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Complexes of Divalent Lanthanides (Yb(II), Eu(II), Sm(II)) with Decaborates

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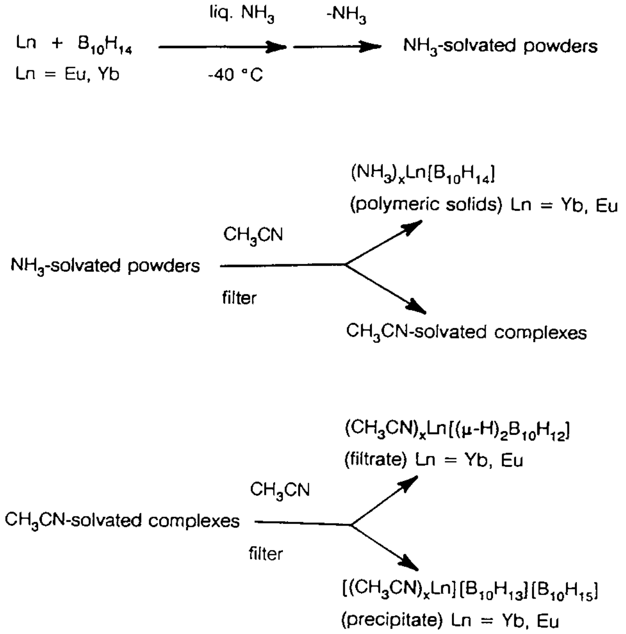
Decaborate complexes of divalent lanthanides are prepared through the reduction of $B_{10}H_{14}$ by elemental lanthanides in liquid NH_3. The products are insoluble in liquid NH_3. Extraction with CH_3CN yields the complexes $(CH_3CN)_6Yb[B_{10}H_{14}]$ and $(CH_3CN)_xEu[B_{10}H_{14}]$, in which the boron cage is bound to the lanthanide dianion through Ln–H–B bonds. Solvent-separated decaborate anions $[B_{10}H_{13}]^-$ and $[B_{10}H_{15}]^-$ are also observed in the CH_3CN extracts. Reductions of $B_{10}H_{14}$ by lanthanide amalgams, Ln(Hg) (Ln = Sm, Yb), in 1,2-dimethoxyethane (DME) produce small amounts of the DME-soluble salts containing the solvent-separated decaborate anions $[B_{10}H_{13}]^-$ and $[B_{10}H_{15}]^-$. The major reaction product is insoluble in DME, but extraction with CH_3CN yields salts with the solvent-separated $[B_{10}H_{13}]^-$ and $[B_{10}H_{15}]^-$. Solvent-free $Eu[B_{10}B_{10}]$ and $Yb[B_{10}B_{10}]$ are prepared by decomposing in vacuum at 200 °C NH_3- and also CH_3CN-solvated salts of $Eu[B_{10}H_{14}]$ and $Yb[B_{10}H_{14}]$. Further decomposition of $Yb[B_{10}H_{10}]$ at temperatures above 600 °C in vacuum leads to the formation of YbB_6.

Introduction

The chemistry of the divalent lanthanides, Ln(II), is relatively unexplored compared to that of the trivalent lanthanides. Low-valent lanthanide species are postulated as intermediates in catalytic processes,[1,2] and Ln(II) compounds act as unique reducing agents in organic systems,[3-6] yet little specific information is available concerning bonding modes and tendencies for ligation of these cations. It has been suggested that the chemistry of divalent lanthanides might be different from that of trivalent lanthanides.[7] Trivalent lanthanides tend to act as hard Lewis acids, forming ionic bonds to the most electronegative species available. Divalent lanthanides on the other hand appear to behave as somewhat softer Lewis acids, in some instances forming dative bonds with neutral phosphorus donors in the presence of oxygen bases.[8] Loss of coordinated ligands from lanthanide centers leave vacant coordination sites which give rise to intermolecular interactions resulting in polymeric solids.[9] Bulky $C_5R_5^-$ ligands are generally used[10-12] to block potential coordination sites and circumvent this problem.

We are interested in developing the chemistry of divalent lanthanide derivatives of borane anions, with the intent of possibly converting such complexes to metal borides. Such precursor materials should contain ligands that stabilize the lanthanide borane so that decomposition does not easily occur, yet these ligands should be sufficiently labile that they can be readily removed when it is appropriate to do so. While the cyclopentadienide ion forms complexes that are frequently too stable for studies that involve cleanly stripping ligands from the metal to form borides, we find that acetonitrile and pyridine are ideally suited for our purposes. Coordination of CH_3CN and C_5H_5N to Ln(II) decreases the tendency toward polymerization, promotes solubility, and allows in some cases isolation of discrete, neutral, monomeric complexes. In an earlier study we prepared the structurally characterized borohydride complexes of CH_3CN- and C_5H_5N-ligated Yb(II) and Eu(II)[13a] and also produced metal borides from these complexes. Hawthorne and co-workers[20] found CH_3CN and dimethylformamide to be useful solvents and ligands in the preparation of lanthanide–carborane complexes.

Scheme I. Synthesis and Separation of Products from $Ln/B_{10}H_{14}$ Reactions in Liquid Ammonia



In a preliminary account,[13b] we described the reduction of $B_{10}H_{14}$ by Yb and Eu in liquid NH_3 to produce Ln(II) compounds that contain the decaborate anion $[B_{10}H_{14}]^{2-}$. Heating these salts to 200 °C in vacuum produced *closo*-$[B_{10}H_{10}]^{2-}$ complexes of these lanthanides. We also described the structure of the monomeric coordination complex $(CH_3CN)_6Yb[B_{10}H_{14}]$. Its structure was determined from a single-crystal X-ray analysis (Figure 1).[13b] Ytterbium in this compound is eight-coordinate in the solid state. It has two Yb–H–B bridges and six CH_3CN ligands. Isolation of Yb(II) bound to six CH_3CN ligands is unusual, since it is often difficult to isolate heavily solvated lanthanide species intact. Described here are details of our reduction studies of $B_{10}H_{14}$ by $Ln(NH_3)$ (Ln = Yb, Eu) and also lanthanide amalgams, Ln(Hg) (Ln = Sm, Yb).

