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METHYLTRIHYDROBORATE COMPLEXES OF THE
LANTHANIDES AND ACTINIDES

R.S. Shinomoto
(Ph.D. Thesis)

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MASTER

to my parents

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Methyltrihydroborate Complexes of the Actinides and Lanthanides

Ronald Steven Shinomoto

ABSTRACT

The reaction of MCl_n ($M = Zr, Hf, U, Th, Np$) with $LiBH_3CH_3$ in chlorobenzene produces volatile, hexane-soluble $M(BH_3CH_3)_n$. Crystal structures confirm that they are monomeric, tetrahedral species. The $U(IV)$ and $Th(IV)$ methyltrihydroborates readily form Lewis base adducts. The adducts prepared include $U(BH_3CH_3)_4 \cdot THT$, $Th(BH_3CH_3)_4 \cdot L$ ($L = THF$ (tetrahydrofuran), THT (tetrahydrothiophene), SMe_2 , OMe_2), $U(BH_3CH_3)_4 \cdot 2L$ ($L = THF$, pyridine, NH_3), $Th(BH_3CH_3)_4 \cdot 2L$ ($L = THF$, THT , py, NH_3), $M(BH_3CH_3)_4 \cdot L-L$ ($M = U, Th$; $L-L = dme$ (1,2-dimethoxyethane), $bnte$ (bis(1,2-methylthio)ethane), $tmed$ (N,N,N',N' -tetramethylethylenediamine), $dmpe$ (1,2-dimethylphosphinoethane)) and $Th(BH_3CH_3)_4 \cdot 1/2 OEt_2$. $U(BH_3CH_3)_4 \cdot 2THF$ has a pseudo-octahedral geometry with THF groups trans to each other. The adducts $[Th(BH_3CH_3)_4 \cdot THF]_2$ and $Th(BH_3CH_3)_4 \cdot 1/2 OEt_2$ are dimers in the solid state. The metal atoms are linked by a $M-H-BH(CH_3)-H-M$ bridge with the unique hydrogen directly bridging the two metal atoms. The dimer $U(BH_3CH_3)_4 \cdot THT$ is bridged by THT groups. CI mass spectrometry suggests $Th(BH_3CH_3)_4 \cdot L$ ($L = THT, OMe_2, SMe_2$) is a dimer in the solid state. A steric model has been used to justify the stoichiometry and structures of $M(BH_3CH_3)_4$ and $M(BH_3)_4$ ($M = U, Th$) base adducts. The bidentate base adducts of $U(BH_3CH_3)_4$ show dynamic behavior. The pseudo-octahedral species have two nonequivalent BH_3CH_3 sites in the solid state, two trans and two cis to the bidentate ligand. These two sites exchange rapidly at room temperature in solution but exchange can be slowed appreciably at lower

temperatures so as to observe two nonequivalent BH_2CH_3 sites on the ^1H NMR time scale. A twisting mechanism has been proposed based on measured ΔG values for two site exchange. The U(III) species, $\text{U}(\text{BH}_2\text{CH}_3)_2\cdot 2\text{dmpe}$, has also been prepared by thermal decomposition of $\text{U}(\text{BH}_2\text{CH}_3)_4\cdot \text{dmpe}$ in toluene in the presence of excess dmpe. It has a pseudo-pentagonal bipyramidal geometry with two of the BH_2CH_3 groups occupying axial positions.

The reaction of MCl_3 ($\text{M} = \text{Ho}, \text{Yb}, \text{Lu}$) with LiBH_2CH_3 in diethyl ether produces volatile, toluene-soluble $\text{M}(\text{BH}_2\text{CH}_3)_2\cdot \text{OEt}_2$. Other Lewis base adducts prepared from $\text{M}(\text{BH}_2\text{CH}_3)_2\cdot \text{OEt}_2$ include $\text{Ho}(\text{BH}_2\text{CH}_3)_2\cdot \text{L}$ ($\text{L} = \text{THT}, \text{THF}, \text{py}$), $\text{Ho}(\text{BH}_2\text{CH}_3)_2\cdot 2\text{L}$ ($\text{L} = \text{THT}, \text{THF}, \text{py}$), $\text{Ho}(\text{BH}_2\text{CH}_3)_2\cdot \text{tmed}$, $\text{Ho}(\text{BH}_2\text{CH}_3)_2\cdot 3/2 \text{ L-L}$ ($\text{L-L} = \text{dmpe}, \text{bmte}$), $\text{Yb}(\text{BH}_2\text{CH}_3)_2\cdot 3/2 \text{ dmpe}$, $\text{Yb}(\text{BH}_2\text{CH}_3)_2\cdot \text{L}$ ($\text{L} = \text{THF}, \text{dme}$), $\text{Yb}(\text{BH}_2\text{CH}_3)_2\cdot 2\text{THF}$, and $\text{Lu}(\text{BH}_2\text{CH}_3)_2\cdot \text{THF}$. The species $\text{Yb}(\text{BH}_2\text{CH}_3)_2\cdot \text{OEt}_2$ has a pseudo-tetrahedral structure and $\text{Ho}(\text{BH}_2\text{CH}_3)_2\cdot 2\text{py}$ has a trigonal bipyramidal geometry with the pyridines occupying both axial positions.

By structural criteria, the bonding in actinide and lanthanide methyltrihydroborate complexes is primarily ionic in character even though they display covalent-like physical properties. Spectroscopic measurements indicate that there is some degree of covalent bonding in $\text{U}(\text{BH}_2\text{CH}_3)_4$.

Chapter 1

INTRODUCTION

The study of metal tetrahydroborates with d transition metals, lanthanides, and actinides has taken on renewed interest because the compounds formed exhibit unusual covalent physical properties (volatility and solubility in nonpolar solvents).^{1, 2} Covalent lanthanide and actinide compounds are a matter of some controversy. Therefore the preparation and study of actinide and lanthanide complexes that exhibit covalent physical properties are of current interest.

The tetrahydroborate ligand usually coordinates to the metal through tridentate or bidentate bridging hydrogen atoms:

bidentate coordination

tridentate coordination

In addition two unusual types of ligation have been observed. One is monodentate coordination of the tetrahydroborate,

found only in structurally characterized $\text{Cu}(\text{PPh}_2\text{Me})_2\text{BH}_4$.³ The other unusual type of ligation is found in $\text{Co}_2(\text{BH}_4)_2(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)_2 \cdot 1/2 \text{C}_6\text{H}_6$.⁴ In this case a $\text{Co-H-BH}_2\text{-H-Co}$

type of linkage is found in addition to direct bridging of the cobalt atoms by one hydrogen atom:

The tetrahydroborate may be described as being both tridentate and chelating to both Co atoms.

The Zr(IV), Hf(IV), Np(IV), and Pu(IV) tetrahydroborates exhibit high volatility^{2, 5} and are monomeric species in which all of the tetrahydroborate groups coordinate to the metal through tridentate ligation. Tetravalent Th, Pa, and U tetrahydroborate exhibit lower volatility^{2, 5, 6} and are polymeric, bridging through bidentate tetrahydroborate groups. Two terminal tridentate tetrahydroborates and four bridging bidentate tetrahydroborates surround the metal.⁷

Zirconium(IV) and hafnium(IV) tetrahydroborates were originally prepared by reacting the tetravalent fluoride double salts; e. g., NaZrF_6 and NaHfF_6 , with $\text{Al}(\text{BH}_3)_3$.^{5a} Np(IV), Pu(IV), Th(IV), Pa(IV), and U(IV) tetrahydroborate were originally prepared by reacting the tetravalent fluoride with $\text{Al}(\text{BH}_3)_3$.^{2, 5, 6} Due to the inherent hazards in working with $\text{Al}(\text{BH}_3)_3$,⁸ alternate methods of preparation have been attempted. $\text{U}(\text{BH}_3)_4$ has been successfully prepared by reacting UCl_4 with LiBH_4 in a vacuum ball mill.⁹ $\text{Zr}(\text{BH}_3)_4$ and $\text{Th}(\text{BH}_3)_4$ have been prepared by reacting the tetravalent chloride with LiBH_4 in diethyl ether.^{10, 11}

Recently in our laboratory, attempts were made to prepare $U(BH_3)_4$ by reacting UF_4 with $LiBH_4$ in diethyl ether.^{12a} This method proved unsuccessful because a diethyl ether adduct of $U(BH_3)_4$ was obtained upon sublimation. Direct treatment of $U(BH_3)_4$ with THF or *n*-propyl ether produced $U(BH_3)_4 \cdot 2THF$ or $U(BH_3)_4 \cdot O(n-Pr)_2$, respectively.^{12b,c} The formation of these Lewis base adducts is not surprising since actinide ions, which have a high charge-to-radius ratio, are hard Lewis acids. The structure of these complexes is fascinating because of the different types of tetrahydroborate ligation involved in these complexes. $U(BH_3)_4 \cdot OMe_2$ and $U(BH_3)_4 \cdot OEt_2$ are linear chains in which each U atom is coordinated to three tridentate tetrahydroborates, two bridging bidentate tetrahydroborates, and one ether molecule.^{11a} $U(BH_3)_4 \cdot O(n-Pr)_2$ is a dimer in which one uranium atom is surrounded by four tridentate tetrahydroborates and one bridging bidentate tetrahydroborate while the other uranium atom is coordinated to three tridentate tetrahydroborates, one bridging bidentate tetrahydroborate, and two ether molecules.^{12c} U(III) tetrahydroborate base adducts have been prepared by reacting $U(BH_3)_4 \cdot nTHF$ with 1,2-dimethylphosphinoethane (dmpe) or 2-(diphenylphosphino)pyridine (Ph_2Ppy) to form $U(BH_3)_4 \cdot 2dmpe$ and $U(BH_3)_4 \cdot 2Ph_2Ppy$, respectively.¹³ X-ray crystal structure analyses showed that two of the tetrahydroborate ligands are tridentate while the third is bidentate in $U(BH_3)_4 \cdot 2dmpe$ while all of the tetrahydroborates are tridentate in $U(BH_3)_4 \cdot 2Ph_2Ppy$.

In addition to these base adducts, a number of double salts have been isolated. When $Zr(BH_3)_4$ and $Hf(BH_3)_4$ are treated with $LiBH_4$ in ether, the double salt $Li[M(BH_3)_4]_2$, $M = Zr, Hf$, is obtained.¹¹ The ligation of the tetrahydroborate ligand in these complexes has not been

structurally characterized by X-ray diffraction but appears to be bidentate according to the IR spectra. Similarly when $\text{Th}(\text{BH}_4)_4$ is treated with LiBH_4 in diethyl ether, the following double salts are obtained:¹¹

In these cases the infrared spectra suggest the mode of ligation of the tetrahydroborate ligands to be tridentate. The double salt $(\text{NEt}_4)_2[\text{U}(\text{BH}_4)_6]$ has also been reported.¹⁴ An approximately octahedral geometry for $[\text{U}(\text{BH}_4)_6]^{2-}$ has been proposed with four terminal bidentate and two tridentate tetrahydroborates coordinated to the metal.¹⁵

Organometallic tetrahydroborate complexes are also known. The tris-Cp (cyclopentadienyl) complex, $(\text{C}_5\text{H}_5)_3\text{MBH}_4$, $M = \text{U}, \text{Th}$, has been synthesized by treating $(\eta\text{-C}_5\text{H}_5)_3\text{MCl}$ with excess NaBH_4 in THF or benzene.¹⁵ From assignments of the IR spectrum, it appears to have a C_{3v} structure with a tridentate tetrahydroborate ligand. The bis-Cp complex, $(\text{C}_5\text{H}_5)_2\text{U}(\text{BH}_4)_2$, has been prepared by the following route:¹⁶

This complex has been structurally characterized by X-ray diffraction. The geometry about the metal is approximately tetrahedral with tridentate tetrahydroborate groups.

Undoubtedly these changes in tetrahydroborate ligation are related to steric crowding about the metal. Recently Bagnall and Li have developed a quantitative cone-packing model for steric crowding about U(IV) and Th(IV) complexes, including the $U(BH_4)_4$ base adducts described above.¹⁷ Utilization of this model will be described in Chapters 3 and 4. This model provided a useful basis for explaining the structure, stability, and stoichiometry of f-transition metal complexes that they prepared, specifically complexes of the type $UCp(NCS)_2L_2$ and $M(O_2CR)_4.nL$, $M = U, Th$; $R = CCl_3, CF_3, CHCl_2$; where L is an oxygen-donor base.¹⁷ Application of this steric model tacitly implies that these compounds are primarily ionic in character.¹⁸

Tetrahydroborate complexes of lanthanides are rare. Zange has prepared a number of complexes with formula $Ln(BH_4)_4.nTHF$ ($Ln =$ lanthanide, $n =$ nonintegral number) by treating anhydrous lanthanide chlorides with diborane in THF.¹⁹ A series of complexes, $Ln(BH_4)_4.3THF$ ($Ln = La, Y, Nd, Gd, Er$), can be made by reacting $Ln(OMe)_3$ with B_2H_6 in THF, or by reacting $Ln(OMe)_3$ with $Al(BH_4)_3$ in the absence of solvent, followed by removal of volatiles and extraction with THF.²⁰ The preparation of two organometallic Ce(IV) tetrahydroborates have been reported-- $(\eta^5-C_5H_5)_2CeBH_4$ and $(\pi-indenyl)_2Ce(BH_4)_2$.²¹ It seems surprising that a strong reducing agent like the BH_4^- anion does not reduce Ce(IV) to Ce(III), and the existence of these compounds has recently come under question.²² Attempts to prepare $Ce(BH_4)_4$ will be discussed in Chapter 4. Marks and Grynkevich have prepared the

organometallic lanthanide tetrahydroborate complexes $(\eta^5\text{-C}_5\text{H}_5)_2\text{MBH}_4$ (M = Er, Yb) and $(\eta^5\text{-C}_5\text{H}_5)_2\text{MBH}_4\cdot\text{THF}$ (M = Sm, Er, Yb) by the following route:²³

These compounds, though not structurally characterized by X-ray diffraction, appear to invoke different modes of tetrahydroborate ligation for steric reasons. Based on the IR spectra, the tetrahydroborate ligand in $(\text{C}_5\text{H}_5)_2\text{SmBH}_4\cdot\text{THF}$ appears to be tridentate while it is bidentate in the smaller Er and Yb THF-adduct analogues. For THF-free $(\text{C}_5\text{H}_5)_2\text{MBH}_4$ (M = Er, Yb) complexes, the tetrahydroborate ligand appears to be bidentate, forming a polymeric structure in which the lanthanide ions are bridged as in CH_3ZnBH_4 .²⁴ Several Russian workers have reported the synthesis of homoleptic THF-free lanthanide tetrahydroborates by reacting the anhydrous lanthanide trichloride with NaBH_4 in an aromatic solvent.²⁵ $\text{La}(\text{BH}_4)_3$ and $\text{Ce}(\text{BH}_4)_3$ were successfully prepared by this method. On the basis of IR assignments, tridentate ligation of the tetrahydroborate groups was inferred.²⁵ This seems surprising since the steric environment about the metal would be undercrowded. Therefore a polymeric structure might be expected containing bridging bidentate tetrahydroborate groups that would help fill the coordination sphere about the metal. A polymeric structure is suggested by the fact that these compounds are not

volatile,²⁵ in contrast to other monomeric homoleptic Group IVB and actinide tetrahydroborates, which are highly volatile.^{2,3}

Recently the spectroscopic properties of $U(BH_4)_4$ and $Np(BH_4)_4$ have been studied.^{26,27,28} Since $U(BH_4)_4$ is polymeric in the solid state, samples must be diluted in a diamagnetic matrix such as $Hf(BH_4)_4$, in order to study their spectroscopic properties as symmetric (tetrahedral) monomers.²⁶ Furthermore, the wavefunctions obtained from the optical analysis of the tetrahedral $U(BH_4)_4/Hf(BH_4)_4$ system cannot be used to calculate the magnetic susceptibility of the lower symmetry $U(BH_4)_4$ polymer. Therefore studies on analogous monomeric compounds with very similar physical properties were desired. An ideal candidate is $U(BH_2CH_3)_4$. Like $U(BH_4)_4$, it is volatile,²⁹ but unlike $U(BH_4)_4$ in the solid state, it is a symmetric monomeric species, thus facilitating spectral studies. It also possesses ideal physical characteristics; i. e., solubility in hydrocarbon solvents, thus making chemical studies more feasible. Solubility in hydrocarbon solvents is a highly desired physical property since reactions with soft Lewis bases; e. g., CO, olefins, and acetylenes, can be attempted.

In the following chapters, we will describe the preparation of $U(BH_2CH_3)_4$ and other methyltrihydroborates as well as Lewis base adducts of actinide and lanthanide methyltrihydroborates.

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Chapter 2

THE METHYLTRIHYDROBORATES OF ZR, HF, U, TH, NPIntroduction

There are two structural types of actinide tetrahydroborates, polymeric and monomeric.^{1, 2} The former include $\text{Th}(\text{BH}_4)_4$, $\text{Pa}(\text{BH}_4)_4$, and $\text{U}(\text{BH}_4)_4$, while the latter include $\text{Pu}(\text{BH}_4)_4$ and $\text{Np}(\text{BH}_4)_4$. In the polymeric tetrahydroborates there are two types of tetrahydroborate groups, bidentate and tridentate. Each metal is surrounded by four bidentate and two tridentate groups. Each of the bidentate groups are bound to the metal via hydrogen bridge bonds and use their remaining two hydrogen atoms to link neighboring metal atoms in a polymeric structure of C_2 symmetry at the metal. The tridentate groups are connected to the metal by three hydrogen bridge bonds while the last hydrogen atom lies on the M-B axis and is in a terminal position. In the monomeric tetrahydroborates, the metal is surrounded tetrahedrally by four tridentate groups. As symmetric monomeric compounds are useful for spectroscopic and magnetic measurements, it was desirable to find analogous monomeric compounds of Th, Pa, and U.

During the Manhattan project, Schlesinger et al. reported the synthesis and isolation of methyl derivatives of uranium tetrahydroborate, the mono and tetra(methyltrihydroborate) derivatives, $\text{U}(\text{BH}_4)_4$, BH_3CH_3 , and $\text{U}(\text{BH}_3\text{CH}_3)_4$.³ $\text{U}(\text{BH}_3\text{CH}_3)_4$ would be an ideal candidate for spectroscopic and magnetic measurements since if monomeric, it would be totally symmetric. $\text{U}(\text{BH}_3\text{CH}_3)_4$ was originally synthesized by the reaction of $\text{U}(\text{BH}_4)_4$ with excess trimethylboron:

This reaction also produces $\text{U}(\text{BH}_2\text{CH}_3)_x(\text{BH}_4)_{4-x}$ as products, but excess trimethylboron drives the reaction to $\text{U}(\text{BH}_2\text{CH}_3)_4$. Our attempts with the above synthesis resulted in low yields and substantial unreacted starting materials. Therefore an alternative method of synthesis of $\text{U}(\text{BH}_2\text{CH}_3)_4$ and other methyltrihydroborates was sought.

Synthesis

In attempting to find an alternate method of making $\text{U}(\text{BH}_2\text{CH}_3)_4$, the reaction of UF_4 with $\text{Al}(\text{BH}_2\text{CH}_3)_3$ or $\text{Al}(\text{BH}_2\text{Me}_2)_3$ was considered, analogous to the reaction of UF_4 with $\text{Al}(\text{BH}_4)_3$ to make $\text{U}(\text{BH}_4)_4$. To prepare $\text{Al}(\text{BH}_2\text{CH}_3)_3$ or $\text{Al}(\text{BH}_2\text{Me}_2)_3$, the gas phase reaction of $\text{Al}(\text{BH}_4)_3$ with $\text{B}(\text{CH}_3)_3$ was tried. Unfortunately, pure $\text{Al}(\text{BH}_2\text{CH}_3)_3$ or $\text{Al}(\text{BH}_2\text{Me}_2)_3$ could not be isolated by trap-to-trap distillation. A good deal of the $\text{Al}(\text{BH}_4)_3$ remained unreacted. Only a very small amount of $\text{U}(\text{BH}_2\text{CH}_3)_4$ was obtained by reacting the partially B-methylated $\text{Al}(\text{BH}_4)_3$ mixture with UF_4 . Thus this method proved unsatisfactory.

Recently it was shown that $\text{Zr}(\text{BH}_4)_4$ could be prepared in high yields by the reaction of ZrCl_4 and LiBH_4 in enough diethyl ether to form a slurry.⁵ Therefore an analogous reaction between ZrCl_4 and LiBH_2CH_3 , prepared by the method of Wartik and Schlesinger (see Chapter 5), was attempted in diethyl ether. Within a couple of hours the reaction mixture turned dark, eventually turning black. $\text{Zr}(\text{BH}_2\text{CH}_3)_4$ was isolated from the reaction mixture in 40% yields. Based on the results of this reaction, the analogous reaction of UCl_4 with LiBH_2CH_3 in diethyl ether was tried. Unfortunately only a very small yield of $\text{U}(\text{BH}_2\text{CH}_3)_4$ was obtained. When ThCl_4 was reacted with LiBH_2CH_3 in

diethyl ether, the base adduct $[\text{Th}(\text{BH}_2\text{CH}_3)_4]_2\cdot\text{OEt}_2$ was acquired (see Chap. 3). The diethyl ether could be completely removed from $[\text{Th}(\text{BH}_2\text{CH}_3)_4]_2\cdot\text{OEt}_2$ by repeated crystallization from hexane, but the process is a long and tedious one. Therefore the use of a noncoordinating solvent was sought. It was found that the following reaction works satisfactorily:

Physical Properties

All methyltrihydroborates are volatile solids, which may be sublimed under vacuum at room temperature and are also soluble in non-coordinating hydrocarbons. These two properties make methyltrihydroborates ideal starting reagents since they can be easily purified and reactions can be run in many different solvents.

All methyltrihydroborates are extremely reactive, especially towards oxidation, and only the most nonacidic solvents can be used. It is unwise to store methyltrihydroborates in solvents for any period of time as decomposition inevitably occurs. It is desirable to work with grease-free systems with teflon stopcocks and Viton O-ring connections whenever possible for optimum purity. In disposing of unwanted material, careful quenching with methanol under vacuum is recommended, followed by careful exposure to air, and washing with water and dilute HCl.

Crystal Structures and Characterization*

It was found that $\text{Zr}(\text{BH}_2\text{CH}_3)_4$, $\text{Np}(\text{BH}_2\text{CH}_3)_4$, $\text{Th}(\text{BH}_2\text{CH}_3)_4$, and $\text{U}(\text{BH}_2\text{CH}_3)_4$ are all monomeric (see Figs. 1 and 2). $\text{Zr}(\text{BH}_2\text{CH}_3)_4$,

crystallizes in the space group $P4_2/n$ with $Z = 2$. It is tetragonal with unit cell parameters $a = 10.311(6)$ Å, $c = 5.851(3)$ Å. $\text{Th}(\text{BH}_3\text{CH}_3)_4$ crystallizes in the space group $P\bar{1}$ with $Z = 8$. It is triclinic with unit cell parameters $a = 18.403(6)$ Å, $b = 16.910(6)$ Å, $c = 8.834(3)$ Å, $\alpha = 88.06(4)^\circ$, $\beta = 90.83(4)^\circ$, $\gamma = 88.08(4)^\circ$. $\text{U}(\text{BH}_3\text{CH}_3)_4$ crystallizes in the space group $P2_1/n$ with $Z = 8$. It is monoclinic with unit cell parameters $a = 18.228(6)$ Å, $b = 16.749(6)$ Å, $c = 8.765(2)$ Å, $\beta = 90.69(4)^\circ$. $\text{Np}(\text{BH}_3\text{CH}_3)_4$ crystallizes in the space group $P4_2/n$ with $Z = 2$. It is tetragonal with $a = 10.552(6)$ Å, $c = 5.950(3)$ Å. In all four compounds, the metal atom is tetrahedrally coordinated to the four methyltrihydroborate groups with twelve hydrogen atoms from the BH_3CH_3 ligands surrounding the metal (Fig. 1). Both $\text{Zr}(\text{BH}_3\text{CH}_3)_4$ and $\text{Np}(\text{BH}_3\text{CH}_3)_4$ consist of a body-centered packing of molecules (Fig. 3), and the coordination is similar to those found for unsubstituted tetrahydroborates.² The Zr-B distances in $\text{Zr}(\text{BH}_3\text{CH}_3)_4$ and $\text{Zr}(\text{BH}_4)_4$ are 2.335(3) and 2.34(3) Å, respectively.⁷ The Np-B distances in $\text{Np}(\text{BH}_3\text{CH}_3)_4$ and $\text{Np}(\text{BH}_4)_4$ are 2.487(6) and 2.46(3) Å, respectively.² Selected bond distances and angles are presented in Tables I and II, respectively. $\text{Th}(\text{BH}_3\text{CH}_3)_4$ and $\text{U}(\text{BH}_3\text{CH}_3)_4$ are almost crystallographically isomorphous. The uranium compound is in a monoclinic space group, but in the Th compound the b axis is inclined to the ac plane by about 2° , which results in a triclinic space group. Whereas in the uranium compound the unit cell contains two crystallographically different but chemically identical molecules, the thorium compound contains four. Within these structures the M-B bond lengths deviate less than 2σ (for U) and 3σ (for Th) from their respective average, and the B-M-B angles in both structures are all

within 3° of being tetrahedral. The M-B-C angles are close to 180°, indicative of tridentate ligation of the methyltrihydroborate group.

The average triply bridged U-B distance is 2.48 ± 0.03 Å. These may be compared to triply bridged distances found in $U(BH_3)_4$,¹ 2.52(1) Å; $U(BH_3)_4 \cdot OEt_2$,^a 2.53 Å; and $U(BH_3)_4 \cdot 2THF$,^b 2.56(4) Å. These last three compounds are all 14-coordinate and thus it is expected that the U(IV) ionic radius would be slightly greater for these compounds than the 12-coordinate $U(BH_3CH_3)_4$.⁹

These compounds were characterized by IR and proton NMR spectroscopy. The data are presented in the Experimental Section (Chapter 5). From the assignments of Marks et al.,¹⁰ and Banks and Edelstein,¹¹ the infrared spectrum shows the presence of B-H bridging stretches at ~ 2100 cm⁻¹ and bridge deformation at ~ 1250 cm⁻¹, and the complete absence of B-H_{tridentate} stretches at ~ 2500 cm⁻¹. The other bands listed are due to the presence of the methyl group. The IR spectrum of $Hf(BH_3CH_3)_4$ is very similar to that of the structurally characterized $Zr(BH_3CH_3)_4$, $U(BH_3CH_3)_4$, and $Th(BH_3CH_3)_4$, suggesting it has a structure that is similar to these compounds. The PMR spectrum of $Zr(BH_3CH_3)_4$ shows a quartet due to the three bridging trihydroborate protons (for ¹¹B, I = 3/2) with nearly the same chemical shift as that of $Zr(BH_3)_4$.¹² The bridging protons are broadened due to quadrupole relaxation by ¹¹B. This obscures boron-hydrogen spin-spin coupling. The PMR spectrum of $Hf(BH_3CH_3)_4$ is very similar to $Zr(BH_3CH_3)_4$ with the exception that the bridging protons are shifted about 1 ppm upfield. A similar shift is also found when the PMR spectra of $Zr(BH_3)_4$ and $Hf(BH_3)_4$ are compared.¹² The PMR spectrum of the methyl protons of both complexes are broadened due to unresolved spin-spin coupling and

quadruple relaxation with ^{10,11} B. The PMR spectrum of the methyl protons of diamagnetic Th(BH₃CH₃)₄ are split into a quartet due to coupling between ¹H and ¹¹B. The PMR spectrum of the bridging protons of U(BH₃CH₃)₄ are shifted far downfield due to paramagnetic U(IV).

