyl (Cy)}$$

The compounds, other than *trans*-$(i\text{-}Pr_3P)_2Pd(H)BH_4$, are all indefinitely stable at room temperature under argon. The palladium compound, $(i\text{-}Pr_3P)_2Pd(H)(BH_4)$, decomposes at room temperature in a matter of hours. All of the complexes are benzene soluble except for $(Cy_3P)_2Pd(H)BH_4$ which is relatively insoluble in all solvents. Again a bidentate geometry is assignable to the tetrahydroborate ligands by means of infrared spectroscopic analogies. Proposed structures for these complexes are similar to **16**. No tetrahydroborate complex of platinum has yet been synthesized.



16

In the same work in which they initially reported the phosphine hydride tetrahydroborates of ruthenium and cobalt mentioned earlier (vide supra), Holah and co-workers[40a] reported the complex hydridotetrahydroboratotris(triphenylphosphine)nickel(II), $(Ph_3P)_3Ni(H)BH_4$, prepared by mixing sodium tetrahydroborate, nickel(II) chloride, and triphenylphosphine in solution. Chemical details and properties of this complex were not reported. These workers withdrew the original formulation of the complex as $(Ph_3P)_3Ni(H)(BH_4)$ in a subsequent work[40c] and amended the tetrahydroborate complex to $(Ph_3P)_3Ni(BH_4)$. The same yellow-brown species is produced regardless of the nature of the Ni(II) aquated halide, i.e., chloride, bromide, or iodide. Extensive physical studies of this complex resulted in the alteration of its chemical formula. Speculation as to the nature of the linkage of the tetrahydroborate ligand was absent.

I. Copper, Silver, Gold

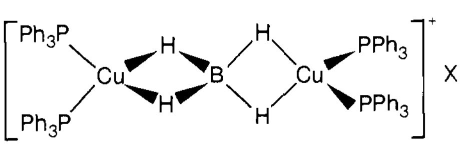
Both cuprous and cupric chloride react with lithium tetrahydroborate at low temperatures in diethyl ether to produce $Cu(BH_4)$.[51-54] At -45 °C the compound is a nonvolatile white powder which is air sensitive and decomposes to copper metal, diborane, and hydrogen at -12 °C.

Lippard and Ucko[34] have shown that this compound may be stabilized by the addition of soft Lewis bases to form complexes of the type $(R_3E)_2Cu(BH_4)$ (eq 24) where R_3E may be a phosphine, arsine, or stibine ligand. When the ligands are triarylphosphines a marked increase in thermal stability is observed. Trialkylphosphines and triarylarsines and -stibines form unstable species, however, which decompose immediately.

$$4R_3E + CuCl + 2Na(BH_4) \rightarrow (R_3E)_2Cu(BH_4) \qquad (24)$$

An interesting reaction of the complex $(Ph_3P)_2CuBH_4$ occurs when solutions of this compound are treated with gaseous HF.[55] The resultant product, $(Ph_3P)_2CuBF_4$, is similar to that obtained when $(C_5H_5)_2TiBH_4$ is reacted with $BF_3{\cdot}O(C_2H_5)_2$ to give $(C_5H_5)_2TiBF_4$.[22] It is not known how general this reaction pattern is.

Known tetrahydroborate complexes of copper include $(Ph_2PCH_2CH_2PPh_2)Cu(BH_4)$,[56] $(Ph_3P)_2Cu(BH_4)$, (o-phen)$(PPh_3)Cu(BH_4)$,[57] and the cationic species $[(Ph_3P)_2CuBH_4Cu(PPh_3)_2]^+X^-$, where X^- may be ClO_4^-, BF_4^-, or $B(C_6H_5)_4^-$.[57] It has been proposed that these cationic dimers have two copper atoms bridged by a tetrahydroborate ligand functioning in a bidentate manner toward both metals (**17**).[57] In all of the neutral complexes the tetrahydroborate apparently functions as a bidentate donor ligand (**18**).[34] The x-ray structure of $(Ph_3P)_2Cu(BH_4)$ is discussed in section V.



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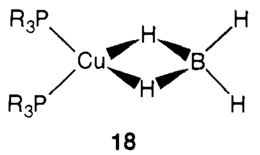
$X^- = BF_4^-, B(C_6H_5)_4^-$



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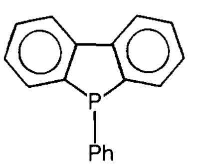
A tetrahydroborate complex of copper containing the phosphine ligand 5-phenyl-5*H*-dibenzophosphazole (DBP) (**19**) was synthesized by the treatment of cupric chloride with the phosphine ligand and sodium tetrahydroborate.[40a] The complex formed, $(DBP)_2CuBH_4$, was characterized by chemical analyses and infrared spectroscopy. Further data of a chemical and physical nature await publication.



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Silver(I) tetrahydroborate has been prepared by the reaction of silver salts with alkali tetrahydroborates in diethyl ether or ammonium hydroxide solutions at low (<-30 °C) temperatures.[58] This compound decomposes thermally above -30 °C. Like its copper homolog, stabilization may be effected by the addition of triphenylphosphine to form $(Ph_3P)_2Ag(BH_4)$, a colorless solid. [59] No attempt was made to identify the bonding in the tetrahydroborate group. Presumably the bonding in $(Ph_3P)_2Ag(BH_4)$ is quite similar to that in the copper homolog,[34] including the bidentate BH_4 ligation.

At -120 °C in diethyl ether, gold(III) chloride reacts with excess lithium tetrahydroborate to form the extremely thermally unstable species $Au(BH_4)_3$.[22] At temperatures in excess of this the compound decomposes to metallic gold, diborane, and hydrogen. This instability precludes extensive studies into the chemistry and physical characteristics of the compound.

J. Zinc, Cadmium, Mercury

Zinc bis(tetrahydroborate) has been synthesized in two ways:[60,61]

$$ZnCl_2 + 2MBH_4 \xrightarrow{(C_2H_5)_2O} Zn(BH_4)_2 + 2LiCl \qquad (25)$$

$$(M = Li, K)$$

$$B_2H_6 + ZnH_2 \rightarrow Zn(BH_4)_2 \qquad (26)$$

The white insoluble solid decomposes above 50 °C and hydrolyzes vigorously[61] when allowed to come in contact with water. Evidently there was no further physical characterization attempted. It has also been reported by Russian workers that the complex tetrahydroborate, $Na[Zn(BH_4)_3]{\cdot}O(C_2H_5)_2$, decomposes at 80 °C to yield $Zn(BH_4)_2$,[62a] a temperature which seems to be far in excess of that quoted earlier[60] as the upper limit of stability of this compound. Nöth, Wiberg, and Winter [62b] have reported that various anionic zinc tetrahydroborates can be synthesized by the reactions:

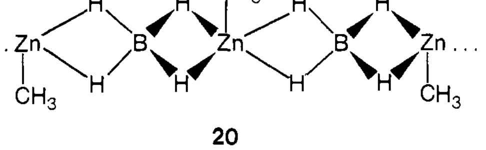
$$\begin{array}{ccc} Zn(BH_4)_2 & & LiZn(BH_4)_3 \\ \text{or} & \xrightarrow[Et_2O \text{ or } THF]{LiBH_4 \text{ or } NaBH_4} & Li_2Zn(BH_4)_4 \\ ZnCl_2 & & NaZn(BH_4)_3 \end{array} \qquad (27)$$

The sodium compound can also be prepared by the reaction of diborane with $NaZn(OCH_3)_3$ or $Na_2Zn(OCH_3)_4$. Based upon infrared spectra, the authors proposed that all of these compounds have bidentate BH_4^- coordination. Somewhat different products were obtained when potassium and barium were the counterions (eq 28–29).

$$ZnCl_2 \text{ or } Zn(BH_4)_2 \xrightarrow{KBH_4} K_2Zn_3(BH_4)_8 \qquad (28)$$

$$ZnCl_2 \text{ or } Zn(BH_4)_2 \xrightarrow{Ba(BH_4)_2} BaZn_3(BH_4)_8 \qquad (29)$$

There is a recent report of a vibrational spectroscopic study of the compound $(CH_3)Zn(BH_4)$.[63] The authors suggest that the most likely structure is the polymeric solid pictured as **20**, with



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bridging BH_4^- groups interacting in a bidentate fashion with two adjacent $ZnCH_3$ cations. The vibrational spectra are quite complex. There is some indication that the tetrahydroborate group in the solid zinc species is more ionic than those bridging BH_4 units in solid $Be(BH_4)_2$[64] (see section V).

Cadmium bis(tetrahydroborate), $Cd(BH_4)_2$, may be synthesized in diethyl ether at 0 °C:[54]

$$CdCl_2 + 2LiBH_4 \rightarrow Cd(BH_4)_2 + 2LiCl \tag{30}$$

This compound is air sensitive and thermally unstable, decomposing above 25 °C into its three constituent elements.[54]

Nöth and Winter have prepared compounds of the formulation $Cd(BH_4)_2{\cdot}L$, where L may be THF, pyridine, or ammonia.[65] This was accomplished by the action of diborane on $Cd(OCH_3)_2$ in a tetrahydrofuran solution containing the ligand of choice. These compounds have increased stability over the pure cadmium tetrahydroborate species although no suggestions concerning the tetrahydroborate bonding were advanced.

K. Lanthanides

Tetrahydroborate complexes of the lanthanide series are relatively rare. A series of complexes of the formulation $M(BH_4)_3{\cdot}n$THF (n is a nonintegral number) was prepared by Zange by the treatment of anhydrous lanthanide trichlorides with an excess of diborane in THF.[66] Tris(tetrahydroborates) of samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium were prepared in this manner. Unfortunately, the compounds are rather insoluble, intractable solids and little chemistry was performed on them.

Chlorobis(tetrahydroborates) of samarium, gadolinium, terbium, dysprosium, erbium, and ytterbium have been prepared by the reaction of 2 equiv of lithium tetrahydroborate with 1 equiv of the respective anhydrous metal trichloride.[10a,67] These systems tend to be no more responsive to chemical reactants than were the tris(tetrahydroborates). Rossmanith reported a similar europium compound $EuBr(BH_4)_2{\cdot}2.4$THF, prepared in a analogous manner, and with similar properties.[68]

Organometallic tetrahydroborates of cerium(IV) have been recently reported.[69] The compounds $(\eta^5\text{-}C_5H_5)_3Ce(BH_4)$ and $(\pi\text{-indenyl})_2Ce(BH_4)_2$ were prepared by the reactions of the corresponding cerium chlorides, $(\eta^5\text{-}C_5H_5)_3CeCl$ and $(\pi\text{-indenyl})_2CeCl_2$, respectively, with an excess of $NaBH_4$ in refluxing THF under nitrogen. The compounds are nonvolatile solids, stable in a dry, inert atmosphere at room temperature. The authors propose that the tetrahydroborate ligands are bidentate. This is based on their interpretation of the infrared spectra.[69] It is surprising that a strong oxidant such as ceric ion is not reduced when reacted with the BH_4^- anion.

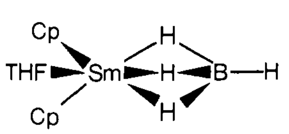
A number of lanthanide complexes of the formulation $(\eta^5\text{-}C_5H_5)_2MBH_4$ (M = Er, Yb) and $(\eta^5\text{-}C_5H_5)_2MBH_4{\cdot}$THF (M = Sm, Er, Yb) have been prepared by the reaction of the complexes $(\eta^5\text{-}C_5H_5)_2$ MCl with excess sodium tetrahydroborate in THF (eq 31).[70]

$$(C_5H_5)_2MCl + NaBH_4 \xrightarrow{\text{THF}} (C_5H_5)_2MBH_4 \cdot \text{THF}$$

M = Sm, Er, Yb

$$\xrightarrow[-\text{THF}]{\Delta} \begin{matrix}(C_5H_5)_2MBH_4 \\ M = \text{Er, Yb}\end{matrix} \tag{31}$$

The THF is readily and reversibly removed from the Er and Yb compounds; however, attempts to remove it from the Sm analog have resulted in decomposition to tris(cyclopentadienyl)samarium. Infrared and Raman results (see section III) suggest that the tetrahydroborate ligand is bonded in a tridentate fashion to the samarium ion (**21**) in $(C_5H_5)_2SmBH_4{\cdot}$THF, whereas in the erbium and ytterbium (**22**) analogs its bonding mode appears to be bidentate. The simplest explanation for this is the increase in the ionic radius of the central metal upon going from Yb^{3+} and Er^{3+} to Sm^{3+}. Vibrational data on the nonadducted bis(cyclopentadienyl)lanthanide tetrahydroborates are consistent with a polymeric structure in which BH_4^- bridges lanthanide ions (section III) as in $(CH_3)Zn(BH_4)$.[63]



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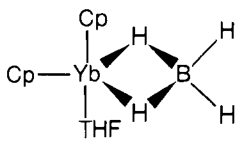

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L. Actinides

Both $U(BH_4)_4$[71] and $Th(BH_4)_4$[15a] were first prepared by the reaction of the corresponding anhydrous metal tetrafluoride with gaseous aluminum tetrahydroborate. Ehemann and Nöth[21] have reported that the thorium compound can be most conveniently synthesized by reacting ThF_4 with $LiBH_4$ in diethyl ether and under vacuum, subliming the resulting precipitate. The uranium compound is a volatile green solid which decomposes at 100 °C forming an involatile brown solid which was presumed to be $U(BH_4)_3$. $U(BH_4)_4$ is only slowly hydrolyzed in air in contrast to the corresponding behavior of $Zr(BH_4)_4$ and $Hf(BH_4)_4$. The gas-phase infrared spectrum of $U(BH_4)_4$ is nearly identical with the spectra of $Zr(BH_4)_4$ and $Hf(BH_4)_4$,[72] indicating that it possesses four tridentate tetrahydroborate ligands (see section III). In the solid state, however, the uranium is coordinated to four bridging (between adjacent uranium ions) bidentate tetrahydroborates and two tridentate terminal tetrahydroborates,[73] quite dissimilar to the proposed gas-phase structure (see section V).

The thorium compound, $Th(BH_4)_4$,[15a] is a colorless solid which melts at 203 °C and is less volatile than $U(BH_4)_4$. It is, unlike $Zr(BH_4)_4$ and $Hf(BH_4)_4$, hydrolyzed only slowly in air. It is very soluble in ethereal solvents, forming bisetherates from which the ether may be removed on heating. Isomorphism with $U(BH_4)_4$ has been proven,[15] indicating that thorium here is most likely also tetradecacoordinate (see section V) with both bridging and terminal tetrahydroborate ligands.[73] The structure of $U(BH_4)_4$ is detailed in section V.

Further treatment of $Th(BH_4)_4$ with $LiBH_4$ in diethyl ether results in formation of the ionic complexes $Li[Th(BH_4)_5]{\cdot}m(O(C_2H_5)_2)$ and $Li_2[Th(BH_4)_6]{\cdot}n(O(C_2H_5)_2)$:[21]

$$LiBH_4 + Th(BH_4)_4 \xrightarrow{O(C_2H_5)_2} Li[Th(BH_4)_5] \cdot m(O(C_2H_5)_2) \tag{32}$$

$$2LiBH_4 + Th(BH_4)_4 \xrightarrow{O(C_2H_5)_2} Li_2[Th(BH_4)_6] \cdot n(O(C_2H_5)_2) \tag{33}$$

$$m, n = 1, 2, \cdots$$

The ether can be easily removed by heating in vacuo. These reactions are similar to the reactions of $Zr(BH_4)_4$ and $Hf(BH_4)_4$ with $LiBH_4$ to form $[M(BH_4)_5]^-$ anions (vide supra). However, the increased Lewis acidity and larger size of thorium(IV) evidently facilitates expansion of the coordination sphere about the metal to accommodate not only a sixth BH_4^- ligand but ether molecules as well.[21] Based upon infrared spectra, tridentate ligation was assigned to BH_4^- coordination.

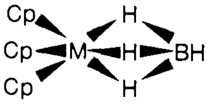
The complexes $(R_4N^+)[Th(BH_4)_5^-]{\cdot}m(O(C_2H_5)_2)$ are also known where R_4N^+ is a tetrabutylammonium or trioctylpropylammonium cation.[21] These are prepared as in eq 34 and have properties similar to the $Li^+[Th(BH_4)_5^-]{\cdot}m(O(C_2H_5)_2)$ complexes. Again, the ether can be removed by pumping. Infrared spectra have been interpreted in terms of tridentate BH_4^- coordination.

$$(R_4N^+)(BH_4^-) + Th(BH_4)_4$$

$$\xrightarrow{O(C_2H_5)_2} (R_4N^+)[Th(BH_4^-)_5] \cdot m(O(C_2H_5)_2) \tag{34}$$

A homoleptic complex of neptunium(IV), $Np(BH_4)_4$, was prepared by Hoekstra and Katz.[15b] Details of its chemistry are lacking.

The organoactinide(IV) compounds $(C_5H_5)_3M(BH_4)$ have been synthesized where the central metal is either uranium or thorium. The reaction was carried out by treatment of the highly useful precursor $(\eta^5\text{-}C_5H_5)_3MCl$[74] with an excess of $NaBH_4$.[75] For M = U, the red crystalline solid is mildly volatile and highly air sensitive.[76] The covalent tetrahydroborate binds to the uranium atom through three bridging hydrides. The corresponding thorium(IV) complex, $(C_5H_5)_3Th(BH_4)$,[77,78] is a white solid, which may be purified by vacuum sublimation at 120 °C indicating reasonable volatility and covalency. From infrared spectra the bonding of the tetrahydroborate ligand appears to be tridentate.[77] The thorium and uranium compounds are very similar chemically and physically and the proposed structures are illustrated as **23**.



23

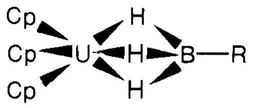
Treatment of both $U(BH_4)_4$ and $(C_5H_5)_3U(BH_4)$ with trialkyl- or triarylboranes results in the replacement of the hydride ligand in the terminal position with an alkyl or aryl group.[76,79]

$$U(BH_4)_4 + B(CH_3)_3 \rightarrow U(BH_4)_3(H_3BCH_3) + U(H_3BCH_3)_4 \quad (35)$$

$$(C_5H_5)_3U(BH_4) + R_3B \rightarrow (C_5H_5)_3U(H_3BR) \quad (36)$$

$$R = C_2H_5, \text{ phenyl}$$

These compounds are all volatile, air-unstable solids. $U(BH_4)_3(H_3BCH_3)$ is a green solid which is even more volatile than $U(BH_4)_4$. The compound $U(H_3BCH_3)_4$ is a less volatile lavender solid which melts at 73 °C. The organouranium compounds $(\eta^5\text{-}C_5H_5)_3U(H_3BCH_2CH_3)$ and $(\eta^5\text{-}C_5H_5)_3U(H_3BC_6H_5)$ are both air-unstable brick-red solids. Their volatility and physical characteristics are similar to the unsubstituted tetrahydroborate. Again, ligation is through a triple hydrogen bridge (**24**).



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$R = C_2H_5, C_6H_5$

M. Generalizations

At the conclusion of this section there are a number of important general points to be made regarding both the methods of synthesis and the properties of the compounds.

The most common and obviously most facile means of preparation of covalent metal tetrahydroborates is the reaction of an excess of an alkali tetrahydroborate with the corresponding metal halide. This suffers the disadvantage of effecting concomitant reduction of the metal ion in certain cases, e.g., $(C_5H_5)_2Ti(BH_4)$ and $(C_5H_5)_2V(BH_4)$. The second most popular means of preparation is the treatment of a solution of a metal alkoxide with diborane. The only drawback here is the inconvenience of handling diborane. This method has been used in only an isolated number of cases and is far less popular than method 1.