Results

Reductions in Liquid Ammonia. Liquid-ammonia solutions of Eu and Yb provide effective homogeneous media for reducing $B_{10}H_{14}$ to $[B_{10}H_{14}]^{2-}$, similar to its reduction by sodium in liquid

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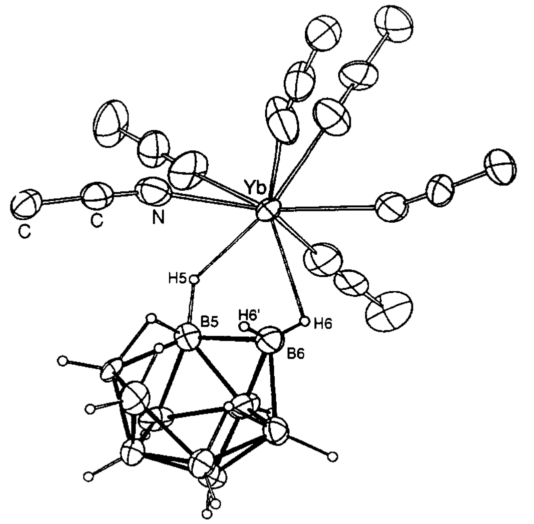


Figure 1. Molecular structure of $(CH_3CN)_6Yb[(\mu\text{-}H)_2B_{10}H_{12}]$, showing 50% thermal ellipsoids.

ammonia.[14] The products are insoluble in liquid NH_3. Components of these solids were extracted with CH_3CN or C_5H_5N. Acetonitrile proved to be the better solvent. Extraction with CH_3CN yields the complexes $(CH_3CN)_6Yb[B_{10}H_{14}]$ and $(CH_3CN)_xEu[B_{10}H_{14}]$. Small amounts of the solvent-separated anions $[B_{10}H_{13}]^-$ and $[B_{10}H_{15}]^-$ were also present in the extracts. Remaining CH_3CN-insoluble residues appear to be $(NH_3)_3Yb[B_{10}H_{14}]$ and $(NH_3)_xEu[B_{10}H_{14}]$ (Scheme I).

Initial extraction by CH_3CN of the ammonia-solvated Yb(II) powder gave a bright orange solution leaving behind a lavender colored solid that is believed to be polymeric $(NH_3)_3Yb[B_{10}H_{14}]$. Its infrared spectrum in Nujol contains bands characteristic[15] of $[B_{10}H_{14}]^{2-}$ and NH_3, but not CH_3CN. Thermal decomposition of $(NH_3)_3Yb[B_{10}H_{14}]$ at 200 °C in vacuum produces ammonia and hydrogen gas in the ratio $3/2NH_3/H_2$ and solid $Yb[B_{10}H_{10}]$.

The ^{11}B NMR spectrum of the orange filtrate from the extraction with CH_3CN indicated that it contained a mixture of boron hydride species. Cooling the filtrate to 0 °C and filtering again allowed separation of a small amount of bright yellow solid from the orange filtrate. This solid was slightly soluble in CH_3CN, forming a pale yellow solution. Analysis of the ^{11}B NMR spectrum of this solution indicated that it contained equimolar ratios of $[B_{10}H_{13}]^-$ and $[B_{10}H_{15}]^-$. Chemical shifts and coupling constants of these ions were in accord with those reported for the alkali metal salts,[16,17] which suggest that these ions are not coordinated to $[(CH_3CN)_xYb]^{2+}$ but exist as solvent-separated ions.

Analysis of the ^{11}B NMR spectrum of the remaining, purified orange filtrate from the procedure above and X-ray analysis[13b] of crystals obtained from this filtrate revealed that it contained $(CH_3CN)_6Yb[B_{10}H_{14}]$, with a $[B_{10}H_{14}]^{2-}$ unit coordinated to Yb(II). The ^{11}B NMR spectrum of the filtrate in CH_3CN is shown in Figure 2, along with the spectrum of free $[B_{10}H_{14}]^{2-}$.[18] Upon coordination of Yb(II) to $[B_{10}H_{14}]^{2-}$ the C_{2v} symmetry of the free anion is reduced to apparent C_s symmetry. The four signals of the free anion are of intensity 2:4:2:2, whereas the spectrum of the coordinated anion consists of six signals of intensity 1:1:4:1:1:2. The triplet that represents the $-BH_2$ groups at the equivalent 6 and 9 positions of the boron cage in the free anion split into a downfield doublet and a triplet in the coordinated decaborate, while the doublet that represents the -BH groups at the equivalent 2 and 4 positions of the cage in the free anion split into a pair of doublets in the coordinated decaborate. This pattern of signals is consistent with binding of the decaborate cage through a single bridge hydrogen from the $B(6)H_2$ group to Yb(II). Changing a terminal hydrogen to a B–H–Yb bridge causes this boron signal to become a doublet, shifting to lower field, while the $B(9)H_2$ group on the other side of the cage is unaffected and remains a triplet. Binding of Yb(II) to a hydrogen of the $B(6)H_2$ group also causes nonequivalence of the B(2) and B(4) borons. The signal that represents the equivalent B(5), B(7), B(8), and B(10) atoms in the free anion was expected to split into two signals representing B(5), B(10) and B(7), B(8) in the coordinated anion, but such splitting was not observed. Coincidental overlap of the signals is confirmed by a 2-D ^{11}B–^{11}B NMR experiment (Figure 3).

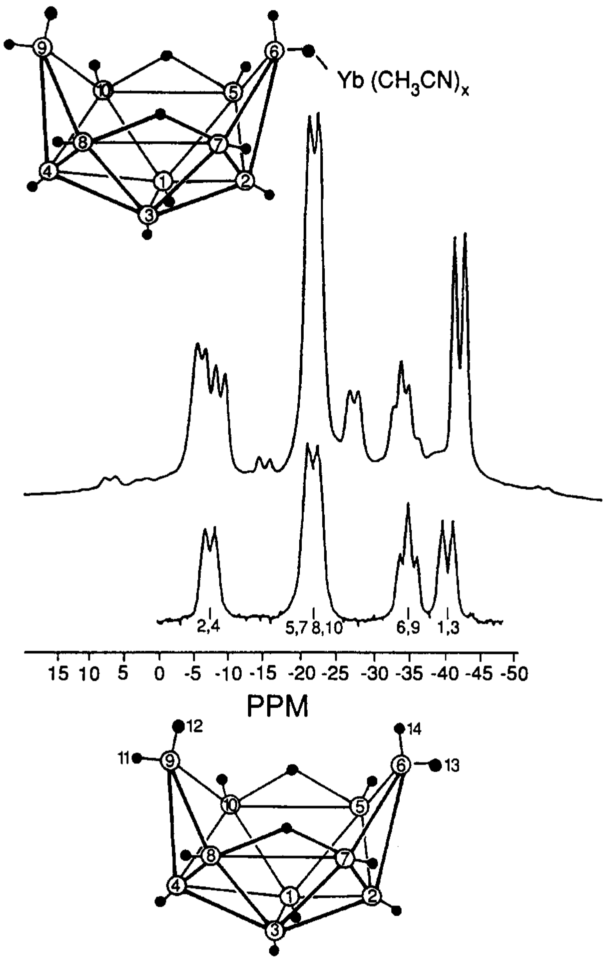
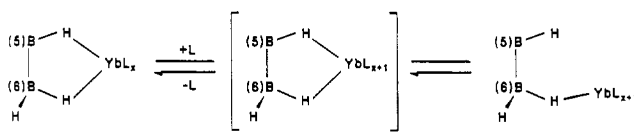


Figure 2. Boron-11 NMR spectra of (a, top) $(CH_3CN)_6Yb[(\mu\text{-}H)_2B_{10}H_{12}]$ in CH_3CN and (b, bottom) $Na_2[B_{10}H_{14}]$ in D_2O.