Thus we see replacement of the BH₄ group by the BH₃CH₃ group results in formation of monomeric compounds. Nevertheless, the crystal structure of Np(BH₃CH₃)₄ is like that of Zr(BH₃CH₃)₄ rather than that of U(BH₃CH₃)₄, despite the fact that the ionic radius of U(IV) is only 0.02 Å larger than Np(IV) while Zr(IV) is 0.12 Å smaller.¹³

According to Raymond and Pauling's structural definition of ionicity,¹⁴ these compounds are primarily ionic since bond lengths can be predicted by adding ionic radii. For instance, assuming an ionic radius of 1.36 Å for the methyltrihydroborate¹⁵ and an ionic radius of 0.98 Å, 1.21 Å, 1.17 Å, and 1.10 Å for Zr(IV), Th(IV), U(IV), and Np(IV), respectively,¹³ we would predict a Zr(IV)-B bond length of 2.34 Å (compared to the actual bond distance of 2.335(3) Å), a Th(IV)-B bond length of 2.57 Å (cf. 2.56(5) Å), a U(IV)-B bond length of 2.53 Å (cf. 2.49(2) Å), and a Np(IV)-B bond length of 2.46 Å (cf. 2.487(6) Å).

Optical and Magnetic Properties

Despite structural characterizations that indicate these compounds are primarily ionic, this does not mean that there is no covalent character involved in the bonding. Unless covalency is the dominant feature of the bonding, it cannot be expected to appear as a structural effect.^{14a} Spectroscopic measurements indicate that there is a certain degree of covalency involved in the bonding of these compounds. An assumption was made that the electronic structure of U(BH₃CH₃)₄ and U(BH₄)₄ are similar. This is valid since their optical spectra in C₆D₆

are similar, although the bands in $U(BH_3CH_3)_4$ seem to be shifted to a slightly higher energy (see Fig. 4). Using the eigenvectors obtained from a reanalysis of the data of the high resolution optical data of $U(BD_4)_4$ in single crystals of $Hf(BD_4)_4$ of Keiderling and Bernstein,¹⁶ Rajnak et al.¹⁷ fitted the magnetic susceptibility data of $U(BH_3CH_3)_4$ by using an orbital reduction factor of $k = 0.85$. This may be compared to the reduction of the spin orbit coupling constant for U^{4+} free ion to that of $U(BD_4)_4/Hf(BD_4)_4$, where $k = \epsilon_{crystal}/\epsilon_{free\ ion} = 0.91$. Thus use of this crystal field model indicates that the degree of covalency in the bonding of $U(BH_3CH_3)_4$ is greater than that of $U(BH_4)_4$.

To determine the degree of f-orbital covalency, it is necessary to evaluate contact and pseudo-contact contributions to the observed isotropic shifts in NMR spectra of paramagnetic compounds. For $U(BH_3CH_3)_4$, there is no pseudo-contact (dipolar) contribution to the observed isotropic shifts since they average out to zero in cubic symmetry. We have measured the isotropic shifts with respect to temperature in 1H , ^{13}C , and ^{11}B NMR spectra of $U(BH_3CH_3)_4$. The data are presented in Tables III through V. A plot of the isotropic shift vs. $1/T$ is presented in Figs. 5 through 8. The analysis of this data in terms of the isotropic hyperfine coupling constants at the various nuclei is in progress.¹⁸ MO calculations need to be made to interpret the data.

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Table I. Selected Interatomic Distances (Å)

	Zr(BH ₃ CH ₃) ₄	Np(BH ₃ CH ₃) ₄
M-B	2.335(3)	2.487(6)
-4H(1)	2.08(3)	2.22
-4H(2)	2.04(3)	2.15
-4H(3)	2.07(3)	2.16
B-C	1.573(5)	1.563(8)
-H(1)	1.15(3)	1.05
-H(2)	1.12(3)	1.06
-H(3)	1.15(3)	1.09
C-H(4)	0.84(5)	0.96
-H(5)	1.00(4)	0.96
-H(6)	0.85(5)	0.94

U(BH ₃ CH ₃) ₄			
U(1)-B(1)	2.50(4)	U(2)-B(5)	2.50(3)
-B(2)	2.46(4)	-B(6)	2.44(4)
-B(3)	2.49(4)	-B(7)	2.50(3)
-B(4)	2.50(4)	-B(8)	2.43(3)
B(1)-C(1)	1.65(4)	B(5)-C(5)	1.62(4)
B(2)-C(2)	1.66(4)	B(6)-C(6)	1.67(4)
B(3)-C(3)	1.59(4)	B(7)-C(7)	1.63(4)
B(4)-C(4)	1.60(4)	B(8)-C(8)	1.70(4)

Th(BH ₃ CH ₃) ₄			
Th(1)-B(1)	2.57(6)	Th(3)-B(9)	2.56(6)
-B(2)	2.54(7)	-B(10)	2.55(7)
-B(3)	2.57(6)	-B(11)	2.71(7)
-B(4)	2.49(6)	-B(12)	2.58(6)
Th(2)-B(5)	2.57(6)	Th(4)-B(13)	2.61(6)
-B(6)	2.50(6)	-B(14)	2.49(6)
-B(7)	2.51(8)	-B(15)	2.57(6)
-B(8)	2.52(5)	-B(16)	2.56(5)
B(1)-C(1)	1.76(8)	B(9)-C(9)	1.65(7)
B(2)-C(2)	1.59(7)	B(10)-C(10)	1.65(8)
B(3)-C(3)	1.76(7)	B(11)-C(11)	1.57(8)
B(4)-C(4)	1.73(7)	B(12)-C(12)	1.57(7)
B(5)-C(5)	1.63(7)	B(13)-C(13)	1.63(7)
B(6)-C(6)	1.70(7)	B(14)-C(14)	1.66(8)
B(7)-C(7)	1.55(8)	B(15)-C(15)	1.62(9)
B(8)-C(8)	1.64(6)	B(16)-C(16)	1.63(7)

Table II. Selected Angles (deg)

$M(BH_3CH_3)_n$			
		M = Zr	M = Np
B-M-B ^a		109.6(2)	109.7(3)
B-M-B ^b		109.4(1)	109.4(2)
M-B-C		179.9(3)	178.7(5)
H(1)-B-H(2)		96(2)	108
H(1)-B-H(3)		104(2)	92
H(2)-B-H(3)		99(2)	95
H(4)-C-H(5)		101(4)	95
H(4)-C-H(6)		113(5)	108
H(5)-C-H(6)		101(5)	108
$U(BH_3CH_3)_n$			
B(1)-U(1)-B(2)	110(1)	B(6)-U(2)-B(8)	109(1)
B(1)-U(1)-B(3)	110(1)	B(7)-U(2)-B(8)	109(1)
B(1)-U(1)-B(4)	108(1)	U(1)-B(1)-C(1)	178(2)
B(2)-U(1)-B(3)	108(1)	U(1)-B(2)-C(2)	178(2)
B(2)-U(1)-B(4)	112(2)	U(1)-B(3)-C(3)	177(2)
B(3)-U(1)-B(4)	109(1)	U(1)-B(4)-C(4)	176(3)
B(5)-U(2)-B(6)	110(1)	U(2)-B(5)-C(5)	177(2)
B(5)-U(2)-B(7)	111(1)	U(2)-B(6)-C(6)	175(3)
B(5)-U(2)-B(8)	111(1)	U(2)-B(7)-C(7)	179(2)
B(6)-U(2)-B(7)	108(1)	U(2)-B(8)-C(8)	175(3)
$Th(BH_3CH_3)_n$			
B(1)-Th(1)-B(2)	110(2)	B(13)-Th(4)-B(16)	109(2)
B(1)-Th(1)-B(3)	111(2)	B(14)-Th(4)-B(15)	109(2)
B(1)-Th(1)-B(4)	107(2)	B(14)-Th(4)-B(16)	108(2)
B(2)-Th(1)-B(3)	106(2)	B(15)-Th(4)-B(16)	109(2)
B(2)-Th(1)-B(4)	115(2)	Th(1)-B(1)-C(1)	175(4)
B(3)-Th(1)-B(4)	107(2)	Th(1)-B(2)-C(2)	178(4)
B(5)-Th(2)-B(6)	107(2)	Th(1)-B(3)-C(3)	174(4)
B(5)-Th(2)-B(7)	108(2)	Th(1)-B(4)-C(4)	171(4)
B(5)-Th(2)-B(8)	108(2)	Th(2)-B(5)-C(5)	177(4)
B(6)-Th(2)-B(7)	110(2)	Th(2)-B(6)-C(6)	171(4)
B(6)-Th(2)-B(8)	116(2)	Th(2)-B(7)-C(7)	174(5)
B(7)-Th(2)-B(8)	107(2)	Th(2)-B(8)-C(8)	177(4)
B(9)-Th(3)-B(10)	106(2)	Th(3)-B(9)-C(9)	179(4)
B(9)-Th(3)-B(11)	109(2)	Th(3)-B(10)-C(10)	175(5)
B(9)-Th(3)-B(12)	108(2)	Th(3)-B(11)-C(11)	171(4)
B(10)-Th(3)-B(11)	111(2)	Th(3)-B(12)-C(12)	171(5)
B(10)-Th(3)-B(12)	111(2)	Th(4)-B(13)-C(13)	174(4)
B(11)-Th(3)-B(12)	112(2)	Th(4)-B(14)-C(14)	172(4)
B(13)-Th(4)-B(14)	111(2)	Th(4)-B(15)-C(15)	175(4)
B(13)-Th(4)-B(15)	112(2)	Th(4)-B(16)-C(16)	178(4)

a) At position 1/2-x, 1/2-y, z.

b) At position y, 1/2-x, 1/2-z.

Table III. ^1H NMR Data for $\text{U}(\text{BH}_3\text{CH}_3)_4$.

$T(^{\circ}\text{K})$	$1/T(\text{K}^{-1})$	CH_3	Shift (ppm)* BH_3
192	5.21×10^{-3}	+23.17	+219.44
196	5.10	+22.80	+216.41
200	5.00	+22.35	+212.28
204	4.90	+22.07	+209.94
213	4.69	+21.41	+203.89
217	4.61	+20.92	+199.80
220	4.55	+20.80	+198.33
231	4.33	+19.90	+190.51
240	4.17	+19.20	+184.38
241	4.15	+19.19	+183.48
249	4.02	+18.59	+178.77
258	3.88	+17.93	+173.25
259	3.86	+17.85	+172.35
269	3.72	+17.24	+167.07
281	3.56	+16.50	+160.69
283	3.53	+16.42	+159.67
295.5	3.38	+15.81	+154.51
298	3.36	+15.68	+153.00

* Referenced with respect to $\text{Th}(\text{BH}_3\text{CH}_3)_4$. Positive sign indicates downfield shift.

Table IV. ^{13}C NMR Data for $\text{U}(\text{BH}_3\text{CH}_3)_4$.

$T(^{\circ}\text{K})$	$1/T(\text{K}^{-1})$	Shift (ppm) *
201	4.98×10^{-3}	+90.92
225	4.44	+84.61
245	4.08	+80.58
276	3.62	+73.95
305	3.28	+68.42

* Referenced with respect to $\text{Th}(\text{BH}_3\text{CH}_3)_4$. Positive sign indicates downfield shift.

Table V. ^{11}B NMR Data for $\text{U}(\text{BH}_3\text{CH}_3)_4$.

$T(^{\circ}\text{K})$	$1/T(\text{K}^{-1})$	Shift (ppm)*
213	4.69×10^{-3}	+110.02
248	4.03	+104.75
273	3.66	+101.89
298	3.36	+99.78
323	3.10	+97.42

* Referenced with respect to $\text{Th}(\text{BH}_3\text{CH}_3)_4$. Positive sign indicates downfield shift.

Fig. 1. ORTEP drawing of $\text{Zr}(\text{BH}_3\text{CH}_3)_2$.

XBL 814-9355A

Fig. 2. ORTEP drawing of $U(BH_3CH_3)_4$.

;

Fig. 3. ORTEP drawing showing packing of $\text{Zr}(\text{BH}_3\text{CH}_3)_4$ units. The central molecule is displaced by $1/2a$, $1/2b$, $1/2c$ from the corner molecules.

XBL 812-8218

Fig. 4. Optical absorption spectra of $U(BH_3)_4$ and $U(BH_3CH_3)_4$ in C_6D_6 at room temperature.

XBL 835-242A

Fig. 5. Isotropic shift vs. $1/T$ for methyl protons of $U(BH_3CH_3)_4$.

Methyl Protons of $U(BH_3CH_3)_4$

34

Fig. 6. Isotropic shift vs. $1/T$ for bridging protons of $U(BH_3CH_3)_n$.

Bridging Protons of $\text{U}(\text{BH}_3\text{CH}_3)_4$

Fig. 7. Isotropic shift vs. $1/T$ for ^{13}C of $\text{U}(\text{BH}_3\text{CH}_3)_4$.

^{13}C of $\text{U}(\text{BH}_3\text{CH}_3)_4$

38

Shift (ppm)

Fig. 8. Isotropic shift vs. $1/T$ for ^{11}B of $\text{U}(\text{BH}_3\text{CH}_3)_4$.

^{11}B of $\text{U}(\text{BH}_3\text{CH}_3)_4$

40

Shift (ppm)

XCG 8410-13384

Chapter 3

LEWIS BASE ADDUCTS OF $\text{Th}(\text{BH}_2\text{CH}_3)_4$ AND $\text{U}(\text{BH}_2\text{CH}_3)_4$ Introduction

Lewis base adducts of uranium tetrahydroborate are known,¹ and the formation of a Lewis base adduct of $\text{Th}(\text{BH}_2\text{CH}_3)_4$, $[\text{Th}(\text{EH}_2\text{CH}_3)_4]_2 \cdot \text{OEt}_2$ has been reported in Chapter 2. In addition a number of additional Lewis base adducts of $\text{Th}(\text{BH}_2\text{CH}_3)_4$ and $\text{U}(\text{BH}_2\text{CH}_3)_4$ have been synthesized. A quantitative cone-packing model for steric crowding has been applied to explain the coordination and stoichiometry of these complexes and will be reported in this chapter. Comparisons with Lewis base adducts of $\text{Th}(\text{BH}_3)_4$ and $\text{U}(\text{BH}_3)_4$ will be discussed.

Discussion

In earlier attempts to make $\text{Th}(\text{BH}_2\text{CH}_3)_4$ and $\text{U}(\text{BH}_2\text{CH}_3)_4$, ethereal solvents were used, analogous to the preparation of $\text{Zr}(\text{BH}_2\text{CH}_3)_4$ from ZrCl_4 and LiBH_2CH_3 in diethyl ether. Reaction of UCl_4 with LiBH_2CH_3 in ether and subsequent sublimation produced a small yield of the desired $\text{U}(\text{BH}_2\text{CH}_3)_4$. However, when the same reaction was carried out in THF, $\text{U}(\text{BH}_2\text{CH}_3)_4 \cdot 2\text{THF}$ was sublimed out of the reaction mixture. Reaction of ThCl_4 with LiBH_2CH_3 in ether and THF produced species with empirical formulas $\text{Th}(\text{BH}_2\text{CH}_3)_4 \cdot 1/2 \text{OEt}_2$ and $\text{Th}(\text{BH}_2\text{CH}_3)_4 \cdot 2\text{THF}$, respectively, after sublimation. A diethyl ether adduct of $\text{U}(\text{BH}_2\text{CH}_3)_4$ apparently forms when $\text{U}(\text{BH}_2\text{CH}_3)_4$ is dissolved in ether, judging from its green color. However, it decomposes to $\text{U}(\text{BH}_2\text{CH}_3)_4$ when isolated and dried under vacuum at room temperature. It was also found that when one equivalent of THF is added to $\text{Th}(\text{BH}_2\text{CH}_3)_4$ in hexane, the adduct $\text{Th}(\text{BH}_2\text{CH}_3)_4 \cdot \text{THF}$ is

formed. X-ray crystal structure determinations of $\text{Th}(\text{BH}_3\text{CH}_3)_2 \cdot 1/2 \text{OEt}_2$ and $\text{Th}(\text{BH}_3\text{CH}_3)_2 \cdot \text{THF}$ were performed.²

Surprisingly both $\text{Th}(\text{BH}_3\text{CH}_3)_2 \cdot 1/2 \text{OEt}_2$ and $\text{Th}(\text{BH}_3\text{CH}_3)_2 \cdot \text{THF}$ were found to be dimers. $[\text{Th}(\text{BH}_3\text{CH}_3)_2]_2 \cdot \text{OEt}_2$ crystallizes in the space group $\text{P2}_1/\text{c}$ with $Z = 4$. It is monoclinic with unit cell parameters $a = 20.163(5) \text{ \AA}$, $b = 10.353(3) \text{ \AA}$, $c = 14.583(3) \text{ \AA}$, $\beta = 104.47(3)^\circ$. $[\text{Th}(\text{BH}_3\text{CH}_3)_2 \cdot \text{THF}]_2$ crystallizes in the space group $\text{P2}_1/\text{n}$ with $Z = 4$. It is also monoclinic with unit cell parameters $a = 12.506(4) \text{ \AA}$, $b = 11.533(4) \text{ \AA}$, $c = 11.662(4) \text{ \AA}$, $\beta = 99.06(2)^\circ$. In both complexes, the thorium atoms are bridged by two methyltrihydroborate groups, and each Th atom is bonded to 3 additional terminal BH_3CH_3 groups. In the diethyl ether complex, only one of the thorium atoms has an ether ligand whereas in the tetrahydrofuran complex, both thorium atoms have THF ligands (Figs. 1 and 2).

The non-bridging BH_3CH_3 groups are of the terminal tetrahydroborate-type bond found in $\text{U}(\text{BH}_4)_3$, in which the metal atom is connected to the boron atom in the BH_4 group through three hydrogen bridges.³ The Th-B distances range from 2.47 to 2.61 $\text{\AA}$ with an average distance of $2.58 \pm 0.04 \text{ \AA}$ and are comparable to the average distance of $2.56 \pm 0.05 \text{ \AA}$ in $\text{Th}(\text{BH}_3\text{CH}_3)_2$.⁴ Selected bond distances and angles are presented in Tables I and II, respectively.

The geometry of the double bridge is illustrated in Figs. 3 and 4. The three hydrogen atoms of BH_3 connect the Th and B atoms. The Th atoms each contact two hydrogen atoms from two BH_3 groups and share two hydrogens from the two BH_3 groups for a total of four hydrogen contacts. The Th-H distances to the unshared atoms are approximately 2.4 $\text{\AA}$. The Th-H distances to the shared atoms are 2.7 $\text{\AA}$ in the

tetrahydrofuran complex; the shared Th-H distances in the asymmetric ethyl ether complex show variations from 2.5 to 2.8 Å. The geometry of the bridging portion of the two complexes is different (Figs. 3 and 4). In the ethyl ether complex (Fig. 3), the bridging hydrogens H(1) and H(24) are cis to each other, and the four atoms, Th(1), B(1), Th(2), and B(8), do not form a plane. In the tetrahydrofuran complex (Fig. 4), the hydrogen atoms H(12) and H(12)' are trans to each other across a center of symmetry, and the four atoms Th, B(4), Th', and B(4)' define an exact plane.

In the ethyl ether structure, the coordination numbers are 13 and 14 for Th(1) and Th(2), respectively. In the tetrahydrofuran complex, the coordination of both Th atoms is 14. It appears the steric requirements of the base affect the bonding mode of the methyltrihydroborate ligand. Because of its bulkier nature, diethyl ether has only enough room to coordinate to one of the Th atoms while the less bulky THF can coordinate to both Th atoms. In previous studies,^{1a,c} similar results were found for the $U(BH_4)_4$ ether complexes, where the methyl and ethyl ether complexes are symmetric polymeric species in which all U atoms are 14-coordinate, each coordinated to one ether group, while the n-propyl ether complex is an asymmetric dimeric species, where one U atom is 14-coordinate while the other is 13-coordinate. The 14-coordinate U atom is surrounded by four terminal tetrahydroborate groups and one bridging bidentate tetrahydroborate group. The 13-coordinate U atom is surrounded by three terminal tridentate tetrahydroborate groups, one bridging bidentate tetrahydroborate group, and two n-propyl ether groups. The

lower coordination number of the 13-coordinate U atom may be due to the presence of the bulky n-propyl ether groups.

In the dimeric Ti complexes described above, the methyltrihydroborate ligand serves in a unique bridging capacity since it cannot form bidentate hydrogen bridges between adjacent metal atoms like the $U(BH_3)_4$ ether complex due to the presence of the methyl group. Almost concurrently, Holah et al.⁵ reported a similar type of bridging for the tetrahydroborate ligand in the complex,

There is no evidence for magnetically nonequivalent methyltrihydroborate sites in solution. 1H ^{11}B , ^{11}B 1H , and ^{13}C 1H NMR spectra show only one trihydroborate proton, one ^{11}B , and one ^{13}C (methyltrihydroborate) peak down to $-80^\circ C$, respectively. This can result from either a solution structure different from the solid state structure, or a site exchange process rapid on the 1H NMR time scale. There is evidence for both.

In order to elucidate whether terminal and bridging methyltrihydroborates could be distinguished by NMR if the time resolution were increased, solution studies have been carried out using paramagnetic $U(BH_3CH_3)_4$. While the analogous uranium dimers have not been isolated, a 1:1 mixture of $U(BH_3CH_3)_4$ and THF can be probed by NMR to determine what possible species exist in solution. The low temperature 1H NMR spectrum of $U(BH_3CH_3)_4$ and one equivalent of THF in toluene- d_6 is reported in Table III. At low temperatures ($<-30^\circ C$), peaks with identical chemical shifts to authentic compounds can be observed for $U(BH_3CH_3)_4$ and $U(BH_3CH_3)_4 \cdot 2THF$. In addition a third

species is present, having integrated intensities 3:3:1:1--

$U(BH_3CH_3)_4 \cdot THF$. There is no evidence (down to $-96^\circ C$) for nonequivalent methyltrihydroborate sites, and so $U(BH_3CH_3)_4 \cdot THF$ is probably monomeric in solution. K_{eq} (by integration) for the equilibrium,

is ~ 20 at $-80^\circ C$. This indicates that the Th dimers isolated in the solid state are likely to have a more complex solution state.

Upon mixing equimolar amounts of $U(BH_3CH_3)_4$ and $Th(BH_3CH_3)_4$ in toluene- d_6 and recording the 1H variable temperature NMR spectra, well resolved peaks are seen at low temperatures for both the Th and U compounds. As the solution temperature is raised, the BH_3 peaks broaden and the CH_3 peaks coalesce, becoming one time averaged signal. The observed rate is dependent on concentration. If under identical conditions Zr is substituted for Th (decreasing the ionic radius by $0.15 \text{ \AA}$), no exchange is observed up to $80^\circ C$. Zr is too small to accomodate bridging methyltrihydroborates. The resultant chemical shifts of the Th/U exchange process is the weighted average of the individual species (within experimental error). These observations are consistent with an associative BH_3CH_3 exchange process, and show that rapid methyltrihydroborate site exchange via a transient dimeric species is a possible explanation for the lack of nonequivalent sites observed in the NMR spectra of the diamagnetic thorium dimers.

There is also no evidence for a bridging structure in the solid state IR spectrum as reported by Holah et al. for

$Co_2(BH_4)_2(Ph_2P(CH_2)_5PPh_2)_2 \cdot 1/2 C_6H_6$.⁵ The IR spectra are consistent

only with tridentate ligation of the methyltrihydroborate group to the metal. IR peaks are observed at $\sim 2100\text{ cm}^{-1}$ (tridentate B-H₃ stretch) and $\sim 1250\text{ cm}^{-1}$ (tridentate bridge deformation).

The other two bis-THF adducts, $\text{U}(\text{BH}_3\text{CH}_3)_4 \cdot 2\text{THF}$ and $\text{Th}(\text{BH}_3\text{CH}_3)_4 \cdot 2\text{THF}$ can achieve a coordination number of 14 if all four methyltrihydroborates are tridentate. An X-ray crystal structure determination of $\text{U}(\text{BH}_3\text{CH}_3)_4 \cdot 2\text{THF}$ confirms this (see Fig. 5). Its structure is similar to that of $\text{U}(\text{BH}_4)_4 \cdot 2\text{THF}$.^{1b} $\text{U}(\text{BH}_3\text{CH}_3)_4 \cdot 2\text{THF}$ crystallizes in the space group C2cb with $Z = 8$. It is orthorhombic with unit cell parameters $a = 10.116(4)\text{ \AA}$, $b = 16.072(4)\text{ \AA}$, $c = 12.911(3)\text{ \AA}$. The four BH_3CH_3 groups and 2 THF groups form a distorted octahedron about the uranium. The THF groups are trans to each other. The U-B-C angles are close to 180° , indicative of tridentate ligation to the metal. The average U-B bond length ($2.57 \pm 0.02\text{ \AA}$) compares favorably with the tridentate U-B distance found for $\text{U}(\text{BH}_4)_4 \cdot 2\text{THF}$ ($2.56(4)\text{ \AA}$). It is larger than that found for $\text{U}(\text{BH}_3\text{CH}_3)_4$ ($2.48 \pm 0.03\text{ \AA}$),^a presumably due to its larger coordination number (14 vs. 12). The U-O bond distance ($2.485(6)\text{ \AA}$) is also close to that of $\text{U}(\text{BH}_4)_4 \cdot 2\text{THF}$ ($2.47(1)\text{ \AA}$).^{1b} Selected bond distances and angles are given in Tables I and II, respectively.

Because of the fact that $\text{U}(\text{BH}_3\text{CH}_3)_4$ and $\text{Th}(\text{BH}_3\text{CH}_3)_4$ appear to act as good Lewis acids, reactions with other Lewis bases were attempted. Bis-adducts of $\text{U}(\text{BH}_3\text{CH}_3)_4$ and $\text{Th}(\text{BH}_3\text{CH}_3)_4$ have been prepared with pyridine and NH_3 . However, $\text{Th}(\text{BH}_3\text{CH}_3)_4$ forms both a bis- and mono-adduct with THT (tetrahydrothiophene). Attempted preparation of mono-adducts of pyridine and NH_3 (by adding one equivalent of pyridine or NH_3) only resulted in isolation of the bis-adduct from toluene. If the

toluene solution was pumped dry and sublimed, only $An(BH_3CH_3)_4$ ($An = U, Th$) and the corresponding bis-adduct were obtained. These results suggest that an equilibrium like that found for $U(BH_3CH_3)_4 \cdot 2THF$ (see p. 45) is taking place with $K_{eq} \ll 1$. The less soluble bis-adduct crystallizes out of solution ($U(BH_3CH_3)_4$ and $Th(BH_3CH_3)_4$ are very soluble in toluene), shifting the equilibrium to the left (towards $An(BH_3CH_3)_4$ ($An = U, Th$) and the bis-adduct), which results in more of the bis-adduct crystallizing out. $U(BH_3CH_3)_4$ forms only a mono-adduct with THT while $Th(BH_3CH_3)_4$ forms only a mono-adduct with OMe_2 and SMe_2 . $U(BH_3CH_3)_4$ does not form a stable adduct with these last two bases. Judging by their IR spectra, all bis-adducts are probably 14-coordinate monomeric species like $U(BH_3CH_3)_4 \cdot 2THF$ since all of the methyltrihydroborate groups appear to be tridentate.