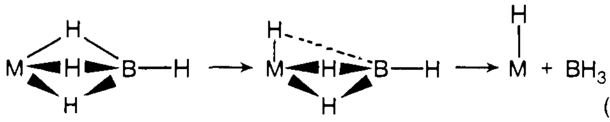
Those factors which stabilize covalent metal tetrahydroborate complexes with respect to thermal decomposition are most likely both thermodynamic and kinetic. The thermodynamic factor concerns how readily the metal can be reduced by BH_4^-

$$M^{n+}BH_4^- \rightarrow M^{(n-1)+} + BH_3 + \tfrac{1}{2}H_2 \quad (37)$$

or how stable the complex is with respect to a metal hydride and diborane.

$$M^{n+}BH_4^- \rightarrow M^{n+}H^- + BH_3 \quad (38)$$

For homoleptic tetrahydroborates these factors are readily appreciated. For example, obvious routes to $Ti(BH_4)_4$ yield $Ti(BH_4)_3$, whereas for zirconium and hafnium, the thermally stable $M(BH_4)_4$ product is isolated. This is consistent with the fact that Ti(IV), under most conditions, is more easily reduced than Zr(IV) and Hf(IV).[80] Likewise, at the right of the periodic table, relatively strong oxidants such as Au(III) yield highly unstable tetrahydroborates, $(Au(BH_4)_3)$. The complexation of ligands such as phosphines stabilizes unstable complexes such as $Cu(BH_4)$ and $Ag(BH_4)$. Here it is likely that soft, electron-releasing ligands decrease the oxidative tendencies of the metal ion. Furthermore, the bulky ligands may play an important kinetic role in stabilizing the tetrahydroborate by saturating and immobilizing the metal coordination sphere. If the reaction coordinate for the decomposition process requires expansion of the metal coordination sphere, e.g., for B–H bond scission (eq 39), then bulky ligands may impede this process by crowding the available space around the metal. Saturation and coordination sphere immobilization appear to play an important role in stabilizing other types of organometallics.[81–84]



(39)

N. Catalytic Properties of Tetrahydroborate Complexes

One facet of the chemistry of transition metal tetrahydroborates which is yet to receive due attention is the catalytic activity, both homogeneous and heterogeneous, which certain of these complexes possess. Catalytic activity of covalent metal tetrahydroborates was alluded to in the Introduction. There is considerable experimental evidence indicative of the action of tetrahydroborates as effective catalysts for polymerization, oligomerization, and hydrogenation of olefins.[3–7] In this subsection that specific activity will be explored in greater detail.

Baum and Fraser determined that a 6% (w/v) solution of $Ti(BH_4)_3$ in petroleum ether functioned efficiently as a polymerization catalyst for 1-olefins.[3] Treatment of the ethylene at high pressures (250–300 psi) for several hours with this homogeneous titanium system yielded predominantly unbranched polyethylene. $TiCl(BH_4)_2$ afforded similar results. Similarly, $Ti(BH_4)_3{\cdot}3THF$ polymerized ethylene to polyethylene efficiently.[7] Increased efficiency for this system was attained when the titanium tetrahydroborate was mixed with $(C_2H_5)_3Al$ and then allowed to interact with the olefin of choice. Propylene and butadiene were also efficiently polymerized by $Ti(BH_4)_3{\cdot}3THF$ as well as by $Ti(BH_4)_3{\cdot}OP(NMe_2)_3$, $Ti(BH_4)_3{\cdot}(\text{dioxane})$, $Ti(BH_4)_3{\cdot}Sb(C_9H)_3$, $V(BH_4)(OMe)_2(\tfrac{1}{2}OP(NMe_2)_3)$, Cr(borohydride)·THF and $V(BH_4)(OMe)_2{\cdot}HMPA$ (HMPA = hexamethylphosphoramide).[7] A catalyst system consisting of a solution of $Zr(BH_4)_4$ in cyclohexane plus VCl_4 in $(CCl_2)_2$ and $AlBr_3$ in $(CCl_2)_2$ was found to effectively copolymerize ethylene and propylene.[4] The catalytic activity occurred after a relatively short (7.5 min) time period and afforded a highly soluble, high viscosity copolymer in good yield. The preceding examples are extracted from the patent literature and, as such, are devoid of mechanistic considerations. They do serve to illustrate the capacity of covalent tetrahydroborates to function as highly active polymerization catalysts. The efficiency of all these systems is apparently increased upon addition of a foreign Lewis acid. Only the final example was of a heterogeneous catalyst. The titanium systems were apparently homogeneous.

TABLE I. Normal Modes and Spectral Activities for Various Mononuclear MBH_4 Configurations

Structure	Normal modes	Activity[a]
I (C_{3v})	$4A_1$	IR, R
	4E	IR, R
II (C_{2v})	$5A_1$	IR, R
	A_2	R
	$3B_1$	IR, R
	$3B_2$	IR, R
III (C_{3v})	$4A_1$	IR, R
	4E	IR, R
IV (T_d)	A_1	R
	E	R
	$2T_2$	IR, R

[a] IR = infrared active; R = Raman active.

The patent literature has a number of other examples of the use of tetrahydroborates as catalysts for various types of chemical transformations. Mason[85] found that a mixture of sodium tetrahydroborate and nickel phosphinoacetates or nickel phosphinobenzoates catalyzes the oligomerization of ethylene. Gleim[86] ascertained that petroleum sludges and residues could be quantitatively refined to lower boiling hydrocarbons and freed from asphaltenes, metal impurities, and sulfur- and nitrogen-containing compounds by the hydrorefinement of these residues *catalyzed* by group 4, 5, and 6 metal tetrahydroborates.

Hydrogenation is an important process and there have been examples of metal tetrahydroborates functioning as hydrogenation catalysts. In very recent work, Nakajima and co-workers found that $Co(H)(BH_4)(P(C_6H_{11})_3)_2$ homogeneously catalyzes both the hydrogenation and isomerization of olefins at atmospheric pressure and room temperature.[42] Benzene solutions of hex-1-ene were hydrogenated in 30 min at room temperature by the cobalt complex. For olefins where isomerization is possible, that process drastically slowed the hydrogenation reaction. McQuillen and co-workers found that $RhCl_2(BH_4)(DMF)(py)_2$ was a very effective hydrogenation catalyst for cycloalkenes and nitro compounds.[87]

Recently, Miller and co-workers noted that a toluene solution of a mixture of *trans*-$Ni(H)(BH_4)(P(C_6H_{11})_3)_2$ and *trans*-$NiCl_2(P(C_6H_{11})_3)_2$ catalyzes the isomerization of *cis*-1,4-hexadiene in 47% yield to *trans*-2-methyl-1,3-pentadiene and trace amounts of *trans,cis*- and *cis,cis*-2,4-hexadienes.[88] As in the previous two examples of catalytic hydrogenation,[42,87] the function of the BH_4^- ligand in the actual catalytic process was not elucidated.

Green and Munakata have found that the complex $Ni(H)(BH_4)(P(C_6H_{11})_3)_2$ also functions as an oligomerization catalyst for 1,3-butadiene.[89] The chief product of the reaction was octa-1,3,5-triene. When methanol was added to the reaction mixture, $Pd(H)(BH_4)(P(C_6H_{11})_3)_2$ behaved in much the same manner to yield octa-1,3,7-triene as well as minor amounts of methoxyoctadienes (as did the nickel complex). In the absence of methanol the catalytic action of both complexes is much less clean and a number of isomeric butadiene dimers were formed. These authors were the first to actually postulate a mechanism for the activity of the complex tetrahydroborates. The mechanism is illustrated in Scheme I. The elimination of $H_3BP(C_6H_{11})_3$ activates the metal ion and facilitates complexation of butadiene. The subsequent elimination of hydrogen frees two additional coordination sites on the metal so that a second butadiene molecule may coordinate from whence oligomerization in the metal coordination sphere may occur. It also reduces the metal to the zerovalent state.

SCHEME I. Scheme for Catalytic Cycle[89]

$$\textit{trans}\text{-}NiH(BH_4)(PCy_3)_2 \xrightarrow{C_4H_6} NiH_2(PCy_3)(C_4H_6) + H_3BP(C_6H_{11})_3$$

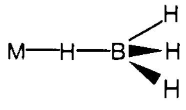
$$\Big\downarrow{-H_2}$$

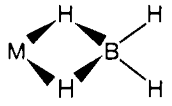
$$Ni(PCy_3)(\text{butadiene adducts})$$

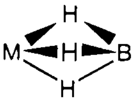
While Green and Munakata elucidate well the function of the tetrahydroborate ligand in the oligomerization process, the question of how tetrahydroborates behave in the other catalytic processes mentioned earlier, i.e., hydrogenation, polymerization, and isomerization, remains unanswered. There are a number of functions the BH_4^- ligand could fulfill in catalysis, homogeneous and heterogeneous: BH_4^- may (1) reduce the central metal to a lower oxidation state; (2) provide a source of hydrogen forming, in effect, a metal hydride (Green and Munakata, vide supra); (3) provide a variable coordination sphere for the metal atom by a series of bidentate ⇌ tridentate (or vice versa) fluctuations effectively acting as a "gate keeper" toward the coordinative saturation of the metal; (4) simply function as a ligand which activates other ligands bound to the same metal. Whatever the function the bound tetrahydroborate fulfills, the inescapable fact is that covalent metal tetrahydroborates have proven to be effective catalysts for a number of important processes. There remains a great deal of quantitative and mechanistic research to be done before the role of $M-BH_4$ systems may be classified as understood.

III. Vibrational Spectroscopy

The mode of attachment of the tetrahedral BH_4^- ligand to a metal ion in a metal tetrahydroborate is a fundamental and important structural feature of the complex. A priori, four possible ligation patterns are conceivable for a mononuclear complex: monodentate (I), bidentate (II), tridentate (III), and ionic (IV). As will be discussed in detail in section V, only structures II and III have been observed in diffraction studies.


I


II


III

$M^+ \quad BH_4^-$

IV

The latter technique, when employing x-radiation, has considerable limitations in locating hydrogen atoms near heavy metals. In addition, diffraction with any kind of radiation does not yield particularly useful structural data in solutions or in powders. As will be seen in section IV, nuclear magnetic resonance has far too slow a timescale in most cases to yield meaningful structural information on tetrahydroborate complexes. In contrast, vibrational spectroscopy (infrared and laser Raman) can provide useful data on the metal–ligand coordination geometry and bonding; for the majority of compounds it allows a ready distinction to be drawn among structures I–IV.[77] Furthermore the data can be easily acquired and interpreted by nonspecialists.

A. Mononuclear Complexes

Consideration of an isolated MBH_4 unit yields the normal modes and spectral activities shown in Table I for the various ligation geometries. The structurally diagnostic bands are in the 2500–1000-cm^{-1} region and involve principally the stretching and deformation of B–H bonds, and some stretching of M–H bonds. The assignment of bands to various changes in internal coordinates, characteristic of a given metal-BH_4 ligation geometry, follows from analyses of model compounds (including isotopic substitution) with known structures.[77,90–93] The terminal

TABLE II. Infrared-Active Fundamental Vibrational Transitions Commonly Observed for Mononuclear MBH_4 Configurations

Structure	Approx freq, cm^{-1}	Type of internal coordinate change	Symmetry type	Comments
I (monodentate)	2300–2450	$B-H_t$ stretching	A_1, E	Strong, probably a doublet
	~2000	$B-H_b$ stretching	A_1	Strong
	~2000–1700	$M-H_b$ stretching	A_1	May be very broad
	1000–1150	BH_3 deformation	A_1, E	Strong band, possibly with weaker one at slightly higher frequency
II (bidentate)	2400–2600	$B-H_t$ stretching	A_1, B_1	Strong doublet, 50–80 cm^{-1} splitting
	1650–2150	$B-H_b$ stretching	A_1, B_2	Strong band, possible shoulder
	1300–1500	Bridge stretching	A_1	Strong, broad
	1100–1200	BH_2 deformation	B_2	Strong
III (tridentate)	2450–2600	$B-H_t$ stretching	A_1	Strong singlet
	2100–2200	$B-H_b$ stretching	A_1, E	Doublet, 50–80 cm^{-1} splitting
	1150–1250	Bridge deformation	E	Strong
IV (ionic)	2200–2300	$B-H_t$ stretching	T_2	Strong, broad
	1050–1150	BH_2 deformation	T_2	Strong, broad

TABLE III. Raman-Active Fundamental Vibrational Transitions Commonly Observed for Mononuclear MBH_4 Configurations

Structure	Approx freq, cm^{-1}	Type of internal coordinate change	Symmetry type	Comments
I (monodentate)	2300–2450	$B-H_t$ stretching	A_1	Strong
	~2000	$B-H_b$ stretching	A_1	Strong
	~2000–1700	$M-H_b$ stretching	A_1	May be broad
	1000–1150	BH_3 deformation	A_1	Strong
II (bidentate)	2400–2600	$B-H_t$ stretching	A_1	Strong singlet, possible shoulder
	1650–2150	$B-H_b$ stretching	A_1	Medium-strong band
	1300–1500	Bridge stretching	A_1	Strong, broad
	1100–1200	BH_2 deformation	A_1, B_2	Medium-strong, possibly a doublet
III (tridentate)	2450–2600	$B-H_t$ stretching	A_1	Strong singlet
	2100–2200	$B-H_b$ stretching	A_1	Strong singlet, possible shoulder
	1200–1250	Bridge deformation	A_1	Strong singlet
IV (ionic)	2200–2300	$B-H_t$ stretching	A_1	Strong, broad
	1150–1250	BH_2 deformation	E	Weak

hydrogen–boron stretch (ν_{B-H_t}) and bridge hydrogen–boron stretch (ν_{B-H_b}) are the two most easily recognized coordinate changes, and are expected to be relatively "pure"; i.e., unmixed with other low-frequency modes belonging to the same irreducible representation, since they involve principally motion of a very light atom bonded to a relatively heavy (^{10}B or ^{11}B) atom. Similarly, because of the large number of intervening bonds (and spacial separation of groups), it is reasonable to assume that the structurally diagnostic vibrations of one BH_4 group in a complex are not coupled to similar vibrations in another BH_4 group (or other ligand) in the same complex. In addition, it is assumed that the structurally diagnostic normal coordinates involve insufficient motion of the boron atoms to produce a large multiplicity of well-separated bands arising from the two boron isotopes (^{11}B, 81.2% abundant; ^{10}B, 18.8% abundant). These assumptions were an integral part of the vibrational criteria which we proposed.[77] Their validity has since been supported both by the confirmation of predictions as well as by normal coordinate analysis.[94]

Table II sets out criteria for structure assignments, based on infrared spectra. Laser Raman spectra are a useful adjunct to infrared spectra; in general, we[77,95] and others[91,92,94,96] have found the totally symmetric modes to be the most intense and, of course, polarized in solution. The development of apparatus which prevents laser damage by rapidly spinning the sample[98a,b] will doubtless allow the study of many more tetrahydroborates in the future. Raman structural correlations, which are based upon less available data than the infrared criteria, are set out in Table III.

For structure I, $H_3B-H-BH_3^-$ is the only available model compound,[97] since monodentate metal complexes are unknown at present. The structure should exhibit two (A_1 and E) ν_{B-H_t} transitions at ca. 2300–2450 cm^{-1}. Only a single ν_{B-H_b} band is expected; it would probably occur in the 2000-cm^{-1} range. The energy of the metal-hydrogen stretching frequency is difficult to predict; however, judging from results on linearly bridged (M–H–M) metal hydrides, it could be as low in frequency as ca. 1600 cm^{-1},[99,100] and, in addition, may be broadened to the point of invisibility at room temperature.[100,101] The cause of the broadness in M–H–B and other metal tetrahydroborate bridging modes is apparently analogous to the broadening seen in hydrogen-bonded systems. In the present case it would then arise from strong coupling of the ν_{M-H_b} mode with the low-frequency M–B stretching mode via mechanical and/or electrical anharmonicity.[101b,c] In the region 1000–1150 cm^{-1}, monodentate tetrahydroborates should exhibit one (A_1) or possibly two (A_1, E, the latter being weak) BH_3 deformation modes.[77]

Referring to structure II, which is the most common, two strong $B-H_t$ stretches (symmetrically (A_1) and antisymmetrically (B_1) coupled) are expected at 2400–2600 cm^{-1}. In addition, analogous A_1 and B_2 $B-H_b$ stretches are predicted at 2150–1650 cm^{-1}; these are sometimes overlapped. However, the presence of greater than one band should always be apparent in Raman[77] (especially with depolarization) and matrix infrared studies.[90] The position of these bands appears to be diagnostic of the electronic nature of the metal–ligand interaction (vide infra). A band which is composed of bridge expansion and M–H stretching is usually observed at 1300–1500 cm^{-1} (frequently broad) and a BH_2 deformation at 1050–1150 cm^{-1}. The principal differences between type I and type II spectra, then, should occur in the ν_{B-H_b} region and the B–H deformation region. Several examples of bidentate tetrahydroborate infrared spectra are pre-

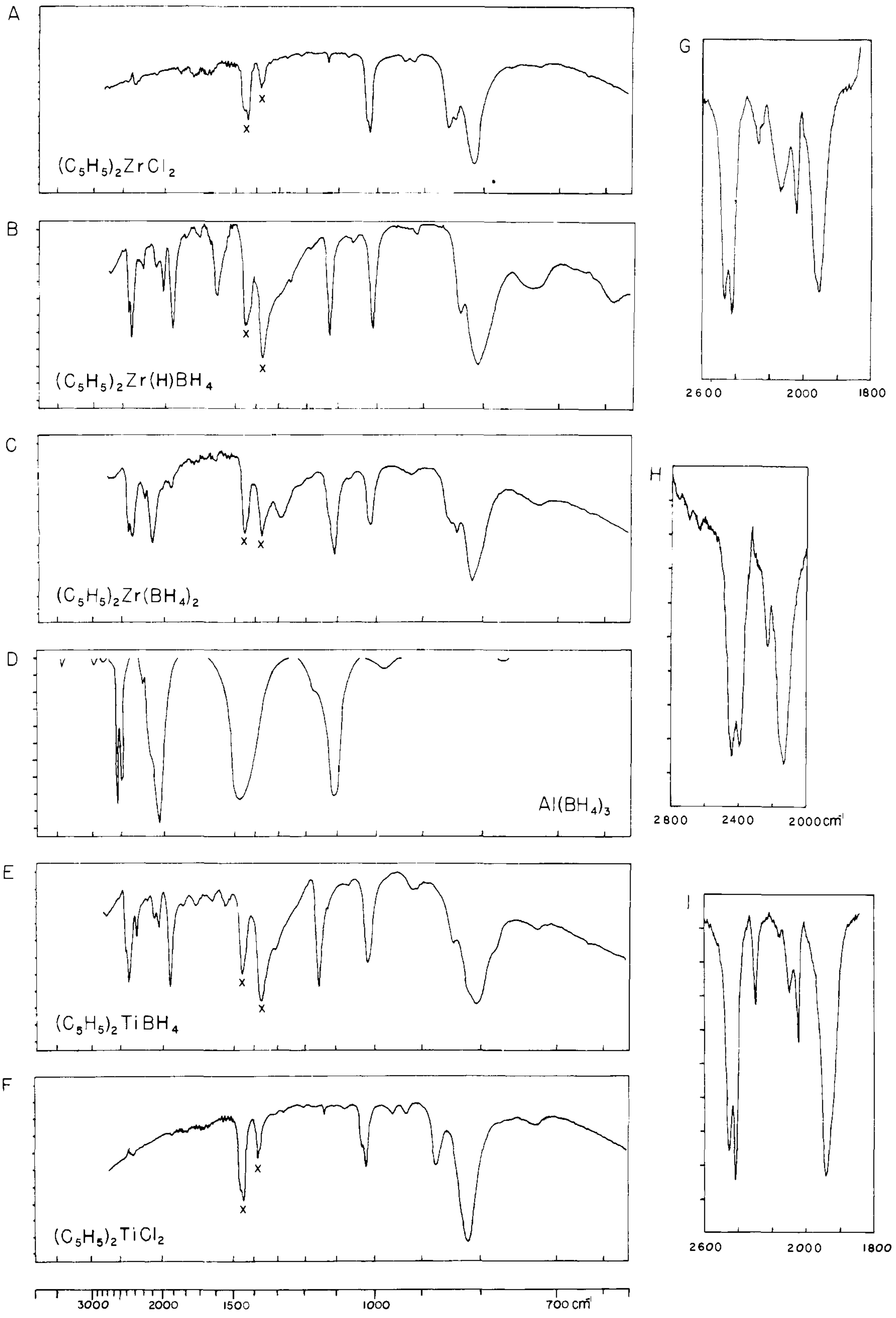


Figure 2. Infrared spectra of some bidentate tetrahydroborate complexes and their chloride analogues from ref 77: (A) the spectrum of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ as a Nujol mull; (B) the spectrum of $(\eta^5\text{-}C_5H_5)_2Zr(H)(BH_4)$ as a mull in Nujol; (C) the spectrum of $(\eta^5\text{-}C_5H_5)_2Zr(BH_4)_2$ as a Nujol mull; (D) the gas-phase spectrum of $Al(BH_4)_3$ reproduced from ref 93; (E) the spectrum of $(\eta^5\text{-}C_5H_5)_2Ti(BH_4)$ as a mull in Nujol; (F) the spectrum of $(\eta^5\text{-}C_5H_5)_2TiCl_2$ as a Nujol mull (sharp bands marked X are due to Nujol); (G) the spectrum in the B–H stretching region of $(\eta^5C_5H_5)_2Zr(H)(BH_4)$ as benzene solution; (H) the spectrum of $(\eta^5\text{-}C_5H_5)_2Zr(BH_4)_2$ as a solution in benzene; (I) the spectrum of $(\eta^5\text{-}C_5H_5)_2Ti(BH_4)$ as a benzene solution.

sented in Figure 2, along with information necessary to subtract vibrations due to other ligands on the metal. More details about the complete molecular structures of several of these compounds are deferred until section V.