Scheme II. Proposed Liquid (L = CH_3CN) Displacement of Ln–H–B(5) Bond in $(CH_3CN)_6Yb[(\mu\text{-}H)_2B_{10}H_{12}]$ in CH_3CN Solution with Only Borons 5 and 6 of the $[B_{10}H_{14}]^{2-}$ Unit and Their Attached Hydrogens Shown



The complex $(CH_3CN)_6Yb[B_{10}H_{14}]$ crystallizes as $(CH_3CN)_6Yb[(\mu\text{-}H)_2B_{10}H_{12}]$ (Figure 1) with two additional molecules of CH_3CN solvation.[13b] This X-ray structure confirms the presence of the B(6)–H–B bridge bond inferred from the ^{11}B NMR spectrum and also shows a B(5)–H–Yb bridge bond. This additional binding is undoubtably weaker, since it is not observed in solution and the Yb–B(5) distance (3.03 (2) Å) is 0.19 Å longer than the Yb–B(6) distance (2.84 (2) Å). In CH_3CN solution a solvent molecule could replace the B(5)–H–Yb bond by entering the Yb^{2+} coordination sphere. Such an exchange could proceed via Scheme II. Paramagnetism of the europous ion precluded

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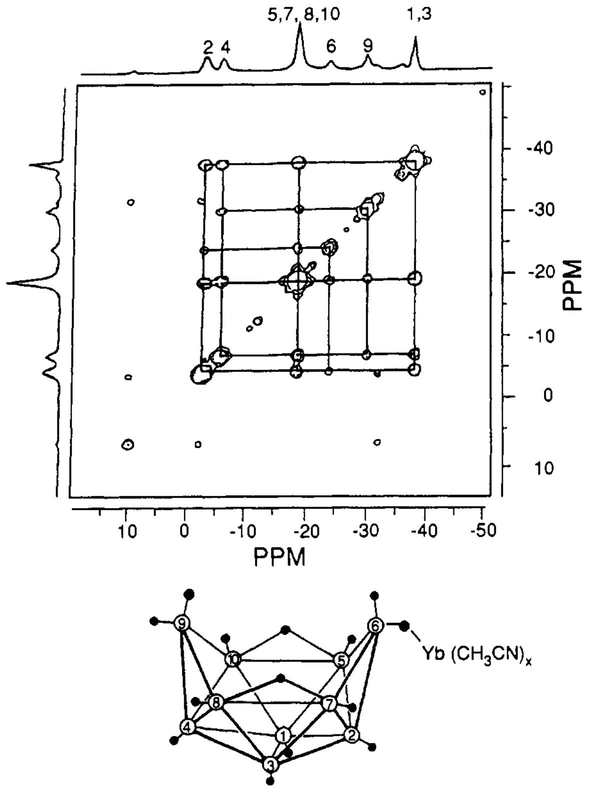
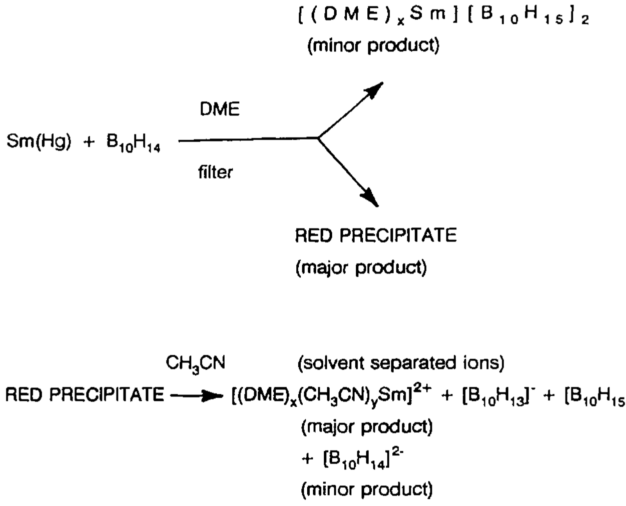


Figure 3. ^{2}D ^{11}B–^{11}B NMR spectrum of $(CH_3CN)_6Yb[(\mu\text{-}H)_2B_{10}H_{12}]$ in CD_3CN.

Scheme III. Synthesis and Separation of Products from $Sm(Hg)/B_{10}H_{14}$ Reactions in DME



NMR analyses of the Eu(II) complexes.

Reductions by Amalgams. Lanthanide amalgam reductions of $B_{10}H_{14}$ in 1,2-dimethoxyethane, DME, gave results different from those of reductions in liquid NH_3. These reactions were slower due to their heterogeneous nature. Reactions and separation of products for Sm(Hg) are shown in Scheme III.

Main products from the reductions by amalgams were colored precipitates: red products from Sm(Hg) and yellow-green products from Yb(Hg). These solids were heavily contaminated with Hg and would not dissolve in Et_2O, THF, NH_3, or *N,N,N′,N′*-tetramethylethylenediamine, TMEDA. A small amount of DME-soluble material was also formed in each reaction. The solution containing Yb(II) was pale yellow, while the solution containing Sm(II) was thermochromic, changing from emerald-green at −78 °C to green-red in color at room temperature. Removal of solvent from these solutions yielded solids that decomposed more rapidly, in vacuum and under nitrogen at room temperature, than the solutions. After 1 day under N_2 or vacuum, H_2 gas and $B_{10}H_{14}$ present along with some of the original material were the only identifiable species.

The ^{11}B NMR spectrum of the DME solution obtained from the reduction of $B_{10}H_{14}$ by Yb amalgam contained equimolar ratios of $[B_{10}H_{13}]^-$ and $[B_{10}H_{15}]^-$. Their chemical shifts and coupling constants were nearly identical to those reported for the alkali metal salts of these ions.[16,17] Thus this solution appears to consist of $[(DME)_xYb]^{2+}$ in the presence of the solvent-separated $[B_{10}H_{13}]^-$ and $[B_{10}H_{15}]^-$ anions.

Although Sm(II) is paramagnetic, an interpretable ^{11}B NMR spectrum was obtained from the DME solution produced in the reduction of $B_{10}H_{14}$ by Sm amalgam.[19] The solution apparently contained only $[B_{10}H_{15}]^-$, which, on the basis of chemical shifts, appeared to be solvent separated from Sm(II). It is surprising that no evidence for the presence of $[B_{10}H_{13}]^-$ was observed as in solutions derived from reductions by Yb amalgam.

DME-insoluble solids from the reduction reactions by Ln(Hg) (Ln = Yb, Sm) were slowly solublized by extraction with CH_3CN. The first extracts were more intensely colored than subsequent ones. Initial extracts from solutions containing Yb(II) were yellow-orange, similar in color to solutions of $(CH_3CN)_6Yb[B_{10}H_{14}]$ but not as intensely colored. Initial extracts containing Sm(II) were green-black.