To determine the effect of steric factors on the stability of Th and U methyltrihydroborate adducts, the cone-packing model for steric crowding about uranium and thorium as recently developed by Bagnall and Li has been utilized.⁶ It is first necessary to define two types of steric crowding--first- and second-order steric crowding. The former refers to the crowding caused by the atoms or groups of atoms directly coordinated to the metal. The latter refers to crowding caused by the remaining atoms of the coordinating groups, which are not themselves directly bonded to the metal. The cone-packing model utilized by Bagnall and Li offers a quantitative measure of first-order crowding only. They define the cone angle factor (caf) as the solid angle of the cone comprising the metal center at the apex and the primary coordinating atom divided by 4π . They also define a fan angle. For monodentate ligands, the fan angle, $\theta = \sin^{-1}(R_0/b)$ (see Fig. 6) and

the cone angle factor = $1/4\pi \int_0^\theta \int_0^{2\pi} \sin\theta \cdot d\theta d\phi = 1/2 (1 - \cos\theta)$. R_O is 1.40 Å for oxygen, 1.5 Å for nitrogen, 1.85 Å for sulfur, and 1.9 Å for phosphorous.⁷ For the tridentate tetrahydroborate and methyltrihydroborate ligands, the fan angle, $\theta = \tan^{-1}(R_O/b)$ (see Fig. 7) and the caf is defined as before. $R_O = R_H + l$, where $R_H = 1.2 \text{ Å}$ ⁷ and l is defined as in Fig. 7. For bidentate methyltrihydroborate or tetrahydroborate groups, the two coordinating protons are treated as two monodentate ligands. To account for the overlap of the two coordinating protons, 0.006 is subtracted from their combined caf's.⁸ $\sum \text{caf}$ is defined as the sum of the caf's of all of the primary coordinating atoms or groups of atoms about the metal. Bagnall and Li calculated $\sum \text{caf}$'s for 17 U(IV) complexes. An average $\sum \text{caf}$ of 0.80 ± 0.03 was found. Thus the region of stability is defined as being from 0.74 to 0.86. The fact that about 95% of these complexes falls between 0.74 and 0.86 is a clear indication that steric crowding is an essential factor in actinide coordination chemistry.⁶

To extend this model to the U(IV) and Th(IV) methyltrihydroborate complexes, caf calculations were made on them. The results are tabulated in Table IV. Asterisked complexes are based on estimates from known bond distances found in similar compounds. All of the $\sum \text{caf}$'s fall between 0.74 and 0.86. Thus Bagnall and Li's steric model appears to work very well for the U(IV) and Th(IV) methyltrihydroborate complexes. However the model works less well in predicting the instability of certain complexes. As seen in Table V, the hypothetical complexes listed have $\sum \text{caf}$'s that lie within the region of stability, with the exception of the hypothetical bis-adduct, $U(BH_3CH_3)_2 \cdot 2THT$, which has a high $\sum \text{caf}$ of 0.868. Either these complexes are unstable

due to second-order crowding (for instance, the diethyl ether adduct of $U(BH_3CH_3)_4$) or non-steric reasons are responsible for their instability. Further studies are needed to resolve this question. The instability of the hypothetical symmetric dimer $[Th(BH_3CH_3)_4 \cdot OEt_2]_2$ may be attributed to second order crowding between diethyl ether groups.

Caf calculations are more useful in explaining why the hemi-etherate of $Th(BH_3CH_3)_4$ and $[Th(BH_3CH_3)_4 \cdot THF]_2$ are dimers and not monomers. Hypothesizing a monomeric 13-coordinate structure in which the metal is coordinated to four tridentate methyltrihydroborates and the oxygen atom of ether or THF, the calculated Δ_{caf} value is low (see Table VI)--the monomeric complex is unstable due to undercrowding. Caf calculations of other mono-adducts of $U(BH_3CH_3)_4$ and $Th(BH_3CH_3)_4$ indicate that they are more stable as dimers (see Table IV) than as 13-coordinate monomers (see Table VI).

Of all the mono-adducts, only the mono-THT adduct of $U(BH_3CH_3)_4$ shows some unusual dynamic behavior by 1H NMR. In the 1H NMR, we see one BH_3CH_3 site, which coalesces and then splits into two different BH_3CH_3 sites of equal population at $-90^\circ C$ (see Table VII). Because this is inconsistent with the dimeric structure of $[Th(BH_3CH_3)_4 \cdot THF]_2$, where we would expect a 1:1:2 ratio for the different BH_3CH_3 sites, the X-ray crystal structure of the mono-THT adduct of $U(BH_3CH_3)_4$ was determined.

The crystal structure confirmed that $[U(BH_3CH_3)_4 \cdot THT]_2$ is dimeric with a different structure than $[Th(BH_3CH_3)_4 \cdot THF]_2$. It crystallizes in the space group $P2_1/c$ with $Z = 8$. It is monoclinic with unit cell parameters $a = 12.054(2)$ Å, $b = 16.332(3)$ Å, $c = 18.545(3)$ Å, $\beta = 108.82(2)^\circ$. The two U atoms are bridged by THT groups, not BH_3CH_3 ,

groups (see Figure 8). The plane of the two bridging THT groups is perpendicular to the plane containing the U(1), U(2), S(1), S(2) atoms. All of the BH₃CH₃ groups are tridentate. The average U-B distance is 2.54 ± 0.04 Å, which compares favorably with the average U-B_{tridentate} bond length of 2.57 ± 0.04 Å found in U(BH₃CH₃)₄·2THF. The two average U-S bond lengths are 3.14 ± 0.03 and 3.26 ± 0.03 Å. Selected bond distances and angles are presented in Tables I and II, respectively. There are two different BH₃CH₃ sites of equal population, those that are pointed towards the THT groups and those that are pointed away. This explains why two different BH₃CH₃ sites of equal population are found in the ¹H NMR spectra. The mono-THT adduct of U(BH₃CH₃)₄ is probably not a monomer in solution like U(BH₃CH₃)₄·THF since nonequivalent BH₃CH₃ sites were not observed in the NMR spectrum for the latter. It may be asked why [U(BH₃CH₃)₄·THT]₂ adopts this unusual dimeric structure. Steric factors do not seem to play a role here since the {caf's for the actual and hypothetical (U atoms bridged by BH₃CH₃ groups) structures are nearly identical (see Tables IV and VI). Bridging by THT groups may occur so that a lone pair is donated to each metal without bringing the metal atoms too close to each other as would be the case with THF with its smaller sp³ orbitals. To see whether [Th(BH₃CH₃)₄·THT]₂ has a similar bridging structure as [U(BH₃CH₃)₄·THT]₂, [Th(BH₃CH₃)₄·THT]₂ was analyzed by CI (chemical ionization) mass spectrometry. Its mass spectrum (see Table VIII) suggests it has a bridging structure like [Th(BH₃CH₃)₄·OEt]₂ since it has a major peak at m/e = 666 (Th₂(BH₃CH₃)₈)⁺, a peak which is found in the mass spectrum of [Th(BH₃CH₃)₄·OEt]₂ (Table IX). The corresponding peak (U₂(BH₃CH₃)₈)⁺, m/e = 678 is clearly absent in the mass spectrum

of $[\text{U}(\text{BH}_3\text{CH}_3)_4\text{THT}]_2$ (Table X). We cannot conclusively say that the bridging structure of $[\text{Th}(\text{BH}_3\text{CH}_3)_4\text{THT}]_2$ is different from $[\text{U}(\text{BH}_3\text{CH}_3)_4\text{THT}]_2$, since the fragmentation pattern of a uranium species may be different from its thorium analogue due to U(IV)'s ability to reduce to U(III) easily. However if we assume that $[\text{Th}(\text{BH}_3\text{CH}_3)_4\text{THT}]_2$ is not bridged by THT groups, it may be because Th(IV) has a slightly larger ionic radius than U(IV). The Th atoms may be brought in too close to each other by the bridging THT groups. The other mono-adducts, $\text{Th}(\text{BH}_3\text{CH}_3)_4\text{OME}_2$ and $\text{Th}(\text{BH}_3\text{CH}_3)_4\text{SMe}_2$ also were analyzed by CI mass spectrometry (Tables XI and XII). Fragmentation patterns also suggest that these adducts have a bridging structure like $[\text{Th}(\text{BH}_3\text{CH}_3)_4]_2\text{OEt}_2$ since a major peak at $m/e = 666$ is found in both spectra.

In addition to the above monodentate base adducts, bidentate base adducts of $\text{U}(\text{BH}_3\text{CH}_3)_4$ and $\text{Th}(\text{BH}_3\text{CH}_3)_4$ were prepared with dme (1,2-dimethoxyethane), tmed (N,N,N',N'-tetramethylethylenediamine), dmpe (1,2-dimethylphosphinoethane), and bmte (bis(1,2-methylthio)ethane). Studies by ^1H NMR spectroscopy of these four $\text{U}(\text{BH}_3\text{CH}_3)_4$ complexes indicate some interesting dynamic behavior is taking place. To elucidate and confirm their interpretation, crystal structure determinations were made on all four complexes.

The four complexes of $\text{U}(\text{BH}_3\text{CH}_3)_4$ are all monomers (see Figs. 9 through 12). $\text{U}(\text{BH}_3\text{CH}_3)_4\text{dme}$ crystallizes in the space group $P4/n$ with $Z = 8$. It is tetragonal with unit cell parameters $a = 21.822(8) \text{ \AA}$, $c = 7.681(5) \text{ \AA}$. $\text{U}(\text{BH}_3\text{CH}_3)_4\text{tmed}$ crystallizes in the space group $P2_1/n$ with $Z = 4$. It is monoclinic with unit cell parameters $a = 10.206(4) \text{ \AA}$, $b = 15.436(6) \text{ \AA}$, $c = 12.880(5) \text{ \AA}$, $\beta = 92.25(3)^\circ$. $\text{U}(\text{BH}_3\text{CH}_3)_4\text{dmpe}$

crystallizes in the space group $P2_1/c$ with $Z = 4$. It is monoclinic with unit cell parameters $a = 9.439(3)$ Å, $b = 14.023(4)$ Å, $c = 16.596(2)$ Å, $\beta = 97.48(4)^\circ$. $U(BH_3CH_3)_4 \cdot bmtc$ crystallizes in the space group $P\bar{1}$ with $Z = 2$. It is triclinic with unit cell parameters $a = 8.937(4)$ Å, $b = 13.692(4)$ Å, $c = 8.186(3)$ Å, $\alpha = 96.46(4)^\circ$, $\beta = 97.64(4)^\circ$, $\gamma = 74.07(4)^\circ$. $U(BH_3CH_3)_4 \cdot dme$, $U(BH_3CH_3)_4 \cdot dmpe$, and $U(BH_3CH_3)_4 \cdot bmtc$ show formal 14-coordination. The U atom is surrounded by a distorted octahedron, whose vertices are occupied by 4 tridentate methyltrihydroborate groups and the 2 coordinating atoms of the bidentate base. The average U-B distance for $U(BH_3CH_3)_4 \cdot dme$, $U(BH_3CH_3)_4 \cdot dmpe$, and $U(BH_3CH_3)_4 \cdot bmtc$ is 2.56 ± 0.02 Å. This is similar to the average tridentate U-B distance found in $U(BH_3CH_3)_4 \cdot 2THF$ (2.57 ± 0.02 Å). All U-B-C angles are close to 180° , as expected for tridentate ligation.

$U(BH_3CH_3)_4 \cdot tmed$ is anomalous in that one of the methyltrihydroborates is coordinated through bidentate ligation, making it formally 13-coordinate. Bidentate coordination, though common for the tetrahydroborates, has until now not been observed for the methyltrihydroborates. Three of the U-B-C angles of $U(BH_3CH_3)_4 \cdot tmed$ are close to 180° , with an average U-B distances of 2.54 ± 0.02 Å, consistent with tridentate coordination. However, for the bidentate BH_3CH_3 group, the U-B-C angle is $142(2)^\circ$ with a U-B distance of $2.72(2)$ Å. This value may be compared to bidentate U-B distances found in $U(BH_4)_4$ (2.86 ± 0.03 Å),² $U(BH_4)_4 \cdot OEt_2$ ($2.89(1)$ Å),^{1a} and $U(BH_4)_4 \cdot OMe_2$ ($2.89(2)$ Å).^{1a} The U-B-H_{terminal} angle is 102° . Selected bond distances and angles are presented in Tables I and II, respectively. As expected, the sterically demanding methyl group is at

a greater angle away from the metal than the terminal hydrogen. The reason for this unusual bonding cannot be attributed to first order steric crowding, since hypothetical complete tridentate coordination would give a $\sum \text{caf}$ of 0.810 (Table VI), which is much smaller than that of $\text{U}(\text{BH}_3\text{CH}_3)_4 \cdot \text{dmpe}$, which has no bidentate methyltrihydroborates. The anomalous bonding observed for one of the BH_3CH_3 groups in $\text{U}(\text{BH}_3\text{CH}_3)_4 \cdot \text{tmed}$ may be attributed to second order crowding or to crystal packing forces. There are an unusually large number of bands in the 2000 to 2400 cm^{-1} region of the IR spectrum (see Chap. 5), indicative of this bidentate bridging mode.

The crystal structure of $\text{Th}(\text{BH}_3\text{CH}_3)_4 \cdot \text{tmed}$ should be determined in order to see whether any of the methyltrihydroborates are bidentate. If steric factors are of importance here, it is expected that all of the methyltrihydroborate groups would be tridentate because of the ionic radius of Th(IV) is larger than that of U(IV). The IR spectrum suggests complete tridentate BH_3CH_3 coordination since bands in the 2000 to 2200 cm^{-1} region are similar to that of methyltrihydroborate complexes containing only tridentate BH_3CH_3 groups.

For $\text{U}(\text{BH}_3\text{CH}_3)_4 \cdot \text{dme}$ the average U(IV)-O bond length (2.58(1) Å) is in range with other U(IV)-O bond lengths found in O-coordinated base adducts of $\text{U}(\text{BH}_3)_4$ and $\text{U}(\text{BH}_3\text{CH}_3)_4$ (2.44(1) Å for $\text{U}(\text{BH}_3)_4 \cdot \text{OME}_2$, ^{1a} 2.485(5) Å for $\text{U}(\text{BH}_3)_4 \cdot \text{OEt}_2$, ^{1a} 2.48(4) Å for $\text{U}(\text{BH}_3)_4 \cdot \text{O}(\text{n-Pr})_2$, ^{1c} 2.47(1) Å for $\text{U}(\text{BH}_3)_4 \cdot 2\text{THF}$, ^{1b} and 2.485(6) Å for $\text{U}(\text{BH}_3\text{CH}_3)_4 \cdot 2\text{THF}$). The average U(IV)-N bond length of 2.73(1) Å is in line with other U(IV)-N(neutral) bond lengths (2.68(2) Å for $\text{U}\{\text{n-C}_5\text{H}_4\}_2\text{CH}_2\}\text{Cl}_2 \cdot \text{bipy}$, ¹⁰ and $\text{UCp}_3\text{NCS.NCMe}$, ¹¹) The average U(IV)-P bond length of 3.02 ± 0.01 Å for $\text{U}(\text{BH}_3\text{CH}_3)_4 \cdot \text{dmpe}$ is also in line with previous U(IV)-P bond lengths

$(3.104 \pm 0.006 \text{ \AA for } \text{U}(\text{OPh})_2\text{dmpe})$.¹² The average U(IV)-S bond length for $\text{U}(\text{BH}_3\text{CH}_3)_2\text{bmte}$ is $3.07(1) \text{ \AA}$. This may be compared to the U(III)-S bond distance of $2.99(1) \text{ \AA}$ found for $(\text{MeC}_5\text{H}_4)_2\text{U.THT}$.¹³ Thus there appears to be no unusual bonding interactions for all four bidentate adducts of $\text{U}(\text{BH}_3\text{CH}_3)_2$.

There also appear to be no significant angular distortions due to the presence of the bidentate base ligand. According to Kepert's points-on-a-sphere repulsion energy calculations for 6-coordinate complexes of the type $\text{M}(\text{unidentate})_4(\text{bidentate})$, it is expected that the greater the normalized bite (normalized bite is defined as the distance between donor atoms in the chelate group divided by the metal-donor atom distance) of the bidentate ligand, the closer the cis unidentate ligands approach the bidentate ligand while the trans ligands move away from it.¹⁴ Treating the methyltrihydroborates as unidentate ligands, this is what is found for $\text{U}(\text{BH}_3\text{CH}_3)_2\text{dme}$ (n. b. (normalized bite) = 1.056), $\text{U}(\text{BH}_3\text{CH}_3)_2\text{dmpe}$ (n. b. = 1.109), and $\text{U}(\text{BH}_3\text{CH}_3)_2\text{bmte}$ (n. b. = 1.142), although angular distortions are very slight. As defined in Fig. 13, ϕ_C for $\text{U}(\text{BH}_3\text{CH}_3)_2\text{dme}$, $\text{U}(\text{BH}_3\text{CH}_3)_2\text{dmpe}$, and $\text{U}(\text{BH}_3\text{CH}_3)_2\text{bmte}$ is 83° , 82° , and 81° , respectively. The angle ϕ_E for these same three compounds is 127° , 128° , and 126° , respectively, the last value being anomalous but not significant. However, $\text{U}(\text{BH}_3\text{CH}_3)_2\text{tmed}$ (n. b. = 1.116) has significantly anomalous ϕ_C and ϕ_E values due to the presence of the bidentate methyltrihydroborate. The ϕ_C and ϕ_E angles are 90° and 124° , respectively.

Because of the similarities in both steric and electronic properties of the four bidentate bases used to prepare the $\text{U}(\text{BH}_3\text{CH}_3)_2$ base adducts, ligand exchange studies were performed by ¹NMR

spectroscopy. Toluene- d_6 solutions of one of the bidentate base adducts were equilibrated with one or two equivalents of another bidentate base. Although no K_{eq} values were obtained because of either rapid and complete exchange of one base for another or no exchange at all, a qualitative order of affinity to the metal was determined. The order found was $dmpe > tmed > bmte \sim dme$. This order is surprising in light of the fact that the hard oxygen-coordinated base, dme , would be expected to have a greater affinity for the hard U(IV) ion than the softer phosphorous-coordinated base, $dmpe$. Recent ligand exchange studies of $(MeC_5H_4)_3U.L$ ($L = THF, py, quinuclidine, PMe_3$) and $(MeC_5H_4)_3M.L$ ($M = Ce, Nd; L = PMe_3, py$) gave similar results--the softer PMe_3 had a greater affinity for the metal than the nitrogen- and oxygen-coordinated bases.¹⁵

Octahedral d transition metal systems with the general formula $M(unidentate)_4(bidentate)$ are rare.¹⁴ Very little is known about the dynamics of these systems, although a brief study on the dynamics of $CH_3TiCl_3.L-L$ ($L-L = bidentate$ base) complexes was done recently.¹⁶ Thus study of the dynamics of the pseudo-octahedral $U(BH_3CH_3)_4.L-L$ systems by 1H NMR was desired. 1H NMR data are summarized in Tables XIII through XVI. In general, at low temperatures, two distinguishable methyl and two distinguishable trihydroborate proton peaks are observed. On increasing the temperature, coalescence occurs, indicating exchange of nonequivalent sites. On further warming, only one averaged methyl and one averaged trihydroborate peak is observed. For $U(BH_3CH_3)_4.dme$, coalescence of methyl peaks occurs at $-40^\circ C$; for $U(BH_3CH_3)_4.bmte$, $-20^\circ C$; for $U(BH_3CH_3)_4.tmed$, $-25^\circ C$; and for $U(BH_3CH_3)_4.dmpe$, $-10^\circ C$. The chemical shift difference between cis and

trans CH₃ protons is -126 ppm at -78°C, for U(BH₃CH₃)₄.dme, -104 ppm at -59°C for U(BH₃CH₃)₄.tmed, -150 ppm at -78°C for U(BH₃CH₃)₄.bmte, and -76 ppm at -66°C for U(BH₃CH₃)₄.dmpe. Approximate rate constants for two site exchange were obtained using the formula, $k = \pi \Delta_{rs} / \sqrt{2}$, where Δ_{rs} is the chemical shift difference between the two sites at coalescence.¹⁷ Substituting these values into the Eyring equation, $k = (k_B T/h) \exp(-\Delta G/RT)$,¹⁷ the following values for ΔG , the free energy of activation of exchange are obtained. For U(BH₃CH₃)₄.dme, ΔG is 9 kcal/mol; For U(BH₃CH₃)₄.tmed, 12 kcal/mol; for U(BH₃CH₃)₄.bmte, 9 kcal/mol; and for U(BH₃CH₃)₄.dmpe, 10 kcal/mol. Thus the order of lability is dme ~ bmte > dmpe > tmed.

There are at least two possible mechanisms for exchange of BH₃CH₃ sites, analogous to the mechanisms proposed for the exchange process of CH₃TiCl₃ adducts in solution.^{16b} The first is that one of the coordinating atoms of the bidentate ligand dissociates and then reattaches itself to the metal in a different sense such that BH₃CH₃ sites are exchanged. The second possibility is a twist mechanism; e. g., a Bailar twist,¹⁸ which scrambles cis and trans positions. Figure 14 illustrates this twist mechanism.

For the dissociation mechanism, we would expect the complexes with the weakest M-L bond strengths to be the most labile. As we mentioned earlier, based on ligand exchange studies, the order of bond strengths is bmte ~ dme < tmed < dmpe. Thus we would expect the order of lability to be bmte ~ dme > tmed > dmpe. This generally agrees with the actual order of lability with one exception, dmpe is more labile than tmed.

The twist mechanism again is controlled by steric crowding. However in this case, secondary crowding from the methyl groups on the coordinating bidentate ligand is more important, with a larger M-L distance reducing steric crowding. In this case, we would expect the order of lability to be $\text{bnte} \geq \text{dme} > \text{dmpe} \geq \text{tmed}$. This matches more closely the actual order $\text{dme} - \text{bnte} > \text{dmpe} > \text{tmed}$ than the dissociation mechanism. Thus it appears that the twist mechanism is more compatible with the data. However, the ΔG values we have measured are only approximations and more detailed NMR studies are needed to determine a more accurate ΔG of exchange value.

During the course of running VT ¹H NMR's of $U(BH_3CH_3)_4$, N- or P-coordinated adducts, it was noted that solutions turned brown at elevated temperatures ($>70^\circ C$). The brown color suggested reduction of U(IV) to U(III). Reduction of U(IV) to U(III) is known to occur when $U(BH_3)_4$ is heated in toluene. Marquet-Ellis et al. have prepared $U(BH_3)_4$ crown etherates by this method.¹⁹ Therefore preparative scale reactions of several $U(BH_3CH_3)_4$ adducts with excess base in toluene at elevated temperatures were run. Of all the reactions attempted, only reaction of excess dmpe with $U(BH_3CH_3)_4$.dmpe at $80^\circ C$ in toluene resulted in successful isolation of a characterizable compound. A possible reaction scheme is given below:

During the course of running VT ¹H NMR's of $U(BH_3CH_3)_4$, N- or P-coordinated adducts, it was noted that solutions turned brown at elevated temperatures ($>70^\circ C$). The brown color suggested reduction of U(IV) to U(III). Reduction of U(IV) to U(III) is known to occur when $U(BH_3)_4$ is heated in toluene. Marquet-Ellis et al. have prepared $U(BH_3)_4$ crown etherates by this method.¹⁹ Therefore preparative scale reactions of several $U(BH_3CH_3)_4$ adducts with excess base in toluene at elevated temperatures were run. Of all the reactions attempted, only reaction of excess dmpe with $U(BH_3CH_3)_4$.dmpe at $80^\circ C$ in toluene resulted in successful isolation of a characterizable compound. A possible reaction scheme is given below:

$U(BH_3CH_3)_2dmpe$ can also be prepared by a method similar to that used by Moody et al. to prepare $U(BH_3)_2dmpe$,²⁰ substituting $LiBH_3CH_3$ for $LiBH_4$. To compare its structure with that of $U(BH_3)_2dmpe$, a crystal structure determination of $U(BH_3CH_3)_2dmpe$ was made.^{9b}

The compound crystallizes in the space group $P4_212$ with $Z = 4$. It is tetragonal with unit cell parameters $a = 11.297(4)$ Å, $c = 23.03(2)$ Å. The U(III) atom is at the center of a distorted pentagonal bipyramid of B and P atoms (see Fig. 15). The equatorial plane consists of 2P(1), 2P(2), B(1), and U. The B(2) atoms are 2.58 Å above and below the pentagonal plane. The borons are bridged to the uranium atoms through tridentate ligation, thus making the uranium atom 13-coordinate. Unlike $U(BH_3)_2dmpe$, the equatorial BH_3CH_3 group is tridentate, not bidentate. The U-P(2) distance of 3.085(3) Å is 0.09 Å shorter than the U-P(1) distance of 3.134(3) Å. This difference can be explained as a steric effect by comparing ligand-ligand contact distances. At the P(2) site, the two methyl carbons C(7) and C(8) are more than 4 Å away from B(1), B(2), and C(1). At the P(1) site, methyl carbons C(3) and C(4) are at a distance of 3.80 Å. Given a van der Waals radius for the methyl group of 2.0 Å, it seems reasonable that methyl-methyl repulsive forces are the reason for the larger U-P(1) bond distance. The average U(III)-B distance is 2.64 Å and is similar to the U(III)-B_{tridentate} distance of 2.68(4) Å found in $U(BH_3)_2dmpe$. Unlike $U(BH_3CH_3)_2dmpe$, $U(BH_3CH_3)_2dmpe$ is fluxional on the NMR time scale (see Table XVII), and no nonequivalent sites could be observed for either the methyltrihydroborate or phosphine ligands down to $-95^\circ C$. If $U(BH_3CH_3)_2dmpe$ and $U(BH_3CH_3)_2dmpe$ are considered to be pseudo-six and seven-coordinate, respectively, then this behavior parallels that

of the d block metals since seven-coordinate complexes are fluxional on the NMR time scale while octahedral d transition metal complexes are rigid on the NMR time scale.²¹

When excess dmpe is added to a toluene solution of $\text{Th}(\text{BH}_2\text{CH}_3)_4$ and heated to -80°C , no reduction occurs. This suggested that the following reaction occurred:

Although $(\text{BH}_2\text{CH}_3)_2\text{dmpe}$ was isolated, the $\text{Th}(\text{IV})$ hydride species could not be isolated. A colorless compound containing BH_2CH_3 and dmpe groups was obtained. However no evidence for a Th-H stretch could be found in the IR spectrum.

In addition to the dmpe methylboranes described above, methylboranes were obtained as side products in other reactions with $\text{U}(\text{IV})$ and $\text{Th}(\text{IV})$ methyltrihydroborates. When excess tmed or pyridine is added to a toluene solution of $\text{An}(\text{BH}_2\text{CH}_3)_4$, $\text{An} = \text{U}, \text{Th}$, the formation of tmed methylborane or pyridine methylborane is observed, respectively. This is similar to what happens when an excess amount of N- or P-coordinated base is added to $\text{Al}(\text{BH}_2)_3$, where boranes and aluminum hydride derivatives are obtained.²²

Because of the ~~interesting variety of structures~~ found for Lewis base adducts of $\text{U}(\text{BH}_2\text{CH}_3)_4$ and $\text{Th}(\text{BH}_2\text{CH}_3)_4$, it was desirable to investigate how ligands substituted for methyltrihydroborates would affect the coordination of the remaining methyltrihydroborates. We

used the following route to prepare the bis-Cp (cyclopentadienyl) substituted $U(BH_3CH_3)_4$:

The IR spectrum shows a B-H_b stretch at 2080 cm^{-1} and 2150 cm^{-1} and bridge deformation at 1235 cm^{-1} , indicative of tridentate ligation. Its structure is probably similar to $UCp_2(BH_3)_2$ ²³ with an approximately tetrahedral configuration of two η^5 -Cp groups and two tridentate methyltrihydroborate groups. Its $\sum\text{caf}$ value based on this hypothetical structure lies within the area of stability (Table XVIII).

Physical Properties

Like the base-free methyltrihydroborates, the adducts are volatile solids with the exception of the dmpe adducts, although the volatility varies from adduct to adduct. $[Th(BH_3CH_3)_4]_2 \cdot OEt_2$, $U(BH_3CH_3)_4 \cdot 2NH_3$, and $U(BH_3CH_3)_4 \cdot 2THF$ are easily sublimed at room temperature and are the most volatile adducts. The other adducts must be heated to temperatures ranging up to 125°C . Because these adducts remain intact at such high temperatures, the Lewis base must be tightly bound to the metal. They are readily soluble in non-coordinating aromatic hydrocarbons. However with the exception of $[Th(BH_3CH_3)_4]_2 \cdot OEt_2$ and $U(BH_3CH_3)_4 \cdot 2dmpe$, they are insoluble or only sparingly soluble in aliphatic hydrocarbons.

Despite these covalent-like physical properties, the adducts of $U(BH_3CH_3)_4$ and $Th(BH_3CH_3)_4$ are probably primarily ionic in character

according to Raymond and Pauling's structural definition of ionic bonding.²⁴ Bond lengths can be reasonably predicted by adding ionic radii and the interactions between ligand and metal are controlled primarily by steric factors since these adducts in general obey the cone-packing model for steric crowding. That is, the steric bulk and number of these ligands are primarily responsible for the geometry and coordination number about the metal. In addition the observed associative BH_3CH_3 exchange process and the lability of these complexes are characteristic of ionic systems.