Structure III infrared spectra are unique in almost all regions. The B–H_t stretching region features a single sharp A_1 band at

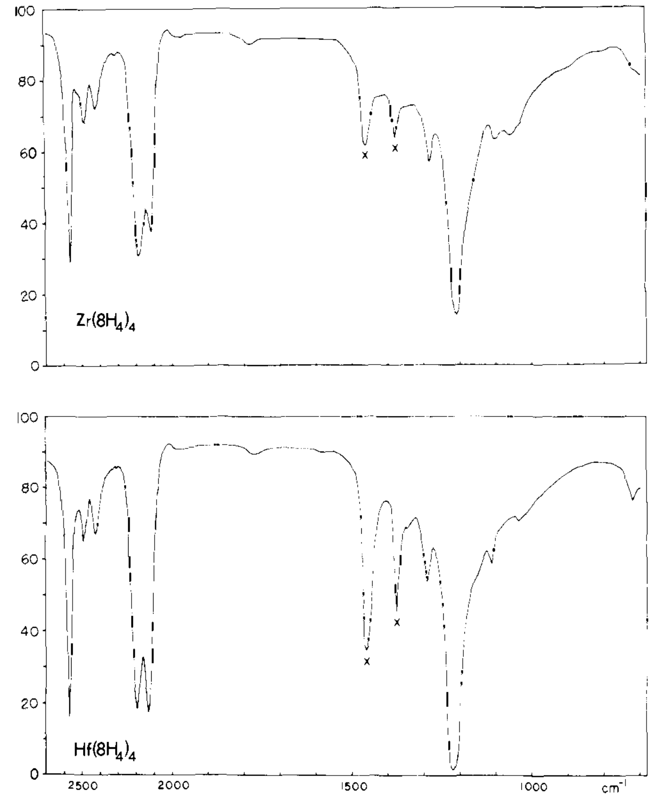


Figure 3. Infrared spectra of $Zr(BH_4)_4$ and $Hf(BH_4)_4$ as solutions in Nujol. The sharp bands due to Nujol are marked X (ref 77).

2450–2600 cm^{-1}; the A_1 and E B–H_b modes invariably appear as a doublet at 2100–2200 cm^{-1}. The only other band of significant intensity is a bridge deformation (1100–1200 cm^{-1}). Figure 3 presents infrared spectra of the tridentate model compounds $Zr(BH_4)_4$ and $Hf(BH_4)_4$, while Figure 4 exhibits spectra of some tridentate organoactinide tetrahydroborates.

The ionic structure IV should exhibit only two bands in the infrared spectrum, a T_2 B–H stretch at 2260–2300 cm^{-1} and a T_2 BH_2 deformation at 1050–1150 cm^{-1}. In cases of site symmetry lower than T_d for the BH_4^- moiety, broadening or splitting of these bands occurs.[102-104] The B–H stretch is frequently broader than the deformation. When very strong solid-state effects are present in, for example, $LiBH_4$, the doubly degenerate, Raman-active BH_2 bend at ca. 1200 cm^{-1} may become infrared active.[103,104]

B. Spectral Anomalies and Trends in Bonding

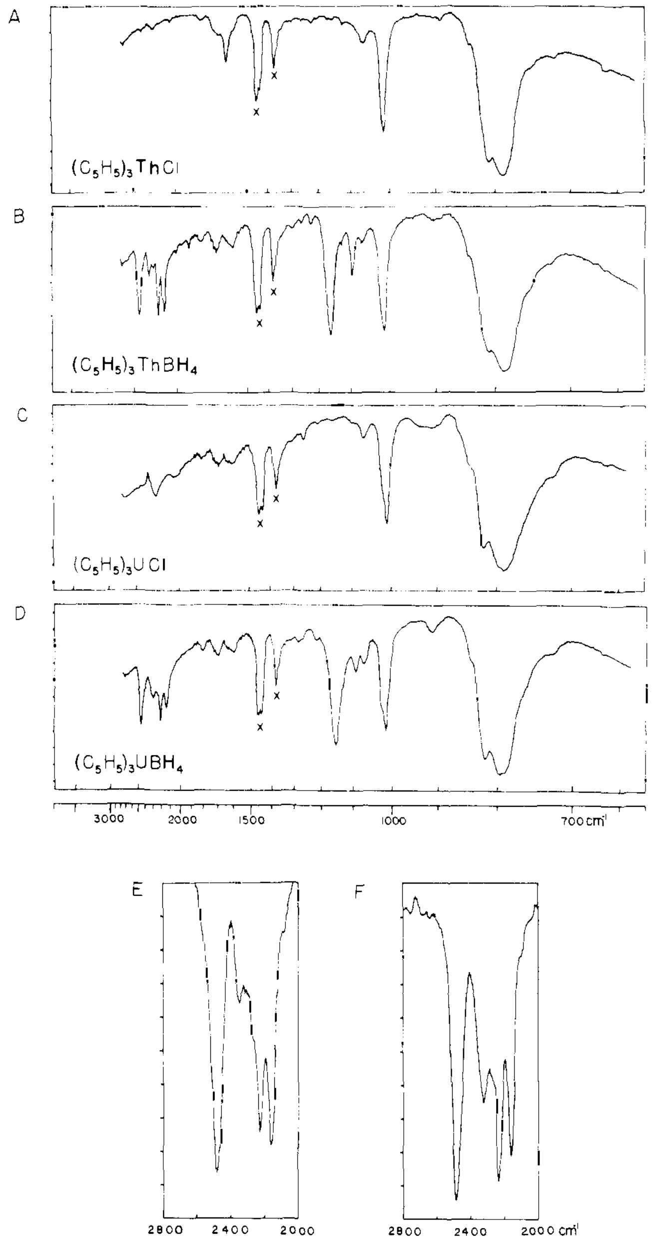
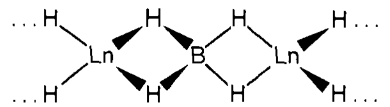


Figure 4. Infrared spectra of typical tridentate tetrahydroborate complexes and their chloride analogues from ref 77: (A) the spectrum of $(\eta^5\text{-}C_5H_5)_3ThCl$ as a Nujol mull; (B) the spectrum of $(\eta^5\text{-}C_5H_5)_3Th(BH_4)$ as a mull in Nujol; (C) the spectrum of $(\eta^5\text{-}C_5H_5)_3UCl$ as a Nujol mull; (D) the spectrum of $(\eta^5\text{-}C_5H_5)_3U(BH_4)$ as a mull in Nujol (sharp bands due to Nujol are marked X); (E) the spectrum of $(\eta^5\text{-}C_5H_5)_3Th(BH_4)$ in the B–H stretching region as a benzene solution; (F) the spectrum of $(\eta^5\text{-}C_5H_5)_3U(BH_4)$ as a benzene solution.

$Ln^+ BH_4^-$

25



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The above considerations are applicable to mononuclear complexes. In several cases, tetrahydroborates are known to have polymeric solid-state structures in which the BH_4^- moiety bridges two metal atoms. In these cases the vibrational spectra are more complex, but are by no means uninformative. For example, infrared and Raman studies of $Be(BH_4)_2$[102] did not reveal the details of the helical polymeric structure[64] (see section V for a discussion) but did reveal type II and type IV BH_4^- units. Scrutiny of the bond distances from the x-ray study reveals that the vibrational data accurately mirrored the strong interactions and simply did not detect the perturbation of the weaker bridging interactions. Another example is the series of compounds $(\eta^5\text{-}C_5H_5)_2LnBH_4$, Ln = Er, Yb.[70] The infrared spectra in the ν_{B-H_t}/ν_{B-H_b} region exhibit only a single band at 2280 cm^{-1}. In addition, a low-frequency band is observed at 1230 cm^{-1}. These results are compatible either with an ionic (IV and **25**) structure[105] or, more likely, a polymeric (**26**) structure. The latter choice is more compatible with vibrational frequencies as well as mass spectral data[70] and coordination numbers usually observed for organolanthanides.[106] A similar situation occurs in CH_3ZnBH_4.[63]

The discussion thus far has focused on elucidating the gross features of MBH_4 coordination. Though such correlations reveal important information about the metal–ligand bond, there are also more subtle trends which are visible within a given coordination geometry as the metal is varied. For example, procession from $(\eta^5\text{-}C_5H_5)_2TiBH_4$ to $(\eta^5\text{-}C_5H_5)_2VBH_4$ (both have bidentate structures) occurs with a marked lowering of ν_{B-H_b} (ca. 300 cm^{-1}) and an increase in the bridge expansion/ν_{M-H} frequency (ca. 80 cm^{-1}) while the vibrations involving the $B(H_t)_2$

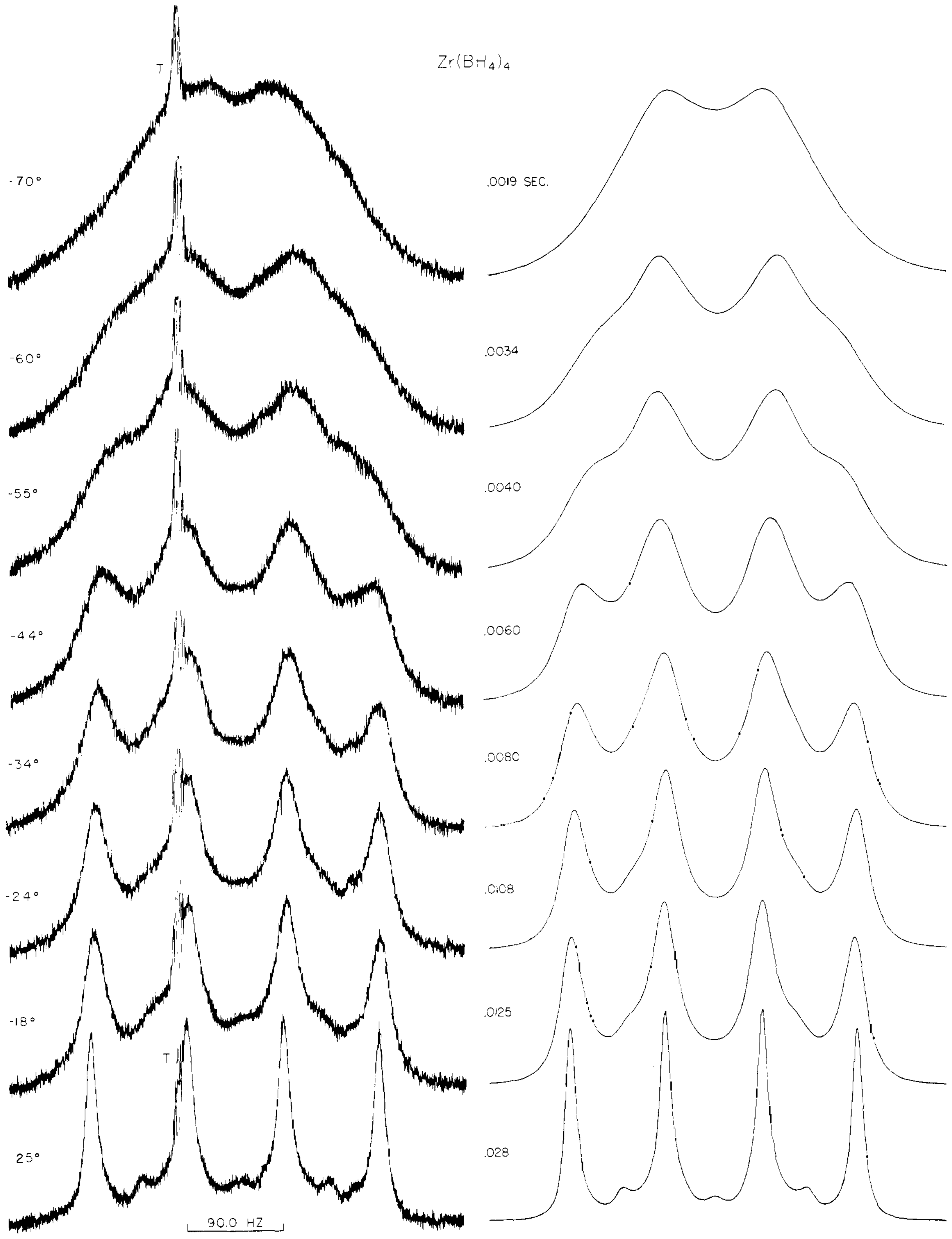
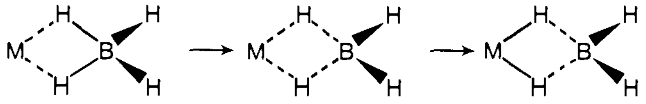


Figure 5. Left: Variable-temperature 90-MHz ^1H NMR spectra of $Zr(BH_4)_4$ as a solution in toluene $-d_8$. The peak marked T is due to traces of $C_6D_5CD_2H$. Right: Computed spectra for the ^{11}B spin-lattice relaxation times (T_1) indicated (from ref 109).

portion of the molecule remain essentially unperturbed.[28] The close proximity of Ti and V in the periodic table rules out mass effects as a major cause of the changes. The trend can be rationalized by considering the effects of increasing metal ion distortion of the isolated BH_4^- unit and decreasing the ionic character of the bonding. An alternative description (see section VI for more details) would involve increasing the donation of electron density from predominantly bonding $B-H_b$ ligand molecular orbitals. The overriding first-order effect should be weakening of bridging B-H bonds and, presumably, strengthening of the M-H and M-B interactions. The description was put



forward to explain the differences between $(C_5H_5)_2TiBH_4$ and $(C_5H_5)_2VBH_4$; it is equally applicable to $(C_5H_5)_2NbBH_4$, which has an infrared spectrum similar to the vanadium complex. Examination of Figure 4 also reveals that the infrared spectrum of $(C_5H_5)_2Zr(BH_4)_2$ is curious in that ν_{B-H_b} is somewhat high in frequency, and the bridge expansion/ν_{M-H} stretch is somewhat low. The above explanation invoking diminished donation from the BH_4 ligands can explain the data. It has been previously pointed out that the electronic demands by the metal on the BH_4 functionality are not as great as in compounds such as $(C_5H_5)_2TiBH_4$.[77]

IV. Nuclear Magnetic Resonance Spectroscopy and Fluxional Behavior

A significant feature of the proton NMR spectra of nearly all covalent metal tetrahydroborates studied to date is the magnetic equivalence of bridge and terminal hydrogen atoms at ambient temperatures. Only one exception to this generalization has been reported.[45] The surprising magnetic degeneracy of bridge and terminal hydrogens is observed for both bidentate and tridentate coordination geometries. It was recognized some time ago that this equivalence was most likely due to rapid (on the NMR time scale) interchange of bridge and terminal hydrogens.[26,107,108] The actual rate of the process and the mechanism of the rearrangement remained a mystery. At room temperature most complexes exhibit in the proton NMR a broad quartet, since ^{11}B (81.2% abundant) has a nuclear spin quantum number of $^3/_2$; occasionally the multiplet due to ^{10}B ($I = 3$, 18.8% abundant) is also observed. The room-temperature spectrum of $Zr(BH_4)_4$ (Figure 5) is typical. For most diamagnetic, nontransition metal or transition metal tetrahydroborates with completely filled or empty d shells, the multiplet is usually centered at τ 7–10. $J_{^{11}B-H}$ is usually 80–90 Hz and $J_{^{10}B-H}$ is 27–30 Hz.[8]

An obvious means to elucidate the nature of the bridge-terminal hydrogen interchange would be to lower the temperature of the sample. This results in collapse of the multiplet and eventual "washing out" of the B–H coupling, as shown in Figure 5. The reason for this spectral collapse has been the source of considerable confusion. It is *not* related to slowing (or speeding up) of the fluxional process. Rather, it is due to rapid spin–lattice relaxation of the ^{11}B and ^{10}B nuclei.[109,110] In solution, a particularly efficient relaxation mechanism for quadrupolar nuclei (i.e., $I > \frac{1}{2}$) is one in which the quadrupole moment of the nucleus interacts with the electric field gradient at the nucleus, the direction of which is fluctuating as a consequence of rapid molecular reorientation.[109,111-114] The rate of spin–lattice relaxation is given by the equation

$$\frac{1}{T_1} = \frac{3}{40}\,\frac{2I+3}{I^2(2I-1)}\,(1 + \eta^2/3)(e^2qQ/h)^2\tau_c \qquad (40)$$

where T_1 = spin–lattice relaxation time, I = nuclear spin quantum number, η = asymmetry parameter at the quadrupolar nucleus

$$= \left(\frac{\partial^2 V}{\partial x^2} - \frac{\partial^2 V}{\partial y^2}\right)\bigg/\frac{\partial^2 V}{\partial z^2}$$

eq = field gradient at the quadrupolar nucleus = $\partial^2 V/\partial z^2$, eQ = nuclear quadrupole moment of the nucleus, e^2qQ/h = nuclear quadrupole coupling constant, and τ_c = rotational correlation time for quadrupolar relaxation.

For axial symmetry about the boron as in $Zr(BH_4)_4$, $\eta = 0$. Thus the magnitude of the chemically interesting nuclear quadrupole coupling constant, which is proportional to the field gradient at boron in the particular molecule, and the rotational correlation time, which is inversely proportional to the tumbling rate of the molecule in solution, will determine the rate of boron spin–lattice relaxation. When this rate becomes sufficiently rapid, i.e., when boron nuclei are making sufficiently rapid transitions between spin states, the coupled protons are no longer able to "distinguish" boron spin states, and isotropic spin–spin coupling is washed out. The phenomena can be treated as a multisite exchange process, and theoretical spectra can be generated for various boron T_1 values[109] (Figure 5). A number of experimental and theoretical results suggest that τ_c varies approximately as $\bar{\eta}/T$,[109,115-117] where $\bar{\eta}$ is the macroscopic viscosity of the solution and T is the temperature. This phenomenonologically applicable hydrodynamic model is sufficiently accurate to illustrate the effect of lowering the solution temperature on the boron T_1, hence the spectral pattern. This effect has been called "thermal decoupling";[110] however, it should be noted that changes in viscosity at constant temperature produce equivalent results (Figure 6). Perhaps "correlation time decoupling" would be a more accurate term. One result of studies on $Zr(BH_4)_4$ and $Hf(BH_4)_4$ was an estimate of e^2qQ/h which follows from application of eq 40 for an estimated correlation time.[109] For a nearly spheroidal molecule the latter quantity can be calculated with reasonable accuracy.[116] The value of the ^{11}B nuclear quadrupole coupling constant for both molecules was found to be 1.7 ± 0.3 MHz, which is surprisingly large (it should be zero for tetrahedral BH_4^-) but still too small to observe by conventional NQR.[118]

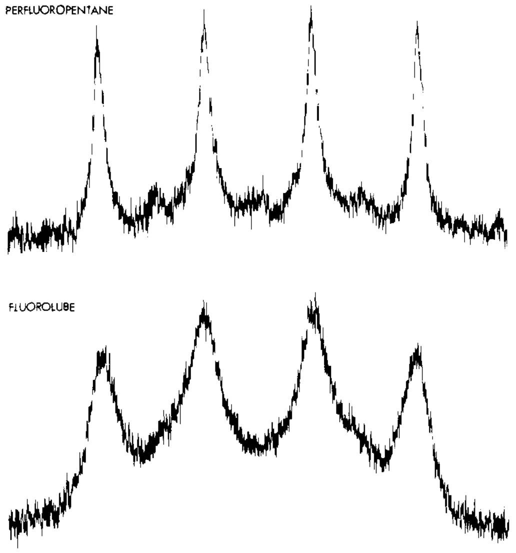


Figure 6. Room-temperature ^1H NMR spectra at 90 MHz of $Zr(BH_4)_4$ solutions as a function of viscosity. The concentration of $Zr(BH_4)_4$ and the line width of internal benzene were approximately the same in the two samples (ref 109).

A convenient way to eliminate quadrupolar effects from covalent metal tetrahydroborate ^1H NMR spectra is by simultaneous, strong radio-frequency irradiation at the ^{11}B frequency. When this is carried out the BH_4 proton spectrum collapses to a sharp singlet. An example is shown in Figure 7A. It is then possible to undertake low-temperature studies without quadrupolar interference. A sharp BH_4 singlet is observed in the case of $Zr(BH_4)_4$, $Hf(BH_4)_4$, $(\eta^5\text{-}C_5H_5)_2Zr(BH_4)_4$, and $(\eta^5\text{-}C_5H_5)_2Zr(H)BH_4$, and there is no evidence that the intramolecular exchange process is slowing at −85 °C in toluene-d_8.[119] Three approaches to the elucidation of the nature of the fluxional process have been pursued. The first was to examine the ^1H NMR spectra of molecules where vibrational or electronic (see section VI) considerations suggested the metal–ligand bonding might be more rigid; i.e., the ground-state metal–ligand configuration might lie in a deeper potential well. The second approach was to alter the NMR time scale. The third approach was to change media: solid-state NMR studies.