The ^{11}B NMR spectrum of the initial CH_3CN extract of the solid from the reduction of $B_{10}H_{14}$ by Yb(Hg) contained equimolar ratios of $[B_{10}H_{13}]^-$ and $[B_{10}H_{15}]^-$ and some $[B_{10}H_{14}]^{2-}$ with chemical shifts that indicated that these anions are solvent separated in solution.[16–18] Residual DME in the initial extracts may result in the formation of mixed-ligand solvent-separated cations such as $[(DME)_xYb(CH_3CN)_y]^{2+}$. Such mixed-ligand cations have been observed in other systems.[21] Later extracts were much paler in color and contained only $[B_{10}H_{13}]^-$ and $[B_{10}H_{15}]^-$ as counterions.

The ^{11}B NMR spectra of initial CH_3CN extracts of the solid obtained from the reduction of $B_{10}H_{14}$ by Sm(Hg) revealed the presence of equimolar ratios of solvent-separated[16,17] $[B_{10}H_{13}]^-$ and $[B_{10}B_{15}]^-$, along with four paramagnetically shifted and broadened resonances as well. The paramagnetically broadened peaks were not observed in later extracts. These broad signals might be due to $[B_{10}H_{14}]^{2-}$ coordinated to or ion-paired with Sm(II).

Thermal Decomposition of Lanthanide(II) Decaborates. Synthesis of $Ln[B_{10}H_{10}]$ complexes (eq 1 was achieved by thermal

$$(L)_xLn[B_{10}H_{14}] \xrightarrow[-L,\,-H_2]{190\ °C,\ vac} Ln[B_{10}H_{10}] \qquad (1)$$

$$Ln = Eu, Yb;\ L = NH_3,\ CH_3CN$$

decomposition of $(CH_3CN)_6Yb[B_{10}H_{14}]$, $(NH_3)_xEu[B_{10}H_{14}]$, and the ammonia-solvated powders produced in the reduction (Scheme I) of $B_{10}H_{14}$. The $Ln[B_{10}H_{10}]$ compounds are ligand free when formed. They are soluble in CH_3CN and C_5H_5N. The ^{11}B NMR spectrum of $Yb[B_{10}H_{10}]$ in C_5H_5N is very similar to that of alkali metal salts[22] of *closo*-$[B_{10}H_{10}]^{2-}$, indicating that this ion is solvent separated in solution.

The decaborate complex $Yb[B_{10}H_{10}]$ was heated in a quartz tube maintained at 10^{-5} Torr to a maximum of 1000 °C over a period of 1 h (eq 2). Although $Yb[B_{10}H_{10}]$ does not possess a

$$Yb[B_{10}H_{10}] \xrightarrow{1000\ °C} YbB_6 + 4B + 5H_2 \qquad (2)$$

Yb to B ratio consistent with any known ytterbium boride, it was thought that it might be possible to lose metal via sublimation to yield the boron-rich YbB_{12} phase. Previous investigators ob-

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served only mixtures of LnB_4 and LnB_6 phases formed during the thermal decomposition of Lanthanide(III) *closo*-decaborates (Ln = Gd, Pr).[23] We found that $Yb[B_{10}H_{10}]$ slowly evolves H_2 in the temperature range 300–500 °C, and no further volatiles are evolved up to 1000 °C. Evidently YbB_6 begins to form as soon as all the H_2 has been lost from the B_{10} cage. A powder X-ray pattern of the residue formed when $Yb[B_{10}H_{10}]$ is heated to 535 °C in vacuum contained broad lines that are assignable to YbB_6. These broad lines indicate that the boride is not yet fully crystalline. After heating of the sample to 1000 °C, the decomposition product exhibited sharp lines for only YbB_6 in the X-ray powder pattern. Amorphous B is probably present as well. A small amount of B_2O_3 was also observed, presumably due to side reactions with the walls of the reaction tube.

Discussion

Homogeneous reduction of $B_{10}H_{14}$ by Ln (Yb, Eu) in liquid NH_3 produces $[B_{10}H_{14}]^{2-}$ as the principle decaborate product. The reaction is relatively rapid, going to completion in about 5 min at −78 °C. On the other hand, heterogeneous reduction of $B_{10}H_{14}$ by Ln(Hg) (Yb, Sm) in DME produces as the major products equal amounts of the decaborates $[B_{10}H_{13}]^-$ and $[B_{10}H_{15}]^-$. This reaction is relatively slow, requiring several hours at room temperature to go to completion. In the heterogeneous reactions it is believed that $B_{10}H_{14}{}^{2-}$ is formed slowly, and as it is formed, it reacts relatively rapidly with unreduced $B_{10}H_{14}$ according to eq 3.

$$[B_{10}H_{14}]^{2-} + B_{10}H_{14} \rightarrow [B_{10}H_{13}]^- + [B_{10}H_{15}]^- \qquad (3)$$

The $[B_{10}H_{14}]^{2-}$ dianion is a sufficiently strong electron donor to coordinate to Yb(II) to form Yb–H–B bridges in $(CH_3CN)_6Yb[B_{10}H_{14}]$ as indicated by NMR spectroscopy and its X-ray structure (Figure 1). It is likely that Ln–H–B bonds also exist in the powders $(NH_3)_xLn[B_{10}H_{14}]$ (Ln = Yb, Eu) and $(CH_3CN)_xEu[B_{10}H_{14}]$. Infrared spectra of these materials, including $(CH_3CN)_6Yb[B_{10}H_{14}]$, contain a very weak band in the range 1650–1580 cm^{-1} that can reflect the B–H–Ln stretch. The monoanions $[B_{10}H_{13}]^-$ and $[B_{10}H_{15}]^-$ do not appear to be sufficiently electron donating to coordinate to the divalent lanthanides studied here. In every case examined, NMR spectra indicated that these ions in solution are apparently solvent separated from the ligated metal cation.

Interestingly, when $[B_{10}H_{14}]^{2-}$ is formed in DME through reduction of $B_{10}H_{14}$ by Yb amalgam and then placed in CH_3CN solution, the ^{11}B NMR spectrum indicates that this anion is solvent separated from the cation. Apparently sufficient DME remains coordinated to the lanthanide cation to favor solvent-separated species instead of the Ln–H–B complexes formed in the reductions in liquid ammonia.