Comparison with Base Adducts of $\text{U}(\text{BH}_3)_4$ and $\text{Th}(\text{BH}_3)_4$

The preparation of several base adducts of $\text{U}(\text{BH}_3)_4$ -- $\text{U}(\text{BH}_3)_4\cdot\text{OME}_2$, $\text{U}(\text{BH}_3)_4\cdot\text{OEt}_2$, $\text{U}(\text{BH}_3)_4\cdot\text{O}(\text{n-Pr})_2$, and $\text{U}(\text{BH}_3)_4\cdot 2\text{THF}$ has been mentioned.¹ A few Lewis base adducts of $\text{Th}(\text{BH}_3)_4$ have also been recently prepared-- $\text{Th}(\text{BH}_3)_4\cdot 2\text{THF}$, $\text{Th}(\text{BH}_3)_4\cdot\text{dme}$, and $\text{Th}(\text{BH}_3)_4\cdot 2\text{NH}_3$. The preparation of the N-coordinated base adduct, $\text{Th}(\text{BH}_3)_4\cdot 2\text{NH}_3$, was at first unexpected because previous attempts to prepare $\text{U}(\text{BH}_3)_4\cdot\text{npy}$ and $\text{U}(\text{BH}_3)_4\cdot\text{nNMe}_3$ were unsuccessful and resulted in the formation of black solids (probably some uranium (III) derivative) and the corresponding borane, $\text{BH}_3\cdot\text{L}$ ($\text{L} = \text{py}$, NMe_3).²⁵ However, these reactions were run in neat solutions of the base while that with $\text{Th}(\text{BH}_3)_4$ was run in hexane with a slight excess of NH_3 . Thus $\text{U}(\text{BH}_3)_4$ in the presence of excess N-coordinated base reacts like $\text{Al}(\text{BH}_3)_3$ and $\text{An}(\text{BH}_3\text{CH}_3)_3$, $\text{An} = \text{U}$, Th . The preparation of N-, P-, and S-coordinated base adducts of $\text{U}(\text{BH}_3)_4$ are in progress.^{26, 26}

As described earlier, X-ray crystal structure determinations of the $\text{U}(\text{BH}_3)_4$ etherates were made. However, no X-ray crystal structure determinations were done on the $\text{Th}(\text{BH}_3)_4$ adducts prepared. From the IR

spectrum, it appears that all of the tetrahydroborate groups are tridentate. Peaks characteristic of tridentate coordination were found at -2500 cm^{-1} ($\text{B-H}_{\text{terminal}}$ stretch), -2200 cm^{-1} ($\text{B-H}_{\text{bridging}}$ stretch), and -1200 cm^{-1} (bridge deformation). Thus it appears that $\text{Th}(\text{BH}_3)_4 \cdot 2\text{THF}$ and $\text{Th}(\text{BH}_3)_4 \cdot 2\text{NH}_3$ have a pseudo-octahedral geometry similar to that of $\text{U}(\text{BH}_3)_4 \cdot 2\text{THF}$ ^{1b} while $\text{Th}(\text{BH}_3)_4 \cdot \text{dme}$ probably has a structure similar to $\text{U}(\text{BH}_3\text{CH}_3)_4 \cdot \text{L}$ ($\text{L} = \text{dme}, \text{bmte}, \text{dmpe}$).⁹

The physical properties of the $\text{U}(\text{BH}_3)_4$ and $\text{Th}(\text{BH}_3)_4$ base adducts are similar to those of $\text{U}(\text{BH}_3\text{CH}_3)_4$ and $\text{Th}(\text{BH}_3\text{CH}_3)_4$ base adducts. They are very air sensitive and display covalent-like properties; e. g., solubility in aromatic hydrocarbons and volatility. The cone-packing model for steric crowding has been applied to these $\text{U}(\text{BH}_3)_4$ and $\text{Th}(\text{BH}_3)_4$ base adducts. As seen in Table XIX, all adducts prepared have $[\text{caf}]$'s that lie between 0.74 to 0.86, the region of stability. Asterisked complexes are based on estimated bond distances. The cone-packing model may explain why $\text{U}(\text{BH}_3)_4 \cdot \text{OME}_2$ and $\text{U}(\text{BH}_3)_4 \cdot \text{OEt}_2$ are polymers and $\text{U}(\text{BH}_3)_4 \cdot \text{O}(\text{n-Pr})_2$ is a dimer. If they were 13-coordinate monomers, their $[\text{caf}]$'s would be low (0.737, see Table XX), and thus would be unstable due to undercrowding. Thus like the $\text{U}(\text{BH}_3\text{CH}_3)_4$ and $\text{Th}(\text{BH}_3\text{CH}_3)_4$ adducts, the $\text{U}(\text{BH}_3)_4$ and $\text{Th}(\text{BH}_3)_4$ adducts are primarily ionic in character since interactions between ligand and metal are primarily controlled by steric factors.

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Table I. Selected Interatomic Distances (Å)

[Th(BH ₃ CH ₃) ₄] ₂ .O(C ₂ H ₅) ₂				[Th(BH ₃ CH ₃) ₄ .OC ₄ H ₉] ₂			
Th(1)-B(2)	2.60(2)	Th(2)-B(5)	2.62(1)	Th-B(1)	2.61(1)		
-B(3)	2.47(2)	-B(6)	2.55(2)	-B(2)	2.61(1)		
-B(4)	2.57(2)	-B(7)	2.58(2)	-B(3)	2.61(3)		
-B(1)	2.92(2)	-B(8)	2.91(2)	-B(4)*	3.11(1)		
-B(8)	2.97(2)	-B(1)	3.07(2)	-B(4)	3.06(1)		
		Th(2)-O	2.59(1)	Th-O	2.534(4)		
B(1)-C(1)	1.57(2)	B(5)-C(5)	1.58(2)	B(1)-C(1)	1.60(1)		
B(2)-C(2)	1.57(2)	B(6)-C(6)	1.55(2)	B(2)-C(2)	1.59(1)		
B(3)-C(3)	1.53(2)	B(7)-C(7)	1.56(2)	B(3)-C(3)	1.57(1)		
B(4)-C(4)	1.59(2)	B(8)-C(8)	1.56(2)	B(4)-C(4)	1.59(1)		
		O-C(9)	1.46(2)	O-C(5)	1.48(1)		
		O-C(11)	1.46(2)	O-C(8)	1.46(2)		
		C(9)-C(10)	1.44(2)	C(5)-C(6)	1.48(2)		
		C(11)-C(12)	1.44(2)	C(6)-C(7)	1.50(2)		
				C(7)-C(8)	1.44(2)		
Th(1)-Th(2)	4.445(1)			Th-Th	4.917(1)		
B(1)-B(8)	3.549(6)			B(4)-B(4)*	3.73(1)		

* Atom at -x, -y, -z.

Table I. Selected Interatomic Distances (Å)

[U(BH ₃ CH ₃) ₂ .THT] ₂			
U(1)-B(3)	2.51(2)	U(2)-B(7)	2.47(2)
-B(1)	2.53(2)	-B(8)	2.51(2)
-B(4)	2.54(2)	-B(5)	2.58(2)
-B(2)	2.58(2)	-B(6)	2.60(2)
-S(1)	3.120(4)	-S(2)	3.164(4)
-S(2)	3.240(5)	-S(1)	3.276(4)
S(1)-C(12)	1.85(2)	S(2)-C(16)	1.87(2)
S(1)-C(9)	1.86(2)	S(2)-C(13)	1.88(1)
B(1)-C(1)	1.60(2)	B(5)-C(5)	1.60(3)
B(2)-C(2)	1.60(2)	B(6)-C(6)	1.58(3)
B(3)-C(3)	1.61(2)	B(7)-C(7)	1.62(3)
B(4)-C(4)	1.66(3)	B(8)-C(8)	1.61(3)
C(9)-C(10)	1.53(3)	C(13)-C(14)	1.48(3)
C(10)-C(11)	1.43(3)	C(14)-C(15)	1.39(3)
C(11)-C(12)	1.51(3)	C(15)-C(16)	1.52(3)
S(1)-S(2)	3.476(5)		

U(BH ₃ CH ₃) ₂ .2THF		U(BH ₃ CH ₃) ₂ .2dmpe	
U	-O	U-B(1)	2.66(1)
	-B(1)	U-2B(2)	2.62(1)
	-B(2)	U-2P(1)	3.174(3)
O	-C(3)	-2P(2)	3.085(3)
O	-C(6)	P(1)-C(3)	1.79(1)
B(1)-C(1)	1.61(2)	-C(4)	1.78(1)
B(2)-C(2)	1.63(2)	-C(5)	1.82(2)
C(3)-C(4)	1.51(2)	P(2)-C(6)	1.83(2)
C(4)-C(5)	1.42(2)	-C(7)	1.79(1)
C(5)-C(6)	1.55(2)	-C(8)	1.79(1)
		B(1)-C(1)	1.64(1)
		B(2)-C(2)	1.64(1)
		C(5)-C(6)	1.43(2)

Table I. Selected Interatomic Distances (Å)

U(BH ₃ CH ₃) ₄ .dme			U(BH ₃ CH ₃) ₄ .tmed		
U	-O(1)	2.60(1)	U	-N(1)	2.72(1)
U	-O(2)	2.55(1)	U	-N(2)	2.74(1)
U	-B(1)	2.57(2)	U	-B(1)	2.56(2)
U	-B(2)	2.55(2)	U	-B(2)	2.72(2)
U	-B(3)	2.58(2)	U	-B(3)	2.55(2)
U	-B(4)	2.52(2)	U	-B(4)	2.51(2)
O(1)-C(5)	1.44(2)		N(1)-C(5)	1.44(2)	
O(1)-C(6)	1.44(2)		N(1)-C(6)	1.47(3)	
			N(1)-C(7)	1.48(3)	
O(2)-C(7)	1.45(2)		N(2)-C(8)	1.44(2)	
O(2)-C(8)	1.39(2)		N(2)-C(9)	1.46(2)	
			N(2)-C(10)	1.46(2)	
B(1)-C(1)	1.61(2)		B(1)-C(1)	1.57(2)	
B(2)-C(2)	1.57(3)		B(2)-C(2)	1.54(3)	
B(3)-C(3)	1.60(3)		B(3)-C(3)	1.58(3)	
B(4)-C(4)	1.60(3)		B(4)-C(4)	1.58(3)	
C(6)-C(7)	1.40(3)		C(7)-C(8)	1.35(3)	

U(BH ₃ CH ₃) ₄ .dme			U(BH ₃ CH ₃) ₄ .bme		
U	-P(1)	3.029(2)	U	-S(1)	3.09(1)
U	-P(2)	3.017(2)	U	-S(2)	3.04(1)
U	-B(1)	2.58(1)	U	-B(1)	2.57(1)
U	-B(2)	2.56(1)	U	-B(2)	2.55(1)
U	-B(3)	2.56(1)	U	-B(3)	2.54(1)
U	-B(4)	2.58(1)	U	-B(4)	2.57(1)
P(1)-C(5)	1.84(1)		S(1)-C(5)	1.80(1)	
P(1)-C(6)	1.82(1)		S(1)-C(7)	1.80(1)	
P(1)-C(7)	1.84(1)				
P(2)-C(8)	1.83(1)		S(2)-C(6)	1.79(1)	
P(2)-C(9)	1.82(1)		S(2)-C(8)	1.80(1)	
P(2)-C(10)	1.82(1)				
B(1)-C(1)	1.60(1)		B(1)-C(1)	1.59(1)	
B(2)-C(2)	1.61(1)		B(2)-C(2)	1.59(1)	
B(3)-C(3)	1.60(1)		B(3)-C(3)	1.59(1)	
B(4)-C(4)	1.60(1)		B(4)-C(4)	1.59(1)	
C(7)-C(8)	1.50(1)		C(6)-C(7)	1.51(1)	

Table II. Selected Angles (deg)

B(1)-Th(1)-B(8)	74.0(3)	O-Th(2)-B(6)	82.2(3)
B(1)-Th(1)-B(2)	143.9(4)	O-Th(2)-B(7)	91.3(3)
B(1)-Th(1)-B(3)	106.4(4)	B(1)-Th(2)-B(5)	98.3(4)
B(1)-Th(1)-B(4)	85.8(4)	B(1)-Th(2)-B(6)	161.3(4)
B(8)-Th(1)-B(2)	83.1(4)	B(1)-Th(2)-B(7)	81.3(4)
B(8)-Th(1)-B(3)	102.1(4)	B(8)-Th(2)-B(5)	27.3(4)
B(8)-Th(1)-B(4)	150.5(4)	B(8)-Th(2)-B(6)	96.8(4)
B(2)-Th(1)-B(3)	105.5(5)	B(8)-Th(2)-B(7)	154.0(4)
B(2)-Th(1)-B(4)	102.5(5)	B(5)-Th(2)-B(6)	96.6(4)
B(3)-Th(1)-B(4)	104.2(5)	B(5)-Th(2)-B(7)	97.8(4)
Th(1)-B(1)-C(1)	132.4(8)	B(6)-Th(2)-B(7)	107.9(4)
Th(1)-B(8)-C(8)	124.7(8)	Th(2)-B(1)-C(1)	124.9(7)
Th(1)-B(2)-C(2)	178.0(1)	Th(2)-B(8)-C(8)	119.7(8)
Th(1)-B(3)-C(3)	176.0(1)	Th(2)-B(5)-C(5)	177.0(1)
Th(1)-B(4)-C(4)	177.0(1)	Th(2)-B(6)-C(6)	178.0(1)
B(1)-Th(2)-B(8)	72.7(3)	Th(2)-B(7)-C(7)	177.0(1)
O-Th(2)-B(1)	81.3(3)	Th(2)-O-C(9)	125.9(6)
O-Th(2)-B(8)	83.8(3)	Th(2)-O-C(11)	120.7(6)
O-Th(2)-B(5)	170.8(3)	C(9)-O-C(11)	113.1(7)

B(4)-Th-B(4)*	74.4(3)	B(2)-Th-B(4)*	95.3(2)
O-Th-B(4)*	76.8(2)	B(3)-Th-B(4)*	88.4(3)
O-Th-B(4)	81.1(2)	B(3)-Th-B(4)*	162.4(3)
O-Th-B(1)	166.2(2)	Th-B(1)-C(1)	178.2(6)
O-Th-B(2)	86.8(2)	Th-B(2)-C(2)	177.7(6)
O-Th-B(3)	91.4(2)	Th-B(3)-C(3)	176.2(7)
B(1)-Th-B(2)	97.9(3)	Th-B(4)-C(4)	125.6(5)
B(1)-Th-B(3)	100.4(3)	Th-B(4)-C(4)	122.2(6)
B(1)-Th-B(4)	96.3(3)	Th-B(4)-Th	105.6(3)
B(1)-Th-B(4)	85.6(3)	Th-O-C(5)	125.6(4)
B(2)-Th-B(3)	100.3(3)	Th-O-C(8)	127.9(5)
B(2)-Th-B(4)	161.7(3)	C(5)-O-C(8)	106.2(6)

* Atom at -x, -y, -z.

Table II. Selected Angles (deg)

[U(BH ₃ CH ₃) ₄ ·THT] ₂			
S(1)-U(1)-S(2)	66.3(1)	S(1)-U(2)-S(2)	65.3(1)
S(1)-U(1)-B(1)	146.5(6)	S(1)-U(2)-B(5)	84.8(5)
S(1)-U(1)-B(2)	76.1(4)	S(1)-U(2)-B(6)	81.9(5)
S(1)-U(1)-B(3)	106.8(5)	S(1)-U(2)-B(7)	172.8(6)
S(1)-U(1)-B(4)	77.4(4)	S(1)-U(2)-B(8)	82.9(5)
S(2)-U(1)-B(1)	80.3(6)	S(2)-U(2)-B(5)	75.0(5)
S(2)-U(1)-B(2)	84.5(4)	S(2)-U(2)-B(6)	76.3(4)
S(2)-U(1)-B(3)	173.0(5)	S(2)-U(2)-B(7)	107.6(6)
S(2)-U(1)-B(4)	84.5(5)	S(2)-U(2)-B(8)	148.1(5)
B(1)-U(1)-B(2)	101.4(7)	B(5)-U(2)-B(6)	151.2(6)
B(1)-U(1)-B(3)	106.8(8)	B(5)-U(2)-B(7)	94.7(7)
B(1)-U(1)-B(4)	100.4(7)	B(5)-U(2)-B(8)	101.0(7)
B(2)-U(1)-B(3)	93.5(7)	B(6)-U(2)-B(7)	95.3(7)
B(2)-U(1)-B(4)	153.5(6)	B(6)-U(2)-B(8)	102.6(7)
B(3)-U(1)-B(4)	94.6(8)	B(7)-U(2)-B(8)	104.3(7)
U(1)-B(1)-C(1)	178(2)	U(2)-B(5)-C(5)	178(1)
U(1)-B(2)-C(2)	177(1)	U(2)-B(6)-C(6)	177(2)
U(1)-B(3)-C(3)	178(2)	U(2)-B(7)-C(7)	177(1)
U(1)-B(4)-C(4)	177(1)	U(2)-B(8)-C(8)	175(1)
U(1)-S(1)-U(2)	114.3(1)	U(1)-S(2)-U(2)	114.1(1)
U(1)-S(1)-C(12)	112.9(6)	U(2)-S(2)-C(16)	113.5(6)
U(1)-S(1)-C(9)	115.2(6)	U(2)-S(2)-C(13)	113.9(6)
C(9)-S(1)-C(12)	96.4(8)	C(13)-S(2)-C(16)	94.3(8)

U(BH₃CH₃)₄·2THF

O	-U	-O ^a	177(1)
O	-U	-B(1)	81.7(5)
O	-U	-B(1) ^c	96.0(5)
O	-U	-B(2) ^a	99.1(5)
O	-U	-B(2) ^b	83.2(5)
B(1)-U	-B(1)	^c	90.3(8)
B(1)-U	-B(2)	^b	91.4(4)
B(1)-U	-B(2) ^a		164.9(4)
B(2)-U	-B(2) ^b		90.8(7)
U	-B(1)-C(1)		174(1)
U	-B(2)-C(2)		175(1)
U	-O	-C(3)	125.4(9)
U	-O	-C(6)	125.8(7)

U(BH₃CH₃)₄·2dmp

P(1)-U-P(1) ^d	72.6(2)
P(1)-U-P(2)	63.4(1)
P(1)-U-B(2)	81.5(3)
P(1)-U-P(2) [†]	83.6(3)
P(2)-U-P(2) [†]	160.6(1)
P(2)-U-B(1)	80.3(1)
P(2)-U-B(2)	89.7(3)
P(2)-U-B(2) [†]	93.5(3)
B(1)-U-B(2)	99.3(2)
B(2)-U-B(2) [†]	161.4(5)
U-B(1)-C(1)	180.0
U-B(2)-C(2)	175.5(7)

- a) Atom at -x, -y, -z.
 b) Atom at x, y, -z.
 c) Atom at -x, -y, z.
 d) Primed atoms at y, x, -z.

Table II. Selected Angles (deg)

U(BH ₃ CH ₃) ₂ .dme			U(BH ₃ CH ₃) ₂ .tmed		
B(1)-	U-B(2)	92.2(6)	B(2)-	U-B(3)	85.3(6)
B(2)-	U-B(3)	93.2(6)	B(2)-	U-B(4)	86.4(7)
B(1)-	U-B(4)	97.4(6)	B(1)-	U-B(4)	94.7(6)
B(3)-	U-B(4)	98.4(6)	B(1)-	U-B(3)	95.2(6)
B(2)-	U-B(4)	107.3(7)	B(1)-	U-B(2)	112.3(6)
B(1)-	U-B(3)	161.0(6)	B(3)-	U-B(4)	168.9(7)
O(1)-	U-O(2)	63.9(4)	N(1)-	U-N(2)	68.0(4)
O(1)-	U-B(4)	86.0(6)	N(2)-	U-B(1)	84.2(5)
O(2)-	U-B(2)	102.9(5)	N(1)-	U-B(2)	95.5(5)
B(1)-	U-X	81.3	B(3)-	U-X	90.3
B(3)-	U-X	82.1	B(4)-	U-X	89.4
C(1)-B(1)-U		176(1)	C(1)-B(1)-U		177(2)
C(2)-B(2)-U		179(2)	C(2)-B(2)-U		142(2)
C(3)-B(3)-U		178(2)	C(3)-B(3)-U		178(2)
C(4)-B(4)-U		178(2)	C(4)-B(4)-U		177(2)

U(BH ₃ CH ₃) ₂ .dmpe			U(BH ₃ CH ₃) ₂ .bmtc		
B(1)-	U-B(2)	110.0(3)	B(1)-	U-B(3)	93.7(6)
B(1)-	U-B(3)	92.0(3)	B(3)-	U-B(4)	94.0(3)
B(1)-	U-B(4)	94.1(3)	B(2)-	U-B(4)	98.8(3)
B(2)-	U-B(3)	99.1(3)	B(1)-	U-B(2)	99.1(3)
B(2)-	U-B(4)	97.9(3)	B(2)-	U-B(3)	107.0(3)
B(3)-	U-B(4)	158.8(3)	B(1)-	U-B(4)	157.5(3)
P(1)-	U-P(2)	67.4(1)	S(1)-	U-S(2)	69.9(2)
P(1)-	U-B(1)	168.2(2)	S(1)-	U-B(2)	85.0(2)
P(1)-	U-B(2)	81.8(2)	S(2)-	U-B(3)	98.2(2)
P(1)-	U-B(3)	86.1(2)	B(1)-	U-X	79.7
P(1)-	U-B(4)	83.9(2)	B(4)-	U-X	79.7
P(2)-	U-B(1)	100.8(2)	C(1)-B(1)-U		177(1)
P(2)-	U-B(2)	149.2(2)	C(2)-B(2)-U		178(1)
P(2)-	U-B(3)	79.6(2)	C(3)-B(3)-U		178(1)
P(2)-	U-B(4)	79.3(2)	C(4)-B(4)-U		178(1)
C(1)-B(1)-U		176.8(6)			
C(2)-B(2)-U		177.7(7)			
C(3)-B(3)-U		178.0(6)			
C(4)-B(4)-U		174.8(6)			

* X is the midpoint of atoms O(1)-O(2), N(1)-N(2), or S(1)-S(2).

Table III. ¹H NMR Data for U(BH₃CH₃)₄ + THF at -80°C^{a,b,c}

Peak	δ	Assignment
1	265.05	BH ₃ , U(BH ₃ CH ₃) ₄ .2THF
2	220.40	BH ₃ , U(BH ₃ CH ₃) ₄
3	143.17	BH ₃ , U(BH ₃ CH ₃) ₄ .THF
4	65.39	THF, U(BH ₃ CH ₃) ₄ .THF
5	34.14	THF, U(BH ₃ CH ₃) ₄ .THF
6	30.91	CH ₃ , U(BH ₃ CH ₃) ₄ .2THF
7	22.86	CH ₃ , U(BH ₃ CH ₃) ₄
8	7.89	CH ₃ , U(BH ₃ CH ₃) ₄ .THF
9	-24.79	THF, U(BH ₃ CH ₃) ₄ .2THF
10	-50.91	THF, U(BH ₃ CH ₃) ₄ .2THF

a) In toluene-d₆.b) Shifts in ppm from Me₄Si. Positive sign indicates downfield shift.c) Concentration = 0.12 g/mL U(BH₃CH₃)₄.

Table IV. $\sum$ Caf Calculations for U and Th Methyltrihydroborate Base Adducts

Compound	Coordination Number	Coordinating Group/Atom	Distance	Caf	$\sum$ Caf
U(BH ₃ CH ₃) ₄ .dme	14	U-BH ₃	2.09 Å	0.163	0.812
		U-O	2.58	0.080	
U(BH ₃ CH ₃) ₄ .tmed	13	U-BH	2.09	0.163	0.799
		U-BH ³	2.23	0.073	
		U-N ²	2.73	0.082	
U(BH ₃ CH ₃) ₄ .dmpe	14	U-BH ₃	2.15	0.155	0.842
		U-P ³	3.02	0.111	
[Th(BH ₃ CH ₃) ₄] ₂ .OEt ₂	13	Th-BH ₃	2.11	0.160	0.724
		Th-BH ₂	2.46	0.121	
		Th-BH ₂	2.44	0.123	
	14	Th-BH ₃	2.15	0.156	0.780
		Th-BH ₂	2.43	0.124	
		Th-BH ₂	2.58	0.109	
		Th-O	2.59	0.079	
[Th(BH ₃ CH ₃) ₄].THF] ₂	14	Th-BH ₃	2.10	0.158	0.783
		Th-BH ₂	2.56	0.111	
		Th-BH ₂	2.53	0.114	
		Th-O	2.53	0.084	
U(BH ₃ CH ₃) ₄ .2dmpe	13	U-BH ₃	2.27	0.145	0.847
		U-P ³	3.13	0.103	
U(BH ₃ CH ₃) ₄ .2THF	14	U-BH ₃	2.09	0.163	0.826
		U-O	2.49	0.087	
Th(BH ₃ CH ₃) ₄ .2THF*	14	Th-BH ₃	2.14	0.159	0.802
		Th-O	2.54	0.083	
[Th(BH ₃ CH ₃) ₄].OMe ₂]*	14	Th-BH ₃	2.10	0.158	0.783
		Th-BH ₂	2.56	0.111	
		Th-BH ₂	2.53	0.114	
		Th-O	2.53	0.084	

(continued)

Table IV. Σ Caf Calculations for U and Th Methyltrihydroborate Base Adducts (continued)

Compound	Coordination Number	Coordinating Group/Atom	Distance	Caf	Σ Caf
$\text{Th}(\text{BH}_3\text{CH}_3)_4 \cdot 2\text{py}^*$	14	Th-BH ₃	2.14	0.159	0.800
		Th-N ₃	2.73	0.082	
$\text{U}(\text{BH}_3\text{CH}_3)_4 \cdot 2\text{py}^*$	14	U-BH ₃	2.09	0.163	0.822
		U-N ₃	2.68	0.085	
$\text{Th}(\text{BH}_3\text{CH}_3)_4 \cdot 2\text{NH}_3^*$	14	Th-BH ₃	2.14	0.159	0.800
		Th-N ₃	2.73	0.082	
$\text{U}(\text{BH}_3\text{CH}_3)_4 \cdot 2\text{NH}_3^*$	14	U-BH ₃	2.09	0.163	0.822
		U-N ₃	2.68	0.085	
$\text{Th}(\text{BH}_3\text{CH}_3)_4 \cdot \text{tmed}^\dagger$	14	Th-BH ₃	2.15	0.158	0.788
		Th-N ₃	2.80	0.078	
$[\text{Th}(\text{BH}_3\text{CH}_3)_4 \cdot \text{SMe}_2]_2^*$	14	Th-BH ₃	2.10	0.158	0.804
		Th-H _{br}	2.56	0.111	
		Th-H _{br}	2.53	0.114	
		Th-S	3.02	0.105	
$\text{Th}(\text{BH}_3\text{CH}_3)_4 \cdot 2\text{THT}^*$	14	Th-BH ₃	2.14	0.159	0.844
		Th-S	3.03	0.104	
$[\text{Th}(\text{BH}_3\text{CH}_3)_4 \cdot \text{THT}]_2^*$	14	Th-BH ₃	2.10	0.158	0.804
		Th-BH ₂	2.56	0.111	
		Th-BH ₂	2.53	0.114	
		Th-S	3.02	0.105	
$[\text{U}(\text{BH}_3\text{CH}_3)_4 \cdot \text{THT}]_2$	14	U-BH ₃	2.09	0.163	0.839
		U-S ₃	3.14	0.096	
		U-S	3.26	0.088	
$\text{Th}(\text{BH}_3\text{CH}_3)_4 \cdot \text{bmte}^*$	14	Th-BH ₃	2.16	0.157	0.822
		Th-S ₃	3.12	0.097	
$\text{U}(\text{BH}_3\text{CH}_3)_4 \cdot \text{bmte}$	14	U-BH ₃	2.11	0.160	0.842
		U-S ₃	3.07	0.101	
$\text{Th}(\text{BH}_3\text{CH}_3)_4 \cdot \text{dmpe}^*$	14	Th-BH ₃	2.20	0.151	0.818
		Th-P ₃	3.07	0.107	

[†] Assuming all methyltrihydroborate groups are tridentate.