The vibrational spectrum of $(\eta^5\text{-}C_5H_5)_2VBH_4$, discussed in the previous section, indicated very strong and covalent metal–ligand interaction in the bidentate geometry.[28] Low-temperature ^1H NMR studies (Figure 7B) revealed, for the first time, slowing of the bridge–terminal hydrogen interchange process. The high-field resonance was assigned to the $(H_b)_2$ signal; the resonance po-

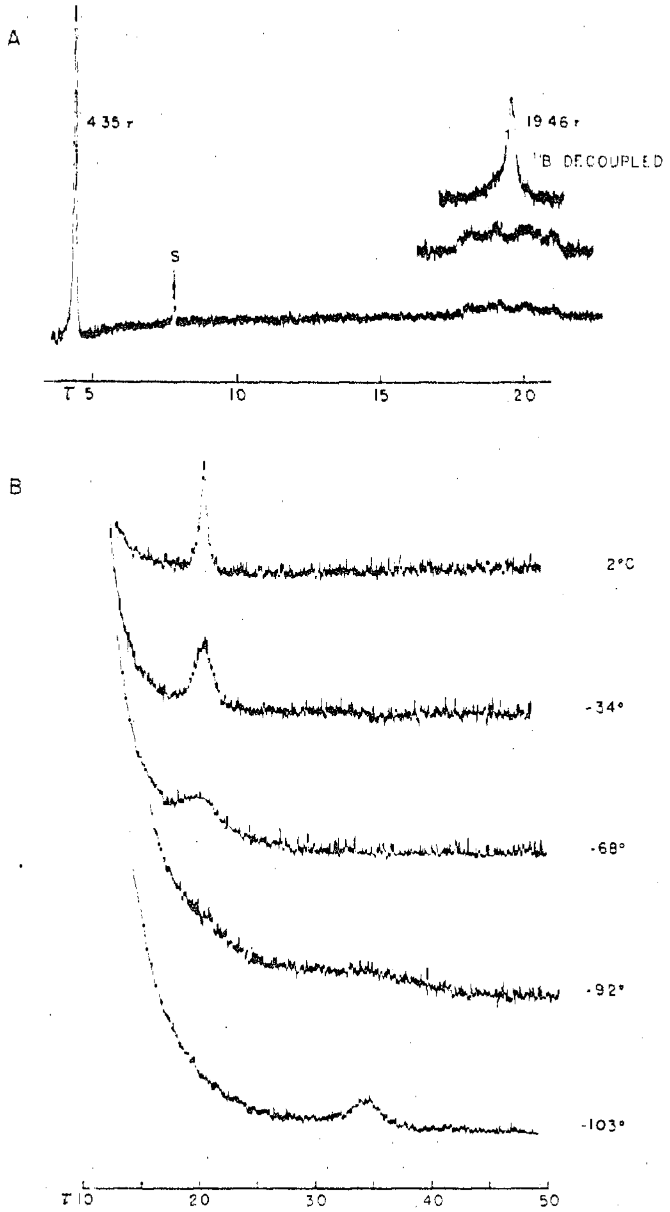


Figure 7. (A) Room-temperature 90-MHz ^1H NMR spectrum of $(\eta^5\text{-}C_5H_5)_2VBH_4$ in toluene-d_8. S denotes solvent. (B) Variable-temperature 90 MHz $^1H\{^{11}B\}$ spectra of $(\eta^5\text{-}C_5H_5)_2VBH_4$ in 3:1 toluene-d_8-diethyl ether (from ref 28).

sition is in the region expected for a hydride of a transition metal with a partially filled d shell.[28,99] The $(H_t)_2$ resonance was obscured by the solvent, but its position was calculated to be ca. τ 5–6, close to the resonance position of the terminal protons in diborane.[120] The free energy of activation at spectral coalescence[121] (−87 ± 7 °C) was calculated to be 7.6 ± 0.3 kcal/mol; assuming log $A = 13$, then $E_a \approx 7.9$ kcal/mol. Interestingly, the analogous $(\eta^5\text{-}C_5H_5)_2NbBH_4$, which has a nearly identical MH_2BH_2 vibrational spectrum, showed no significant broadening of the BH_4 resonance down to −120 °C; hence $E_a \lesssim 5.6$ kcal/mol. The difference in behavior of $(C_5H_5)_2VBH_4$ and $(C_5H_5)_2NbBH_4$ may reflect more the energetics of reaching the transition state than differences in ground-state bonding. For instance, Nb has a larger ionic radius and could more easily accommodate such configurations as a tridentate transition state for the fluxional process. Another intriguing example of a covalent tetrahydroborate with a high barrier to bridge–terminal hydrogen interchange is $Mo(CO)_4BH_4^-$.[35,122] Here it is possible to reach the slow exchange limit (Figure 8) and to observe both the $(H_b)_2$ and $(H_t)_2$ resonances. The field position for the latter is close to that estimated for $(C_5H_5)_2VBH_4$. In this case, $\Delta G_c^\ddagger$ = 10.0 ± 0.2 kcal/mol. Preliminary results indicate even higher barriers in $IrH_2(BH_4)(PR_3)_2$ and $RhH_2(BH_4)(PR_3)_2$ compounds.[45]

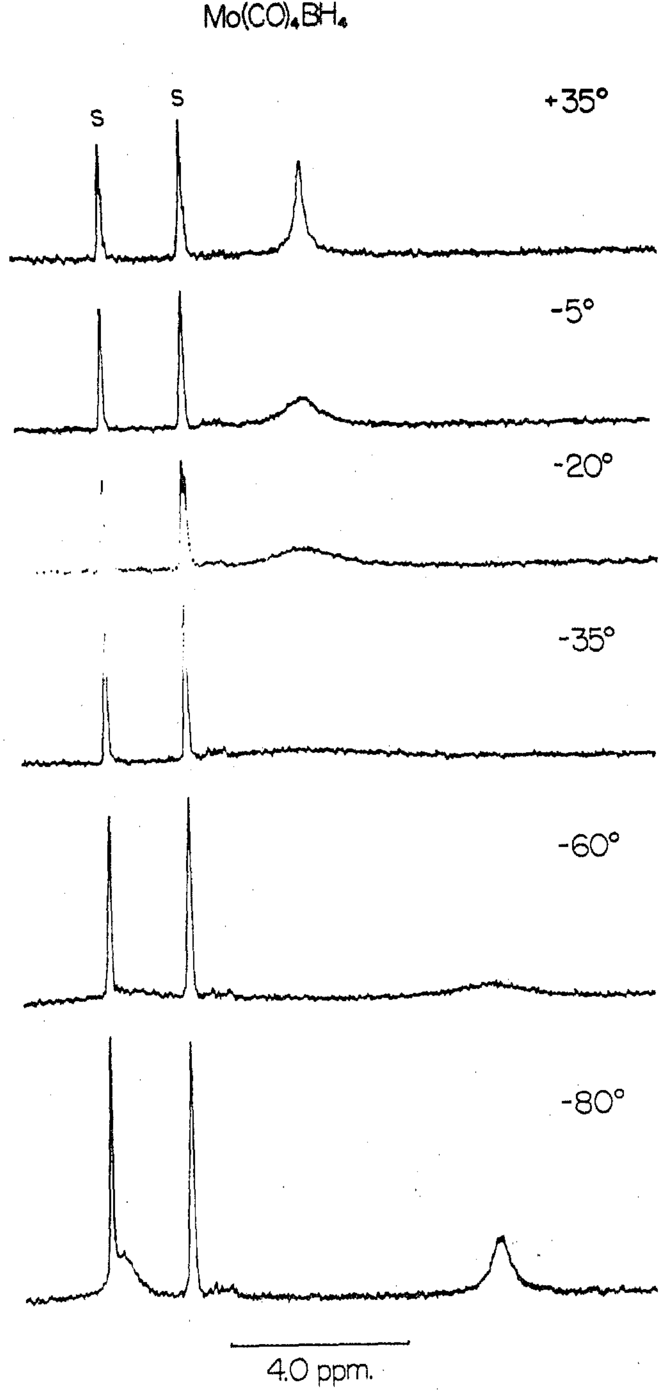


Figure 8. Variable-temperature 60 MHz ^1H NMR spectra of $[(C_6H_5)_3P]_2N^+\text{-}Mo(CO)_4BH_4^-$ with decoupling of ^{11}B. S denotes traces of protonated species in the solvent, tetrahydrofuran-d_8 (ref 122).

Another approach to studying processes which are rapid on the NMR time scale is by altering the NMR time scale. The time resolution of NMR can be increased by expanding the energy separation between the exchanging sites.[76,114,121,123–126] The effect on the spectrum can be appreciated in a simple two-site process by considering the solution to the modified Bloch equations[121] in the fast exchange regime (eq 41) and at spectral coalescence (eq 42).

$$\frac{1}{\tau} = \frac{(\delta\omega)^2}{4}\left[\frac{1}{T_2^{\text{exch}}} - \frac{1}{T_2^{0}}\right]^{-1} \qquad (41)$$

(fast exchange)

$$\frac{1}{\tau} = \pi\delta\omega/\sqrt{2} \qquad (42)$$

(coalescence)

Here τ is the mean preexchange lifetime, and $\delta\omega$ is the frequency separation between exchanging sites. Note the sensitivity of the spectral line width to changes in $\delta\omega$. One way to greatly expand $\delta\omega$ is by studying a paramagnetic compound. Here isotropic (contact and dipolar)[127,128] shifts are expected to greatly increase the frequency separation between exchanging sites. The $5f^2$ system $(\eta^5\text{-}C_5H_5)_3UBH_4$ offers the attractive features cited above, plus very rapid electron spin relaxation, which results in narrow proton line shapes.[76,129,130] Figure 9 presents low-temperature ^{1}H NMR spectra of $(C_5H_5)_3UBH_4$ with decoupling of ^{11}B. The spectral collapse is observed for solutions with several different solvents, but most importantly, no collapse is seen in the related compound $(C_5H_5)_3UH_3BCH_2CH_3$ which could not be fluxional. The low-temperature results for $(C_5H_5)_3UBH_4$ are interpreted as slowing of the bridge–terminal hydrogen interchange process. From the chemical shift data for $(C_5H_5)_3UBH_4$ and the ethyl derivative, the frequency separation between exchanging sites ($\delta\omega$) is calculated to be 15 000–36 000 Hz at the estimated coalescence point, -140 ± 20 °C. This yields $\Delta G_c^{\ddagger} = 5.0 \pm 0.6$ kcal/mol. Thus, the paramagnetic isotropic shifts allow measurements of a rate process which would be too rapid for NMR studies in a diamagnetic compound in solution.

A method of promising utility for studying rapid fluxional processes in the solid state is broad-line NMR.[131–134] The greater range of accessible temperatures facilitates the slowing of rate processes too rapid to slow in solution. In addition, the lattice forces may impose interesting constraints upon molecular motion. The theory for treating broad-line NMR data is well developed.[135–137] In the solid, the major interaction between two nuclear spins is a through-space dipolar coupling of the form

$$\frac{1 - 3\cos^2\theta_{jk}}{r_{jk}^{\;3}} \qquad (43)$$

where θ is the angle between the magnetic field of the spectrometer and the vector between nuclei j and k, and r_{jk} is the internuclear distance. The dipolar interactions, when summed over all proximate spins in the lattice and over all orientations in the polycrystalline sample, usually lead to line shapes which are many times broader than those observed in solution spectra. Rapid intramolecular motion which averages θ over all possible angles reduces the intramolecular dipolar interaction to zero; this leads to drastic narrowing of the line shape. More restricted motion over only certain angles reduces the interaction to an extent which can usually be calculated. Structural data are most easily related to the second moment, $(\Delta H)^2$

$$(\Delta H)^2 = \int_{-\infty}^{\infty} (H - H_{av})^2 f(H)dH \Big/ \int_0^{\infty} f(H)dH \qquad (44)$$

H = magnetic field

H_{av} = center of the resonance

$f(H)$ = line-shape function

of the experimental line shape by the equation of Van Vleck

$$(\Delta H)^2 = {}^6\!/_5\, g_1^{\,2}\beta^2 I_1(I_1 + 1)\frac{1}{N_1}\sum_{j>k}\frac{1}{r_{jk}^{\;6}} + {}^4\!/_{15}\, g_2^{\,2}\beta^2 I_2(I_2 + 1)\frac{1}{N_2}\sum_{j,n}\frac{1}{r_{jn}^{\;6}} \qquad (45)$$

where the first term refers to resonant nuclei and the second term to magnetic nuclei not at resonance. N_1 and N_2 refer to the number of proximate equivalent nuclei, and the other terms have their usual meaning.[135–137] Because accurate neutron diffraction structural data were available for $Hf(BH_4)_4$ at a number of temperatures[138] (see section V), we undertook a broad-line NMR study to determine (a) whether the bridge–terminal hydrogen interchange process occurred in the solid state; (b) if so, what the rate of the process was; (c) whether the behavior in the solid state could be related to the thermal motion detected in the neutron diffraction results.[138] Figure 10 presents the line-width dependence of the $Hf(BH_4)_4$ proton resonance as a function of temperature.[139] These data as well as variable-temperature spin–lattice relaxation time measurements[139] reveal the presence of two rate processes. Second moment calculations suggest that one process is the bridge–terminal hydrogen exchange and that it occurs with an activation energy of 8.4 kcal/mol. This value is fairly close to that found in solution for the other tridentate tetrahydroborate, $(C_5H_5)_3UBH_4$.[76] The nature of the

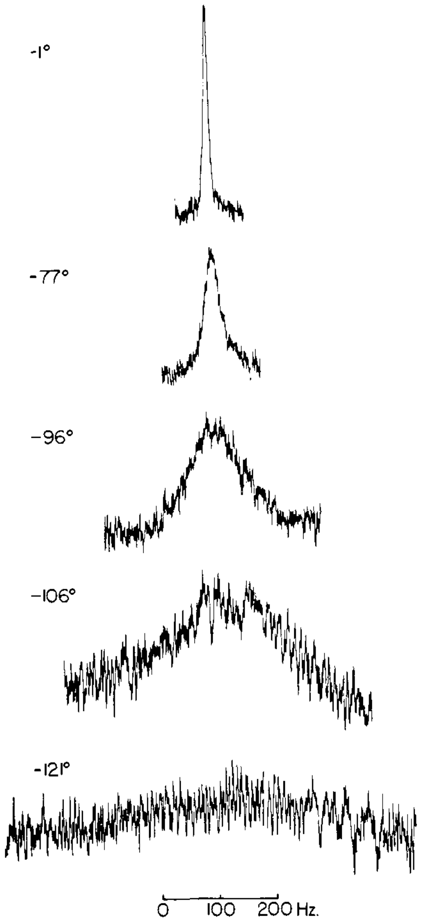


Figure 9. Variable-temperature ^{1}H NMR (90 MHz) spectra of $(\eta^5\text{-}C_5H_5)_3UBH_4$ in the BH_4 region as a solution in 1:3 Me_4Si–diethyl ether, with broad band decoupling of ^{11}B (ref 76).

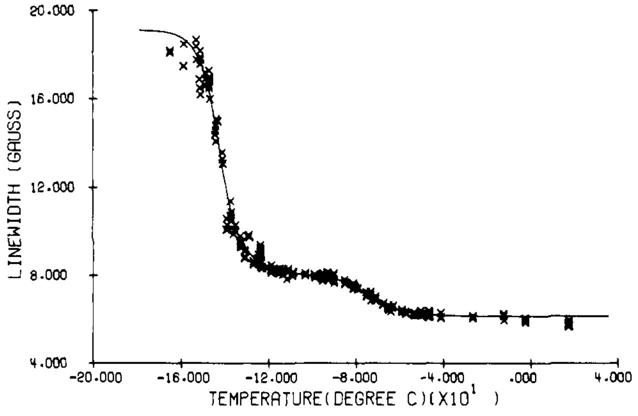
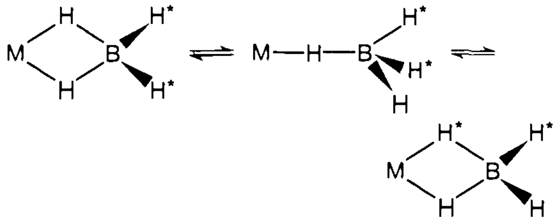


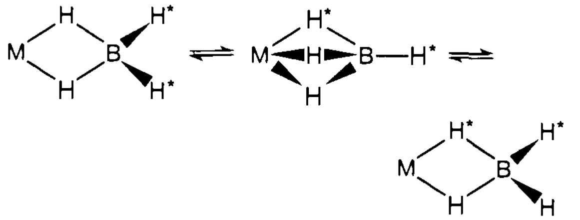
Figure 10. The temperature dependence of the ^{1}H NMR line width of a polycrystalline sample of $Hf(BH_4)_4$ (from ref 139).

second rate process in solid Hf(BH$_4$)$_4$ will be discussed in detail elsewhere;[139] it appears to be a librational motion of the coordinated BH$_4^-$ about its threefold axis and has a barrier of 4.6 kcal/mol. This proposed motion is supported by the thermal parameters obtained in refining the neutron diffraction data.[138]

Though the energetic details of the dynamic hydrogen interchange process in covalent metal tetrahydroborates are now on a quantitative footing, the exact mechanism of the process remains open to speculation. We consider first the various possible pathways which have been proposed and then discuss what information might actually be obtainable by NMR experiments. The first pathway to be suggested for stereochemical nonrigidity in a tetrahydroborate anion which has bidentate BH$_4$ ligation was put forward by Williams[108] for Al(BH$_4$)$_3$. It involved permutation of bridge and terminal hydrogens via a monodentate intermediate or transition state. Subsequently,[24,109] it was pointed out that a bidentate $\rightleftharpoons$ tridentate equilibration offered several attractive features. Not only are both geometries known in the ground state, but one process and its reverse serve to describe a means of hydrogen interchange for both bidentate and tridentate borohydrides.[109] The two cases would simply be traversals of similar but inverted potential energy surfaces. In addition, certain empirical observations (see section VI) suggested that, at least for early transition metals, bidentate and tridentate ligation patterns did not differ greatly in energy.[77] This was in accord with the low activation energy of the hydrogen interchange process.



(46)



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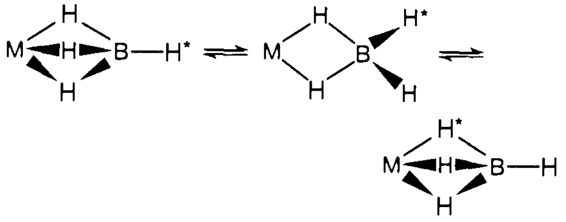
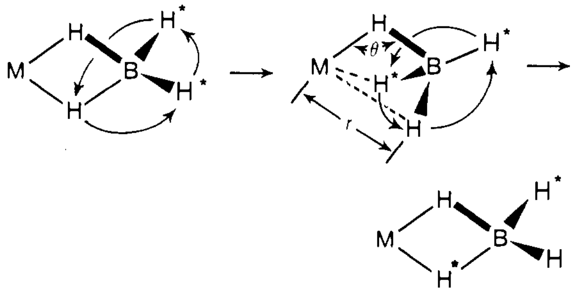


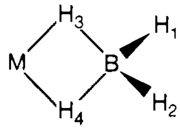
(48)

The above rearrangement pathways as written are not strictly concerted[140] in the sense that bond breaking and bond making are not simultaneous events along the reaction coordinate. It is possible to proceed further and enumerate an entire family of concerted processes for tetrahydroborates with bidentate ground-state geometries by twisting the ligand about one of the B-H$_b$ bonds (darkened) as shown in eq 49. The parameters r and θ could have a range of values and in the two possible extremes define tridentate and monodentate structures. A similar twisting process can be written for a complex with a tridentate ground-state structure; here the midpoint on the reaction coordinate resembles, with the exception of possible dissymmetry in the bridge, a bidentate configuration.



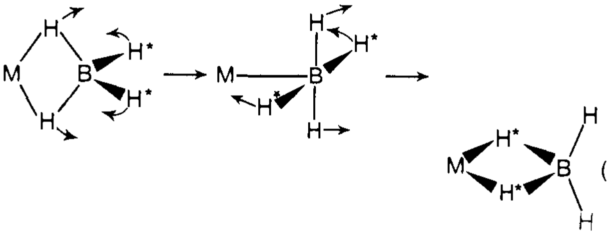
(49)

It is next appropriate to inquire if any NMR experiment could differentiate among the above suggested processes. Since a dynamic NMR experiment does not monitor reaction mechanisms but rather nuclear permutations which may be interpreted in terms of reaction mechanisms, the real question is which nuclear interchange processes could give rise to different spectral band-shape patterns for various rates of site exchange. To answer this question rigorously, resort is made to group theory and combinatorial mathematics as outlined by Klemperer[141] and others.[142] This method is a means of counting the number of molecular "reactions" which are "differentiable" in an NMR experiment by enumerating those permutations of nuclei which alter the spin Hamiltonian of the starting configuration, and partitioning these reactions into equivalency classes. For a C_{2v} bidentate borohydride complex three reactions are, in principal, differentiable. Neglecting the identity reaction and its equivalents, the two permutations of interest are shown below.