While the ligands Et_2O, THF, DME, NH_3, and TMEDA bind to the lanthanide cation of $Ln[B_{10}H_{14}]$ (Ln = Yb, Eu, Sm) to form species that show characteristic ligand bands in Nujol IR spectra, the solids do not appreciably change color and will not dissolve in the liquid ligand even though some of these ligands (DME, NH_3, THF) bind quite strongly to the metal, and heating the complexes to temperatures of over 100 °C in vacuum is usually required to remove them. Acetonitrile and pyridine, however, proved to be excellent solvents for hydrodecaborate and borohydride complexes, forming highly colored, ligated species, for $[B_{10}H_{14}]^{2-}$ and also $[BH_4]^-$.[13a,b,21]

The "special" abilities of C_5H_5N and CH_3CN to dissolve lanthanide complexes have been observed in other systems as well. The cyclooctatetraene complex $(C_8H_8)Yb$ is insoluble in THF, $N(CH_3)_3$, NH_3, NH_2CH_3, and saturated hydrocarbons but dissolves in C_5H_5N to form $(C_8H_8)Yb(C_5H_5N)_3$.[24] The complexes Cp_2Ln (Ln = Sm, Eu, Yb) are insoluble in solvents like THF but dissolve in C_5H_5N.[25] Carborane complexes $(CH_3CN)_4Ln[C_2B_9H_{11}]$ (Ln = Sm, Yb) soluble in CH_3CN have been reported by Hawthorne et al.[26]

The ability of CH_3CN and C_5H_5N to solubilize Ln(II) complexes is reminiscent of their ability to solvate Cu(I) compounds. Cu(I) compounds have extensive solubility in CH_3CN and C_5H_5N, when compared to solvents such as NH_3, H_2O, and $H_2N(CH_2)_2NH_2$.[27] In CH_3CN and C_5H_5N solvents, Cu(I) readily forms the complexes $[(CH_3CN)_4Cu]^+$ and $[(C_5H_5N)_4Cu]^+$.[28,29] These complexes can be compared to the $[(CH_3CN)_xLn]^{2+}$ and $[(C_5H_5N)_xLn]^{2+}$ complex ions in the presence of $[B_{10}H_{13}]^-$, $[B_{10}H_{15}]^-$, and $[B_{10}H_{10}]^{2-}$ in CH_3CN and C_5H_5N solutions. Both Cu(I) [Ar]$3d^{10}$ and Yb(II) [Xe]$4f^{14}$ have closed-shell electronic configurations. For Sm(II) and Eu(II) the contracted nature of the 4f orbitals[30] causes the partially occupied orbitals to behave as core orbitals, giving Sm(II) [Xe]$4f^6$ and Eu(II) [Xe]$4f^7$ *pseudo*-closed-shell configurations and hence similar chemistry. In C_5H_5N, Eu(II) forms preferentially over Eu(III),[25] just as Cu(I) forms instead of Cu(II) in this solvent.[31] The bonding of C_5H_5N and CH_3CN to Ln(II) and Cu(I) ions seem to be through a weak ion–dipole interaction. The C≡N stretches of CH_3CN in the complexes $(CH_3CN)_6Yb[B_{10}H_{14}]$ and $(CH_3CN)_xEu[B_{10}H_{14}]$ are nearly identical with those reported for $[(CH_3CN)_4Cu]PF_6$.[32] Bond distances in the CH_3CN ligands in the Cu(I) and Yb(II) complexes[13a,b,28] are not significantly different from their free ligand values, consistent with weak, dative interaction between the metal and the ligand.

For Yb(II) and Eu(II) colors are independent of the anions $[B_{10}H_{10}]^{2-}$, $[B_{10}H_{14}]^{2-}$, $[BH_4]^-$,[13a] and Cl^- (CH_3CN). Eu(II) and Yb(II) complexes in C_5H_5N or CH_3CN have the same appearance: Yb(II)–CH_3CN, orange; Yb(II)–C_5H_5N, violet; Eu(II)–CH_3CN, yellow; Eu(II)–C_5H_5N, red-orange. These colors are undoubtedly due to metal-to-ligand charge-transfer bands (MLCT) from the Ln(II) ion to the π^* states of the unsaturated C_5H_5N and CH_3CN ligands, just as in the case of Cu(I) complexes. Deacon et al. has previously invoked MLCT bands to explain the visible spectra of some Ln organometallics.[33]

With the exception of the $Ln[B_{10}H_{10}]$ complexes, all of the Ln(II) decaborates are unstable as dry solids. Slow H_2 evolution is observed from solids that are stored under vacuum at room temperature. IR spectra of the freshly prepared solids in Nujol indicate the presence of Ln–H–B bridges. Upon resolvation of a complex that has been dry for some time, additional amounts of H_2 are evolved. ^{11}B NMR spectra of the resulting solutions show numerous unassignable boron resonances, along with signals due to the original compound.

It is suggested that, during the drying process, as ligands are removed from the Ln(II) coordination sphere, the boron hydride transfers H^- to the lanthanide forming an Ln–H intermediate. This hydride could interact with a proton in a neighboring Ln–H–B bond, resulting in elimination of H_2. Such a decomposition mechanism is shown schematically for an $L_xLn[B_{10}H_{14}]$ complex in Scheme IV. In this proposed pathway the decaborate ion is coordinated to the Ln(II) ion as observed in the molecular structure of $(CH_3CN)_6Yb[B_{10}H_{14}]$. As ligands are removed from the lanthanide coordination sphere, one of the terminal hydrogens is transfered to the Ln ion forming a lanthanide hydride species, and migration of B–H–B hydrogens on the boron cage to Yb–H–B

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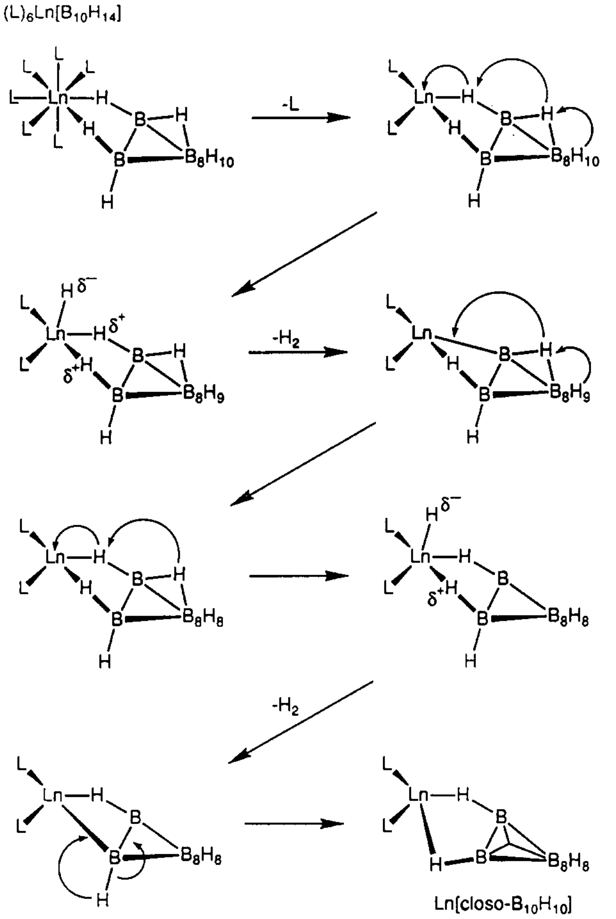
Scheme IV. Proposed H_2 Elimination Mechanism for $L_xLn[B_{10}H_{14}]$ Compounds (Ln = Eu, Yb; L = CH_3CN, C_5H_5N)



sites occurs. The hydride and bridge hydrogen then combine to form H_2, which is eliminated. Loss of hydrogen atoms from the boron cage results in B–B bond formation. This process could continue until all the bridge hydrogens have been eliminated and only the stable *closo*-$[B_{10}H_{10}]^{2-}$ remains. This proposed scheme could account for the relative instabilities of the $Ln[B_{10}H_{14}]$ complexes compared to alkali metal salts of $[B_{10}H_{14}]^{2-}$ since M–H–B bridges are not present in these salts.[34]