Table V. Σ Caf Calculations for Hypothetical U and Th
Methyltrihydroborate Base Adducts

Compound	Coordination Number	Coordinating Group/Atom	Distance	Caf	Σ Caf
$[U(BH_3CH_3)_4 \cdot OMe_2]_2$	14	U-BH ₃	2.05 Å	0.162	0.808
		U-BH ₂	2.51	0.116	
		U-BH ₂	2.48	0.119	
		U-O	2.48	0.087	
$[U(BH_3CH_3)_4]_2 \cdot OEt_2$	13	U-BH ₃	2.06	0.164	0.748
		U-BH ₂	2.41	0.127	
		U-BH ₂	2.39	0.129	
	14	U-BH ₃	2.10	0.160	0.807
		U-BH ₂	2.38	0.130	
		U-BH ₂	2.53	0.114	
$[U(BH_3CH_3)_4 \cdot SMe_2]_2$	14	U-O	2.54	0.083	0.839
		U-BH ₃	2.05	0.165	
		U-BH ₂	2.51	0.116	
		U-BH ₂	2.48	0.119	
$U(BH_3CH_3)_4 \cdot 2THT$	14	U-S	2.97	0.109	0.868
		U-BH ₃	2.09	0.163	
$Th(BH_3CH_3)_4 \cdot 2SMe_2$	14	Th-S	2.98	0.108	0.844
		Th-EH ₃	2.14	0.159	
$Th(BH_3CH_3)_4 \cdot 2OMe_2$	14	Th-S	3.03	0.104	0.902
		Th-BH ₃	2.14	0.159	
		Th-O	2.54	0.083	

Table VI. Σ Caf Calculations for Hypothetical U and Th Methyltrihydroborate Base Adduct Structures

Compound	Coordination Number	Coordinating Group/Atom	Distance	Caf	Σ Caf
Th(BH ₃ CH ₃) ₄ .OEt ₂	13	Th-BH ₃	2.13 Å	0.159	0.720
		Th-O	2.52	0.084	
Th(BH ₃ CH ₃) ₄ .THF	13	Th-BH ₃	2.13	0.159	0.720
		Th-O	2.52	0.084	
Th(BH ₃ CH ₃) ₄ .OMe ₂	13	Th-BH ₃	2.13	0.159	0.720
		Th-O	2.52	0.084	
Th(BH ₃ CH ₃) ₄ .SMe ₂	13	Th-BH ₃	2.13	0.159	0.742
		Th-S	3.01	0.106	
Th(BH ₃ CH ₃) ₄ .THT	13	Th-BH ₃	2.13	0.159	0.742
		Th-S	3.01	0.106	
U(BH ₃ CH ₃) ₄ .THT	13	U-BH ₃	2.08	0.164	0.766
		U-S	2.96	0.110	
U(BH ₃ CH ₃) ₄ .tmed	14	U-BH ₃	2.10	0.162	0.810
		U-N	2.75	0.081	
[U(BH ₃ CH ₃) ₄ .THT] ₂ *	14	U-BH ₃	2.05	0.165	0.839
		U-BH ₂	2.51	0.116	
		U-BH ₂	2.48	0.119	
		U-S	2.97	0.109	

* U atoms bridged by BH₃CH₃ groups.

Table VII. ^1H NMR Data for $[\text{U}(\text{BH}_3\text{CH}_3)_2\cdot\text{THT}]_2$ ^{a,b,c}

T (°C)	BH ₃	CH ₃	THT
-90	-105.68 (12H, s) d	-43.23 (12H, s) 104.82 (12H, s)	-47.23 (8H, s) -23.52 (8H, s)
-72	e	f	-30.75 (8H, s) -11.94 (8H, s)
-54	e	20.41 (24H, s) ^g	-10.79 (8H, s) -3.25 (8H, s)
30	145.17 (24H, s) ^h	13.81 (24H, s) ^g	3.45 (8H, s) 8.77 (8H, s)

a) In toluene-d₆.

b) Shifts in ppm from Me₄Si. Positive sign indicates downfield shift.

c) Concentration = 0.012 g/mL.

d) Other BH₃ peak too far downfield to be observed.

e) BH₃ peak broadened into baseline due to rapid exchange of BH₃CH₃ sites.

f) CH₃ peak broadened into baseline due to rapid exchange of BH₃CH₃ sites.

g) Averaged CH₃ peak.

h) Averaged BH₃ peak.

Table VIII. Mass spectrum of $[\text{Th}(\text{BH}_3\text{CH}_3)_4\cdot\text{THT}]_2$

Relative Abundance	m/e	Assignment
0.0281	666	$\text{Th}_2(\text{BH}_3\text{CH}_3)_7^+$
0.0120	652	$\text{Th}_2(\text{BH}_3\text{CH}_3)_6(\text{CH}_3)^+$
0.1384	407	$\text{Th}(\text{BH}_3\text{CH}_3)_3\text{THT}^+$
0.0614	393	$\text{Th}(\text{BH}_3\text{CH}_3)_2(\text{CH}_3)\text{THT}^+$
0.1295	319	$\text{Th}(\text{BH}_3\text{CH}_3)_3^+$
0.1133	305	$\text{Th}(\text{BH}_3\text{CH}_3)_2(\text{CH}_3)^+$
1.0000	89	$\text{THT}^+ (M + 1)$

Table IX. Mass spectrum of $[\text{Th}(\text{BH}_3\text{CH}_3)_4]_2 \cdot \text{OEt}_2$

Relative Abundance	m/e	Assignment
0.1190	666	$\text{Th}_2(\text{BH}_3\text{CH}_3)_7^+$
0.0365	652	$\text{Th}_2(\text{BH}_3\text{CH}_3)_6(\text{CH}_3)^+$
0.5039	393	$\text{Th}(\text{BH}_3\text{CH}_3)_3(\text{OEt}_2)^+$
0.0729	379	$\text{Th}(\text{BH}_3\text{CH}_3)_2(\text{CH}_3)(\text{OEt}_2)^+$
0.0243	364	$\text{Th}(\text{BH}_3\text{CH}_3)_2(\text{OEt}_2)^+$
0.0121	350	$\text{Th}(\text{BH}_3\text{CH}_3)(\text{CH}_3)(\text{OEt}_2)^+$
0.0137	335	$\text{Th}(\text{BH}_3\text{CH}_3)(\text{OEt}_2)^+$
0.0119	321	$\text{Th}(\text{CH}_3)(\text{OEt}_2)^+$
0.0947	319	$\text{Th}(\text{BH}_3\text{CH}_3)_3^+$
0.0575	305	$\text{Th}(\text{BH}_3\text{CH}_3)_2(\text{CH}_3)^+$
1.0000	75	$\text{OEt}_2^+ (M + 1)$

Table X. Mass spectrum of $[U(BH_3CH_3)_4 \cdot THT]_2$

Relative Abundance	m/e	Assignment
0.0123	413	$U(BH_3CH_3)_3THT^+$
0.0083	399	$U(BH_3CH_3)_2(CH_3)THT^+$
0.0141	325	$U(BH_3CH_3)_3^+$
0.0115	311	$U(BH_3CH_3)_2(CH_3)^+$
1.0000	89	$THT^+ (M + 1)$

Table XI. Mass spectrum of $[\text{Th}(\text{BH}_3\text{CH}_3)_4 \cdot \text{OMe}_2]_2$

Relative Abundance	m/e	Assignment
0.0112	666	$\text{Th}_2(\text{BH}_3\text{CH}_3)_7^+$
0.0105	652	$\text{Th}_2(\text{BH}_3\text{CH}_3)_6(\text{CH}_3)^+$
0.1589	365	$\text{Th}(\text{BH}_3\text{CH}_3)_3\text{OMe}_2^+$
0.0860	351	$\text{Th}(\text{BH}_3\text{CH}_3)_2(\text{CH}_3)\text{OMe}_2^+$
0.0136	336	$\text{Th}(\text{BH}_3\text{CH}_3)_2\text{OMe}_2^+$
0.0840	319	$\text{Th}(\text{BH}_3\text{CH}_3)_3^+$
0.0640	305	$\text{Th}(\text{BH}_3\text{CH}_3)_2(\text{CH}_3)^+$
1.0000	57	$(\text{BH}_2\text{CH}_3)_2^+ (M + 1)$

Table XII. Mass spectrum of $[\text{Th}(\text{BH}_3\text{CH}_3)_6\text{SMe}_2]_2$

Relative Abundance	m/e	Assignment
0.0108	666	$\text{Th}_2(\text{BH}_3\text{CH}_3)_7^+$
0.0075	652	$\text{Th}_2(\text{BH}_3\text{CH}_3)_6(\text{CH}_3)^+$
0.0332	381	$\text{Th}(\text{BH}_3\text{CH}_3)_5\text{SMe}_2^+$
0.0131	367	$\text{Th}(\text{BH}_3\text{CH}_3)_4(\text{CH}_3)\text{SMe}_2^+$
0.0341	319	$\text{Th}(\text{BH}_3\text{CH}_3)_3^+$
0.0281	305	$\text{Th}(\text{BH}_3\text{CH}_3)_2(\text{CH}_3)^+$
1.0000	63	$\text{SMe}_2^+ (M + 1)$

Table XIII. ^1H NMR Data for $\text{U}(\text{BH}_2\text{CH}_3)_4 \cdot \text{dme}^{\text{a},\text{b}}$

T(°C)	BH_2	CH_3	DME
-78	-102.25 (6H, s) (679.5) ^c	-31.20 (6H, s) 94.65 (6H, s)	-56.52 (4H, s) -44.46 (6H, s)
-40	d	e	-47.64 (4H, s) -38.10 (6H, s)
-20.5	d	25.09 (12H, s) ^f	-42.66 (4H, s) -34.20 (6H, s)
25	194.25 (12H, s) ^g	21.43 (12H, s) ^f	-33.84 (4H, s) -27.57 (6H, s)

a) In toluene- d_6 .

b) Shifts in ppm from Me_4Si . Positive sign indicates downfield shift.

c) Estimated δ of other BH_2 peak based on extrapolation from averaged BH_2 peak at 25°C.

d) BH_2 peak broadened into baseline due to rapid exchange of BH_2CH_3 sites.

e) CH_3 peak broadened into baseline due to rapid exchange of BH_2CH_3 sites.

f) Averaged CH_3 peak.

g) Averaged BH_2 peak.

Table XIV. ^1H NMR Data for $\text{U}(\text{BH}_3\text{CH}_3)_4 \cdot \text{bmte}^{\text{a,b}}$

$T(^{\circ}\text{C})$	BH_3	CH_3	BMTE
-78	c	-69.98 (6H, s) 80.49 (6H, s)	-24.54 (4H, s) -9.90 (6H, s)
-32	c	d	-17.53 (4H, s) -8.26 (6H, s)
-22	c	21.78 (12H, s)	-16.64 (4H, s) -7.92 (6H, s)
15	182.94 (12H, s) ^e	19.26 (12H, s) ^f	-13.30 (4H, s) -6.56 (6H, s)

a) In toluene- d_6 .

b) Shifts in ppm from Me_4Si . Positive sign indicates downfield shift.

c) No BH_3 peak found.

d) CH_3 peak broadened into baseline due to rapid exchange of BH_3CH_3 sites.

e) Averaged BH_3 peak.

f) Averaged CH_3 peak.

Table XV. ^1H NMR Data for $\text{U}(\text{BH}_3\text{CH}_3)_4 \cdot \text{TMED}^{\text{a,b}}$

T (°C)	BH_3	CH_3	TMED
-59	-74.50 (6H, s) ^c	-22.83 (6H, s) 81.11 (6H, s)	-40.50 (12H, s) -28.05 (4H, s)
25	d	e	-29.64 (12H, s) -16.74 (4H, s)
54	f	19.39 (12H, s) ^g	-26.40 (12H, s) -14.57 (4H, s)

a) In toluene- d_6 .

b) Shifts in ppm from Me_4Si . Positive sign indicates downfield shift.

c) Other P^{u} , peak not found.

d) BH_3 , peak broadened into baseline due to rapid exchange of BH_3CH_3 sites.

e) CH_3 , peak broadened into baseline due to rapid exchange of BH_3CH_3 sites.

f) Averaged BH_3 , peak not found up to 84°C.

g) Averaged CH_3 , peak.

Table XVI. ^1H NMR Data for $\text{U}(\text{BH}_3\text{CH}_3)_2 \cdot \text{dmpe}^{\text{a,b}}$

$T(^{\circ}\text{C})$	BH_3	CH_3	DMPE
-66	-32.97 (6H, s) 450.14 (6H, s)	-16.20 (6H, s) 60.27 (6H, s)	-15.64 (4H, s) -8.14 (12H, s)
8.5	c	d	-11.14 (4H, s) -6.01 (12H, s)
35	e	16.05 (12H, s) ^f	-9.90 (4H, s) -5.33 (12H, s)

a) In toluene- d_6 .

b) Shifts in ppm from Me_4Si . Positive sign indicates downfield shift.

c) BH_3 peak broadened into baseline due to rapid exchange of BH_3CH_3 sites.

d) CH_3 peak broadened into baseline due to rapid exchange of BH_3CH_3 sites.

e) Averaged BH_3 peak not found up to 93°C .

f) Averaged CH_3 peak.

Table XVII. ^1H NMR Data for $\text{U}(\text{BH}_3\text{CH}_3)_3 \cdot 2\text{dmpe}^{\text{a,b}}$

$T(^{\circ}\text{C})$	BH_3	CH_3	DMPE
-68	144.61 (9H, s)	12.44 (9H, s)	-5.31 (8H, s) -0.57 (12H, s)
-22	125.95 (9H, s)	10.23 (9H, s)	-2.94 (8H, s) -0.08 (24H, s)
25	115.24 (9H, s)	8.92 (9H, s)	-1.09 (8H, s) -0.07 (24H, s)
70	112.99 (9H, s)	8.39 (9H, s)	-0.24 (8H, s) 0.13 (24H, s)

a) In toluene- d_6 .

b) Shifts in ppm from Me_4Si . Positive sign indicates a downfield shift.

Table XVIII. $\sum \text{Caf}$ Calculations for $\text{UCp}_2(\text{BH}_3\text{CH}_3)_2$

Coordination Number	Coordinating Group/Atom	Distance	Caf	$\sum \text{Caf}$
12	U-Cp	2.83 Å	0.207	0.742
	U-BH ₃	2.06	0.164	

Table XIX. $\sum \text{Caf}$ Calculations for U and Th Tetrahydroborate Base Adducts

Compound	Coordination Number	Coordinating Group/Atom	Distance	Caf	$\sum \text{Caf}$
$\text{U}(\text{BH}_4)_4 \cdot 2\text{THF}$	14	U-BH ₃	2.16 Å	0.161	0.818
		U-O	2.48	0.087	
$\text{U}(\text{BH}_4)_4 \cdot \text{OMe}_2$	14	U-BH ₃	2.13	0.163	0.834
		U-BH ₂	2.40	0.128	
		U-O	2.46	0.089	
$\text{U}(\text{BH}_4)_4 \cdot \text{OEt}_2$	14	U-BH ₃	2.13	0.163	0.833
		U-BH ₂	2.40	0.128	
		U-O	2.47	0.088	
$\text{U}(\text{BH}_4)_4 \cdot \text{O}(\underline{n}\text{-Pr})_2$	13	U-BH ₃	2.11	0.165	0.807
		U-BH ₂	2.34	0.063	
		U-O	2.47	0.088	
	14	U-BH ₃	2.11	0.165	0.786
		U-BH ₂	2.34	0.063	
$\text{Th}(\text{BH}_4)_4 \cdot 2\text{THF}^*$	14	Th-BH ₃	2.21	0.157	0.796
		Th-O	2.53	0.084	
$\text{Th}(\text{BH}_4)_4 \cdot \text{dme}^*$	14	Th-BH ₃	2.21	0.157	0.782
		Th-O	2.62	0.077	
$\text{Th}(\text{BH}_4)_4 \cdot 2\text{NH}_3^*$	14	Th-BH ₃	2.21	0.157	0.794
		Th-N	2.72	0.083	

Table XX. $\sum \text{Caf}$ Calculations for Hypothetical U Tetrahydroborate Base Adduct Structures

Compound	Coordination Number	Coordinating Group/Atom	Distance	Caf	$\sum \text{Caf}$
$\text{U}(\text{BH}_3)_4 \cdot \text{OMe}_2$	13	U-BH ₃	2.12 Å	0.160	0.730
		U-O	2.44	0.090	
$\text{U}(\text{BH}_3)_4 \cdot \text{OEt}_2$	13	U-BH ₃	2.12	0.160	0.730
		U-O	2.45	0.090	
$\text{U}(\text{BH}_3)_4 \cdot \text{O}(\underline{n}\text{-Pr})_2$	13	U-BH ₃	2.12	0.160	0.730
		U-O	2.45	0.090	

Fig. 1. ORTEP drawing of $[\text{Th}(\text{BH}_3\text{CH}_3)_4]_2 \cdot \text{O}(\text{C}_2\text{H}_5)_2$.

XBL 835-9692

Fig. 2. ORTEP drawing of $[\text{Th}(\text{BH}_3\text{CH}_3)_4 \cdot \text{THF}]_2$.

Fig. 3. Bridging scheme in $[\text{Th}(\text{BH}_3\text{CH}_3)_6]_2 \cdot \text{O}(\text{C}_2\text{H}_5)_2$.

XBL 835-9689

Fig. 4. Bridging scheme in $[\text{Th}(\text{BH}_3\text{CH}_3)_4\cdot\text{THF}]_2$.

XBL 835-9690

Fig. 5. ORTEP drawing of $U(BH_3CH_3)_4 \cdot 2THF$.

XBL 8410-4299

Fig. 6. The basis for calculation of fan angle for monodentate ligands. The length b is the distance from the center of the metal atom to the center of the coordinating atom.

Fan angle, $\theta = \sin^{-1}(R_o/b)$

Fig. 7. The basis for calculation of fan angle for tridentate methyltrihydroborate or tetrahydroborate groups. R_H is the van der Waals radius of a hydrogen atom, l is the distance from the center of the triangle to the center of one of the bridging hydrogen atoms, and b is the distance from the center of the triangle (c) to the center of the metal.

Top view:

Side view:

$$\text{Fan angle, } \theta = \tan^{-1} (R_o/b)$$

Fig. 8. ORTEP drawing of $[\text{U}(\text{BH}_3\text{CH}_3)_4 \cdot \text{THT}]_2$.

XBL 8410-4301

Fig. 9. ORTEP drawing of $U(BH_3CH_3)_4 \cdot dme$.

Fig. 10. ORTEP drawing of $U(BH_3CH_3)_4 \cdot 4H_2O$.

Fig. 11. ORTEP drawing of $U(BH_3CH_3)_4 \cdot 6H_2O$.

Fig. 12. ORTEP drawing of $U(BH_3CH_3)_6 \cdot bmtc$.

Fig. 13. General stereochemistry for $M(\text{bidentate})(\text{unidentate})_2$,
showing ϕ_C and ϕ_E . Regular octahedral values are $\phi_C = 90^\circ$,
 $\phi_E = 135^\circ$.

Fig. 14. Illustration of twist mechanism. The reference axis with respect to which the twisting is taking place is normal to the plane of the paper. The arrows indicate the directions of twist of the front face with respect to the back face, which is kept fixed.

X = O, N, P, or S

Fig. 15. ORTEP drawing of $U(BH_3CH_3)_3 \cdot 2dmpe$.

Chapter 4

THE LANTHANIDE METHYLTRIHYDROBORATE COMPLEXESIntroduction

Volatile lanthanide tetrahydroborates are relatively rare. A series of nonvolatile compounds, $M(BH_4)_n \cdot nTHF$ ($M = Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu$; $n = \text{nonintegral number}$) were prepared by Zange by treating the anhydrous chlorides with diborane in THF.¹ Rossmanith reported a series of volatile compounds, $M(BH_4)_n \cdot nTHF$ ($n \sim 1$), prepared by the disproportionation of chlorobistetrahydroborates of Y, Dy, and Ho and the dichlorotetrahydroborate of Eu at 120-160°C under vacuum.² More recently Marks et al. reported the synthesis of volatile Cp_2MBH_4 compounds of Er and Yb,³ and Lobkovskii et al. reported the volatile pseudo-lanthanide $Sc(BH_4)_2 \cdot 2THF$.⁴

Recently in this laboratory, attempts were made to prepare $Ce(BH_4)_3$.⁵ Its synthesis was desired since a solid-state transformation takes place between Np and U tetrahydroborate (Np(IV) I. R. (ionic radius) = 0.98 Å, U(IV) I. R. = 1.00 Å, Ce(IV) I. R. = 0.97 Å).⁶ If $Ce(BH_4)_3$ were monomeric, it would probably be volatile like the other Group IVB monomeric tetrahydroborates.⁷ Treatment of CeF_3 or Na_2CeF_6 with $Al(BH_4)_3$ was unsuccessful. No reaction appeared to occur. After removal of $Al(BH_4)_3$, the residue left behind was analyzed by X-ray diffraction. The powder pattern revealed only unreacted CeF_3 and Na_2CeF_6 .⁸

In another attempt to make $Ce(BH_4)_3$, the reaction used by Zange was modified. Because $CeCl_3$ is unknown, $Ce(Oi-Pr)_3$ was substituted. Reaction of $Ce(Oi-Pr)_3$ with diborane in THF only gave the reduced

species, $\text{Ce}(\text{BH}_4)_3 \cdot 3\text{THF}$. Similarly reaction of $\text{Ce}(\text{O}i\text{-Pr})_4$ with $\text{Al}(\text{BH}_4)_3$ gave $\text{Ce}(\text{BH}_4)_3 \cdot 3\text{THF}$ when the reaction residue was recrystallized from THF. From this reaction it appears that $\text{Ce}(\text{IV})$ is unstable in the presence of the tetrahydroborate group. In this sense $\text{Ce}(\text{IV})$ behaves much like $\text{Ti}(\text{IV})$ since reaction of TiCl_4 with LiBH_4 ^{7,8} gives reduced species as does the reaction of $\text{Ti}(\text{OR})_4$ with diborane in THF.^{9,10} Like the other lanthanide tetrahydroborate tristetrahydrofuranates, $\text{Ce}(\text{BH}_4)_3 \cdot 3\text{THF}$ is nonvolatile and rather insoluble in nonethereal solvents. Because of the intractable nature of lanthanide tetrahydroborate complexes, little chemistry has been explored with them. Therefore the $\text{Ln}(\text{BH}_4\text{CH}_3)_3$ (Ln = lanthanide) complexes have been prepared in the hope that they would display more ideal chemical characteristics, such as volatility and solubility in hydrocarbons like their actinide analogues.

Discussion

In an analogous fashion to the preparation of actinide methyltrihydroborates, the preparation of $\text{Yb}(\text{BH}_4\text{CH}_3)_3$ was attempted by stirring YbCl_3 with LiBH_4CH_3 in chlorobenzene, but no volatile product was obtained. On the other hand, when YbCl_3 is stirred with LiBH_4CH_3 in diethyl ether, a volatile white product is recovered, $\text{Yb}(\text{BH}_4\text{CH}_3)_3 \cdot \text{OEt}_2$. Similarly $\text{Lu}(\text{BH}_4\text{CH}_3)_3 \cdot \text{OEt}_2$ and $\text{Ho}(\text{BH}_4\text{CH}_3)_3 \cdot \text{OEt}_2$ are obtained when LiBH_4CH_3 is reacted with LuCl_3 and HoCl_3 , respectively, in diethyl ether. No volatile product is obtained when SmCl_3 is reacted with LiBH_4CH_3 in ether. From its IR spectrum, the mode of ligation of $\text{Yb}(\text{BH}_4\text{CH}_3)_3 \cdot \text{OEt}_2$ appears to be tridentate. A large, broad peak is found at 2100 cm^{-1} with a shoulder at $\sim 2190 \text{ cm}^{-1}$ ($\text{B-H}_{\text{bridging}}$ stretch). In addition a peak is found at 1270 cm^{-1} (bridge

deformation). These peaks are characteristic of tridentate ligation according to Marks et al.¹¹ The IR spectra of $\text{Lu}(\text{BH}_2\text{CH}_2)_3\cdot\text{OEt}_2$ and $\text{Ho}(\text{BH}_2\text{CH}_2)_3\cdot\text{OEt}_2$ are similar to $\text{Yb}(\text{BH}_2\text{CH}_2)_3\cdot\text{OEt}_2$ in these regions. When the etherate is dissolved in THF, pumped dry, and sublimed, mono-THF adducts are obtained; e. g., $\text{Yb}(\text{BH}_2\text{CH}_2)_3\cdot\text{THF}$, $\text{Lu}(\text{BH}_2\text{CH}_2)_3\cdot\text{THF}$, and $\text{Ho}(\text{BH}_2\text{CH}_2)_3\cdot\text{THF}$. Similarly when THT is used, the mono-THT adduct is obtained; e. g., $\text{Ho}(\text{BH}_2\text{CH}_2)_3\cdot\text{THT}$. The IR spectra of these adducts are similar to the lanthanide methyltrihydroborate etherates in the B-H stretching regions, indicative of tridentate ligation of the methyltrihydroborate group. To confirm our analysis of the IR spectra of these mono-adducts, an X-ray crystal structure determination was made of $\text{Yb}(\text{BH}_2\text{CH}_2)_3\cdot\text{OEt}_2$.

The crystal structure confirmed the tridentate coordination of the methyltrihydroborate groups. The compound crystallizes in the space group $P2_1/n$ with $Z = 4$. It is monoclinic with unit cell parameters $a = 10.745(4)$ Å, $b = 15.647(4)$ Å, $c = 9.215(3)$ Å, $\beta = 90.78(2)^\circ$. The metal is surrounded by three tridentate methyltrihydroborates and one ether group in an approximately tetrahedral arrangement, with the methyltrihydroborates bent slightly towards the ether group (see Fig. 1). Selected bond distances and angles are given in Tables I and II, respectively. All Yb-B-C angles are close to 180° , indicative of tridentate ligation. The average Yb-B distance is 2.45 ± 0.04 Å. This may be compared to the pseudo-lanthanide $\text{Y-B}_{\text{tridentate}}$ distance of $2.58(1)$ Å found for $\text{Y}(\text{BH}_2)_3\cdot 3\text{THF}$,¹² and the $\text{Sc-B}_{\text{tridentate}}$ distance of $2.330(5)$ Å found for $\text{Sc}(\text{BH}_2)_3\cdot 2\text{THF}$.¹³ These values compare favorably since the ionic radius of Y(III) is about 0.04 Å longer and Sc(III) about 0.11 Å shorter than that of Yb(III).⁶ The Yb-O distance is

2.24(1) Å, which may be compared with the Y-O distance of 2.350(6) Å and 2.412(7) Å found for $\text{Y}(\text{BH}_3)_2 \cdot 3\text{THF}$ and Sc-O distance of 2.170(2) Å and 2.163(3) Å found for $\text{Sc}(\text{BH}_3)_2 \cdot 2\text{THF}$, again consistent with the changes in ionic radii of the metal.

The cone-packing model for steric crowding about lanthanides was utilized. Li and Fischer calculated $\sum \text{caf}$'s for more than 30 lanthanide(III) complexes. An average $\sum \text{caf}$ of 0.72 ± 0.05 was obtained. Thus the region of stability was defined as being from 0.62 to 0.82.¹³ $\sum \text{caf}$'s were calculated for the mono-adducts of $\text{Ln}(\text{BH}_2\text{CH}_3)_2$, Ln = Ho, Yb, Lu. The results are given in Table III. Complexes with asterisks are based on estimates from known bond distances found in $\text{Yb}(\text{BH}_2\text{CH}_3)_2 \cdot \text{OEt}_2$, correcting for changes in ionic radii. Most of the mono-adducts we have prepared are borderline low. Note that the unknown $\text{Sm}(\text{BH}_2\text{CH}_3)_2 \cdot \text{OEt}_2$ lies below the region of stability (Table IV). Thus this compound may be unstable due to undercrowding.

When the etherates are dissolved in THF, pumped dry, and then recrystallized from toluene, the bis-adducts are obtained; e. g., $\text{Yb}(\text{BH}_2\text{CH}_3)_2 \cdot 2\text{THF}$ and $\text{Ho}(\text{BH}_2\text{CH}_3)_2 \cdot 2\text{THF}$. Similarly when THT or pyridine are used, the bis-THT and bis-py adducts are obtained, respectively; e. g., $\text{Ho}(\text{BH}_2\text{CH}_3)_2 \cdot 2\text{THT}$ and $\text{Ho}(\text{BH}_2\text{CH}_3)_2 \cdot 2\text{py}$. Thus it appears that both the mono- and bis-unidentate base adducts of $\text{Ln}(\text{BH}_2\text{CH}_3)_2$ (Ln = Ho, Yb, Lu) are stable, with the former being volatile. In all cases, the bis-adduct decomposes to the mono-adduct when sublimed at -100°C in vacuo. The geometry of the bis-adducts appears to be trigonal bipyramidal with the base occupying the axial positions, judging by their proton NMR spectra since no nonequivalent BH_2CH_3 sites could be observed down to

-70°C. An X-ray crystal structure analysis of $\text{Ho}(\text{BH}_2\text{CH}_3)_2\cdot 2\text{py}$ confirms this.