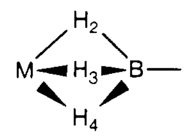
Reaction 1	Reaction 2
(13)(2)(4)	(13) (24)

Each reaction, of course, has other nondifferentiable permutations which are equivalent and which can be readily generated from the given reactions. Reaction 1 and its equivalents[143a] can be interpreted mechanistically as either eq 47, 48, or 49. Each traversal of the reaction coordinate interchanges one bridge and one terminal hydrogen. In contrast, reaction 2 and its equivalents[143b] have not been previously proposed. These operations permute both bridge hydrogens with both terminal hydrogens in each mechanistic event. Topologically, the situation is analogous to that in C_{2v} XPY$_4$ molecules;[144] also, reaction 2 may be interpreted as a Berry pseudo-rotation, and involves an intermediate C_{4v} square pyramid (eq 50). The plausibility of this mechanism is by no means secure. However, there is ample precedent for metal-boron bonds,[145] five-coordinate boron (BH$_5$),[145–147] and a substantial metal-boron overlap in metal tetrahydroborates (see sections V and VI). In any case, reaction 2 is the only process differentiable by NMR from reaction 1.



(50)

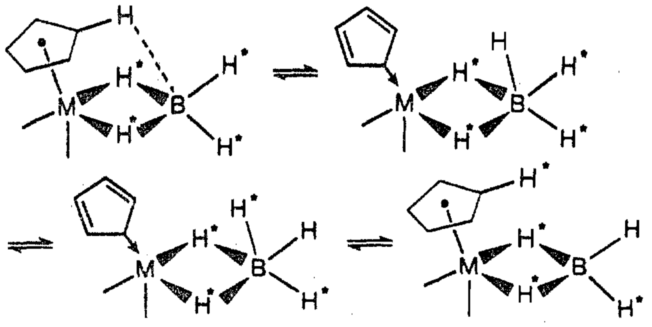
Application of the same permutational arguments to a tetrahydroborate with a tridentate ground-state geometry yields, besides the identity reaction, only one set of nondifferentiable reactions. These consist of the reaction (12)(3)(4) and others



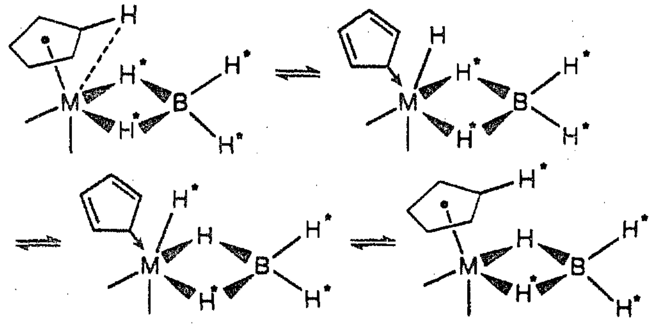
which appear equivalent to the NMR experiment.[148] Thus, in a tridentate system, little mechanistic information follows from such a permutational analysis.

The scope of dynamic molecular processes involving the coordinated tetrahydroborate moiety is not limited to intramolecular bridge–terminal hydrogen interchange. It has also been shown that rapid hydrogen exchange can occur between BH_4 and other ligands coordinated to transition metals. Variable-temperature ^1H NMR spectra of $(\eta^5\text{-}C_5H_5)_2Zr(BH_4)_2$, $(\eta^5\text{-}C_5H_5)_2Hf(BH_4)_2$, and $(\eta^5\text{-}C_5H_5)_2Zr(H)BH_4$ exhibit rapid interchange of C_5H_5 and BH_4 protons at high temperature.[149] An example of boron-decoupled spectra for $(\eta^5\text{-}C_5H_5)_2Zr(H)BH_4$ is presented in Figure 11. Note that at highest temperatures, the metal-bound hydrogen also becomes involved in the transfer process. Thermal decomposition precludes studies at higher temperatures. Dilution studies in all of the above examples support the intramolecularity of the process, as do solid-state infrared spectroscopic experiments with $(C_5H_5)_2Zr(BD_4)_2$.[149] Two possible reaction pathways were put forward[149] to explain the observed site permutation. Direct transfer of a cyclopentadienyl hydrogen to coordinated BH_4^- (Mechanism A) followed by pseudo-rotational scrambling of hydrogens in the coordinated BH_5 moiety and return of a different hydrogen to the carbocyclic ring is one plausible process. It is in some ways analogous to the protonation of BH_4^-.[146,147] Addition of a C–H bond to the metal and subsequent interchange of metal hydride with boron hydride (Mechanism B) are two mechanistic components with firm precedent. Metalation of C–H bonds, including those contiguous with a six-electron π system, is well established,[150] as are rapid bridge–terminal hydrogen interchange processes in metal hydride,[151,152] metalloborane,[110] and borane systems.[110] Mechanism B is supported by the observation of metal hydride exchange in $(C_5H_5)_2Zr(H)BH_4$, albeit at higher temperatures than CH–BH interchange. The metal hydride and the transferred hydride could occupy unique coordination sites which interconvert less rapidly. Alternatively, Mechanism A is operative, and the metal-bound hydride becomes involved via a different route, such as transfer of BH_3 between M–H functionalities. Efforts to obtain further information from spin saturation transfer experiments[153,154] were frustrated by rapid thermal decomposition (especially to traces of paramagnetic products) at high temperatures.

MECHANISM A



MECHANISM B



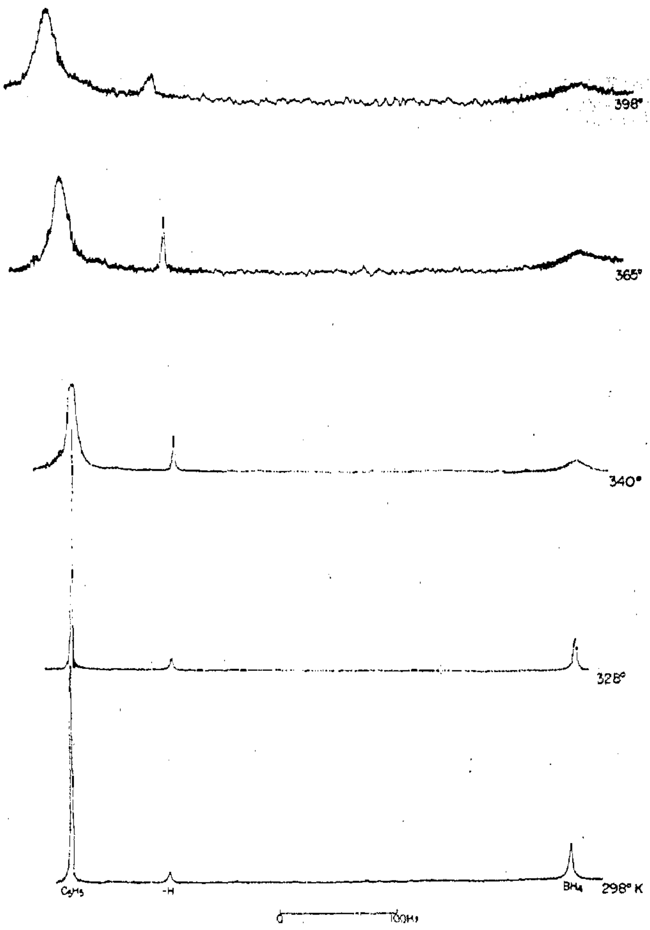
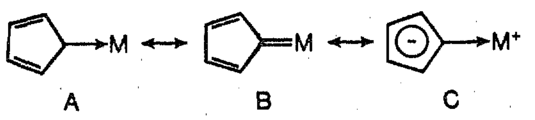
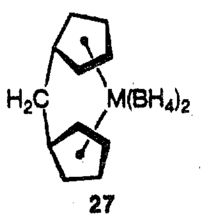


Figure 11. Variable-temperature 90-MHz ^1H NMR spectra of $(\eta^5\text{-}C_5H_5)_2Zr(H)BH_4$ in toluene-d_8 with broad-band decoupling of ^{11}B (ref 149).

Regardless of the exact details of the hydrogen trajectory along the reaction coordinate (in essence, does it stop at the metal along the way?), this work adds to the growing body of evidence that η^5-cyclopentadienyl hydrogens possess considerable lability,[155,156] and that hydrogens bound to multihapto hydrocarbon ligands can be rapidly transferred.[157] In addition, the importance of intermediate carbene complex–ylide species such as A–C is strongly suggested.[149,155] Two more experiments[158] have been conducted to probe further the nature of the unique cyclopentadienyl hydrogen transfer process in tetrahydroborate complexes. Constraining the ring system as in **27** completely inhibits the exchange process on the ^1H NMR time scale. For **28**, exchange of *both* ring and methyl protons is observed.[158]





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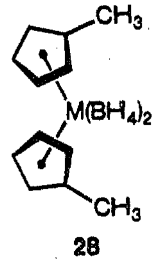


28

V. Structural Studies of Metal Tetrahydroborate Complexes

Any complete understanding of the properties of a molecular system must rest upon a firm structural foundation. For metal tetrahydroborate complexes, precise metrical data are essential for learning more about the bonding. Unfortunately, the most common solid-state structural technique, single-crystal x-ray diffraction, is, in many cases, of only limited utility.[159] Since x-ray scattering is approximately proportional to the square of the atomic number of an atom, accurate location of hydrogen atoms in close proximity to transition metal, lanthanide, and actinide ions is extremely difficult. Furthermore, the tendency of light atoms to have large vibrational amplitudes renders the scattering more diffuse. Though it is unlikely that bridge-terminal BH_4^- hydrogen interchange processes will be fast on the x-ray time scale (ca. 10^{-20} s), it is likely that the potential energy surfaces describing such low activation energy processes will be rather flat. If the potential wells are sufficiently shallow and broad, rather large vibrational amplitudes can be expected (for BH_4^- hydrogens) along certain coordinates. The situation is similar to that encountered in studies of η^5-C_5H_5 metal complexes,[160] where libration about the ring C_5 axis greatly reduces the precision of the carbon and hydrogen coordinates. A more complete discussion of the effect various models for thermal motion have on derived bond distances is presented in ref 159b. Disorder is another closely related problem which arises when there are multiple wells in the potential surface. It is common in η^5-C_5H_5 systems,[160] and though it has not yet been observed in a tetrahydroborate system, such situations as disorder of tridentate tetrahydroborates about the threefold MH_3BH axis do not seem improbable. Besides the above accuracy limitations of x-ray diffraction in the study of tetrahydroborate systems, it should also be recognized that all B–H distances determined by this method are systematically short. This effect is due to bonding and arises because the hydrogen 1s electron density is not spherically symmetrical about the nucleus (as assumed in most x-ray scattering refinement models), but is "pulled" toward the B–H bond. The effect of the aspherical distribution of electron density is to yield B–H bond distances upon refinement which are at least 0.05 Å shorter than those derived for the same compound by electron and neutron diffraction.[161b]

Gas-phase electron diffraction and single-crystal neutron diffraction are two other structural techniques which have been applied to metal tetrahydroborate complexes. The former is useful for relatively simple, volatile complexes. Since electron scattering arises from the electrostatic potentials of the atoms in the molecule, the relative contributions of light atoms to the scattering is considerably greater than in x-ray diffraction.[159b] Also, because the scattering has both electronic and nuclear components, anomalously short bond distances to hydrogen are not obtained. Since data are obtained in the gas phase, disorder is not a problem. However, gas-phase electron diffraction suffers, as compared to solid-state diffraction experiments, from the relatively small amount of information contained in a single radial distribution function. Hence, it is not suitable for complex unsymmetrical molecules. Also gas-phase electron diffraction studies require the complex under examination to be volatile, and not to decompose under the conditions of volatilization. The presence of more than one species in the gas phase, such as in the case of $Be(BH_4)_2$ (vide infra), is a severe complication. In spite of these drawbacks, the method has made a significant contribution to the structural chemistry of metal tetrahydroborate complexes.

For highly accurate metrical data, neutron diffraction[159] is the method of choice. Neutron scattering amplitudes reflect only the nuclear properties of atoms, and the amplitude for hydrogen is sufficiently large to allow precise location of hydrogen nuclei in the presence of heavy atoms. Also, because nuclei scatter, the anomalously short bond distances found in x-ray studies are not encountered. The major drawbacks to neutron studies are the large sizes (0.5 to 5.0 mm on a side) of crystals required to accommodate the low thermal neutron flux produced by even the most advanced reactor facilities, and the relatively small number of facilities around the world equipped for single crystal neutron diffraction. The difficulties in refining diffraction data caused by large amplitudes of thermal motion and/or disorder are common to both x-ray and neutron techniques.

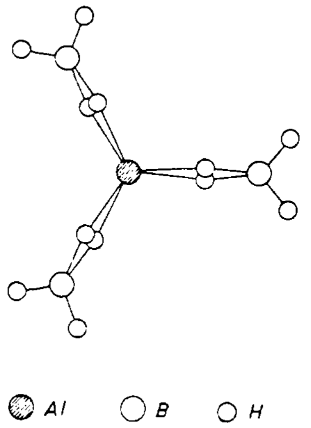
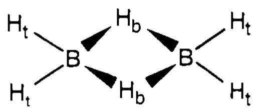


Figure 12. The molecular structure by gas-phase electron diffraction of $Al(BH_4)_3$ (ref 166).

Broad-line nuclear magnetic resonance studies represent a fourth method for obtaining structural data, through analysis of NMR line shapes broadened by nuclear dipole-dipole interactions (section IV). This method yields accurate results for simple, highly symmetrical systems. In cases where there are a large number of spins in unknown spatial orientations, the problem becomes sufficiently complex that it is impossible to derive meaningful structural information. As discussed in section IV, any unsuspected motional processes also influence the line shapes, hence the derived internuclear distances.

The compound which provides a convenient starting point as well as frame of reference for other structural studies is ionic potassium tetrahydroborate. Neutron diffraction data inferred a tetrahedral arrangement for the BH_4^- anion with a B–H distance of 1.260 Å.[162] This is in close agreement with a B–H distance of 1.255 Å calculated from second moment measurements of broad line NMR data on polycrystalline sodium, potassium, and rubidium tetrahydroborates at temperatures ranging from 20 to 293 K.[163]

Another model compound which is appropriate to a discussion of tetrahydroborate structures is diborane B_2H_6. Electron diffraction studies on gaseous diborane[164] and x-ray diffraction studies on crystalline diborane[161a] have been carried out. The molecular structure is indicated in **29**. Bond distances derived by gas-phase electron diffraction (Bartell and Carroll[164]) are B–H_t, 1.196 (8), B–H_b, 1.339 (6), and B–B, 1.775 (3) Å. These can be compared with x-ray diffraction values (Smith and Lipscomb[161a]) of 1.10 (2), 1.25 (2), and 1.776 (10) Å, respectively. For the reasons cited above, the B–H distances obtained by x-ray diffraction are systematically short. The close B–B contact is expected for electron-deficient systems with two-electron three-center bonding. More will be said in section VI. The valence angles around boron are appreciably distorted from tetrahedral with $\angle H_bBH_b$ = 97.0 (3)° and $\angle H_tBH_t$ = 119.0 (9)°.[164]



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The structure of aluminum tris(tetrahydroborate) is presented in Figure 12. It is apparent from this electron diffraction study

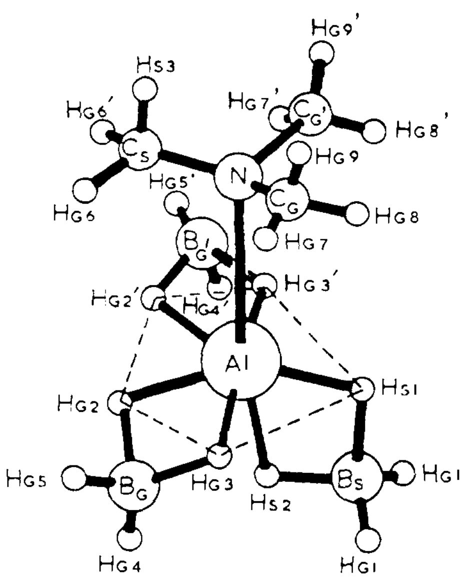


Figure 13. The structure by x-ray diffraction of $(CH_3)_3NAl(BH_4)_3$ at −160 °C from ref 169.

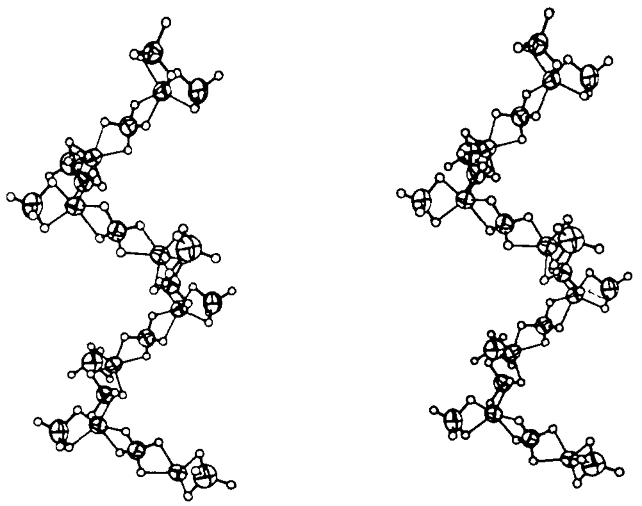
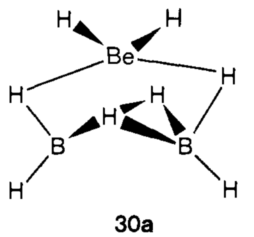


Figure 14. Stereoscopic view of the polymeric structure (by x-ray diffraction) of $Be(BH_4)_2$ from ref 64.

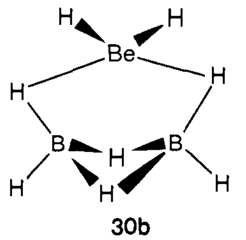
of a gaseous sample of $Al(BH_4)_3$ that each BH_4 ligand is bidentate and the overall coordination geometry around aluminum is that of a trigonal prism with bridging hydrides and a planar AlB_3 arrangement.[166] The molecular symmetry most closely approximates D_{3h} although a slight deformation or twist of the BH_4 groups could reduce this to D_3 symmetry.[166] Some pertinent bond lengths and angles are Al–H_b, 1.801 (6) Å; B–H_b, 1.283 (12) Å; B–H_t, 1.196 (12) Å; H_b–Al–H_b, 73.4 (8)°; H_b–B–H_b, 114.0 (2)°; H_t–B–H_t, 116.2 (2.2)°. The Al–B distance of 2.143 (3) Å is outside the combined covalent radii but is short enough to suggest some direct interaction.

When $Al(BH_4)_3$ is reacted with $:N(CH_3)_3$, the molecular complex $Al(BH_4)_3{\cdot}N(CH_3)_3$ is formed.[167] The x-ray structure of this compound at −160 °C is presented in Figure 13.[168,169] This compound is a prime example of how thermal motion and vibration in covalent tetrahydroborates may dramatically affect structure determination. At room temperature these thermal amplitudes are too great to allow an accurate location of hydrides to be made. However, at low temperature the hydrides were located and again the tetrahydroborates were bidentate. Pertinent structural data are Al–B, 2.218 (13) Å; B–H_b 1.18 (7) and 1.40 (7) Å (H_{s2}); B–H_t, 1.22 (11) Å; Al–H_b, 1.97 (7) Å; B–Al–B, 103.7 (3)°; H_b–Al–H_b, 70.2 (3.2)°; H_b–B–H_t, 116.9 (5.2)°. The mean geometry about aluminum here is that of a pentagonal bipyramid with a bridging hydride ligand capping one pyramid and the trimethylamine capping the opposite face. Within estimated standard deviations it appears that complexation with trimethylamine does not noticeably lengthen the Al–B distance in going from $Al(BH_4)_3$ to $Al(BH_4)_3{\cdot}N(CH_3)_3$.