This scheme might also explain the observed decomposition of the $[B_{10}H_{13}]^-$ and $[B_{10}H_{15}]^-$ complexes. Ln(II) complexes of these anions in CH_3CN and DME are relatively stable in solution when the ions are solvent separated. However, when the solvent is removed from these complexes, loss of coordinated solvent from the Ln(II) cation permits direct bonding of the hydrodecaborate ion. The complex can then eliminate H_2 as shown in Scheme IV. The complex $[(DME)_xSm][B_{10}H_{15}]_2$ exemplifies this point. In DME solution, ^{11}B NMR spectra indicate that the ions are solvent separated. The IR spectrum of this solution contains only one weak absorption in the 2050–1580-cm^{-1} range characteristic of Ln–H–B bonds. Evaporation of the solvent from this compound produces a solid that produces numerous Sm–H–B absorptions in the IR spectrum of a Nujol mull. The solid decomposes upon standing at room temperature.

Experimental Section

General Data. All manipulations were performed under inert atmosphere conditions due to the air- and moisture-sensitive nature of Ln(II) compounds. Standard vacuum line and inert-atmosphere techniques were employed.[35] CH_3CN (Mallinckrodt) was stirred over P_2O_5 for 10 days before being distilled for use. C_5H_5N (Fischer) was dried and distilled from Na immediately prior to use. Hexanes (Baker) were stirred over H_2SO_4 for 2 days, washed with H_2O, dried with CaH_2, and then distilled from Na before use. Tetrahydrofuran, THF (Fischer), and 1,2-dimethoxyethane, DME (Aldrich), were dried with CaH_2 and then distilled from a Na/benzophenone solution immediately prior to use. *N,N,N′,N′*-tetramethylethylenediamine, TMEDA (Aldrich), was dried and distilled from Na metal immediately prior to use. NH_3 (Matheson) was distilled from Na immediately prior to use. Yb metal (Strem) and Sm metal (Strem) were used as received. Eu ingot (Strem) was obtained packed in oil. It was washed with hexanes to remove any oil and then cut into approximately 100-mg strips before use. Tetradecahydrodecaborane, $B_{10}H_{14}$ (Callery), was vacuum sublimed prior to use. Triply distilled mercury (Bethlehem Instruments) was used as received.

All IR spectra were recorded with 2-cm^{-1} resolution using a Mattson-Polaris FT-IR spectrometer. NMR spectra were obtained using a Brucker MSL-300 spectrometer with a boron-free probe equipped for heteronuclear decoupling, operating at 96.3 MHz (^{11}B, $\delta(BF_3{\cdot}OEt_2)$ = 0.00 ppm) and 300 MHz (^1H, δ(TMS) = 0.00 ppm).

X-ray powder data were collected on a Scintag PAD-5 powder X-ray diffractometer. The diffractometer was interfaced with a Data General computer, which contained a JCPDS library file for identification of diffraction patterns.[36]

Reduction of $B_{10}H_{14}$ by Yb in NH_3. In the drybox 141 mg of Yb (0.817 mmol) and 99.6 mg of $B_{10}H_{14}$ (0.815 mmol) are placed with a magnetic stir bar in a 50-mL flask attached to a vacuum line extractor. The extractor is evacuated, and 20 mL of NH_3 is condensed into the reaction flask at −196 °C. The NH_3 is allowed to warm, and a rapid reaction occurs as soon as it melts. A green suspension forms in the first 5 min, with the liberation of H_2 gas. Freezing the reaction flask to −196 °C and toeplerizing the H_2 yields 0.48 mmol (0.36 mmol H_2/mmol Yb), identified as H_2 by its mass spectrum. The green suspension is then thawed and stirred at −33 °C. The reaction mixture becomes more yellow as it is stirred at this temperature, and after 30 min a golden yellow suspension is observed which does not change color further. Removal of the NH_3 under vacuum leaves a yellow solid, which contains a reduced boron hydride and metal-coordinated NH_3 according to its IR spectrum.

The yellow product is treated with 5 mL of CH_3CN condensed onto the solid at −78 °C. Upon melting, NH_3 gas evolution is observed as the CH_3CN displaces coordinated ammonia. The CH_3CN is removed, 15 mL of fresh CH_3CN is condensed into the now orange-brown suspension, and the flask is stirred at room temperature for 20 min. The extractor is then inverted and the suspension is filtered, resulting in a bright orange filtrate of $(CH_3CN)_xYb[B_{10}H_{14}]$ and a purple-brown precipitate. Cooling the filtrate to 0 °C with slow removal of the CH_3CN solvent under dynamic vacuum produces yellow-orange crystals shown to be $(CH_3CN)_6Yb[(\mu\text{-}H)_2B_{10}H_{12}]{\cdot}2CH_3CN$ from a single-crystal X-ray crystallographic study.[13b] The crystalline solid can also be obtained by maintaining a concentrated acetonitrile solution at −30 °C for 1 week. Removal of all solvent causes decomposition of the crystals to a less solvated bright yellow powder with approximate composition $(CH_3CN)_3Yb[B_{10}H_{14}]$. The yield is 96 mg (28%) based on $B_{10}H_{14}$. Anal. Calcd for $C_6H_{23}N_3YbB_{10}$: C, 17.22; H, 5.54; N, 10.04. Found: C, 16.33; H, 5.77; N, 10.66. Infrared data for $(CH_3CN)_3Yb[B_{10}H_{14}]$ (Nujol, NaCl plates): ν_{B-H} 2507 (sh), 2497 (vs), 2454 (s, br), 2365 (m), 2050 (vw), ν_{Yb-H-B} 1616 (vw), ν_{B-B} 1201 (w), 1169 (w), 1075 (w), 1026 (s), 927 (w), $\nu_{C\equiv N}$ 2307 (s, sh), 2265 (s, sh) cm^{-1}. ^{11}B NMR data for $(CH_3CN)_6Yb[(\mu\text{-}H)_2B_{10}H_{12}]{\cdot}2CH_3CN$ in CD_3CN (303 K, ^{11}B–^1H coupling constants in parentheses Hz): −4.3 d (109), −7.1 d (126), −20.0 d (111), −25.6 d (113), −32.2 t (98), −40.3 d (132) ppm. Peak integration gives intensity ratios of approximately 1:1:4:1:1:2, respectively.