$\text{Ho}(\text{BH}_2\text{CH}_3)_2\cdot 2\text{py}$ crystallizes in the space group $P\bar{1}$ with $Z = 2$. It is triclinic with unit cell parameters $a = 9.370(4)$ Å, $b = 12.155(4)$ Å, $c = 8.840(4)$ Å, $\alpha = 80.47(2)^\circ$, $\beta = 107.41(2)^\circ$, $\gamma = 95.15(2)^\circ$. The geometry of the compound is approximately trigonal bipyramidal with the tridentate methytrihydroborates occupying the three equatorial positions and the pyridines the 2 axial positions (see Fig. 2). Selected bond distances and angles are given in Tables I and II, respectively. The average Ho-B distance is 2.50 ± 0.02 Å, which may be compared to the Yb-B distance of 2.45 ± 0.04 Å in $\text{Yb}(\text{BH}_2\text{CH}_3)_2\cdot 0\text{Et}_2$. Accounting for the fact that the ionic radius of Ho(III) is about 0.03 Å larger than Yb(III) and the increase in coordination number is from 10 to 11, this is in very good agreement. The average Ho-N distance is 2.55 ± 0.02 Å. This may be compared to the Yb-N distance of 2.61(1) Å found in $(\text{C}_6\text{H}_5)_2\text{Yb}(\text{NC}_6\text{H}_4\text{N})\text{Yb}(\text{C}_6\text{H}_5)_2$.¹⁴ These values of the distances have been used to approximate bond distances and calculate Δ_{cf} values for other bis-adducts of $\text{Ln}(\text{BH}_2\text{CH}_3)_2$, $\text{Ln} = \text{Ho}, \text{Yb}$. The results are given in Table III. All of the bis-adducts lie well within the region of stability (0.62 to 0.82).

Lanthanide methyltrihydroborate adducts were also prepared with bidentate bases. When $\text{Yb}(\text{BH}_2\text{CH}_3)_2\cdot 0\text{Et}_2$ and $\text{Ho}(\text{BH}_2\text{CH}_3)_2\cdot 0\text{Et}_2$ are reacted with about 2 equivalents of dme and tmed, respectively, only one equivalent of the base coordinates to the metal. However when $\text{Ho}(\text{BH}_2\text{CH}_3)_2\cdot 0\text{Et}_2$ is reacted with 2 equivalents of either bmte or dmpe, one and a half equivalent of base coordinate to the metal. The stoichiometry of these last two species indicates that they are

dimeric, with two lanthanide ions sharing one bidentate base. The Δ_{cal} values for the dme and tmed base adducts lie within the region of stability if the lanthanide ion is assumed to coordinate to two oxygen or two nitrogen atoms, respectively (Table III). However the dmpe and bmtc adducts lie well above the region of stability if each lanthanide ion is assumed to coordinate to three phosphorous or three sulfur atoms, respectively. This may indicate that perhaps the unshared base functions as a monodentate ligand. The bridging structure hypothesized for $\text{Ho}(\text{BH}_2\text{CH}_2)_3 \cdot 3/2 \text{ dmpe}$ and $\text{Ho}(\text{BH}_2\text{CH}_2)_3 \cdot 3/2 \text{ bmtc}$ may occur because the distance between the two coordinating atoms of the bidentate group is long enough to prevent BH_2CH_2 groups on adjacent Ho atoms from being sterically hindered. Dmpe groups that bridge lanthanide ions have been hypothesized for $\text{Yb}(\text{C}_6\text{Me}_6)_2 \cdot \text{dmpe}$.¹⁵ Dme and tmed in $\text{Yb}(\text{BH}_2\text{CH}_2)_3 \cdot \text{dme}$ and $\text{Ho}(\text{BH}_2\text{CH}_2)_3 \cdot \text{tmed}$, respectively, probably can't bridge lanthanide ions because of their shorter O-O or N-N distances. (The N-N, O-O, P-P, and S-S distances are about 2.71, 3.05, 3.35, and 3.51 Å, respectively.¹⁶) The geometry of $\text{Yb}(\text{BH}_2\text{CH}_2)_3 \cdot \text{dme}$ and $\text{Ho}(\text{BH}_2\text{CH}_2)_3 \cdot \text{tmed}$ is probably pseudo-trigonal bipyramidal, with the bidentate base bridging the axial and equatorial sites. This structure is plausible because like the $\text{U}(\text{BH}_2\text{CH}_2)_3$ bidentate base adducts, the base is coordinated to two sites separated by about 90° . This is a valid comparison since the ionic radii of $\text{Ln}(\text{III})$, $\text{Ln} = \text{Ho, Yb}$; and $\text{U}(\text{IV})$ are roughly equivalent.⁶ The structures of these lanthanide bidentate base adducts cannot be readily deduced from their ^1H NMR spectra. X-ray crystal structure analyses are needed to confirm the hypothesized structures.

Recently Marks and Grynkewich have prepared a series of compounds, LnCp_2BH_4 ($\text{Ln} = \text{Er}, \text{Yb}$).¹ Their IR spectra are compatible with a polymeric structure in which the lanthanide ions are bridged by bidentate tetrahydroborate groups as in CH_3ZnBH_4 .¹⁷ Therefore it was of interest to see whether its analogue, $\text{LnCp}_2\text{BH}_2\text{CH}_3$, also polymerizes. $\text{LuCp}_2\text{BH}_2\text{CH}_3$ is prepared by reacting LuCp_2Cl with LiBH_2CH_3 in THF, followed by vacuum sublimation at -200°C . IR peaks characteristic of tridentate ligation are found at 2100 cm^{-1} (doublet due to B-H bridging stretch) and 1174 cm^{-1} (bridge deformation). Thus it is probably a 9-coordinate monomeric species. Its [caf] based on this hypothetical structure is borderline low (Table V).

In summary most of the lanthanide (III) methyltrihydroborate complexes we have prepared lie within the region of stability, although the mono-adducts have [caf] values that are borderline low. Thus like their actinide counterparts, the lanthanide complexes are primarily ionic in character by Raymond and Pauling's structural definition¹⁸ since bond lengths can be reasonably predicted by adding ionic radii and they generally obey the cone-packing model for steric crowding. However it would seem that according to Li and Fischer's steric model, tris-adducts of lanthanide (III) methyltrihydroborates would be stable although their [caf] values would be on the high side (see Table IV). On reflection one should realize that Li and Fischer's model was based predominantly on LnCp_2L_x ($\text{L} = \text{monodentate base}, x = 1, 2$) complexes.¹³ As the number of monodentate ligands is increased, secondary crowding between individual ligands takes on added importance. Thus the nonexistence of tris-adducts of lanthanide (III) methyltrihydroborates is not that surprising.

Chapter 4 References

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Table I. Selected Interatomic Distances (Å)

Yb(BH ₃ CH ₃),.OEt ₂		Ho(BH ₃ CH ₃),.2py	
Yb-O	2.24(1)	Ho-B(1)	2.484(5)
-B(1)	2.41(2)	-B(3)	2.494(6)
-B(2)	2.45(2)	-B(2)	2.519(5)
-B(3)	2.49(1)	-N(1)	2.535(3)
O-C(6)	1.31(3)	-N(2)	2.354(3)
		B(1)-C(1)	1.599(7)
O-C(4)	1.49(3)	B(2)-C(2)	1.601(7)
B(1)-C(1)	1.64(2)	B(3)-C(3)	1.595(8)
B(2)-C(2)	1.58(2)	N(1)-C(4)	1.337(6)
B(3)-C(3)	1.52(1)	N(1)-C(8)	1.334(6)
C(4)-C(5)	1.46(3)	N(2)-C(9)	1.344(6)
C(6)-C(7)	1.52(3)	N(2)-C(13)	1.338(6)
		C(4)-C(5)	1.366(7)
		C(5)-C(6)	1.374(9)
		C(6)-C(7)	1.359(9)
		C(7)-C(8)	1.380(8)
		C(9)-C(10)	1.388(7)
		C(10)-C(11)	1.374(8)
		C(11)-C(12)	1.369(8)
		C(12)-C(13)	1.377(7)

Table II. Selected Angles (deg)

Yb(BH ₃ CH ₃) ₃ .OEt ₂			Ho(BH ₃ CH ₃) ₃ .2py		
O-Yb	-B(1)	102.9(5)	N(1)-Ho	-N(2)	171.3(1)
O-Yb	-B(2)	103.7(5)	N(1)-Ho	-B(1)	95.5(2)
O-Yb	-B(3)	105.1(5)	N(1)-Ho	-B(2)	88.7(1)
B(1)-Yb	-B(2)	112.9(5)	N(1)-Ho	-B(3)	88.9(2)
B(1)-Yb	-B(3)	114.2(5)	N(2)-Ho	-B(1)	93.1(2)
B(2)-Yb	-B(3)	116.2(5)	N(2)-Ho	-B(2)	88.7(1)
Yb-O	-C(4)	120(1)	N(2)-Ho	-B(3)	86.1(2)
Yb-O	-C(6)	128(1)	B(1)-Ho	-B(2)	118.1(2)
C(4)-O	-C(6)	112(2)	B(1)-Ho	-B(3)	114.5(2)
Yb-B(1)-C(1)		179(1)	B(2)-Ho	-B(3)	127.3(2)
Yb-B(2)-C(2)		178(1)	Ho	-B(1)-C(1)	177.4(4)
Yb-B(3)-C(3)		177(1)	Ho	-B(2)-C(2)	177.9(4)
			Ho	-B(3)-C(3)	176.3(5)
			Ho	-N(1)-C(4)	121.5(3)
			Ho	-N(1)-C(8)	122.1(3)
			Ho	-N(2)-C(9)	123.0(3)
			Ho	-N(2)-C(13)	120.5(3)
			C(4)-N(1)-C(8)		116.5(4)
			C(9)-N(2)-C(13)		116.4(4)

Table III. $\sum$ Caf Calculations for Lanthanide Methyltrihydroborate Base Adducts

Compound	Coordination Number	Coordinating Group/Atom	Distance	Caf	$\sum$ Caf
Yb(BH ₃ CH ₃) ₃ .OEt ₂	10	Yb-BH ₃	2.00 Å	0.169	0.617
		Yb-O	2.24	0.110	
Ho(BH ₃ CH ₃) ₃ .OEt ₂ [*]	10	Ho-BH ₃	2.03	0.167	0.607
		Ho-O	2.27	0.106	
Lu(BH ₃ CH ₃) ₃ .OEt ₂ [*]	10	Lu-BH ₃	1.99	0.170	0.621
		Lu-O	2.23	0.111	
Yb(BH ₃ CH ₃) ₃ .THF [*]	10	Yb-BH ₃	2.00	0.169	0.617
		Yb-O	2.24	0.110	
Ho(BH ₃ CH ₃) ₃ .THF [*]	10	Ho-BH ₃	2.03	0.167	0.607
		Ho-O	2.27	0.106	
Lu(BH ₃ CH ₃) ₃ .THF [*]	10	Lu-BH ₃	1.99	0.170	0.621
		Lu-O	2.23	0.111	
Ho(BH ₃ CH ₃) ₃ .THT [*]	10	Ho-BH ₃	2.03	0.167	0.631
		Ho-S	2.75	0.130	
Ho(BH ₃ CH ₃) ₃ .py [*]	10	Ho-BH ₃	2.03	0.167	0.599
		Ho-N	2.52	0.098	
Ho(BH ₃ CH ₃) ₃ .2py	11	Ho-BH ₃	2.04	0.166	0.690
		Ho-N	2.54	0.096	

(continued)

Table III. $\sum$ Caf Calculations for Lanthanide Methyltrihydroborate Base Adducts (continued)

Compound	Coordination Number	Coordinating Group/Atom	Distance	Caf	$\sum$ Caf
Ho(BH ₃ CH ₃) ₃ .2THF ^a	11	Ho-BH ₃	2.04	0.166	0.706
		Ho-O	2.29	0.104	
Yb(BH ₃ CH ₃) ₃ .2THF ^a	11	Yb-BH ₃	2.01	0.169	0.721
		Yb-O	2.26	0.107	
Ho(BH ₃ CH ₃) ₃ .2THT ^a	11	Ho-BH ₃	2.04 A	0.166	0.754
		Ho-S	2.77	0.128	
Yb(BH ₃ CH ₃) ₃ .dme ^a	11	Yb-BH ₃	2.01	0.169	0.701
		Yb-O	2.36	0.097	
Ho(BH ₃ CH ₃) ₃ .tmed ^a	11	Ho-BH ₃	2.04	0.166	0.682
		Ho-N	2.59	0.092	
Ho(BH ₃ CH ₃) ₃ .3/2dmpe ^b	12	Ho-BH ₃	2.06	0.164	0.858
		Ho-P	2.90	0.122	
Yb(BH ₃ CH ₃) ₃ .3/2dmpe ^b	12	Yb-BH ₃	2.03	0.167	0.876
		Yb-P	2.87	0.125	
Ho(BH ₃ CH ₃) ₃ .3/2bmte ^b	12	Ho-BH ₃	2.06	0.164	0.840
		Ho-S	2.89	0.116	

a) Assuming coordination of 2 oxygen or 2 nitrogen atoms to metal.

b) Assuming coordination of 3 phosphorus or 3 sulfur atoms to metal.

Table IV. $\sum \text{Caf}$ Calculations for Hypothetical Lanthanide
Methyltrihydroborate Base Adducts

Compound	Coordination Number	Coordinating Group/Atom	Distance	Caf	$\sum \text{Caf}$
$\text{Sm}(\text{BH}_2\text{CH}_3)_3 \cdot \text{OEt}_2$	10	Sm-BH ₂	2.09 Å	0.161	0.583
		Sm-O	2.33	0.100	
$\text{Ho}(\text{BH}_2\text{CH}_3)_3 \cdot 3\text{py}$	12	Ho-BH ₂	2.06	0.164	0.777
		Ho-N	2.56	0.095	
$\text{Ho}(\text{BH}_2\text{CH}_3)_3 \cdot 3\text{THF}$	12	Ho-BH ₂	2.06	0.164	0.798
		Ho-O	2.31	0.102	
$\text{Yb}(\text{BH}_2\text{CH}_3)_3 \cdot 3\text{THF}$	12	Yb-BH ₂	2.03	0.167	0.819
		Yb-O	2.27	0.106	

Table V. $\sum \text{Caf}$ Calculations for $\text{LuCp}_2\text{BH}_3\text{CH}_3$

Coordination Number	Coordinating Group/Atom	Distance	Caf	$\sum \text{Caf}$
9	Lu-Cp	2.33 Å	0.221	0.614
	Lu-BH ₃	1.97	0.172	

Fig. 1. ORTEP drawing of $\text{Yb}(\text{BH}_2\text{CH}_3)_3 \cdot \text{OEt}_2$.

XBL 8410-4298

Fig. 2. ORTEP drawing of $\text{Ho}(\text{BH}_2\text{CH}_2)_2 \cdot 2\text{py}$.

Chapter 5

EXPERIMENTAL DETAILSGeneral

Infrared spectra were recorded on a Perkin-Elmer IR-238 spectrophotometer as Nujol and fluorolube mulls between KBr windows and calibrated with polystyrene film. Nuclear magnetic spectra were recorded on a JEOL FX 90Q 90-MHz. FT spectrometer and referenced to Me₄Si. Samples were prepared in benzene-d₆ and toluene-d₈. Melting points were determined in sealed argon-filled capillaries and are uncorrected. Elemental analyses were conducted by the analytical laboratories of the University of California, Berkeley.

All manipulations were carried out under an atmosphere of argon on a Schlenk line or in a dry box (Vacuum Atmospheres). Sublimation and trap-to-trap distillation were carried out on a vacuum line equipped with an oil diffusion pump.

Reagent grade diethyl ether, tetrahydrofuran (THF), toluene, and 1,2-dimethoxyethane (dme) were distilled from sodium benzophenone ketyl under argon. Dimethyl ether was purified by passing it through a -78°C trap into a -196°C trap. Chlorobenzene, hexane, tetrahydrothiophene (THT), and dimethyl sulfide were dried over CaH₂ and distilled under argon before use. Pyridine and N,N,N',N'-tetramethylethylenediamine (tmed) were dried over NaOH, and then BaO before use. Ammonia was distilled from liquid NH₃ that was treated with clean Na until a blue solution formed. The bidentate bases 1,2-dimethylphosphinoethane (dmpe)¹ and bis(1,2-methylthio)ethane (bmte)² were prepared according

to the literature and dried over KOH and CaH_2 , respectively.

Benzene- d_6 and toluene- d_8 were degassed and dried over Na.

LiBH_4CH_3 was prepared according to the procedure of Wartik and Schlesinger.¹ $\text{B}(\text{CH}_3)_3$ was prepared by modifying the procedure for the synthesis of $\text{B}(\text{Et})_3$.² In 40 mL of dry mineral oil, 7.2 g (0.10 mol) of $\text{Al}(\text{CH}_3)_3$ was dissolved. A 3.4 g quantity (0.033 mol) of $\text{B}(\text{OCH}_3)_3$ was condensed onto the $\text{Al}(\text{CH}_3)_3$ at -196°C . The mixture was opened to a closed volume of ~1 L and slowly warmed to room temperature. The pressure was monitored with a manometer. After the reaction was completed, the crude $\text{B}(\text{CH}_3)_3$ obtained was pumped into a -196°C trap. This procedure was repeated twice for a total addition of 10.3 g (0.10 mol) of $\text{B}(\text{OCH}_3)_3$. The combined $\text{B}(\text{CH}_3)_3$ collected was purified by passing it through a -132°C trap into a -196°C trap. A yield of 2.1 g (38%) of pure $\text{B}(\text{CH}_3)_3$ was obtained.

NaCp was prepared according to the literature.³ LuCp_2Cl was prepared by using the method of Dubeck et al.⁴ All lanthanide chlorides were prepared according to the procedure of Taylor and Carter.⁵ ZrCl_4 was sublimed under vacuum at 360°C for one day, and UCl_4 and ThCl_4 dried with SOCl_2 and washed with CH_2Cl_2 before use. Cerium (IV) isopropoxide was prepared according to the procedure of Bradley et al.⁶ $\text{Th}(\text{BH}_4)_4$ was prepared by the method of Hoekstra and Katz.⁷

Experimental Procedures for Chapter 2

Preparation of Zr(IV) Methyltrihydroborate

To 0.29 g (8.1 mmol) of LiBH_4CH_3 , were added 0.47 g (2.0 mmol) of ZrCl_4 and 15 mL of chlorobenzene. The mixture was stirred at 40°C for 48 hours under argon and the solvent removed in vacuo to near dryness. $\text{Zr}(\text{BH}_4\text{CH}_3)_4$ was sublimed with pumping at 50°C onto a 0°C cold finger for several hours. A yield of 0.28 g (68%) of colorless crystals of $\text{Zr}(\text{BH}_4\text{CH}_3)_4$ that melt at $90-2^\circ\text{C}$ was recovered. Calculated for $\text{C}_4\text{H}_{12}\text{B}_4\text{Zr}$: C, 23.24; H, 11.70. Found: C, 23.36; H, 11.59. ^1H NMR (25°C , PhH-d_6): δ 0.25 (12H, s), $^{10}\text{CH}_3$; 1.43 (12H, quart), BH_4 . IR Data: 2950cm, 2140cm, 2080s, 1310s, 1230s, 1090cm, 1020cm, 1000cm, 890cm.

Preparation of Hf(IV) Methyltrihydroborate

To 0.80 g (22 mmol) of LiBH_4CH_3 , were added 1.80 g (5.6 mmol) of HfCl_4 and ~20 mL of chlorobenzene. The mixture was stirred for 18 hours and the solvent removed in vacuo to near dryness. $\text{Hf}(\text{BH}_4\text{CH}_3)_4$ was sublimed with pumping at 50°C onto a 0°C cold finger for several hours. A yield of 0.90 g (55%) of colorless crystals of $\text{Hf}(\text{BH}_4\text{CH}_3)_4$ that melt at $97-8^\circ\text{C}$ was recovered. Calculated for $\text{C}_4\text{H}_{12}\text{B}_4\text{Hf}$: C, 16.34; H, 8.23. Found: C, 16.81; H, 8.58. ^1H NMR Data (32°C , PhH-d_6): δ 0.18 (12H, s), $^{10}\text{CH}_3$; 2.31 (12H, quart), BH_4 . IR Data: 2950cm, 2180cm, 2090s, 1320s, 1255s, 1100s, 1000s, 810cm.

Preparation of U(IV) Methyltrihydroborate

To 0.30 g (8.4 mmol) of LiBH_4CH_3 , were added 0.80 g (2.1 mmol) of UCl_4 and 20 mL of chlorobenzene. The mixture was stirred for 2 days under argon and then the solvent removed in vacuo to near dryness. $\text{U}(\text{BH}_4\text{CH}_3)_4$ was sublimed with pumping at 50°C onto a 0°C cold finger for several hours. A yield of 0.41 g (55%) of violet crystals of

$\text{U}(\text{BH}_2\text{CH}_3)_4$, that melt at $72-4^\circ\text{C}$ was obtained. Calculated for $\text{C}_6\text{H}_{12}\text{B}_4\text{U}$: C, 13.59; H, 6.84. Found: C, 13.93; H, 7.08. ^1H NMR (25°C , $\text{PhCH}_3\text{-d}_6$): δ 15.79 (12h, s), CH_3 ; 156.43 (12H, s), BH_2 . IR Data: 2950m, 2130m, 2050s, 1310s, 1270s, 1080s, 1020m, 1000m, 910m.

Preparation of Th(IV) Methyltrihydroborate

To 0.50 g (14.0 mmol) of LiBH_2CH_3 , were added 1.31 g (3.5 mmol) of ThCl_4 and 20 mL of chlorobenzene. The mixture was stirred at 40°C for 48 hours under argon and the solvent removed in vacuo to near dryness. $\text{Th}(\text{BH}_2\text{CH}_3)_4$ was sublimed with pumping at 50°C onto a 0°C cold finger for several hours. A yield of 0.84 g (69%) of colorless crystals of $\text{Th}(\text{BH}_2\text{CH}_3)_4$, that melt at $62-3^\circ\text{C}$ was recovered. Calculated for $\text{C}_6\text{H}_{12}\text{B}_4\text{Th}$: C, 13.83; H, 6.96. Found: C, 13.90; H, 6.85. ^1H NMR Data (25°C , PhH-d_6): δ 0.11 (12H, quart), CH_3 ; 3.43 (12H, quart), BH_2 . IR Data: 2950m, 2165m, 2070s, 1310s, 1260s, 1090m, 1015m, 990m, 870m.

Preparation of Np(IV) Methyltrihydroborate

To 50 mg (1.4 mmol) of LiBH_2CH_3 , were added 135 mg (0.351 mmol) of NpCl_4 and 20 mL of chlorobenzene. The mixture was stirred for 15 hours under argon and the solvent removed in vacuo to dryness. $\text{Np}(\text{BH}_2\text{CH}_3)_4$ was sublimed with pumping at room temperature into a -196°C trap for 12 hours. A yield of 10 mg (8%) of dark green crystals of $\text{Np}(\text{BH}_2\text{CH}_3)_4$ was obtained. Because of the low yield and the radioactivity of the product, no elemental analysis, ^1H NMR spectrum, or IR spectrum was taken.

Experimental Procedures for Chapter 3

Preparation of $[\text{Th}(\text{BH}_2\text{CH}_3)_4]_2\cdot\text{OEt}_2$

To 1.25 g (3.3 mmol) of ThCl_4 , 0.49 g (13.7 mmol) of LiBH_2CH_3 , and 20 mL diethyl ether were added, and the mixture stirred for 24 hours

under argon. The solvent was removed in vacuo to near dryness. The residue remaining was sublimed with pumping at room temperature into a 0°C trap over a 12 hour period. A yield of 0.52 g (37%) of an oil that crystallized after several weeks was obtained. Its ^1H NMR indicates it has the empirical formula, $\text{Th}(\text{BH}_2\text{CH}_2)_2 \cdot 1/2 \text{OEt}_2$. An X-ray crystal structure reveals it is a dimer. Because the diethyl ether could not be completely removed from the sublimate, no satisfactory m. p. and elemental analysis could be obtained. ^1H NMR (25°C , PhH-d_6): δ 0.15 (24H, quart), BH_2CH_2 ; 0.73 (6H, trip), CH_2CH_2 ; 3.28 (4H, quart), CH_2 ; 3.50 (24H, quart), BH_2 . IR Data: 2950m, 2160m 2060s, 1310s, 1250s, 1090s, 990m, 910m, 720m.

Preparation of $\text{Th}(\text{BH}_2\text{CH}_2)_2 \cdot 2\text{THF}$

$\text{Th}(\text{BH}_2\text{CH}_2)_2$ (0.50 g, 1.4 mmol) was dissolved in about 15 mL of THF. The solution was stirred for about half an hour under argon and then the solvent removed in vacuo to dryness. The white residue was transferred into a sublimator and sublimed at 100°C for 12 hours under vacuum. A yield of 0.54 g (76%) white $\text{Th}(\text{BH}_2\text{CH}_2)_2 \cdot 2\text{THF}$ was collected. M. p. = $155-7^{\circ}\text{C}$. Calculated for $\text{C}_{12}\text{H}_{20}\text{B}_2\text{O}_2\text{Th}$: C, 29.31; H, 8.20. Found: C, 29.29; H, 8.06. ^1H NMR (25°C , PhH-d_6): δ 0.51 (12H, quart), CH_2 ; 0.99 (8H, mult), $\text{CH}_2\text{CH}_2\text{O}$; 3.47 (12H, quart), BH_2 ; 3.80 (8H, mult), $\text{CH}_2\text{CH}_2\text{O}$. IR Data: 2950m, 2230m, 2150s, 2080s, 1305s, 1230s, 1105m, 1075m, 1040m, 1000s, 950m, 925m, 915w, 850s, 830s, 725w, 670m.

Preparation of $[\text{Th}(\text{BH}_2\text{CH}_2)_2 \cdot \text{OMe}_2]_2$

To 0.42 g (1.2 mmol) $\text{Th}(\text{BH}_2\text{CH}_2)_2$, 20 mL of dimethyl ether was condensed in at -196°C . It was warmed to -78°C and stirred for several hours. After removal of solvent and sublimation by pumping at room

temperature into a 0 °C trap for 12 hours, 0.29 g (61% yield) was recovered. Its elemental analysis and ^1H NMR were consistent with the empirical formula, $\text{Th}(\text{BH}_2\text{CH}_2)_2\text{OME}_2$. CI mass spectrometry suggests it is a dimer. M. p. = 66-7 °C. Calculated for $\text{C}_{12}\text{H}_{10}\text{B}_2\text{O}_2\text{Th}_2$: C, 18.31; H, 7.68. Found: C, 18.21; H, 7.89. ^1H NMR (25 °C, PhH-d_6): δ 0.27 (24H, quart), BH_2CH_2 ; 2.90 (12H, s), OCH_3 ; 3.50 (24H, quart), BH_2 . IR Data: 2950m, 2190m, 2090s, 1305s, 1250s, 1155m, 1095s, 1040m, 905m, 890m, 720m.