One compound with a rather controversial past in terms of molecular structure is beryllium bis(tetrahydroborate). A gas-phase electron diffraction study of this molecule indicated a BeH_2 fragment coordinated to a diborane molecule. Two possible structural assignments for $Be(BH_4)_2$ are indicated in **30**.[170] From



30a



30b

this study the Be–B distance was found to be 1.83 (6) Å and the B–B distance was 1.74 (10) Å which is very similar to that in diborane (vide supra). The actual hydrogen positions in the gas-phase structure are very poorly resolved but the triangular B–Be–B framework appears certain. Evidently there is still a good deal of controversy surrounding the gas-phase structure of $Be(BH_4)_2$. A very recent gas-phase electron diffraction study[171] of this system has indicated the presence of two distinct species in the gas phase obtained from extremely pure, solid $Be(BH_4)_2$. The evidence for this fact arises from differing electron scattering patterns for gaseous samples which vary only in the means of vaporization of gaseous $Be(BH_4)_2$ from the solid. Although alternative explanations are available, i.e., luminescence of one sample, decomposition, impurities, it is apparent that the molecular structure of gaseous $Be(BH_4)_2$ remains shrouded in mystery at the present and the possibility of molecular isomerism in the gas phase exists.

An x-ray diffraction study of solid $Be(BH_4)_2$ was reported by Marynick and Lipscomb.[64] The structure was found to be that of a helical polymer with Be–B distances of 1.999 (4) Å for the bridging tetrahydroborate ligand and 1.918 (4) Å for the terminal tetrahydroborate unit. The structure is illustrated in Figure 14. The tetrahydroborate ligands are bidentate with B–H distances of 1.07 (4), 1.14 (4), 1.18 (3), and 1.19 (3) Å. Angles are B–Be–B, 124.8 (5)° and B–Be–B_b, 123.5 (5)°, the latter of which is the terminal boron–beryllium-bridging boron angle. The gas-phase and crystalline structures are obviously quite different. The Be–B distance appears to be longer in the solid than in the gas phase.

A recent structural investigation[172] of the compound $(\eta^5$-$C_5H_5)BeBH_4$ warrants comment. The determination was carried out via gas-phase electron diffraction and was refined to a residual value of 8.88%. While rather gross structural features such as a *pentahapto*cyclopentadienyl ring were characterized, the authors were unable to refine the structure to the extent necessary to differentiate between a bidentate or tridentate ligation for the tetrahydroborate ligand. When the structure was refined for a bidentate ligation, molecular parameters were: Be–B, 1.88 (1) Å; B–H_t, 1.17 (3) Å; B–H_b, 1.29 (5) Å; Be–H_b, 1.78 (9) Å; Be–B–H_b, 65 (4)°; H_t–B–H_b, 123 (9)°. When a tridentate BH_4^- was assumed the parameters refined to Be–B, 1.89 (1) Å; B–H_t, 1.16 (2) Å; B–H_b, 1.28 (3) Å; Be–H_b, 1.70 (5) Å; Be–B–H_b, 62 (2)°. The major difference exists in the Be–H_b bond distance. The Be–B distance remains essentially unchanged in both refinements. The Be–B distance found here seems to be longer than that in gaseous $Be(BH_4)_2$ (1.83 (6) Å) but is quite similar to that present in crystalline $Be(BH_4)_2$ (1.918 (4) Å) when one considers the beryllium to boron distance for the terminal bidentate tetrahydroborate. The distance here is significantly

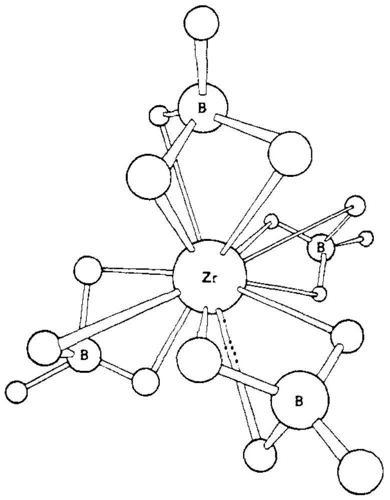


Figure 15. The molecular structure by x-ray diffraction of $Zr(BH_4)_4$ (ref 175).

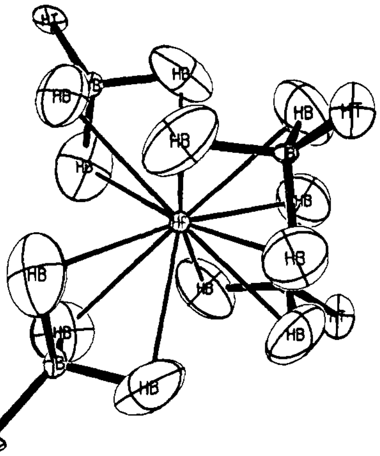


Figure 16. The molecular structure of $Hf(BH_4)_4$ by neutron diffraction (ref 138).

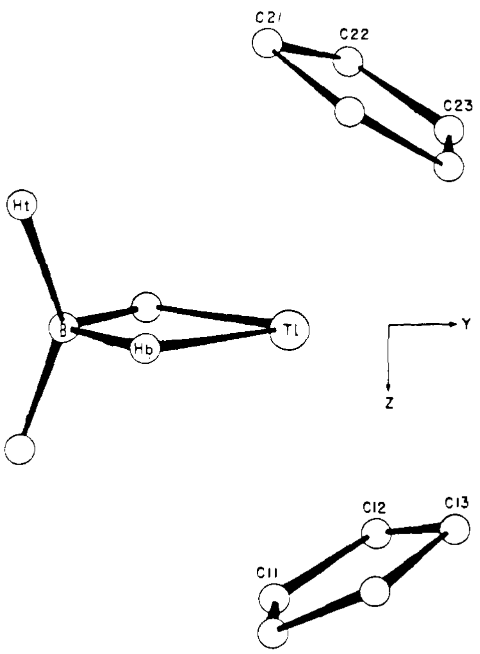


Figure 17. The molecular structure (x-ray diffraction) of $(\eta^5\text{-}C_5H_5)_2TiBH_4$ (from ref 176).

shorter than for the beryllium to boron distance for the bridging tetrahydroborate in crystalline $Be(BH_4)_2$. This is not unexpected when one considers that the bridging BH_4 is feeling similar "pulls" from equivalent berylliums in the helical polymer and might not be expected to approach one beryllium as closely as does the terminal tetrahydroborate. It is also interesting to note that while electron diffraction was unable to differentiate between a tridentate tetrahydroborate or its bidentate counterpart, infrared spectroscopy conclusively proved the existence of a bidentate BH_4 unit in $(\eta^5\text{-}C_5H_5)Be(BH_4)$.[173] As was amply illustrated in section III, vibrational spectroscopy remains a powerful technique for the elucidation of gross structural characteristics, even, in this case, where otherwise reliable diffractometric methods fail.

The first transition metal tetrahydroborate complex to be considered is tetrakis(tetrahydroborato)zirconium(IV), $Zr(BH_4)_4$. The structure as indicated in Figure 15 is a tetrahedron of tridentate tetrahydroborate ligands surrounding the zirconium atom. Both a gas-phase electron diffraction study[174] and an x-ray diffraction study[175] have been performed on this molecule. The electron diffraction study gave bond distances of 2.308 (3) Å for Zr–B, 2.211 (19) Å for $Zr–H_b$, 1.176 (40) Å for $B–H_t$ and 1.272 (10) Å for $B–H_b$. The x-ray diffraction study on a sample cooled to −160 °C gave bond distances of 2.34 Å for Zr–B and 1.2 (4) for $B–H_t$. Although this structure is much less accurate than that performed by electron diffraction, the distances are comparable and there is a strong correlation between the results. The structure consists of 12 bridging hydrides surrounding the zirconium ion in either an icosahedral or cube-octahedral arrangement. The four boron atoms maintain, as mentioned previously, a tetrahedral arrangement about the zirconium atom and the entire molecule has rigorous T_d symmetry.

A low-temperatures (24 K) neutron diffraction study was recently completed on the molecule tetrakis(tetrahydroborato)-hafnium(IV), $Hf(BH_4)$.[138] An ORTEP drawing of the molecule is presented in Figure 16. The actual molecular arrangement of borons and hydrogens is, within experimental error, identical with the arrangement in $Zr(BH_4)_4$. Pertinent bond distances at 24 K are Hf–B, 2.25 (3) Å; $B–H_t$, 1.31 (2) Å; $Hf–H_b$, 2.06 (2) Å; $B–H_b$, 1.19 (2) Å. Bond angles are $Hf–H_b–B$, 83 (1)°; $H_b–B–H_t$, 114 (1)°; $Hf–B–H_b$, 65 (1)°. Each tetrahydroborate ligand is bonded in a tridentate fashion, and the boron atoms form a perfect tetrahedron around the central hafnium atom. Again, rigorous T_d symmetry for the molecular unit obtains.

The single-crystal x-ray structure of $(\eta^5\text{-}C_5H_5)_2Ti(BH_4)$ has also been performed.[176] The tetrahydroborate ligand was found to be bidentate, thus confirming a prediction made solely on the basis of vibrational spectroscopy.[77] The important structural features are Ti–B, 2.37 (1) Å; $Ti–H_b$, 1.75 (8) Å; $B–H_b$, 1.23 (8) Å; $B–H_t$, 1.40 (1) Å; $\angle H_bTiH_b$, 60 (5)°; $\angle H_bBH_b$, 91 (7)°; $\angle H_tBH_t$, 129 (9)°. A drawing of the molecule is given in Figure 17 indicating the bidentate arrangement of the tetrahydroborate ligand. The ability of vibrational spectroscopy to correctly predict gross structural, e.g., *pentahapto*cyclopentadienyl rings and bidentate tetrahydroborates, is again reinforced.

The tetrahydroborate ligand is also bidentate in the compound bis(triphenylphosphine)copper tetrahydroborate.[177,178] The molecular structure is indicated in Figure 18. The copper–boron distance is a relatively short 2.185 (6) Å again suggesting direct copper–boron interaction. Other distances are $Cu–H_b$, 1.82 (3) Å; $B–H_b$, 1.07 (3) Å; $B–H_t$, 1.09 (5) Å. Pertinent bond angles are 59 (2)° for H_bCuH_b, 112 (3)° for H_bBH_b, 113 (4)° for H_tBH_t, and 94 (2)° for CuH_bB.

The x-ray structure of a similar compound, bis(tricyclohexylphosphine)hydridocobalt tetrahydroborate has very recently been communicated.[42] Although structural details are relatively sparse, the important features of this molecule are the Co–B distance 2.13 (1) Å; $Co–H_b$, 1.84 (9) Å; $Co–H_h$, 1.34 (9) Å; $B–H_b$, 1.35 (9) Å; $B–H_t$, 1.29 (9) Å. The tetrahydroborate ligand is bidentate. The structure is illustrated in Figure 19. The coordination

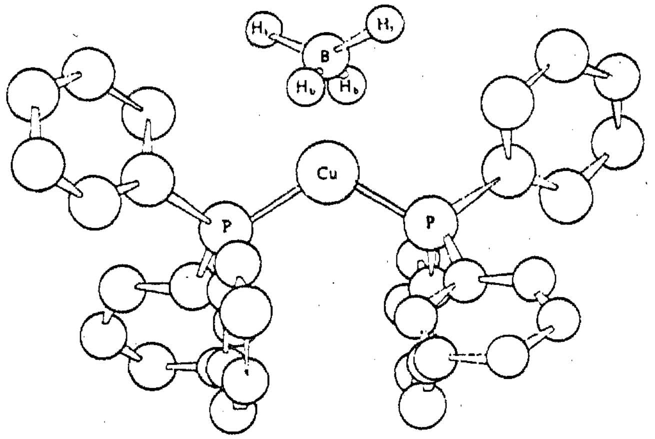


Figure 18. The molecular structure (x-ray diffraction) of $[(C_6H_5)_3P]_2CuBH_4$ (from ref 177).

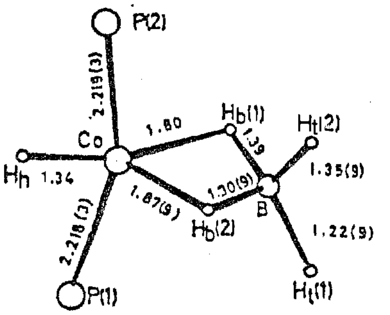


Figure 19. The cobalt coordination geometry in $[(Cy)_3P]_2Co(H)BH_4$ by x-ray diffraction (ref 42).

geometry about cobalt is approximately square pyramidal, with $H_b(2)$ at the axial apex and the other four ligand atoms (2H, 2P) approximately defining the basal plane. The angle P(1)–Co–P(2) was found to be 157.8°. The short Co–B distance is attributed by the authors to the relatively small single bond metallic radius of cobalt, smaller than either titanium or copper, both of which have longer metal–boron distances in, respectively, $(\eta^5\text{-}C_5H_5)_2Ti(BH_4)$ and $[(C_6H_5)_3P]_2Cu(BH_4)$ (vide supra).

Very recently the molecular structure of the compound $(\eta^5\text{-}C_5H_5)_2Nb(BH_4)$[179] has been reported. This is a significant structure determination in that it is the first example of a tetrahydroborate structure of the vanadium–niobium–tantalum triad and allows direct comparison with $(C_5H_5)_2Ti(BH_4)$ to be made. The tetrahydroborate is bidentate. The Nb–B distance is 2.26 (6) Å. Other distances are Nb–H_b, 2.0 (1) Å; B–H_b, 1.1 (2) Å; B–H_t, 1.1 (2) Å. The molecular structure of the compound is illustrated in Figure 20. The actual structure determination and refinement were somewhat inaccurate. It is enough to indicate that the structure of this compound is quite similar to that of the titanium compound. The H_b–Nb–H_b angle is 56 (10)° and the H_b–B–H_b angle is 122 (10)°.

An x-ray crystal structure in press is that of the ionic organometallic compound $([[(C_6H_5)_3P]_2N)^+(Mo(CO)_4(BH_4))^-$.[35] In this compound the tetrahydroborate is bidentate and the bridging hydrides occupy cis positions in the octahedron surrounding the molybdenum atom, the other four vertices being occupied by the carbonyl groups. The Mo–B distance is 2.41 (2) Å. Other bond distances of interest are Mo–H_b, 2.02 (8) Å; B–H_b, 1.20 (10) Å; B–H_t, 1.11 (11) Å. The angle subtended by the atoms H_b, Mo, and H_b is 59 (4)°. The molecular structure of this ionic complex is presented in Figure 21. This is the first structure determination of a compound (ionic or covalent) containing both tetrahydroborates and carbonyl ligands.

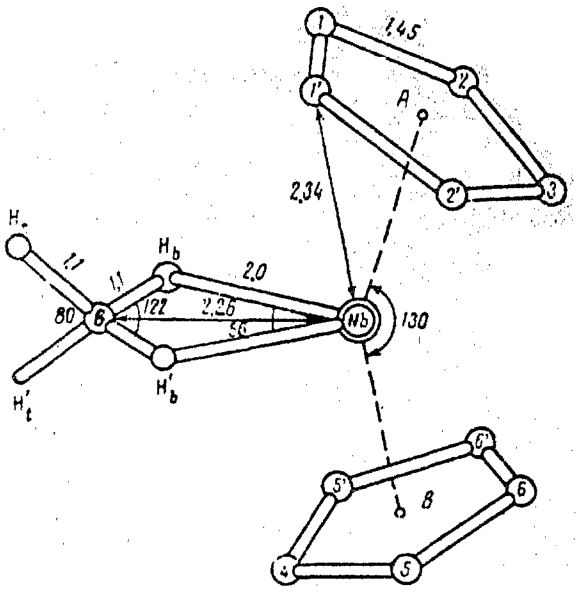


Figure 20. The molecular structure by x-ray diffraction of $(\eta^5\text{-}C_5H_5)_2NbBH_4$ (ref 179).

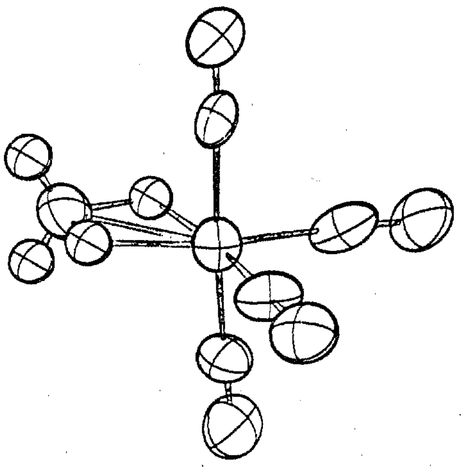


Figure 21. The structure (by x-ray diffraction) of the anionic portion of $[(C_6H_5)_3P]_2N^+Mo(CO)_4BH_4^-$ (from ref 35).

The first and, to date, only crystal structure of a lanthanide or actinide tetrahydroborate is the single-crystal neutron diffraction study at room temperature of the uranium(IV) compound $U(BH_4)_4$.[73] Although a previous single crystal x-ray diffraction study elucidated the gross structural geometry, i.e., uranium and boron atom positions,[180] it was necessary to resort to a neutron diffraction study to accurately locate and refine hydrogen atoms. The polymeric structure of the molecule, which is illustrated in Figure 22, consists of bridging bidentate and terminal tridentate tetrahydroborate ligands. Each uranium atom is coordinated to two terminal tridentate tetrahydroborate ligands and four bridging bidentate tetrahydroborates. Consideration of the bridging hydrides in each of the two distinct types of tetrahydroborate ligands makes each uranium atom formally 14 coordinate. This is also the first example of tetradecacoordination about a metal ion. There is no ready correlation of type of tetrahydroborate group to U–H distance. The structure is not similar to either $Zr(BH_4)_4$ or $Hf(BH_4)_4$, a fact due principally to the ability of uranium to expand its coordination sphere beyond that which either zirconium or hafnium is capable. For the terminal tetrahydroborate group the B–H_t distance is 1.24 (4) Å while the three B–H vectors which bridge boron and uranium atoms are 1.26 (3), 1.09 (4), and 1.34 (3) Å in length. The bridging tetrahydroborate ligand has boron–hydrogen bond distances of 1.29 (3), 1.18 (3), 1.21 (3), and 1.33 (3) Å. The uranium–boron distance for the bidentate bridging ligand is 2.90 (2) Å, while the tridentate terminal tetrahydroborate has a uranium–boron distance of 2.52 Å. For the terminal tridentate tetrahydroborate ligand the uranium–hydrogen bond distances are 2.36 (2), 2.34 (2), and 2.33 (2) Å. The uranium

TABLE IV. Bond Distances,[a] Covalent Radii,[b] Ionic Radii,[c] and Atomic Radii[d] for Covalent Metal Tetrahydroborates

	Distances[a]				Effective ionic radii[b]		Ionic	Atomic
Compound	M–B	M–H_b	B–H_b	B–H_t	r_m(O)	r_m(F)	radii[c]	radii[d]
Tridentate								
$Zr(BH_4)_4$ (gas)[e]	2.308(3)	2.211(19)	1.272(16)	1.176(40)	0.98	0.84	1.55	
$Hf(BH_4)_4$ (neutron)[f]	2.25(3)	2.06(2)	1.19(2)	1.31(2)	0.85	0.71	1.55	
$U(BH_4)_4$ (neutron)[g]	2.52(1)	2.34(2)	1.23(4)	1.24(4)	1.19	1.05	1.75	
Bidentate								
B_2H_6 (gas)[h]	1.775(3)		1.339(6)	1.196(8)	0.26	0.12	0.85	0.90
B_2H_6 (crystal)[t]	1.776(10)		1.25(2)	1.10(2)				
$Be(BH_4)_2$ (gas)[i]	1.83(6)				0.41	0.27	0.85	1.25
$Be(BH_4)_2$ (crystal)(bridges)[j]	1.999(4)	1.61(4)	1.10(4)		0.41	0.27	0.85	1.25
$Be(BH_4)_2$ (crystal)(term)[j]	1.918(4)	1.52(4)	1.18(3)	1.14(4)	0.41	0.27	0.85	1.25
$(C_5H_5)Be(BH_4)$ (gas)[k]	1.88(1)	1.78(9)	1.29(5)	1.17(3)	0.41	0.27	0.85	1.25
$Al(BH_4)_3$ (gas)[l]	2.143(3)	1.801(6)	1.283(12)	1.196(12)	0.67	0.53	1.25	1.30
$Al(BH_4)_3{\cdot}N(CH_3)_3$[m]	2.218(23)	1.97(7)	1.40(7) 1.18(7)	1.22(11)	0.67	0.53	1.25	1.30
$(C_5H_5)_2TiBH_4$[n]	2.37(1)	1.75(8)	1.23(8)	1.40(10)	0.81	0.67	1.40	
$(C_5H_5)_2NbBH_4$[o]	2.26(6)	2.0(1)	1.1(2)	1.1(2)	0.84	0.70	1.45	
$(Ph_3P)_2CuBH_4$[p]	2.185(6)	1.82(3)	1.07(3)	1.09(5)	0.60	0.46	1.35	
$(Cy_3P)_2Co(H)BH_4$[q]	2.13(1)	1.84(9)	1.35(9)	1.29(9)	0.79	0.65	1.35	1.26
$((Ph_3P)_2N)^+(Mo(CO)_4BH_4)^-$[r]	2.41(2)	2.02(8)	1.20(10)	1.11(11)	0.81	0.67	1.45	
$U(BH_4)_4$ (neutron)[g]	2.90(1)	2.41(2)	1.25			1.05	1.75	
Ionic								
$K^+(BH_4^-)$[s](neutron)			1.260(2)					

[a] Given in ångstroms; averaged where appropriate, with estimated standard deviations given in parentheses. [b] Reference 181. [c] Ionic radii were taken from ref 182 and were taken for appropriate ions of similar oxidation state and coordination number. r_m(O) refers to metal oxides and r_m(F) refers to metal fluorides. [d] Reference 183. [e] Electron diffraction data of ref 174. [f] Neutron diffraction data of 138. [g] Neutron diffraction data of ref 73. [h] Electron diffraction data of ref 164. [i] Electron diffraction data from ref 170. [j] X-ray data from ref 65. [k] Electron diffraction data from ref 172 assuming bidentate ligation. [l] Electron diffraction data from ref 166. [m] X-ray data from ref 169. [n] X-ray data, ref 176. [o] X-ray data, ref 179. [p] X-ray data, ref 177 and 178. [q] X-ray data, ref 42. [r] X-ray data, ref 35. [s] Neutron diffraction data, ref 162. [t] X-ray data, ref 161a.