Continued washing of the purple-brown precipitate leaves an insoluble lavender solid $(NH_3)_3Yb[B_{10}H_{14}]$ and a pale, yellow extract. The $(NH_3)_3Yb[B_{10}H_{14}]$ is believed to be polymeric. It is insoluble in standard polar and nonpolar solvents. The number of coordinated NH_3 molecules was determined by heating a sample to 190 °C for 2 h. NH_3 and H_2 were given off in the molar ratio 3/2 NH_3/H_2, and $Yb[B_{10}H_{10}]$ remained behind as a solid. Infrared data for $(NH_3)_3Yb[B_{10}H_{14}]$ (Nujol, NaCl plates): ν_{N-H} 3322 (s), 3248 (s), 3171 (m), 3150 (m), ν_{B-H} 2465 (vs), 2390 (s), 2330 (m), 2257 (w), ν_{Yb-H-B} 1690 (vw, br), 1589 (w, sh), ν_{B-B} 1235 (s), 1179 (m), 1030 (m) cm^{-1}.

The pale, yellow extract mentioned above contains an equimolar amount of solvent-separated $[B_{10}H_{13}]^-$ and $[B_{10}H_{15}]^-$ on the basis of an integrated ^{11}B NMR spectrum. ^{11}B NMR in CH_3CN at 303 K (coupling constants in parentheses in Hz): $[B_{10}H_{13}]^-$, +8.2 d (157), +3.7 d (120), −3.7 d (142), −34.0 d (134) ppm; $[B_{10}H_{15}]^-$, −13.2 d (137), −18.9 d (103), −19.5 d (132), −21.3 d (153) ppm. In CH_3CN the extract very slowly

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decomposes at elevated temperatures. The resulting solid from removal of solvent decomposes much more rapidly when it is maintained at room temperature under N_2 or in vacuum. Noticeable amounts of H_2 and $B_{10}H_{14}$ are the only identifiable decomposition products after the solid is allowed to stand at room temperature in vacuum for 24 h.

Reduction of $B_{10}H_{14}$ by Eu in NH_3. In a reduction reaction similar to that described above, 135 mg (0.888 mmol) of Eu is reacted with 108.6 mg (0.887 mmol) of $B_{10}H_{14}$ in liquid NH_3. The reaction product is a pea-green NH_3-solvated solid. Addition of CH_3CN to this solid and subsequent filtration allows separation of the brilliant yellow filtrate from insoluble pale green $(NH_3)_xEu[B_{10}H_{14}]$. Cooling the filtrate to 0 °C and filtering allows separation of $[(CH_3CN)_xEu][B_{10}H_{13}][B_{10}H_{15}]$ as a yellow-white solid. Removal of the CH_3CN from the bright yellow filtrate produces a film, which becomes bright yellow $(CH_3CN)_xEu[B_{10}H_{14}]$ upon washing with hexanes. Infrared data (Nujol, NaCl plates): ν_{B-H} 2526 (s), 2503 (vs), 2448 (s), 2379 (m), 2031 (vw), ν_{Eu-H-B} 1600 (vw), ν_{B-B} 1204 (w), 1176 (w), 1073 (w), 1024 (s), 927 (w), $\nu_{C\equiv N}$ 2307 (s, sh), 2265 (s, sh) cm^{-1}.

$Yb[B_{10}H_{10}]$. In a drybox the ammonia-solvated powder from the $Yb/B_{10}H_{14}$ in NH_3 above is loaded into a 50-mL flask and fitted with a vacuum line adaptor. The flask is evacuated to 10^{-5} Torr, and a heating mantle/sand bath is used to slowly heat the flask. At 100 °C NH_3 gas is evolved, and at 160 °C evolution of H_2 begins. By the time the temperature has reached 190 °C (2 h), no more gas evolution is observed and the pea-green complex is obtained quantitatively as a powdery solid. Anal. Calcd for $B_{10}H_{10}Yb$: B, 37.12; H, 3.46; Yb, 59.42. Found: B, 35.73; H, 3.40; Yb, 59.15. Infrared data (Nujol, NaCl plates): ν_{B-H} 2525 (sh), 2456 (vs, br) ν_{Yb-H-B} 1588 (vw), ν_{B-B} 1076 (w), 1016 (mw), 974 (w) cm^{-1}. ^{11}B NMR data in C_5D_5N (353 K, B–H coupling constants in parentheses Hz): +3.1 d (143), −24.9 d (118) ppm. Intensity ratios are 1:4, respectively. No B–H coupling is observed for the upfield signal below 333 K. This spectrum is in good agreement with that of alkali metal salts of *closo*-$[B_{10}H_{10}]^{2-}$ salts.[21,22] ^1H NMR data in C_5D_5N (303 K): +4.90 q (142), +1.77 s, br ppm. Intensity ratios are approximately 1:4, respectively.

$Eu[B_{10}H_{10}]$ In a procedure identical to that used for the formation of *closo*-$Yb[B_{10}H_{10}]$ above, the NH_3-solvated powder from the preparation of $B_{10}H_{14}$ with Eu is thermally decomposed. The salt $Eu[B_{10}H_{10}]$ remains behind as a gray-green powder in essentially pure form. Anal. Calcd for $B_{10}H_{10}Eu$: B, 40.02; H, 3.73; Eu, 56.25. Found: B, 38.21; H, 3.46; Eu, 55.55. Infrared data (Nujol, NaCl plates): ν_{B-H} 2503 (s), 2456 (vs, br), ν_{Eu-H-B} 1602 (vw), ν_{B-B} 1086 (w), 1019 (mw), 974 (w) cm^{-1}.