Preparation of $[\text{Th}(\text{BH}_2\text{CH}_2)_2\text{THF}]_2$

To 0.27 g (0.78 mmol) $\text{Th}(\text{BH}_2\text{CH}_2)_2$, dissolved in 20 mL hexane, 0.063 mL (0.78 mmol) THF was added with stirring. It was stirred for several hours, pumped dry, and sublimed at 100 °C in vacuo. A yield of 0.25 g (85%) of colorless crystals was recovered that melts at 112-4 °C. Its elemental analysis and ^1H NMR indicate it has the empirical formula, $\text{Th}(\text{BH}_2\text{CH}_2)_2\text{THF}$. An X-ray crystal structure reveals it is a dimer. Calculated for $\text{C}_{12}\text{H}_{12}\text{B}_2\text{O}_2\text{Th}_2$: C, 22.90; H, 7.69. Found: C, 23.06; H, 7.77. ^1H NMR (25 °C, PhH-d_6): δ 0.36 (24H, quart), BH_2CH_2 ; 0.99 (8H, mult), $\text{CH}_2\text{CH}_2\text{O}$; 3.44 (24H, quart), BH_2 ; 3.67 (8H, mult), $\text{CH}_2\text{CH}_2\text{O}$. IR Data: 2950m, 2200m, 2100s, 1305s, 1245s, 1085m, 1005m, 970m, 915m, 845s, 720w, 670w.

Preparation of $\text{U}(\text{BH}_2\text{CH}_2)_2\text{2THF}$

To 0.75 g (2.0 mmol) UCl_4 and 0.30 g (8.4 mmol) LiBH_2CH_3 , about 5 mL of THF was added. It was stirred for 12 hours. The THF was pumped off and the yellow brown residue transferred to a sublimator. It was sublimed at 75 °C. A yield of 0.17 g (17%) of emerald crystals was obtained. Its elemental analysis and ^1H NMR were consistent with the formula $\text{U}(\text{BH}_2\text{CH}_2)_2\text{2THF}$. M. p. = 95-8 °C. Calculated for $\text{C}_{12}\text{H}_{10}\text{B}_2\text{O}_2\text{U}$:

C, 28.96; H, 8.10. Found: C, 28.92; H, 7.87. ^1H NMR Data (32°C , PhH-d_6 , 1.2×10^{-3} g/mL): δ 5.51 (8H, s), $\text{CH}_2\text{CH}_2\text{O}$; 10.63 (12H, s), CH_3 ; 11.08 (8H, s), $\text{CH}_2\text{CH}_2\text{O}$; 127.34 (12H, doub), BH_3 . IR Data: 2950m, 2230m, 2140s, 2080s, 1340m, 1300s, 1225s, 1100m, 1065m, 1040m, 1010s, 950w, 925m, 850s, 835m, 735m, 670m.

Preparation of $\text{Th}(\text{BH}_3\text{CH}_3)_2 \cdot 2\text{py}$

$\text{Th}(\text{BH}_3\text{CH}_3)_4$ (0.55 g, 1.6 mmol) was dissolved in 20 mL hexane, to which 0.26 mL (3.2 mmol) of pyridine was added dropwise with stirring, giving a white ppt. The solvent was removed in vacuo, and the white residue transferred to a sublimator. It was sublimed at 125°C under vacuum for 12 hours, giving 0.56 g (70% yield) of $\text{Th}(\text{BH}_3\text{CH}_3)_2 \cdot 2\text{py}$. M. p. = $161^\circ\text{C}(\text{dec})$. Calculated for $\text{C}_{14}\text{H}_{24}\text{B}_2\text{N}_2\text{Th}$: C, 33.18; H, 6.78; N, 5.53. Found: C, 33.05; H, 6.61; N, 5.39. ^1H NMR (25°C , PhH-d_6): δ 0.53 (12H, quart), CH_3 ; 3.85 (12H, quart), BH_3 ; 6.40 (4H, mult), CHCHN ; 6.65 (2H, mult), CHCHCHN ; 8.78 (4H, mult), CHN . IR Data: 2950m, 2220m, 2140s, 1595m, 1440s, 1300s, 1230s, 1150w, 1095w, 1070m, 1065m, 1040m, 1010w, 1000m, 950m, 750m, 720w, 685m, 620m.

Preparation of $\text{U}(\text{BH}_3\text{CH}_3)_2 \cdot 2\text{py}$

$\text{U}(\text{BH}_3\text{CH}_3)_4$ (0.55 g, 1.6 mmol) was dissolved in 20 mL hexane, to which 0.26 mL (3.2 mmol) of pyridine was added dropwise with stirring, giving a light green ppt. The solvent was removed in vacuo, and the residue transferred to a sublimator. It was sublimed under vacuum at 100°C for 12 hours. A yield of 0.49 g (62%) of deep green crystals of $\text{U}(\text{BH}_3\text{CH}_3)_2 \cdot 2\text{py}$ was obtained. M. p. = $106-8^\circ\text{C}(\text{dec})$. Calculated for $\text{C}_{14}\text{H}_{24}\text{B}_2\text{N}_2\text{U}$: C, 32.86; H, 6.70; N, 5.48. Found: C, 33.17; H, 6.67; N, 5.34. ^1H NMR Data (30°C , PhH-d_6 , saturated): δ -17.17 (4H, s), CHN ; -3.54 (4H, s), CHCHN ; 1.02 (2H, s), CHCHCHN ; 20.57 (12H, s), CH_3 ;

184.32 (12H, s), BH_3 . IR Data: 2950m, 2310w, 2120s, 1595m, 1485w, 1435s, 1300s, 1220s, 1150w, 1100m, 1065m, 1040m, 1005w, 1000m, 955m, 750s, 690s, 620m.

Preparation of $\text{Th}(\text{BH}_3\text{CH}_3)_4 \cdot \text{dme}$

$\text{Th}(\text{BH}_3\text{CH}_3)_4$ (0.22 g, 0.63 mmol) was dissolved in 10 mL dme. The solution was stirred for about half an hour and then the solvent removed in vacuo to dryness. The white residue was transferred into a sublimator and sublimed at 125 °C under vacuum for 12 hours. A yield of 0.13 g (47%) of $\text{Th}(\text{BH}_3\text{CH}_3)_4 \cdot \text{dme}$ was obtained. M. p. = 180-2 °C(dec). Calculated for $\text{C}_8\text{H}_{14}\text{B}_4\text{O}_2\text{Th}$: C, 21.95; H, 7.83. Found: C, 22.08; H, 7.57. ^1H NMR (25 °C, $\text{PhH}-d_6$): δ 0.44 (12H, quart), BH_3CH_3 ; 2.70 (4H, s), CH_2 ; 2.96 (6H, s), OCH_3 ; 3.51 (12H, quart), BH_3 . IR Data: 2950m, 2190m, 2100s, 1300s, 1230s, 1080s, 1035s, 950m, 850s, 820m, 720w, 660m.

Preparation of $\text{U}(\text{BH}_3\text{CH}_3)_4 \cdot \text{dme}$

A quantity of 0.25 g (0.71 mmol) $\text{U}(\text{BH}_3\text{CH}_3)_4$ was dissolved in 10 mL of dme. The solution was stirred for 24 hours and the solvent removed in vacuo to dryness. The blue green residue was transferred into a sublimator and sublimed under vacuum at 125 °C. A yield of 0.17 g (54%) of blue green, finely crystalline $\text{U}(\text{BH}_3\text{CH}_3)_4 \cdot \text{dme}$ was recovered. M. p. = 141-2 °C(dec). Calculated for $\text{C}_8\text{H}_{14}\text{B}_4\text{O}_2\text{U}$: C, 21.66; H, 7.72. Found: C, 21.60; H, 7.75. ^1H NMR Data (25 °C, PhCH_3-d_6): δ -33.84 (6H, s), OCH_3 ; -27.57 (4H, s), CH_2 ; 21.43 (12H, s), BH_3CH_3 ; 194.25 (12H, s), BH_3 . IR Data: 2950m, 2190m, 2100s, 1300s, 1230s, 1080s, 1035s, 950m, 850s, 820m, 720w, 660m.

Preparation of $\text{Th}(\text{BH}_3\text{CH}_3)_4 \cdot 2\text{NH}_3$

$\text{Th}(\text{BH}_3\text{CH}_3)_4$ (0.31 g, 0.89 mmol) was dissolved in 10 mL hexane. Excess NH_3 was condensed in at -78 °C, a white ppt. forming immediately.

The reaction mixture was allowed to stir at -78°C for several hours. Hexane and excess NH_3 were pumped off. The white residue left behind was sublimed at 75°C under vacuum. A yield of 0.14 g (43%) $\text{Th}(\text{BH}_2\text{CH}_3)_4 \cdot 2\text{NH}_3$ was obtained. M. p. = $111-2^{\circ}\text{C}(\text{dec})$. Calculated for $\text{C}_6\text{H}_{12}\text{B}_4\text{N}_2\text{Th}$: C, 12.59; H, 7.93; N, 7.34. Found: C, 12.71; H, 6.86; N, 6.27. ^1H NMR Data (25°C , $\text{PhH}-d_6$): δ 0.43 (12H, quart), CH_3 ; 0.51 (6H, s), NH_3 ; 2.78 (12H, quart), BH_2 . IR Data: 3300m, 3270s, 2950m, 2210m, 2135s, 2080s, 1305s, 1260s, 1235s, 1210s, 1085s, 950s, 800s, 720m, 595m, 525m.

Preparation of $\text{U}(\text{BH}_2\text{CH}_3)_4 \cdot 2\text{NH}_3$

$\text{U}(\text{BH}_2\text{CH}_3)_4$ (0.45 g, 1.3 mmol) was dissolved in 5 mL hexane. Excess NH_3 was condensed in at -78°C , forming a light green ppt. It was stirred at -78°C for 6 hours. The excess NH_3 and hexane were pumped off and the residue sublimed in vacuo at 50°C and collected on a 0°C cold finger. A yield of 0.26 g (53%) of green $\text{U}(\text{BH}_2\text{CH}_3)_4 \cdot 2\text{NH}_3$ was obtained. M. p. = $90-1^{\circ}\text{C}(\text{dec})$. Calculated for $\text{C}_6\text{H}_{12}\text{B}_4\text{N}_2\text{U}$: C, 12.40; H, 7.80; N, 7.23. Found: C, 12.47; H, 7.25; N, 7.11. ^1H NMR Data (32°C , $\text{PhH}-d_6$, 2.8×10^{-2} g/mL): δ -118.04 (6H, s), NH_3 ; 20.02 (12H, s), CH_3 ; 175.26 (12H, doub), BH_2 . IR Data: 3300m, 3270m, 2950m, 2100m, 2060s, 2030s, 1305s, 1230s, 1070s, 950s, 765m, 720m, 580w, 530m.

Preparation of $\text{Th}(\text{BH}_2\text{CH}_3)_4 \cdot \text{tmed}$

To 0.33 g (0.95 mmol) of $\text{Th}(\text{BH}_2\text{CH}_3)_4$ dissolved in 15 mL hexane, about 0.15 mL (0.95 mmol) of tmed was added, a white ppt. forming. It was stirred for an hour and then the solvent removed in vacuo. The residue left behind was sublimed at 100°C under vacuum, giving 0.23 g (56% yield) of white $\text{Th}(\text{BH}_2\text{CH}_3)_4 \cdot \text{tmed}$. M. p. = $177-80^{\circ}\text{C}(\text{dec})$. Calculated for $\text{C}_{12}\text{H}_{24}\text{B}_4\text{N}_2\text{Th}$: C, 25.90; H, 8.70; N, 6.04. Found: C,

26.02; H, 8.93; N, 6.04. ^1H NMR Data (25°C , PhH-d_6): δ 0.31 (12H, quart), BH_2CH_2 ; 1.78 (4H, s), CH_2 ; 2.08 (12H, s), NCH_2 ; 3.60 (12H, quart), BH_2 . IR Data: 2950m, 2150s, 1300m, 1225m, 1080s, 1035m, 1010m, 1000m, 940s, 910m, 790s, 765m, 720w, 590m, 505m, 480m, 455m.

Preparation of $\text{U}(\text{BH}_2\text{CH}_2)_4\cdot\text{tmed}$

To 0.23 g (0.65 mmol) of $\text{U}(\text{BH}_2\text{CH}_2)_4$, dissolved in 15 mL hexane, 0.10 mL (0.65 mmol) of tmed was added, a yellow green ppt. forming. It was stirred for about 30 minutes and pumped dry. The residue was dissolved in 10 mL toluene and the solution filtered, reduced in volume to 3 mL, and cooled at -20°C . Yellow green crystals were isolated and washed with cold (-78°C) ether. A yield of 0.12 g (39%) of yellow green $\text{U}(\text{BH}_2\text{CH}_2)_4\cdot\text{tmed}$ was recovered. M. p. = $113-5^\circ\text{C}(\text{dec})$. Calculated for $\text{C}_{10}\text{H}_{20}\text{B}_4\text{N}_2\text{U}$: C, 25.57; H, 8.58; N, 5.96. Found: C, 25.44; H, 8.67; N, 5.89. ^1H NMR Data (25°C , $\text{PhCH}_3\text{-d}_6$): δ -29.64 (4H, s), CH_2 ; -16.74 (12H, s), NCH_2 . IR Data: 2950m, 2390m, 2300m, 2210s, 2150s, 2110s, 2040m, 1880w, 1300s, 1280w, 1230s, 1125m, 1110w, 1095w, 1070m, 1035w, 1010m, 1000m, 960w, 945m, 915w, 860w, 790s, 770m, 720w, 680w, 620w, 595w, 495w, 475w, 455w.

Preparation of $[\text{Th}(\text{BH}_2\text{CH}_2)_4\cdot\text{SMe}_2]_2$

$\text{Th}(\text{BH}_2\text{CH}_2)_4$ (0.30 g, 0.86 mmol) was dissolved in 15 mL SMe_2 . After stirring for 30 minutes, it was pumped dry at 50°C for several hours. The residue was transferred into a sublimator and sublimed in vacuo at 75°C . A yield of 0.07 g (~20%) was obtained. Its elemental analysis and ^1H NMR is consistent with the empirical formula, $\text{Th}(\text{BH}_2\text{CH}_2)_4\cdot\text{SMe}_2$. CI mass spectrometry suggests it is a dimer. M. p. = $114-7^\circ\text{C}$. Calculated for $\text{C}_8\text{H}_{16}\text{B}_4\text{S}_2\text{Th}$: C, 17.59; H, 7.38; S, 7.83. Found: C, 17.67; H, 7.58; S, 7.87. ^1H NMR Data (25°C , PhH-d_6): δ

0.24 (24H, quart), BH_2CH_2 ; 1.83 (12H, s), SCH_2 ; 3.50 (24H, quart), BH_2 .
 IR Data: 2950m, 2190m, 2100s, 1420w, 1305s, 1240s, 1090m, 1030w, 985m, 895m, 850w, 800w, 720w, 675w.

Preparation of $\text{Th}(\text{BH}_2\text{CH}_2)_2 \cdot 2\text{THT}$

$\text{Th}(\text{BH}_2\text{CH}_2)_2$ (0.29 g, 0.83 mmol) was dissolved in 10 mL toluene. About 0.2 mL (2.3 mmol) of THT was added with stirring. It was concentrated to 2 mL and cooled at -20°C . Large, rock-like crystals were obtained. The supernate was removed and the crystals washed with cold (-78°C) hexane. A yield of 0.12 g (27%) was obtained. M. p. = $102-3^\circ\text{C}$. Calculated for $\text{C}_{12}\text{H}_{10}\text{B}_4\text{S}_2\text{Th}$: C, 27.51; H, 7.70; S, 12.24. Found: C, 27.97; H, 7.66; S, 11.86. ^1H NMR Data (25°C , PhH-d_6): δ 0.35 (12H, quart), BH_2CH_2 ; 1.35 (8H, mult), $\text{CH}_2\text{CH}_2\text{S}$; 2.85 (8H, mult), $\text{CH}_2\text{CH}_2\text{S}$; 3.46 (12H, quart), BH_2 . IR Data: 2950m, 2190s, 2100s, 1300s, 1230s, 1090s, 1030w, 955m, 880m, 810m, 720w, 670m.

Preparation of $[\text{Th}(\text{BH}_2\text{CH}_2)_2 \cdot \text{THT}]_2$

To 0.30 g (0.86 mmol) $\text{Th}(\text{BH}_2\text{CH}_2)_2$ dissolved in 15 mL hexane, 0.07 mL (0.8 mmol) THT was added with stirring, a white ppt. forming. It was stirred for several hours and then pumped dry. The residue was crystallized from 8 mL toluene at -20°C . The crystals were washed with cold (-78°C) ether. A yield of 0.05 g (~10%) was obtained. ^1H NMR and analysis indicate it has the empirical formula, $\text{Th}(\text{BH}_2\text{CH}_2)_2 \cdot \text{THT}$. CI mass spectrometry suggests it is a dimer. M. p. = $145-8^\circ\text{C}$. Calculated for $\text{C}_{12}\text{H}_{10}\text{B}_4\text{S}_2\text{Th}_2$: C, 22.06; H, 7.40; S, 7.4. Found: C, 21.79; H, 7.08; S, 6.8. ^1H NMR Data (25°C , PhH-d_6): δ 0.28 (24H, quart), BH_2CH_2 ; 1.28 (8H, mult), $\text{CH}_2\text{CH}_2\text{S}$; 2.80 (8H, mult), $\text{CH}_2\text{CH}_2\text{S}$; 3.50 (24H, quart), BH_2 . IR Data: 2950m, 2190m, 2100s, 1305s, 1240s, 1085s, 955w, 880m, 805m, 720w, 660w.

Preparation of $[U(BH_3CH_3)_2]_2 \cdot THT]_2$

$U(BH_3CH_3)_2$ (0.32 g, 0.91 mmol) was dissolved in hexane. About 0.16 mL (1.8 mmol) THT was added. After stirring for a couple of hours, the solution was filtered and pumped dry. The residue was dissolved in toluene and the solution concentrated to 3 mL and cooled at $-20^\circ C$. Dark green crystals were obtained, which were washed with cold ($-78^\circ C$) hexane. A yield of 0.08 g (20%) was obtained. Its elemental analysis and 1H NMR indicate it has the empirical formula, $U(BH_3CH_3)_2 \cdot THT$. An X-ray crystal structure reveals it is a dimer. M. p. = $92-4^\circ C$. Calculated for $C_{16}H_{24}B_4S_2U_2$: C, 21.76; H, 7.30; S, 7.26. Found: C, 21.76; H, 7.17; S, 6.89. 1H NMR Data ($30^\circ C$, $PhCH_3-d_6$, 1.2×10^{-2} g/mL): δ 3.45 (8H, s), CH_2CH_2S ; 8.77 (8H, s), CH_2CH_2S ; 13.81 (24H, s), CH_3 ; 145.17 (24H, doub), BH_3 . IR Data: 2950m, 2160s, 2080s, 1300s, 1240s, 1070m, 1030w, 960w, 890w, 800m, 725m, 665w.

Preparation of $Th(BH_3CH_3)_2 \cdot bmtc$

To 0.27 g (0.78 mmol) $Th(BH_3CH_3)_2$, dissolved in 15 mL hexane, 0.10 mL (0.8 mmol) bmtc was added with stirring, a white ppt. forming. The solvent was pumped off and the residue dissolved in toluene and the solution concentrated to 3 mL and cooled at $-20^\circ C$. Colorless crystals were obtained, which were washed with ether. A yield of 0.14 g (38%) was obtained. M. p. = $160-3^\circ C$ (dec). Calculated for $C_8H_{12}B_2S_2Th$: C, 20.46; H, 7.30; S, 13.65. Found: C, 20.94; H, 7.29; S, 13.75. 1H NMR Data ($25^\circ C$, $PhH-d_6$): δ 0.37 (12H, quart), BH_3CH_3 ; 1.71 (6H, s), SCH_3 ; 2.10 (4H, s), CH_2 ; 3.44 (12H, quart), BH_3 . IR Data: 2950m, 2200s, 2110s, 1410w, 1405w, 1300s, 1260w, 1235s, 1085s, 1020m, 965m, 900m, 800w, 720m.

Preparation of $U(BH_3CH_3)_2 \cdot bmtc$

To 0.30 g (0.85 mmole) $U(BH_3CH_3)_2$, dissolved in 15 mL hexane, 0.10 mL (0.85 mmol) of bmtc was added with stirring. After stirring for 10 minutes, the hexane was pumped off. The residue was redissolved in toluene; the solution was filtered and pumped down to 3 mL. It was cooled at $-20^\circ C$. Deep green crystals were isolated and washed with cold ($-78^\circ C$) ether. A yield of 0.23 g (57%) of deep green $U(BH_3CH_3)_2 \cdot bmtc$ was obtained. M. p. = $134-6^\circ C$ (dec). Calculated for $C_8H_{12}B_2S_2U$: C, 20.20; H, 7.20; S, 13.48. Found: C, 20.60; H, 7.32; S, 13.39. 1H NMR Data ($25^\circ C$, $PhH-d_6$): δ -12.28 (4H, s), CH_2 ; -6.22 (6H, s), SCH_3 ; 18.78 (12H, s), BH_3CH_3 ; 178.0 (12H, s), BH_3 . IR Data: 2950m, 2180s, 2100s, 1430w, 1410w, 1405w, 1300s, 1260w, 1235s, 1075s, 1030m, 960s, 900w, 880w, 840w, 720w.

Preparation of $U(BH_3CH_3)_2 \cdot dmpe$ ¹²

To 0.24 g (0.68 mmol) $U(BH_3CH_3)_2$, dissolved in 20 mL pentane, 0.11 mL (0.66 mmol) of dmpe was added with stirring, giving a green ppt. The solution was stirred for 5 minutes and then pumped to dryness. The green residue was dissolved in 10 mL toluene, and the solution filtered and concentrated to 3 mL. It was cooled at $-20^\circ C$. Within 3 hours, green crystals had formed. They were washed with 2 mL cold ether. A yield of 0.16 g (48%) of $U(BH_3CH_3)_2 \cdot dmpe$ was obtained. M. p. = $131-2^\circ C$ (dec). Calculated for $C_{10}H_{16}B_2P_2U$: C, 23.85; H, 8.01. Found: C, 23.42; H, 8.25. 1H NMR Data ($25^\circ C$, $PhH-d_6$): δ -10.3 (4H, s), CH_2 ; -5.56 (12H, s), PCH_3 . IR Data: 2950m, 2100s, 1415w, 1300m, 1285m, 1220s, 1075s, 940s, 925s, 890m, 865m, 830m, 795m, 735m, 705m, 645m.

Preparation of $U(BH_3CH_3)_2 \cdot 2dmpe$

To 0.12 g (0.24 mmol) $U(BH_3CH_3)_2 \cdot dmpe$ dissolved in 10 mL toluene, 0.40 mL (2.4 mmol) $dmpe$ was added with stirring. The solution was heated at $80^\circ C$ for several hours, during which it turned deep brown. After cooling to room temperature, the toluene was pumped off and the brown residue dissolved in 15 mL hexane. The solution was filtered and cooled slowly to $-20^\circ C$ overnight. Fine brown black needles were obtained. They were isolated and washed twice with cold ($-78^\circ C$) hexane. A yield of 0.06 g (10%) $U(BH_3CH_3)_2 \cdot 2dmpe$ was recovered. M. p. = $130-2^\circ C$. Calculated for $C_{12}H_{20}B_2P_2U$: C, 28.83; H, 8.07. Found: C, 29.01; H, 8.25. 1H NMR Data ($25^\circ C$, $PhCH_3-d_6$): δ -1.09 (8H, s), CH_2 ; -0.07 (24H, s), PCH_3 ; 8.92 (9H, s), BH_3CH_3 ; 115.24 (9H, s), BH_3 . IR Data: 2950m, 2310w, 2165m, 1420w, 1290m, 1260w, 1215m(br), 1140w, 1075w, 940m, 930m, 890m, 825w, 730m, 720m, 700m, 690m, 640m.

Preparation of $Th(BH_3CH_3)_2 \cdot dmpe$

To 0.60 g (1.7 mmol) $Th(BH_3CH_3)_2$ dissolved in 10 mL hexane, 0.28 mL (1.7 mmol) of $dmpe$ was added with stirring, giving a white ppt. It was stirred for 5 minutes and then pumped to dryness. The white residue was dissolved in 10 mL toluene; the solution was filtered and concentrated to 5 mL. It was cooled at $-20^\circ C$. After several hours, colorless crystals formed. The supernate was removed and the colorless crystals washed with 5 mL cold ($-78^\circ C$) ether. A yield of 0.20 g (38%) of colorless $Th(BH_3CH_3)_2 \cdot dmpe$ was obtained. M. p. = $192-4^\circ C$. Calculated for $C_{12}H_{20}B_2P_2Th$: C, 24.14; H, 8.10. Found: C, 24.09; H, 8.00. 1H NMR Data ($25^\circ C$, $PhH-d_6$): δ 0.32 (12H, quart), BH_3CH_3 ; 0.91 (12H, mult), PCH_3 ; 1.14 (4H, mult), CH_2 ; 3.27 (12H, quart), BH_3 . IR

Data: 2950m, 2190m, 2110s, 1435w, 1415m, 1405w, 1300s, 1285m, 1225s, 1085s, 940s, 925s, 890m, 865m, 830m, 795m, 740m, 705m, 645m.

Preparation of $\text{UCp}_2(\text{BH}_3\text{CH}_3)_2$

To 1.1 g (2.9 mmol) of UCl_4 and 0.21 g (5.8 mmol) of LiBH_3CH_3 , about 50 mL of THF were added. The reaction mixture was stirred for 48 hours. To the reaction mixture, 5.8 mmol of NaCp (2.0 mL of 2.9 M NaCp) were added and the mixture stirred for 12 hours. The insolubles were filtered off and the filtrate pumped to dryness. The green residue was transferred into a sublimator and the residue sublimed under vacuum at 125°C . A yield of 0.28 g (23%) of green yellow crystals of $\text{UCp}_2(\text{BH}_3\text{CH}_3)_2$ that melt at $169-71^\circ\text{C}$ was recovered. Calculated for $\text{C}_{12}\text{H}_{22}\text{B}_2\text{U}$: C, 33.84; H, 5.21. Found: C, 33.95; H, 5.40. ^1H NMR Data (25°C , PhH-d_6): δ -9.89 (6H, s), CH_3 ; 2.45 (10H, s), C_5H_5 . IR Data: 2920s, 2150m, 2080s, 1300s, 1235s, 1080m, 1010s, 960w, 885w, 830w, 780s, 720w, 660w.

Preparation of $\text{Th}(\text{BH}_3)_4 \cdot 2\text{THF}$

To 0.27 g (0.73 mmol) $\text{Th}(\text{BH}_3)_4$, 10 mL of THF was added. After complete dissolution, the solution was pumped dry. The residue was dissolved in toluene, and the solution filtered, reduced in volume to 5 mL, and cooled at -20°C . A yield of 0.14 g (35%) $\text{Th}(\text{BH}_3)_4 \cdot 2\text{THF}$ was obtained. M. p. = $129-33^\circ\text{C}$ (dec). Calculated for $\text{C}_8\text{H}_{22}\text{B}_4\text{O}_2\text{Th}$: C, 22.06; H, 7.40. Found: C, 22.47; H, 7.25. ^1H NMR (25°C , PhH-d_6): δ 0.93 (8H, mult), $\text{CH}_2\text{CH}_2\text{O}$; 3.81 (8H, mult), $\text{CH}_2\text{CH}_2\text{O}$; 4.04 (16H, quart), BH_3 . IR Data: 2950m, 2480s, 2320m, 2200s, 2140m, 1345m, 1250m, 1165s, 1090m, 1035m, 995s, 955w, 925m, 915m, 820s, 720w, 670m.

Preparation of $\text{Th}(\text{BH}_4)_4 \cdot \text{dme}$

$\text{Th}(\text{BH}_4)_4$ (0.06 g, 0.55 mmol) was dissolved in 5 mL dme. The solvent was pumped off, and the white residue remaining dissolved in toluene. The solution was filtered, reduced in volume to 1 mL, and cooled at -20°C . A very small yield (0.01 g, $\sim 5\%$) of $\text{Th}(\text{BH}_4)_4 \cdot \text{dme}$ was obtained. Calculated for $\text{C}_4\text{H}_{12}\text{B}_4\text{O}_3\text{Th}$: C, 12.6; H, 6.9. Found: C, 12.6; H, 7.1. ^1H NMR Data (25°C , $\text{PhH}-d_6$): δ 2.61 (4H, s), CH_2 ; 2.92 (6H, s), CH_3 ; 3.99 (16H, quart), BH_4 . IR Data: 2950m, 2490s, 2320m, 2230s, 2160m, 1290m, 1250m, 1160s, 1090m, 1070m, 1020s, 850s, 810m, 720m.