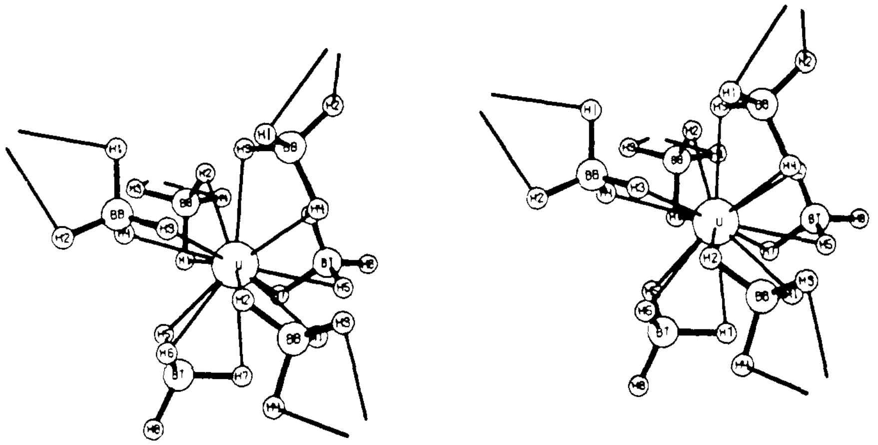


Figure 22. Stereoscopic view of the uranium coordination geometry in $U(BH_4)_4$ by neutron diffraction (ref 73).

to hydrogen distances for the bridging tetrahydroborate ligand which functions as a bidentate ligand toward two uranium atoms and in which all four hydrides are bridging are 2.44 (3), 2.46 (2), 2.36 (2), and 2.36 (2) Å. At first appearance the U–H distances for the tridentate tetrahydroborate appear to be somewhat shorter than similar bond distances for the bidentate bridging tetrahydroborate. The differences in U–H distances are not striking, however, and the authors point out that metal–boron distances imply considerably more about bonding patterns. The positions of the hydrides are, as mentioned earlier, obscured by a good deal of uncertainty.

At this point and in this regard it would be wise to compare structural data for the molecules studied to date. Table IV presents bond distances and Table V bond angles. It is first of interest to discuss what factors govern metal–BH_4^- distances as the metal ion and tetrahydroborate ligation geometry are varied. If the influence on metal–ligand interaction of such factors as metal electronic configuration, π-bonding tendency, and coordinative saturation (see section VI) are not important or do not fluctuate grossly from compound to compound, then the metal–boron distance (which is usually the most accurate metal–BH_4^- parameter in an x-ray structure determination) might be expected to vary in some systematic and calculable way with metal ion size and mode of BH_4^- attachment. This hypothesis was first put forward by Bernstein et al.[73] Also presented in Table IV are several commonly used measures of metal ion size, viz. Shannon and Prewitt effective ionic radii,[181] Bragg and Slater ionic radii, and atomic radii[183] for the metal atom; all values are given for the metal in the closest possible oxidation state and coordination number. Figure 23 illustrates the relationship of metal–boron distances from Table IV to the Shannon–Prewitt effective ionic radii based on metal fluorides. These radii were chosen because they span the greatest number of metal ions and are internally consistent.[181] Considering the variety of

TABLE V. Bond Angles in Covalent Metal Tetrahydroborates[a]

Compound	H_bMH_b	H_bBH_b	MH_bB	H_bBH_t	H_tBH_t
		Tridentate			
$Zr(BH_4)_4$[b]		108.4			
$Hf(BH_4)_4$ (neutron)[c]			83(1)	114(1)	
$U(BH_4)_4$ (neutron)[d]		107	82(1)	113	
		Bidentate			
B_2H_6 (gas)[o]		97.0(3)			119.0(9)
B_2H_6 (crystal)[e]		90(1)			124(1)
$Be(BH_4)_2$ (crystal)(bridge)[f]	67(2)	109(2)			
$Be(BH_4)_2$ (crystal)(term.)[f]	76(2)	106(2)		105(3)	127(3)
$(C_5H_5)Be(BH_4)$ (gas)[g]				123(9)	
$Al(BH_4)_3$ (gas)[h]	73.4(8)	114.0(2)			116.2(2.2)
$Al(BH_4)_3 \cdot N(CH_3)_3$[i]	70.2(3.2)	105.6(4.6)		116.9(5.2)	117.0(6.6)
$(C_5H_5)_2Ti(BH_4)$[j]	60(5)	91(7)	104(5)	108(3)	129(9)
$(C_5H_5)_2Nb(BH_4)$[k]	56(10)	122(10)			
$(Ph_2P)_2Cu(BH_4)$[l]	59(2)	112(3)	94(2)	107(3)	113(4)
$(Cy_3P)_2Co(H)BH_4$[m]					
$((Ph_3P)_2N)^+(Mo(CO)_4BH_4)^-$[n]	59(4)	112(6)	95(5)	107(8)	113(7)
$U(BH_4)_4$ (neutron)[d]		110	99(1)		

[a] Averaged where appropriate; estimated standard deviations of the last significant figure are given in parentheses. [b] See ref 174. [c] Reference 140. [d] Reference 73. [e] Reference 161a. [f] Reference 65. [g] Reference 171. [h] Reference 166. [i] Reference 167. [j] Reference 176. [k] Reference 179. [l] References 177 and 178. [m] Reference 42. [n] Reference 35. [o] Reference 164.

metal oxidation states, coordination numbers, and supporting ligands, the overall correlation is surprisingly linear. In addition it can be seen that, for a given metal ion, tridentate BH_4^- coordination allows closer M-B approach. This can also be demonstrated geometrically.[73] It also appears that when the tetrahydroborate ligand bridges two metal ions, the metal-boron distance is lengthened somewhat. This may reflect electrostatic effects. Within the bidentate structures, there are cases where M-B distances vary more than might be expected for comparable ionic radii. Although there is a great similarity in metal ion coordination environment for $(C_5H_5)_2Ti(BH_4)$ and $(C_5H_5)_2Nb(BH_4)$, as well as in ionic radius ($r_{Nb}-r_{Ti}$ = 0.03 Å), the difference in M-B distance, $d_{Nb}-d_{Ti} = -0.11$ (6) Å, is rather large in magnitude and not of the expected sign. This discrepancy may well reflect differences in metal-ligand bonding which were apparent in the vibrational spectra of these two compounds (section III). It is unfortunate that the niobium diffraction structure was not more accurate. It is far more difficult to rationalize other deviations from linearity in Figure 23, but these could be due to differences in bonding, metal ligation, and oxidation state, as well as in the applicability of metal fluoride effective ionic radii to complexes with soft ligands.

As discussed already, the metal-H_b distances are subject to considerable error. As can be seen in Table IV, these parameters vary from ca. 1.75 to 2.21 Å for transition metal complexes. Typical metal-hydrogen distances for transition metal hydride complexes are in the range 1.6-1.8 Å.[159a] Thus it appears that the M-H_b distances are slightly longer, which may reflect the electrostatic "pull" of the boron and/or the multicenter, electron-deficient character of the bonding. For example, B-H_b in diborane is ca. 0.14 Å longer than B-H_t (Table IV). Attempts to graph the M-H_b distances vs. the effective ionic radii reveal a very rough linearity with considerable uncertainty introduced by the large estimated errors for most of the M-H_b distances.

A final area of interest is the deviation (or lack of same) of the geometries of the coordinated BH_4^- ligands from "free" anionic BH_4^- which has H-B-H angles of 109° 28' and B-H bond lengths of 1.26 (2) Å. For instance, in diborane[164] the H_bBH_b angle closes to 97.0 (3)° and the H_tBH_t angle opens to 119.0 (9)°, both of which differ significantly from the ideal tetrahedral angle found in BH_4^-. The B-H_b bond length also increases to 1.339 (6) Å and the B-H_t distance is decreased to 1.196 (8) Å. Thus the bond length of B-H_b is lengthened (within experimental error) to the same extent that B-H_t is shortened. It would be of great interest to gauge to what degree the BH_4^- ligand is distorted from tetrahedral symmetry in the metal complexes since this might provide some quantitative measure (using diborane as a model) of the covalency of the metal-ligand bonding. Unfortunately, the accuracy of the hydrogen atom positions in most of the structures will be seen to permit only limited qualitative conclusions. First, it appears that B-H_b is generally longer than B-H_t in the bidentate structures studied by electron diffraction (Table IV). However, for the ten bidentate structures Be-Mo in Table IV, the average B-H_b distance, 1.24 (7) Å, is not significantly longer than the average B-H_t distance, 1.19 (8) Å. Only in the electron diffraction studies is it apparent that B-H_b is longer than the 1.260 (2) Å of BH_4^- and that B-H_t is shorter. Comparing parameters for bidentate and tridentate ligation geometries, no clear-cut trend can be discerned, nor is it possible to say whether B-H_b and B-H_t distances are significantly different within the tridentate series. Considering tetrahydroborate valence angles H_bBH_b and H_tBH_t (Table V), conclusions are again tenuous. The average $\angle H_bBH_b$ for the seven structures where data are available (Be-Mo) is 106.9 (4.9)°, which is not significantly different from tetrahedral. The average angle H_tBH_t for six structures is 118.9 (6.0)°, which may indicate the same type of distortion as found in diborane. Thus, it appears that in some main group metal bi-

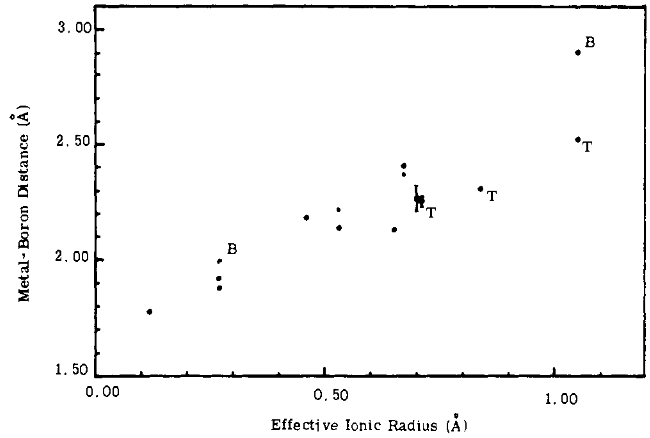


Figure 23. Plot of metal-boron distances (Table IV) vs. Shannon-Prewitt effective ionic radii. T denotes tridentate BH_4^- coordination; B denotes bidentate coordination in which BH_4^- bridges two metal ions. Error bars are only shown for unusually large estimated standard deviations.

dentate structures BH_4^- distorts in the direction found in diborane. However, little can be said about the magnitude of this distortion, and for the transition metal tetrahydroborate complexes it is not even certain that a distortion exists. These results point out the critical need for highly accurate structural data in this area, and also underscore the potential of vibrational spectroscopy to provide a sensitive and convenient tool for studying structure and bonding.

VI. Bonding

An understanding of the nature of the metal ion–tetrahydroborate ligand interaction can hopefully lead to a better understanding of those factors which govern the physical and chemical properties of coordinated BH_4^- and to some predictability as to which compounds will exist and what their properties will be. Traditionally, inorganic chemists have approached problems related to metal–ligand bonding either from a valence-bond, effective atomic number viewpoint, in which complex stability is a function of how closely the empirical "electron count" approaches the next heaviest noble gas, or from a quantum chemical viewpoint, in which the symmetries, spacial extensions, and energies of metal and ligand orbitals determine the characteristics of the metal–ligand interaction. It has usually been assumed that advancing theory and computational power would steadily strengthen the latter approach. In this section we strive to better understand the type of ligand BH_4^- actually is by considering aspects of both of the above approaches. The aim is to place tetrahydroborate within the framework of other ligands commonly found in organometallic compounds.

The valence bond theory–noble gas formalism approach to interpreting valency and predicting stoichiometry in organometallic compounds is based upon evaluating the number of electrons "donated" to the metal ion by the ligands in the coordination sphere.[184,185] Though any basis in bonding theory may be more fortuitous than rigorous,[184,185] this approach has commendable predictive power for diamagnetic complexes of transition metals near the center of the periodic table. It is still the most reliable "rule of thumb" available to synthetic organometallic chemists for anticipating the stability of desired compounds (much of this stability may be kinetic rather than thermodynamic[83,186]). Although the number of transition metal organometallics deviating from 18 (or 16) electron valence configurations is relatively small, it is by no means negligible or trivial.[186] In cases where the number of electrons provided by a particular ligand is not evident from valence bond considerations (e.g., available lone pairs) resort is made to the inductive procedure of comparing the ambiguous system to a similar one where the electron donation is conceptually less ambiguous.

The search for possible carbon-containing analogues to the tetrahydroborate ligand based purely upon empirical grounds brings to light an interesting relationship to the *trihapto*allyl ligand. It is possible to enumerate two parallel sets of transition metal complexes which differ only in the transposition of BH_4^- and η^3-allyl.[77] That is BH_4^- and η^3-allyl bond, to some extent, analogously.[77] Such a relationship suggests in the effective atomic number sense that BH_4^- anion is a four-electron donor or, equivalently, that neutral BH_4 is a three-electron donor. Since this observation was first made,[77] a large number of new tetrahydroborate complexes have been reported (section II). All conform to the above regularity save those which are paramagnetic or contain early transition metals. In general, the noble gas formalism is more frequently violated for such systems.[184] In regard to metal–ligand geometry, it was noted[77] (with surprise) that not only bidentate but also tridentate tetrahydroborates possess η^3-allyl analogues, viz. $M(BH_4)_4$ vs. $M(C_3H_5)_4$, M = Zr, Hf. It was pointed out at that time that near equality of electron donor power in the bidentate and tridentate configurations was in accord with the small energy difference between structures demanded if the fluxional behavior indeed takes place via bidentate-tridentate equilibration. These analogies between BH_4^- and η^3-allyl were presented simply as empirical observations (not as a "hypothesis",[187] "corollary",[187] or, when taken in context, a generalization), and it was suggested that more compounds were needed to test further the relationship of formal electron count to ligation geometry.

In valence bond terms, the four-electron donating ability of a bidentate BH_4^- might be rationalized by the presence of the two electron pairs in the B–H bridge bonds, which could be shared with the metal ion. This would imply that the tridendate ligation geometry allows BH_4^- to function as a six-electron donor. Unfortunately, no well-characterized transition metal complex exists at present to test this proposition; it can be shown by symmetry arguments that six-electron donation is implausible in the only known tridentate transition metal compounds, viz., the $M(BH_4)_4$ series, M = Zr, Hf.[187] At this point it should be emphasized that such empirical electron-counting schemes were originally derived for, and are applicable at best to, more "normal" ligands such as CO and olefins and should not be carried too far. Even in those cases it provides little insight into the electronic nature of the metal–ligand interaction and into what determines complex stability and stoichiometry. The three-center bonding found in covalent tetrahydroborate complexes renders the situation even more difficult. For these reasons resort must be made to an alternative molecular orbital approach, which provides an appealing description of multicenter bonding in boron hydrides.[188–190] Though the arguments here will be qualitative, they also provide the starting point for a quantitative treatment.

To consider in molecular orbital terms how BH_4^- can interact with a metal ion, it is necessary to determine which molecular orbitals of the ligand have the appropriate symmetry to overlap with available metal orbitals.[191,192] For bidentate (C_{2v}) and tridentate (C_{3v}) MBH_4 configurations, it is straightforward to construct tetrahydroborate molecular orbitals of proper symmetry using projection operator techniques.[192] The symmetry-adapted linear combinations of the atomic orbitals are shown in Figure 24. These are derived purely from symmetry considerations. The exact composition (eigenvectors) and energies (eigenvalues) of the molecular orbitals will depend on atomic orbital energies and overlaps. Tables VI and VII present molecular orbitals for BH_4^- which were derived by the authors from INDO-SCF[193] calculations and will suffice for qualitative remarks. The molecular orbital compositions and energies are in substantial agreement with the calculations of Hegstrom, Palke, and Lipscomb.[194] Also indicated are metal atomic orbitals belonging to the same irreducible representations in the point group (C_{2v} or C_{3v}).[195] The actual number of symmetry-compatible metal atomic orbitals may, of course, be somewhat less in real complexes containing additional ligands and having a different symmetry. However, the functions in the tables do give the maximum number of metal atomic orbitals which can interact. Turning now to the BH_4^- results, it is seen that in *both* bidentate and tridentate situations, the tetrahydroborate ligand has four filled molecular orbitals available (eight electrons) to donate electron density to the metal ion. In both cases these consist of two orbitals of appropriate symmetry for forming metal–ligand σ bonds (cylindrical symmetry about the metal–ligand axis) and two for forming π bonds (the metal–ligand axis lies in a nodal plane). In both cases, the three highest energy filled orbitals are degenerate in the isolated BH_4^- ion and consist of one σ- and two π-bonding molecular orbitals. All of these filled orbitals are B–H bonding or nonbonding in character. The tetrahydroborate molecular orbital next highest in energy is, in both bidentate and tridentate geometries, a singly degenerate one which is σ-bonding with respect to the metal and antibonding in terms of B–H interaction. In both bidentate and tridentate systems, the INDO calculations show the highest lying molecular orbitals to

TABLE VI. Symmetry-Adapted BH_4^- Molecular Orbitals for Bidentate (C_{2v}) Coordination

Representation	Molecular orbital					Energy[a] (au)	Metal orbitals
$a_1{}^b$	$0.368H_{1s}{}^{b}$	$+0.368H_{1s}{}^{b'}$	$+0.368H_{1s}{}^{t}$	$+0.368H_{1s}{}^{t'}$	$+0.677B_{2s}$	−0.689	$s, p_z, d_{z^2}, d_{x^2-y^2}, f_{z^3}, f_{z(x^2-y^2)}$
$a_1{}^b$	$0.396H_{1s}{}^{b}$	$+0.396H_{1s}{}^{b'}$	$-0.396H_{1s}{}^{t}$	$-0.396H_{1s}{}^{t'}$	$-0.609B_{2p_z}$	−0.287	$s, p_z, d_{z^2}, d_{x^2-y^2}, 1_{z^3}, f_{z(x^2-y^2)}$
$b_2{}^b$	$-0.561H_{1s}{}^{b}$	$+0.561H_{1s}{}^{b'}$			$+0.609B_{2p_y}$	−0.287	$p_y, d_{yz}, f_{yz^2}, f_{y(3x^2-y^2)}$
$b_1{}^b$			$0.561H_{1s}{}^{t}$	$-0.561H_{1s}{}^{t'}$	$+0.609B_{2p_x}$	−0.287	$p_x, d_{xz}, f_{xz^2}, f_{x(x^2-3y^2)}$
a_1	$0.339H_{1s}{}^{b}$	$+0.339H_{1s}{}^{b'}$	$+0.339H_{1s}$	$+0.339H_{1s}{}^{l}$	$-0.736B_{2s}$	+0.654	$s, p_z, d_{z^2}, d_{x^2-y^2}, f_{z^3}, f_{z(x^2-y^2)}$
a_1	$0.305H_{1s}{}^{b}$	$+0.305H_{1s}{}^{b'}$	$-0.305H_{1s}{}^{l}$	$-0.305H_{1s}{}^{1'}$	$+0.793B_{2p_z}$	+0.695	$s, p_z, d_{z^2}, d_{x^2-y^2}, f_{z^3}, f_{z(x^2-y^2)}$
b_2	$-0.431H_{1s}{}^{b}$	$+0.431H_{1s}{}^{b'}$			$-0.793B_{2p_y}$	+0.695	$p_y, d_{yz}, f_{yz^2}, f_{y(3x^2-y^2)}$
b_1			$0.431H_{1s}{}^{1}$	$-0.431H_{1s}{}^{t'}$	$-0.793B_{2p_x}$	+0.695	$p_x, d_{xz}, f_{xz^2}, f_{x(x^2-3y^2)}$

[a] 1 au = 27.21 eV = 627 kcal/mol. [b] Occupied molecular orbital.