Yb(Hg) and $B_{10}H_{14}$. In a drybox a 50-mL flask with a magnetic stir bar is charged with 173 mg (1.00 mmol) of Yb metal and 10 mL of Hg and fitted with a vacuum line adaptor. The mixture is stirred until all of the metal dissolves (ca. 3 h). Then the flask is charged with 122 mg (1.00 mmol) of $B_{10}H_{14}$ in the drybox. The flask is then cooled to −78 °C and evacuated, and 15 mL DME is condensed onto the mixture. The flask is warmed to room temperature and stirred. As soon as the reaction begins, the mixture turns yellow-green in color. After 8 h a large quantity of a pea-green precipitate is formed. The resulting suspension is siphoned off the mercury in the drybox and placed in a 50-mL flask connected to a vacuum line extractor. Filtration of the suspension yields a pea-green solid as the major product and a pale yellow filtrate. The ^{11}B NMR spectrum of the filtrate indicates that it contains an equimolar ratio of $[B_{10}H_{13}]^-$ and $[B_{10}H_{15}]^-$ with no apparent influence from the Yb^{2+} (NMR in DME-d_{10} at 303 K (coupling constants in parentheses in Hz): $[B_{10}H_{13}]$, +7.5 d (149), +3.0 d (124), −3.9 d (134), −34.6 d (overlaps w/$B_{10}H_{14}$ impurity) ppm; $[B_{10}H_{15}]^-$, −13.6 d (141), −19.0 d (∼102), −19.6 d (∼116), −21.3 d (∼138) ppm). Removing the solvent from this filtrate produces a waxy pale yellow solid which decomposes to give H_2 and $B_{10}H_{14}$ upon standing at room temperature in vacuum. The pea-green solid isolated from the reaction above is heavily contaminated with mercury. A clean receiving flask is connected to the extractor, and CH_3CN is condensed onto the solid. The solid is only slightly soluble in this solvent, and filtration gives a pale yellow-orange solution. ^{11}B NMR analysis of the filtrate shows that it contains equimolar quantities of $[B_{10}H_{13}]^-$ and $[B_{10}H_{15}]^-$ as the main product and very small amounts of free $[B_{10}H_{14}]^{2-}$ observed only in the initial extracts. The $[B_{10}H_{14}]^{2-}$ is thought to be solvent separated in this case due to the presence of mixed-ligand ether–amine cations, $[(DME)_x(CH_3CN)_yYb]^{2+}$. Such cations have been observed in other mixed-solvent systems.[20] NMR in CH_3CN at 303 K (coupling constants in parentheses in Hz): $[B_{10}H_{13}]^-$, 8.1 d (144), +3.8 d (122), −3.7 d (132), −7.0 d (144), −33.9 d (138) ppm; $[B_{10}H_{15}]^-$, −13.3 d (140), −19.0 d (∼107), −19.5 d (∼125), −21.3 d (∼150) ppm; $[B_{10}H_{14}]^{2-}$, −4.7 d (overlaps w/$[B_{10}H_{13}]^-$), −19.7 d (overlaps w/$[B_{10}H_{13}]^-$), −31.6 t (85), −38.3 d (131) ppm. Removal of the solvent from this filtrate yields a bright-yellow solid. The yellow solid slowly decomposes at room temperature in vacuum to give H_2 and $B_{10}H_{14}$ as the only identifiable products.

Sm(Hg) and $B_{10}H_{14}$. In a drybox, a 50-mL flask with a magnetic stir bar is charged with 150 mg of Sm (1.00 mmol) and 10 mL of Hg and fitted with a vacuum line adaptor. The amalgam is formed, and then the flask is charged with 122 mg of $B_{10}H_{14}$ (1.00 mmol) in the drybox. DME is condensed onto the mixture, and the reaction is allowed to proceed at room temperature. A red-green color forms immediately. After 6 h a large quantity of red precipitate has formed. The DME solution is a dark green-red color, and the mercury is quite mobile. The resulting suspension is siphoned off the mercury and placed in a 50-mL flask connected to a vacuum line extractor. Filtration of the suspension yields a large quantity of a red solid, with a red-green filtrate, a color characteristic of Sm(II). On the basis of the ^{11}B NMR spectrum the filtrate consists of a mixture of $[B_{10}H_{15}]^-$ and residual $B_{10}H_{14}$ starting material. The ^{11}B NMR spectrum of the $[B_{10}H_{15}]^-$ in DME-d_{10} at 303 K (−13.1 d (140), −18.6 d (∼105), −19.2 d (∼110), −20.9 d (∼137 Hz) ppm) is unperturbed with respect to that obtained from alkali metal salts of this anion.[17] Removal of solvent yields a small quantity of purple solid which quickly decomposes at room temperature in vacuum, forming H_2 and $B_{10}H_{14}$ as the only identifiable products. A quantity of this purple solid was washed with hexanes to remove the residual $B_{10}H_{14}$. A portion was dissolved in DME, and the IR spectrum of the solution was observed. IR data (DME between NaCl plates): ν_{B-H} 2527 (vs), 2384 (s), 2301 (w), ν_{Sm-H-B} 1925 (vw) cm^{-1}. The IR spectrum of another portion of the purified solid was also obtained. IR data (Nujol, NaCl plates): ν_{B-H} 2519 (vs, br), 2382 (w), 2348 (w), 2308 (w), 2315 (w), ν_{Sm-H-B} 2058 (vw), 2035 (vw), 1910 (vw), 1634 (vw, d), 1616 (vw, d), 1559 (vw, d), ν_{B-B} 1291 (vw), 1251 (w), 1206 (vw), ν_{DME} 1106 (m), 1057 (vs), 1020 (m), 855 (s) cm^{-1}.

The red precipitate produced in the reduction reaction is heavily contaminated with mercury. A receiving flask is connected to the extractor, and CH_3CN is condensed onto the solid. The solid is only slightly soluble in this solvent, and filtration gives a pale, green-black solution. Removal of the solvent from this filtrate yields a green-black solid, that contains both coordinated DME and CH_3CN on the basis of its IR spectrum. ^{11}B NMR analysis of the filtrate shows that it contains equimolar quantities of $[B_{10}H_{13}]^-$ and $[B_{10}H_{15}]^-$ ions (8.8 d (153), +4.0 d (116), −3.0 d (135), −5.0 d (overlaps w/$B_{10}H_{14}$ impurity), −12.5 d (140), −18.0 d (108), −18.7 d (120), −20.4 d (145 Hz), −33.3 d (overlaps w/$B_{10}H_{14}$ impurity) ppm. A very small quantity of another product observed only in the initial extracts of the CH_3CN filtration shows ^{11}B NMR resonances paramagnetically shifted and broadened, which is attributed to the complex $[(DME)_x(CH_3CN)_ySm][B_{10}H_{14}]$. (Chemical shifts in CH_3CN at 303 K are concentration dependent, and signals are broad ($\Delta\nu_{1/2}$ 450–1075 Hz), with no B–H coupling observed. Typical values for the four observed signals are 5.1, −35.2, −40.1, and −62.0 ppm.)

YbB_6. About 100 mg of $Yb[B_{10}H_{10}]$ is loaded into a 15-mm quartz tube fitted with a vacuum line adaptor. The flask is evacuated to 10^{-5} Torr and then heated via an external tube furnace to 1000 °C over a 1-h period. A −196 °C trap is in series with the reaction vessel to collect any condensible gases evolved. Gradual H_2 evolution is observed from 325 to 500 °C, but no Yb metal sublimes from the tube. The X-ray powder diffraction pattern of the resulting black powder contains sharp lines for YbB_6[36] and several less intense peaks attributed to B_2O_3 due to reaction of boron with the quartz tube. A broad hump at low diffraction angles is attributed to amorphous B. Powder X-ray data for YbB_6 [d, Å (I); for Cu Kα]: 4.126 (30), 2.933 (45), 2.400 (21), 2.063 (11), 1.856 (19), 1.690 (12), 1.468 (5), 1.384 (8), 1.315 (7), 1.254 (6).

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