Preparation of $\text{Th}(\text{BH}_4)_4 \cdot 2\text{NH}_3$

To 0.41 g (1.4 mmol) of $\text{Th}(\text{BH}_4)_4$ dissolved in 20 mL ether, ~ 2 mmols NH_3 was condensed in. The reaction mixture was stirred at -78°C for 30 minutes, a white ppt. forming. The solvent and excess NH_3 was pumped off and the residue sublimed at -100°C in vacuo for 12 hours. A yield of 0.10 g (22%) $\text{Th}(\text{BH}_4)_4 \cdot 2\text{NH}_3$ was recovered. M. p. = $111-2^\circ\text{C}(\text{dec})$. Calculated for $\text{H}_{12}\text{B}_4\text{N}_2\text{Th}$: H, 6.81; N, 8.61. Found: H, 6.28; N, 7.51. ^1H NMR Data (25°C , $\text{PhH}-d_6$): δ 0.55 (6H, s), NH_3 ; 3.57 (16H, quart), BH_4 . IR Data: 3300s, 3260s, 3150m, 2460s, 2220s, 1590s, 1240s, 1165s, 1090s, 880w, 720m, 590m.

Attempted Preparation of $\text{U}(\text{BH}_4\text{CH}_3)_4 \cdot \text{nOMe}_2$

To 0.30 g (8.4 mmol) LiBH_4CH_3 and 0.80 g UCl_4 (2.1 mmol), 20 mL of dimethyl ether was condensed in at -196°C . It was stirred for 12 hours at -78°C . The solvent was then pumped off and the residue extracted into toluene; the solution was filtered and cooled at -20°C . No crystals were obtained, only a fine brown suspension. The toluene was

pumped off and the oily residue sublimed in vacuo. Only $U(BH_3CH_3)_2$ was recovered.

Attempted Preparation of $U(BH_3CH_3)_2 \cdot nOEt_2$

To 0.30 g (8.4 mmol) $LiBH_3CH_3$ and 0.80 g (2.1 mmol) UCl_4 , 5 mL of diethyl ether was added. It was stirred for 12 hours. The ether was pumped off and the deep brown residue extracted into toluene; the solution was filtered and cooled at $-20^\circ C$. No crystals were obtained, only a very fine brown suspension. The toluene was pumped off and the residue sublimed in vacuo at room temperature. Only $U(BH_3CH_3)_2$ was recovered.

Attempted Preparation of $U(BH_3CH_3)_2 \cdot nSMe_2$

$U(BH_3CH_3)_2$ (0.13 g, 0.37 mmol) was dissolved in 5 mL SMe_2 , forming a green solution. It was allowed to equilibrate for several hours. The solvent was pumped off and the green residue sublimed in vacuo at room temperature. Only $U(BH_3CH_3)_2$ was recovered.

Experimental Procedures for Chapter 4

Preparation of $LuCp_2BH_3CH_3$

A quantity of 1.88 g (5.52 mmol) of $LuCp_2Cl$ was dissolved in about 40 mL of THF, to which a solution containing 0.28 g (7.8 mmol) of $LiBH_3CH_3$ dissolved in about 20 mL of THF was added. The reaction mixture was stirred for 12 hours, a cloudy suspension of $LiCl$ forming. The THF was removed in vacuo to dryness. The residue was transferred into a sublimator and sublimed under vacuum at $200^\circ C$ for 12 hours. Calculated for $C_{11}H_{13}BLu$: C, 39.55; H, 4.83. Found: C, 39.59; H, 4.70. 1H NMR Data ($25^\circ C$, $PhH-d_6$): δ 0.26 (3H, mult), CH_3 ; 6.07 (10H, s), C_5H_4 . IR Data: 2920s, 2130s, 2060s, 1355m, 1300m, 1174m, 1090m, 1010s, 985m, 895m, 845m, 810w, 795s, 775s.

Preparation of Lu(BH₃CH₃)₃.OEt₂

To 0.77 g (21.5 mmol) of LiBH₃CH₃, 2.04 g (7.3 mmol) of LuCl₃, and about 40 mL of diethyl ether were added. The reaction mixture was stirred for 48 hours under argon. The solvent was removed in vacuo to dryness. The grey residue was transferred into a sublimator and sublimed under vacuum at 50 °C onto a cold finger. A yield of 0.97 g (38%) of white Lu(BH₃CH₃)₃.OEt₂ was obtained that melts at 62-4 °C. Calculated for C₆H₁₂B₃O₂Lu: C, 25.04; H, 8.41. Found: C, 25.90; H, 8.44. ¹H NMR Data (25 °C, PhH-d₆): δ 0.39 (9H, quart), BH₃CH₃; 0.78 (6H, mult), CH₂CH₃; 1.71 (9H, quart), BH₃; 3.27 (4H, mult), CH₂. IR Data: 2930s, 2830s, 2600m, 2465m, 2100s, 1310s, 1275s, 1095s, 1000m, 960m, 910m, 845s, 810m, 675m.

Preparation of Yb(BH₃CH₃)₃.OEt₂

To 0.81 g (22.6 mmol) LiBH₃CH₃, 2.11 g (7.5 mmol) YbCl₃, and 40 mL ether were added. It was stirred for 2 days. The solvent was pumped off and the residue transferred into a sublimator. It was heated at 50 °C in vacuo onto a cold finger. A yield of 1.01 g (40%) of white, crystalline Yb(BH₃CH₃)₃.OEt₂ was obtained that melts at 59-60 °C. Calculated for C₆H₁₂B₃O₂Yb: C, 25.19; H, 8.46. Found: C, 25.06; H, 8.44. ¹H NMR Data (30 °C, PhH-d₆): δ -162.83 (9H, s), BH₃; -25.07 (9H, s), BH₃CH₃; 36.38 (6H, s), CH₂CH₃; 92.65 (4H, s), CH₂. IR Data: 2950m, 2640w, 2430w, 2190m, 2100s, 1310s, 1270s, 1190m, 1145m, 1085s, 1030s, 990m, 970w, 890m, 825m, 770m, 720m.

Preparation of Ho(BH₃CH₃)₃.OEt₂

To 0.77 g (21.5 mmol) LiBH₃CH₃, 1.94 g (7.2 mmol) HoCl₃, and 40 mL ether were added. It was stirred for 2 days. After pumping off the solvent and transferring into a sublimator, it was sublimed at 50 °C in

vacuo onto a cold finger. A yield of 0.90 g (38%) pale orange crystals of $\text{Ho}(\text{BH}_2\text{CH}_2)_3\text{OEt}_2$ was obtained. M. p. = $61-2^\circ\text{C}$. Calculated for $\text{C}_7\text{H}_{28}\text{B}_3\text{HoO}_7$: C, 25.82; H, 8.67. Found: C, 25.94; H, 8.81. ^1H NMR Data (32°C , PhH-d_6): δ -220.70 (4H, s), CH_2 ; -95.61 (6H, s), CH_2CH_2 ; 84.80 (9H, s), BH_2CH_2 . IR Data: 2950m, 2570m, 2420m, 2190s, 2090s, 1350w, 1305s, 1260s, 1190m, 1145m, 1085s, 1020s, 985m, 960m, 890m, 825s, 770s, 495m, 470m.

Preparation of $\text{Lu}(\text{BH}_2\text{CH}_2)_3\text{.THF}$

To 0.33 g (0.98 mmol) $\text{Lu}(\text{BH}_2\text{CH}_2)_3\text{.OEt}_2$, 10 mL THF was added. It was allowed to equilibrate overnight. The THF was pumped off and the white residue transferred into a sublimator. It was heated at 100°C in vacuo for several hours. A yield of 0.27 g (68%) of white $\text{Lu}(\text{BH}_2\text{CH}_2)_3\text{.THF}$ was recovered that melts at $110-2^\circ\text{C}$. Calculated for $\text{C}_7\text{H}_{28}\text{B}_3\text{LuO}_7$: C, 25.20; H, 7.85. Found: C, 25.42; H, 7.75. ^1H NMR Data (30°C , PhH-d_6): δ 0.41 (9H, quart), CH_3 ; 0.81 (4H, mult), $\text{CH}_2\text{CH}_2\text{O}$; 1.84 (9H, quart), BH_2 ; 3.33 (4H, mult), $\text{CH}_2\text{CH}_2\text{O}$. IR Data: 2950m, 2190w(sh), 2100s, 1310s, 1265s, 1175w, 1090s, 1035w, 995s, 960m, 920m, 850s, 720w, 680w.

Preparation of $\text{Ho}(\text{BH}_2\text{CH}_2)_3\text{.THF}$

To 0.37 g (1.1 mmol) $\text{Ho}(\text{BH}_2\text{CH}_2)_3\text{.OEt}_2$, 10 mL of THF was added and it was allowed to equilibrate for one hour. The solvent was removed and the residue left behind was sublimed with pumping at 100°C . A yield of 0.21 g (59%) pale orange $\text{Ho}(\text{BH}_2\text{CH}_2)_3\text{.THF}$ that melts at $94-6^\circ\text{C}$ was obtained. Calculated for $\text{C}_7\text{H}_{28}\text{B}_3\text{HoO}_7$: C, 25.98; H, 8.10. Found: C, 26.56; H, 8.27. ^1H NMR Data (32°C , PhH-d_6): δ -178.61 (4H, s), $\text{CH}_2\text{CH}_2\text{O}$; -87.81 (4H, s), $\text{CH}_2\text{CH}_2\text{O}$; 77.11 (9H, s), CH_3 . IR Data: 2950m,

2180w(sh), 2100s, 1305s, 1260s, 1175w, 1085m, 1035w, 1000m, 955w, 915m, 850s, 720m, 670m.

Preparation of $\text{Yb}(\text{BH}_2\text{CH}_2)_3 \cdot \text{THF}$

To 0.40 g (1.2 mmol) $\text{Yb}(\text{BH}_2\text{CH}_2)_3 \cdot \text{OEt}_2$, 10 mL of THF was added and allowed to equilibrate for one hour. After removal of solvent, the remaining residue was sublimed in vacuo at 100°C . A yield of 0.23 g (58%) of white $\text{Yb}(\text{BH}_2\text{CH}_2)_3 \cdot \text{THF}$ that melts at $100-2^\circ\text{C}$ was obtained. Calculated for $\text{C}_7\text{H}_{12}\text{B}_3\text{YbO}$: C, 25.34; H, 7.90. Found: C, 25.54; H, 7.86. ^1H NMR Data (28°C , $\text{PhH}-d_6$): δ -160.4 (9H, s), BH_2 ; -29.4 (9H, s), CH_2 ; 38.3 (4H, s), $\text{CH}_2\text{CH}_2\text{O}$; 82.2 (4H, s), $\text{CH}_2\text{CH}_2\text{O}$. IR Data: 2950m, 2190w(sh), 2090s, 1310s, 1260s, 1180w, 1090m, 1035w, 1000m, 960w, 915w, 850s, 720w, 675m.

Preparation of $\text{Ho}(\text{BH}_2\text{CH}_2)_3 \cdot 2\text{THF}$

$\text{Ho}(\text{BH}_2\text{CH}_2)_3 \cdot \text{OEt}_2$ (0.48 g, 1.5 mmol) was dissolved in 10 mL THF. It was pumped to dryness and redissolved in 10 mL toluene; the solution was filtered, reduced to 2 mL volume, and cooled at -20°C . Pale orange crystals were obtained, which were isolated and washed with cold (-78°C) ether. A yield of 0.17 g (29%) of $\text{Ho}(\text{BH}_2\text{CH}_2)_3 \cdot 2\text{THF}$ that melts at $133-4^\circ\text{C}$ was obtained. Calculated for $\text{C}_{11}\text{H}_{18}\text{B}_3\text{HoO}_2$: C, 33.4; H, 8.7. Found: C, 33.0; H, 8.6. ^1H NMR Data (32°C , $\text{PhH}-d_6$, 3.3×10^{-2} g/mL): δ -148.08 (9H, s), BH_2 ; -35.83 (8H, s), $\text{CH}_2\text{CH}_2\text{O}$; -13.15 (8H, s), $\text{CH}_2\text{CH}_2\text{O}$; 31.67 (9H, s), CH_2 . IR Data: 2950m, 2180m, 2110s, 1345w, 1300s, 1255s, 1170w, 1085s, 1035m, 1005s, 940m, 920m, 850s, 720m, 665m.

Preparation of $\text{Yb}(\text{BH}_2\text{CH}_2)_3 \cdot 2\text{THF}$

$\text{Yb}(\text{BH}_2\text{CH}_2)_3 \cdot \text{OEt}_2$ (0.42 g, 1.3 mmol) was dissolved in 10 mL THF. It was pumped to dryness and redissolved in 10 mL toluene; the solution was filtered and reduced in volume to 2 mL. It was cooled at -20°C .

Colorless crystals were isolated, which were washed with cold (-78°C) ether. A yield of 0.09 g (17%) of $\text{Yb}(\text{BH}_2\text{CH}_3)_3 \cdot 2\text{THF}$ that melts at $111-4^{\circ}\text{C}$ was obtained. Calculated for $\text{C}_{11}\text{H}_{14}\text{B}_3\text{O}_2\text{Yb}$: C, 32.71; H, 8.49. Found: C, 33.10; H, 8.39. ^1H NMR Data (32°C , PhH-d_6 , 8.4×10^{-3} g/mL): δ -69.21 (9H, s), BH_2 ; -7.77 (8H, s), THF; 8.10 (8H, s), THF; 26.36 (9H, s), CH_3 . IR Data: 2950m, 2350m, 2120s, 1305s, 1260s, 1135w, 1085s, 1030w, 1010s, 950w, 920w, 855s, 800m, 720w, 670w.

Preparation of $\text{Ho}(\text{BH}_2\text{CH}_3)_3 \cdot 3/2 \text{ dmpe}$

$\text{Ho}(\text{BH}_2\text{CH}_3)_3 \cdot \text{OEt}_2$ (0.59 g, 1.8 mmol) was dissolved in 10 mL toluene. Dmpe (0.60 mL, 3.6 mmol) was added with stirring. The solution was filtered, reduced to low volume (~ 2 mL), and cooled at -20°C . Pale orange crystals were obtained. They were washed with cold (-78°C) ether. A yield of 0.45 g (52%) $\text{Ho}(\text{BH}_2\text{CH}_3)_3 \cdot 3/2 \text{ dmpe}$ that melts at $169-71^{\circ}\text{C}$ was recovered. Calculated for $\text{C}_{12}\text{H}_{14}\text{B}_3\text{HoP}_3$: C, 30.23; H, 8.88. Found: C, 29.82; H, 9.33. ^1H NMR Data (32°C , PhH-d_6 , 5.2×10^{-2} g/mL): δ -138.34 (9H, s), BH_2 ; -22.48 (6H, s), CH_2 ; -13.42 (18H, s), PCH_3 ; 32.15 (9H, s), BH_2CH_3 . IR Data: 2950m, 2180s, 2100s, 1430m, 1415m, 1295s, 1280m, 1260s, 1075s, 940s, 900s, 865m, 825m, 800m, 730s, 720w, 705w, 700s, 645m, 465m.

Preparation of $\text{Ho}(\text{BH}_2\text{CH}_3)_3 \cdot \text{tmed}$

$\text{Ho}(\text{BH}_2\text{CH}_3)_3 \cdot \text{OEt}_2$ (0.49 g, 1.5 mmol) was dissolved in 10 mL toluene. Tmed (0.50 mL, 3.0 mmol) was added with stirring. The solution was filtered, reduced to 5 mL, and cooled at -20°C . Pale orange crystals were obtained. They were washed with cold (-78°C) ether. A yield of 0.33 g (60%) $\text{Ho}(\text{BH}_2\text{CH}_3)_3 \cdot \text{tmed}$ that melts at $149-50^{\circ}\text{C}$ was obtained. Calculated for $\text{C}_8\text{H}_{14}\text{B}_3\text{HoN}_2$: C, 29.40; H, 9.32; N, 7.62. Found: C, 29.41; H, 9.34; N, 7.69. ^1H NMR Data (32°C , PhH-d_6 , $1.3 \times$

10^{-3} g/mL): δ -102.81 (9H, s), BH₃; -89.03 (4H, s), CH₂; 18.25 (12H, s), NCH₃; 42.43 (9H, s), BH₂CH₃. IR Data: 2950m, 2200m, 2140s, 2060m, 1405w, 1360w, 1350w, 1300s, 1280w, 1250s, 1160m, 1115m, 1095w, 1085w, 1070m, 1040m, 1010m, 1000m, 995w, 940s, 795s, 770m, 720m.

Preparation of Yb(BH₂CH₃)₃.3/2 dmpe

Yb(BH₂CH₃)₃.0Et₂ (0.45 g, 1.3 mmol) was dissolved in 5 mL toluene. To this solution, 0.43 mL (2.6 mmol) of dmpe was added. The solution turned deep yellow. It was filtered and reduced in volume until slightly cloudy (~1 mL). It was cooled to -20°C. Yellow crystals were obtained. They were washed with cold (-78°C) ether. A yield of 0.09 g (~10%) Yb(BH₂CH₃)₃.3/2 dmpe was obtained. M. p. = 172-4°C. Calculated for C₁₂H₂₂B₃P₃Yb: C, 29.72; H, 8.73. Found: C, 30.19; H, 8.72. ¹H NMR Data (32°C, PhH-d₆, 1.6 x 10⁻² g/mL): δ -80.04 (9H, s), BH₃; -10.83 (6H, s), CH₂; 1.91 (18H, s), PCH₃; 17.16 (9H, s). BH₂CH₃. IR Data: 2950m, 2180m, 2100s, 1305s, 1260s, 1180m, 1100m, 1080m, 940s, 900s, 860m, 825w, 800w, 735s, 720s, 700m.

Preparation of Yb(BH₂CH₃)₃.dme

Yb(BH₂CH₃)₃.0Et₂ (0.42 g, 1.3 mmol) was dissolved in 10 mL dme. The solution was then pumped to near dryness, to which 5 mL toluene was added. The solution was filtered and reduced to 2 mL, to which 1 mL dme was added. It was cooled at -20°C. Colorless crystals were obtained. They were washed with hexane. A yield of 0.22 g (48%) of Yb(BH₂CH₃)₃.dme that melts at 132-3°C was obtained. Calculated for C₇H₂₀B₃O₂Yb: C, 24.04; H, 8.07. Found: C, 23.63; H, 8.23. ¹H NMR Data (32°C, PhH-d₆, 4.2 x 10⁻³ g/mL): δ -171.88, -104.97, -29.29, -15.33, -14.03, -4.43, 1.50, 25.81, 27.04, 52.52. Spectrum could not

be interpreted. IR Data: 2950m, 2180m(sh), 2110s, 1305s, 1260s, 1185m, 1085s, 1025s, 940w, 865m, 855s, 815m, 770w, 720m.

Preparation of $\text{Ho}(\text{BH}_2\text{CH}_2)_3 \cdot 3/2 \text{ bmt}$

$\text{Ho}(\text{BH}_2\text{CH}_2)_3 \cdot \text{OEt}_2$ (0.51 g, 1.6 mmol) was dissolved in ~2 mL toluene, to which 0.20 mL (1.7 mmol) bmt was added. The solution was filtered and cooled to -20°C . Pale orange crystals of $\text{Ho}(\text{BH}_2\text{CH}_2)_3 \cdot 3/2 \text{ bmt}$ were obtained. They were washed with cold (-78°C) ether. M. p. = $147-52^\circ\text{C}$. Calculated for $\text{C}_9\text{H}_{13}\text{B}_3\text{S}_3\text{Yb}$: C, 24.86; H, 7.64; S, 22.12. Found: C, 24.43; H, 7.60; S, 22.01. ^1H NMR Data (34°C , PhH-d_6): δ -120.36 (9H, s), BH_2 ; -7.02 (4H, s), CH_2 ; -5.93 (6H, s), SCH_3 ; 73.56 (9H, s), BH_2CH_2 . IR Data: 2950m, 2190m, 2110s, 1420m, 1420m, 1300s, 1255s, 1155w, 1150w, 1085s, 1025m, 970w, 960m, 940m, 900s, 840m, 800m, 770w, 720m, 660m, 650m, 450w.

Preparation of $\text{Ho}(\text{BH}_2\text{CH}_2)_3 \cdot 2\text{THT}$

To 0.42 g (1.3 mmol) $\text{Ho}(\text{BH}_2\text{CH}_2)_3 \cdot \text{OEt}_2$ dissolved in 10 mL toluene, 0.23 mL (2.6 mmol) THT was added. The solution was filtered, concentrated to 1 mL, and cooled at -20°C . A crystalline mass was obtained. It was washed with cold (-78°C) ether. A yield of only 0.08 g (14%) of pale orange $\text{Ho}(\text{BH}_2\text{CH}_2)_3 \cdot 2\text{THT}$ was obtained. M. p. = $60-3^\circ\text{C}$. Calculated for $\text{C}_{11}\text{H}_{15}\text{B}_3\text{HoS}_2$: C, 30.88; H, 8.01. Found: C, 30.35; H, 8.15. ^1H NMR Data (34°C , PhH-d_6): δ -9.48 (8H, s), $\text{CH}_2\text{CH}_2\text{S}$; -42.30 (8H, s), $\text{CH}_2\text{CH}_2\text{S}$; 89.37 (9H, s), CH_3 . IR Data: 2950m, 2190m, 2100s, 1305s, 1255s, 1130w, 1085m, 1035w, 955m, 880m, 810m, 775w, 720m, 670m, 520m, 475w.

Preparation of $\text{Ho}(\text{BH}_2\text{CH}_2)_3 \cdot \text{THT}$

$\text{Ho}(\text{BH}_2\text{CH}_2)_3 \cdot \text{OEt}_2$ (0.40 g, 1.2 mmol) was dissolved in 5 mL THT. After equilibrating for several minutes, the excess THT was pumped off

at 50 °C for an hour until the residue was near dryness. The pale orange residue was sublimed in vacuo at -100 °C for several hours. A yield of 0.25 g (61%) of pale orange crystals of $\text{Ho}(\text{BH}_2\text{CH}_2)_3\text{THT}$ was recovered. M. p. = 98-9 °C. Calculated for $\text{C}_7\text{H}_{28}\text{B}_3\text{HoS}$: C, 24.75; H, 7.71. Found: C, 24.61; H, 8.05. ^1H NMR Data (32 °C, PhH-d_6): δ -140.73 (4H, s), $\text{CH}_2\text{CH}_2\text{S}$; -59.26 (4H, s), $\text{CH}_2\text{CH}_2\text{S}$; 96.18 (9H, s), CH_3 . IR Data: 2950m, 2170s, 2090s, 1305s, 1250s, 1130w, 1080s, 1015m, 950m, 875m, 805m, 715m, 605m, 520w.

Preparation of $\text{Ho}(\text{BH}_2\text{CH}_2)_3\text{.2py}$

$\text{Ho}(\text{BH}_2\text{CH}_2)_3\text{.OEt}_2$ (0.37 g, 1.1 mmol) was dissolved in 5 mL toluene, to which 0.19 mL (2.4 mmol) pyridine was added with stirring. The solution was filtered, reduced to 3 mL volume and cooled to -20 °C. Pale orange crystals were obtained. They were washed with cold (-78 °C) ether. A yield of 0.21 g (43%) of $\text{Ho}(\text{BH}_2\text{CH}_2)_3\text{.2py}$ was obtained. M. p. = 132-4 °C(dec). Calculated for $\text{C}_{13}\text{H}_{28}\text{B}_3\text{HoN}_2$: C, 38.11; H, 6.89; N, 6.83. Found: C, 36.65; H, 6.93; N, 6.33. ^1H NMR Data (32 °C, PhH-d_6 , 2.3×10^{-2} g/mL): δ -206.53 (9H, s), BH_2 ; -30.65 (4H, s), NCH; -1.77 (4H, s), NCHCH; 3.13 (2H, s), NCHCHCH; 22.95 (9H, s), CH_3 . IR Data: 2950m, 2360m, 2310w, 2130s, 1630m, 1595s, 1570w, 1485s, 1440s, 1365w, 1300s, 1255s, 1220s, 1150m, 1135w, 1125w, 1090w, 1065s, 1035s, 1015w, 1000s, 980w, 945w, 925w, 750s, 720s, 700s, 620s, 470w, 425s.

Preparation of $\text{Ho}(\text{BH}_2\text{CH}_2)_3\text{.py}$

$\text{Ho}(\text{BH}_2\text{CH}_2)_3\text{.OEt}_2$ (0.19 g, 0.58 mmol) was dissolved in 5 mL toluene. Pyridine (0.05 mL, 0.6 mmol) was added with stirring. The solution was pumped to dryness. The residue was sublimed in vacuo at 125 °C for several hours. A yield of 0.06 g (~30%) $\text{Ho}(\text{BH}_2\text{CH}_2)_3\text{.py}$ was recovered. M. p. = 115-9 °C. Calculated for $\text{C}_6\text{H}_{22}\text{B}_3\text{HoN}$: C, 29.06; H,

7.01; N, 4.24. Found: C, 29.31; H, 7.19; N, 3.95. ^1H NMR Data (32°C , PhH-d_6 , 2.6×10^{-3} g/mL): δ -50.61 (9H, s), BH₂; -8.93 (2H, s), NCH; -5.66 (2H, s), NCHCH₂; -1.91 (1H, s), NCHCHCH₂; 32.15 (9H, s), CH₃. IR Data: 2950m, 2120s, 1630m, 1620m, 1600s, 1570w, 1485s, 1440s, 1360w, 1305s, 1255w, 1230w, 1215s, 1150m, 1085s, 1065s, 1035s, 1005s, 945m, 875w, 870w, 750s, 720w, 690s, 620s, 465w, 425s.

Attempted Preparation of $\text{Ce}(\text{BH}_4)_3$

First Method

To 0.30 g (2.1 mmol) of $\text{Ce}(\text{O}i\text{-Pr})_3$, dissolved in 10 mL THF, an excess amount of B_2H_6 (about 45 mmol) was condensed in at -196°C . The reactants were allowed to warm to room temperature, during which a deep red solution resulted. After 2 hours, the solution turned from dark red to pale yellow. The volatiles were removed in vacuo, leaving behind a white solid. The solid was recrystallized from THF by slow evaporation and cooling in a -78°C bath. The IR shows bridging and terminal B-H stretches. Proton NMR reveals the compound is paramagnetic. This indicates presence of Ce(III). An elemental analysis confirmed the formula of the white crystals as $\text{Ce}(\text{BH}_4)_3 \cdot 3\text{THF}$.

Second Method

To 0.16 g (1.1 mmol) of $\text{Ce}(\text{O}i\text{-Pr})_3$, an excess amount (about 10 mmol) of $\text{Al}(\text{BH}_4)_3$, was condensed in at -196°C . Upon warming to -42°C , the reaction mixture turned red brown. After careful warming to room temperature, the reaction mixture turned dark yellow. The volatiles were removed in vacuo, leaving behind an off white residue. Sublimation only yielded unreacted $\text{Al}(\text{BH}_4)_3$, and $\text{Al}(\text{BH}_4)_2(\text{O}i\text{-Pr})$. The white residue left behind was recrystallized from THF. Its IR, ^1H NMR, and elemental analysis indicate it is $\text{Ce}(\text{BH}_4)_3 \cdot 3\text{THF}$.

Chapter 5 References

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CONCLUSIONS AND FUTURE WORK

In our investigation of actinide and lanthanide methyltrihydroborate complexes, we have seen that by a structural definition these compounds are primarily ionic despite their covalent-like physical properties. However this does not rule out the possibility of some covalent character to the bonding in these complexes. Spectroscopic studies on $U(BH_3CH_3)_4$ indicate there is some degree of covalent bonding in this compound. Similar studies on the yet-to-be prepared $Pa(BH_3CH_3)_4$, an f^1 system, are also desirable.

Because of the interesting variety of structures found for methyltrihydroborate or tetrahydroborate complexes, structural characterization by X-ray diffraction of many of the existing complexes; for example, $[Th(BH_3CH_3)_4 \cdot THT]_2$, $[Th(BH_3CH_3)_4 \cdot OMe_2]_2$, $[Th(BH_3CH_3)_4 \cdot SMe_2]_2$, and the bidentate base adducts of $Ln(BH_3CH_3)_3$ ($Ln = Ho, Yb$), should be undertaken. Finally the preparation and study of soft Lewis base adducts of actinide and lanthanide tetrahydroborates and methyltrihydroborates should be pursued.