TABLE VII. Symmetry-Adapted BH_4^- Molecular Orbitals for Tridentate (C_{3v}) Coordination

Representation	Molecular orbital					Energy[a] (au)	Metal orbitals
$a_1{}^b$	$0.369H_{1s}{}^{b}$	$+0.369H_{1s}{}^{b'}$	$+0.369H_{1s}{}^{b''}$	$+0.369H_{1s}{}^{t}$	$+0.678B_{2s}$	−0.688	$s, p_z, d_{z^2}, d_{x^2-y^2}, f_{z^3}, f_{x(x^2-3y^2)}$
$a_1{}^b$	$0.227H_{1s}{}^{b}$	$+0.227H_{1s}{}^{b'}$	$+0.227H_{1s}{}^{b''}$	$-0.690H_{1s}{}^{t}$	$-0.610B_{2p_z}$	−0.287	$s, p_z, d_{z^2}, d_{x^2-y^2}, f_{z^3}, f_{x(x^2-3y^2)}$
e^b		$-0.561H_{1s}{}^{b'}$	$+0.561H_{1s}{}^{b''}$		$+0.609B_{2p_y}$	−0.287	$p_x, p_y, d_{xz}, d_{yz}, f_{xz^2}, f_{yz^2}, f_{xyz}, f_{z(x^2-y^2)}$
e^b	$0.647H_{1s}{}^{b}$	$-0.323H_{1s}{}^{b'}$	$-0.323H_{1s}{}^{b''}$		$+0.609B_{2p_x}$	−0.287	$p_x, p_y, d_{xz}, d_{yz}, f_{xz^2}, f_{yz^2}, f_{xyz}, f_{z(x^2-y^2)}$
a_1	$0.341H_{1s}{}^{b}$	$+0.341H_{1s}{}^{b'}$	$+0.341H_{1s}{}^{b''}$	$+0.341H_{1s}{}^{1}$	$-0.735B_{2s}$	+0.652	$s, p_z, d_{z^2}, d_{x^2-y^2}, f_{z^3}, f_{x(x^2-3y^2)}$
a_1	$0.191H_{1s}{}^{b}$	$+0.191H_{1s}{}^{b'}$	$+0.191H_{1s}{}^{b''}$	$-0.511H_{1s}{}^{1}$	$+0.793B_{2p_z}$	+0.695	$s, p_z, d_{z^2}, d_{x^2-y^2}, f_{z^3}, f_{x(x^2-3y^2)}$
e		$-0.431H_{1s}{}^{b'}$	$+0.431H_{1s}{}^{b''}$		$-0.793B_{2p_y}$	+0.695	$p_x, p_y, d_{xz}, d_{yz}, f_{xz^2}, f_{yz^2}, f_{xyz}, f_{z(x^2-y^2)}$
e	$0.497H_{1s}{}^{b}$	$-0.251H_{1s}{}^{b'}$	$-0.251H_{1s}{}^{b''}$		$-0.793B_{2p_x}$	+0.695	$p_x, p_y, d_{xz}, d_{yz}, f_{xz^2}, f_{yz^2}, f_{xyz}, f_{z(x^2-y^2)}$

[a] 1 au = 27.21 eV = 627 kcal/mol. [b] Occupied molecular orbital.

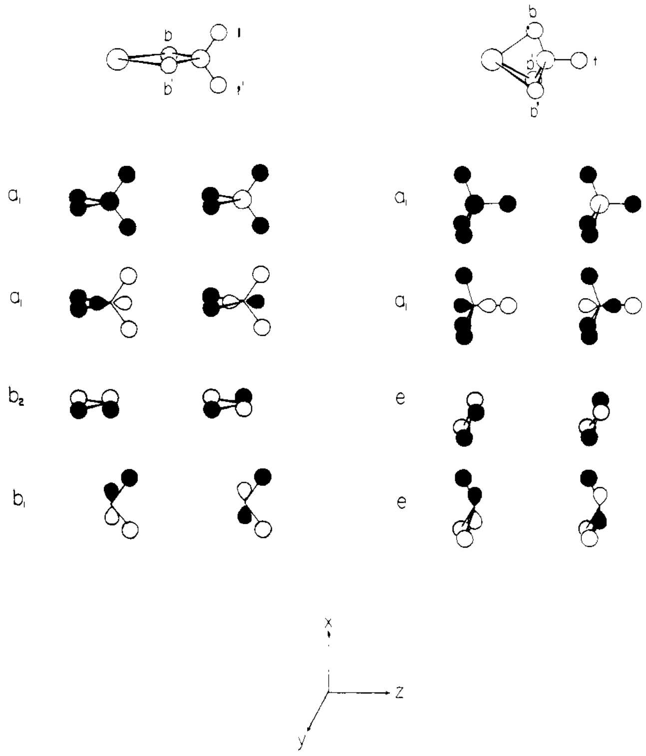
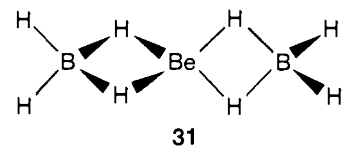


Figure 24. Symmetry-adapted linear combinations of atomic orbitals used to form BH_4^- molecular orbitals for bidentate (C_{2v}) and tridentate (C_{3v}) coordination. For each structure the left-hand column consists of bonding molecular orbitals, the right-hand, antibonding. Eigenvalues and eigenvectors are given in Tables VI and VII.

be a triply degenerate set consisting of one orbital of σ-bonding symmetry, and two of π-bonding symmetry. These orbitals are antibonding or nonbonding with respect to B–H interaction.

The manner in which the ligand molecular orbitals interact with metal orbitals will depend on the symmetries, energies, and spacial extensions of the metal orbitals. Any quantitative discussion of this information and the resulting molecular orbitals for any transition metal complexes requires the results of calculations which have not been carried out or which are still in progress.[196] Qualitatively, it is evident that *both* bidentate and tridentate structures have three filled molecular orbitals of relatively high energy available for electron donation. In this sense, both geometries are potential six-electron donors. However, it does appear (Figure 24) that the overlap of metal orbitals with the bidentate BH_4^- filled b_1 molecular orbital will not be very great.

Overlap of boron and metal orbitals should be significant in both bidentate and tridentate geometries. This is to be expected for what are essentially two-electron three-center bonds. The overlap may be somewhat larger in the tridentate case since, as was seen in the structural discussion (section V), this configuration allows a somewhat shorter metal–boron contact. *Ab initio* calculations relevant to this discussion have been published for B_2H_6[197] and $Be(BH_4)_2$.[198,200] A substantial B–B overlap population[199] (0.29–0.34) was found in the former case, which can be compared to a B–H_{bridge} overlap population of 0.39–0.42. For $Be(BH_4)_2$, Marynick and Lipscomb reported B–Be overlap populations of 0.25–0.35 and B–H_{bridge} and Be–H_{bridge} overlap populations of 0.46–0.61 and 0.18–0.34, respectively. The ranges reflect differences in the assumed structures. Interestingly, these authors as well as Ahlrichs[200] found that, within the accuracy of their calculations, structures **31–33** differed



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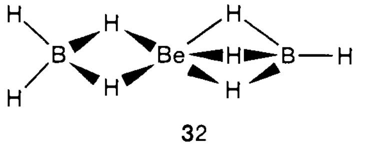

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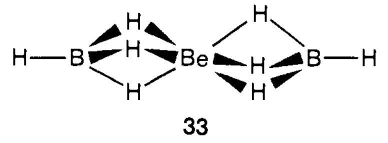

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TABLE VIII. Symmetry-Adapted Allyl$^-$ π Molecular Orbitals C_s Symmetry

Representation	Molecular orbital			Energy[a] (au)	Metal orbitals
a' [b]	$0.527C'_{2p_z}$	$+0.667C''_{2p_z}$	$+0.527C'''_{2p_z}$	-0.329	s, p_y, p_z, $d_{x^2-y^2}$, d_{z^2}, d_{yz}, f_{z^3}, $f_{z(x^2-y^2)}$ f_{yz^2}, $f_{y(3x^2-y^2)}$
a'' [b]	$0.707C'_{2p_z}$		$-0.707C'''_{2p_z}$	$+0.013$	s, p_y, p_z, $d_{x^2-y^2}$, d_{z^2}, d_{yz}, f_{z^3}, $f_{z(x^2-y^2)}$, f_{yz^2}, $f_{y(3x^2-y^2)}$
a'	$0.472C'_{2p_z}$	$-0.745C''_{2p_z}$	$+0.472C'''_{2p_z}$	$+0.542$	p_x, d_{xy}, d_{xz}, f_{xz^2}, $f_{x(x^2-3y^2)}$, f_{xyz}

[a] 1 au = 27.21 eV = 627 kcal/mol. [b] Occupied molecular orbital.

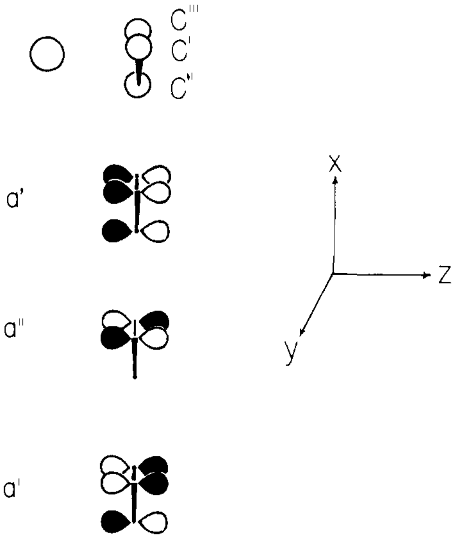


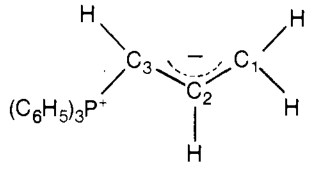
Figure 25. Symmetry-adapted (C_2 symmetry) linear combinations of π atomic orbitals for η^3-allyl molecular orbitals. The compositions and energies of the resulting orbitals are given in Table VIII.

negligibly in energy. In this system there appears to be approximate equality of electron donation in bidentate and tridentate ligation geometries. The calculations correspondingly reveal that passing from bidentate structure **31** to tridentate structure **33** is accompanied by an increase in Be-B overlap population (0.25 to 0.35) and a decrease in Be-H_{bridge} overlap population (0.34 to 0.18).

Preliminary extended Hückel calculations[196] have been performed on $Mo(CO)_4BH_4^-$, holding the $Mo(CO)_4$ fragment rigid, and varying the BH_4^- coordination from monodentate, to bidentate, to tridentate. Hoffmann and Weber find[196] that the bidentate geometry (which is the experimentally determined ground-state structure[35]) is more stable than the monodentate by ca. 10 kcal/mol, and more stable than the tridentate by ca. 20 kcal/mol. It should be emphasized that in these initial calculations, the $Mo(CO)_4$ fragment was, at all times, maintained in the geometry found in the x-ray structure, rather than allowing it to relax to the lowest energy configuration.

It is now appropriate to inquire whether there is any electronic or geometrical basis for the aforementioned empirical analogy between BH_4^- and η^3-allyl. The reasons appear to reflect both similarities in electronic structure and ligation "bite". Figure 25 presents the π molecular orbitals of the allyl anion. The orbital energies and compositions were calculated by the INDO-SCF approximation and are shown in Table VIII.[201] The $C_3H_5^-$ set consists of a filled allyl-metal σ-bonding orbital (a') at slightly lower energy than what are clearly analogous orbitals (Figure 24) in bidentate (a_1) and tridentate (a_1) BH_4^-. The next and highest occupied allyl π molecular orbital (a″) is π-bonding with respect to the metal and is somewhat higher in energy than the corresponding π-bonding tetrahydroborate orbital in the bidentate (b_2) and tridentate (e) situations. The lowest unoccupied allyl molecular orbital (a') is also π-bonding in its interaction with the metal and is at lower energy than the comparable BH_4^- orbitals, i.e., b_2 for the bidentate and e for the tridentate. Thus, the η^3-allyl anion can donate four electrons to a metal ion, two from a σ-bonding and two from a π-bonding molecular orbital. The bidentate BH_4^- ligand possesses two filled molecular orbitals of the same character as allyl (the third filled, π-bonding orbital (b_1) is probably not quite as available for overlap); the tridentate BH_4^- ligand, on the other hand, has one σ- and two π-bonding molecular orbitals available for donation. Both allyl and BH_4^- ligands also have empty orbitals of σ and π symmetry available for back-bonding. Within the accuracy of the INDO/2 calculations, the molecular orbital energies suggest (obviously more detailed calculations are desirable) that η^3-allyl is potentially both a better donor and acceptor than bidentate tetrahydroborate.

Structurally, there is also evidence that η^3-allyl and BH_4^- afford analogous bonding. A particularly relevant pair of molecular structures for comparison consists of $Mo(OC)_4(BH_4)^-$ [35] and the allylic complex $Mo(CO)_4[\eta^3\text{-}C_3H_4P(C_6H_5)_3]$.[202] The latter compound contains an η^3-allyl ligand with one hydrogen replaced by a quaternary phosphonium unit (**34**). The Mo–C distances for the allylic fragment are Mo–C_1, 2.49 (1) Å; Mo–C_2, 2.31 (1) Å; and Mo–C_3, 2.38 (1) Å. Such distances lead to a "bite" angle (∠C_1–Mo–C_3) of 60.5 (2)°, which is rather close to that (∠H_b–Mo–H_b') found in $Mo(CO)_4BH_4^-$, 59 (4)°. It is also instructive to examine how the two ligands perturb the $Mo(CO)_4$ fragment (**35**) and **36**).



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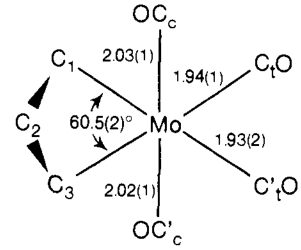

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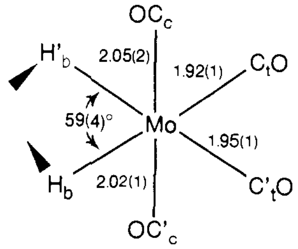

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As can be judged from the Mo–C distances, the η^3-allyl and BH_4 ligands induce a very similar electronic reorganization in the $Mo(CO)_4$ unit upon coordination. The bond angles about the molybdenum reveal relatively minor differences in the bonding. For $Mo(CO)_4BH_4^-$, the only significant deviation of the OCMoCO angles from octahedral symmetry is a closing of ∠C_tMoC_t' to 84.5 (5)°. In allyl, the bulkiness of the trihapto ligand and the appendant triphenylphosphonium moiety appears to cause a slight bending back of the axial carbonyls; ∠C_cMoC_c' = 168 (1)°. At present there are no other precise structure determinations available which allow the comparison of η^3-allyl and tetrahydroborate ligation.

The foregoing observations suggest that there is a demonstrable basis for an analogy between BH_4^- and η^3-$C_3H_5^-$. Such an analogy may be useful in guiding a large number of future chemical experiments.

VII. Addendum

James, Smith, and Shurvell[205] have presented vibrational spectroscopic evidence that $Zr(BH_4)_4$ may be distorted from T_d to T symmetry. Such a distortion could arise from rotation of BH_4 ligands about the H_t–B–Zr axes. Though there is certainly evidence that such a distortion may require relatively little energy,[138,139,175] the arguments presented by James, Smith, and Shurvell are based upon very weak bands in the vibrational spectra, which may be overtones and/or combinations rather than fundamentals arising from lowered symmetry (the spectra were not shown in this article). Hopefully further studies will clarify this point.

Smith, James, and Dilts[206] have reported TG–DTA studies on $(C_5H_5)_2Zr(BH_4)_2$. The thermal decomposition of this compound is complex and appears to consist of a number of stages; the only volatile product of thermolysis is H_2. These authors also report Raman spectra of both $(C_5H_5)_2Zr(BH_4)_2$ and $(C_5H_5)_2Zr(BD_4)_2$, which are interpreted in terms of bidentate tetrahydroborate groups and η^5-C_5H_5 ligands, in agreement with previous assignments (see section III).

Carbon-13 NMR studies[35] of a ca. 15% ^{13}CO-enriched sample of $([(C_6H_5)_3P]_2N)^+Mo(CO)_4(BH_4)^-$ have revealed that the $Mo(CO)_4$ framework is completely rigid on the NMR time scale.[35] Axial–equatorial CO interchange does *not* occur in concert with H_b–H_t exchange, and $\Delta G^{\ddagger}$ for the former process is at least 9 kcal/mol higher. This result places considerable restrictions both upon the possible mechanisms of H_b–H_t exchange and on the lifetimes of conceivable nonrigid pentacoordinate (monodentate BH_4^-) or heptacoordinate (tridentate BH_4^-) intermediates. This is further evidence that the fluxional process occurs with very minimum electronic and stereochemical perturbation of the metal ion coordination sphere. The concerted process of eq 49 must be considered a plausible pathway.

Marynick[207] has published further molecular orbital calculations on the gas-phase structure of $Be(BH_4)_2$. These are ab initio calculations with a Gaussian basis set of double-ζ quality. Only linear (BBeB) geometries with tridentate BH_4^- groups were considered. The minimum energy structure predicted by these calculations is a D_{3d} bis(tridentate) HBH_3BeH_3BH one, which is calculated to be 7.8 kcal/mol more stable than a similar D_{3d} structure determined by electron diffraction[171] and differing only in several bond lengths and angles. A C_{3v} HBH_3BeH_3BH structure in which the two tridentate tetrahydroborate units are not maintained at the same distance is 11.4 kcal/mol less stable.

It has been reported[208] that $(C_5H_5)_2NbBH_4$ reacts with carboxylic acids to yield, among other products, the related Nb(IV) carboxylates (eq 51).

$$(C_5H_5)_2NbBH_4 + 2RCO_2H \rightarrow (C_5H_5)_2Nb(O_2CR)_2 \qquad (51)$$

Dapporto, Midolini, Orlandini, and Sacconi[209] have reported interesting tetrahydroborate derivatives of the formula P_3CuBH_4 and P_3CoBH_4, where the tridentate ligand $P_3 = CH_3C[CH_2P(C_6H_5)_2]_3$. These compounds were prepared by reaction of the divalent metal salts with P_3 and BH_4^-. An x-ray structure of the Co derivative reveals it to be bidentate with B–H_t = 1.63 (17) and 1.41 (18) Å, B–H_b = 1.27 (16) and 1.38 (17) Å, Co–H_b = 1.55 (15) and 1.45 (15) Å, and Co–B = 2.21 (3) Å. The ligand "bite" angle, H_b–Co–H_b is again small, 66.3 (88)°. The angle H_bBH_b is 76.2 (95)°. Vibrational assignments in the B–H stretching region were confirmed with the BD_4^- derivatives.

The complex $Cr(BH_4)_2 \cdot 2THF$ has been produced in a pure state by the reaction of $Cr(O^tBu)_4$ with B_2H_6 in tetrahydrofuran at −40 °C.[210] The blue crystals are indefinitely stable at −20 °C but decompose at room temperature. The infrared spectrum suggests bidentate tetrahydroborate coordination. The complex $(C_5H_5)Cr(BH_4)_2$ was detected mass spectrometrically among the products of the reaction between $(C_5H_5)CrCl_2 \cdot THF$ and $NaBH_4$;[211] it could not be isolated in the pure state.

The synthesis of the complex $(CH_3)_3Ta(BH_4)_2$ has been mentioned as unpublished work in a recent review article.[212] Nöth and co-workers have reported the isolation of a number of new Lewis base adducts of $Ti(BH_4)_3$.[213] The reaction of $TiCl_4$ with $LiBH_4$ in diethyl ether yields the volatile complex $Ti(BH_4)_3 \cdot (C_2H_5)_2$. This reacts with bases (B) to form the derivatives $Ti(BH_4)_3 \cdot nB$ where for B = THF, n = 1 or 2; B = pyridine, n = 2; B = dimethoxyethane, n = 1; and B = 1,2-dimethoxybenzene, n = 1. The thermal stability of these compounds varies greatly with B. In diethyl ether solution Ti(IV) tetraalkoxides react with B_2H_6 to form $ROTi(BH_4)_2$ complexes. The same reaction in tetrahydrofuran yields $Ti(BH_4)_3 \cdot 2THF$. This adduct is converted to $Ti(BH_4) \cdot THF$ upon sublimation.

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VIII. References and Notes

(1) The term *tetrahydroborate* has been adopted for use by *Chemical Abstracts* and is recommended by the American Chemical Society to be used in lieu of *borohydride* as a representation of the BH_4^- anion and ligand. Our desire for uniformity prompts us to maintain this terminology throughout the article.
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