Chemical vapor deposition (CVD) of thin films is a technique often used in the manufacture of microelectronics, as well as hard and optical coating. Before useful thin films can be deposited, however, appropriate CVD precursors must first be synthesized. Several metal methylborohydride complexes have been reported,\(^1\) most of which are volatile. Yet, unlike many metal borohydride complexes, no reports exist of methylborohydride complexes being used as CVD precursors. Another interesting class of CVD precursors is the metal aminodiboranates,\(^2\) primarily those containing \(N,N\)-dimethylaminodiboranate. Magnesium \(N,N\)-dimethylaminodiboranate has, to date, been the most promising candidate for a single source MgB\(_2\) CVD precursor.\(^3\) Expansion of the currently available ligand set to include sterically bulky or electron withdrawing \(N\)-alkyl groups may further enhance the performance of these CVD precursors.

The complex sodium methylborohydride, NaH\(_3\)BCH\(_3\), can be prepared in high yield (83\%) by the addition of trimethylboroxine, (H\(_3\)C)\(_3\)B\(_3\)O\(_3\), to sodium aluminum hydride, NaAlH\(_4\). The subsequent reaction of two equivalents of sodium methylborohydride with the alkaline earth bromides: MgBr\(_2\), CaBr\(_2\), SrBr\(_2\), and BaBr\(_2\) in 1,2-dimethoxyethane, DME, affords the new alkaline earth methylborohydride DME adducts: \([\text{Mg}(\text{H}_3\text{BCH}_3)(\text{DME})]_2\), \([\text{Ca}(\text{H}_3\text{BCH}_3)(\text{DME})]_2\), \([\text{Sr}(\text{H}_3\text{BCH}_3)(\text{DME})]_3\), and \([\text{Ba}(\text{H}_3\text{BCH}_3)(\text{DME})]_3\). \([\text{Mg}(\text{H}_3\text{BCH}_3)(\text{DME})]_2\) sublimes between 80 and 90 °C at 10 mTorr, making it a candidate for the CVD of MgB\(_2\) thin films, while the larger alkaline earth methylborohydrides do not sublime up to 120 °C. \([\text{Mg}(\text{H}_3\text{BCH}_3)(\text{DME})]_2\) is an asymmetrically bridged dimer in the solid state where each Mg center has a terminal \(\kappa^2\)H-methylborohydride, a bridging \(\kappa^2\)H-methylborohydride, a bridging \(\kappa^1\)H-methylborohydride and a chelating DME. The other alkaline earth methylborohydrides have two \(\kappa^2\)H-methylborohydrides and two chelating DME for the Ca complex and three chelating DME for the Sr and Ba complexes.

![Figure 1: Structure of the \([\text{Mg}(\text{H}_3\text{BCH}_3)(\text{DME})]_2\) dimer.](image-url)
Rare earth methylborohydride THF adducts are prepared by the reaction of a rare earth halide (Sc, Y, Nd, Gd, Er) with 3 – 4 equivalents of sodium methylborohydride in THF. The scandium and yttrium complexes are isolated by sublimation at 50 °C, while the neodymium, gadolinium, and erbium complexes are isolated by sublimation at 60 °C. In the solid state, scandium methylborohydride has three $\kappa^3$H-methylborohydrides and one coordinated THF. The yttrium, gadolinium, and erbium complexes crystallize as charge separated ion pairs: $[\text{RE}(\text{H}_3\text{BCH}_3)_2(\text{THF})_4]$, $[\text{RE}(\text{H}_3\text{BCH}_3)_4]$, where the cation has two $\kappa^3$H-methylborohydrides and four coordinated THF and the anion consists of four $\kappa^3$H-methylborohydrides. A similar structure has been reported for the yttrium borohydride THF adduct, $[\text{Y(BH}_4)_2(\text{THF})_4][\text{Y(BH}_4)_4]$. The neodymium methylborohydride complex is a methylborohydride bridged dimer, $[\text{Nd(H}_3\text{BCH}_3)_3(\text{THF})_2]_2$, where each Nd center has two $\kappa^3$H-methylborohydrides, two bridging $\kappa^2$H-methylborohydrides and two THF. In addition to the Sc, Y, Nd, Gd, and Er THF adducts, the neodymium DME adduct, $\text{Nd(H}_3\text{BCH}_3)_3(\text{DME})_{1.5}$, has also been synthesized by a similar method. This complex can be sublimed under vacuum at 115 °C. The Er complex has been used in preliminary CVD experiments which demonstrate the ability to grow thin films between 250 and 350 °C using this new precursor.

![Figure 2: Structure of [Gd(H$_3$BCH$_3$)$_2$(THF)$_4$][Gd(H$_3$BCH$_3$)$_4$]](image-url)

The synthesis of sodium aminodiboranates with sterically bulky or electron withdrawing substituents on nitrogen has been achieved by treating the amine-borane with either BH$_3$·THF or by thermolysis at elevated temperatures followed by the addition of BH$_3$·THF, which produced $\mu$-aminodiborane. The $\mu$-aminodiborane can then be ring opened with NaH, similar to what has been reported by Keller for the synthesis of sodium $N,N$-dimethylaminodiboranate. Implementing this method, the sterically bulky aminodiboranates: sodium $N$-isopropyl-$N$-methylaminodiboranate, sodium $N,N$-disopropylaminodiboranate, sodium $cis$-$2,6$-dimethylpiperdinyldiboranate, sodium $tert$-butylaminodiboranate, and sodium $N$-isopropylaminodiboranate have been prepared. The aminodiboranates with electron withdrawing substituents on nitrogen: sodium $N$-benzylaminodiboranate, sodium $N$-benzyl-$N$-methylaminodiboranate, and sodium 2,2-difluoroethylaminodiboranate were also able to be prepared by the addition of BH$_3$·THF to the appropriate amine-borane followed by treatment with sodium hydride. Unfortunately, these aminodiboranates decompose slowly at room temperature.
Magnesium cis-2,6-dimethylpiperidinyldiboranate was able to be synthesized by treatment of MgBr₂ with two equivalents of sodium cis-2,6-dimethylpiperidinyldiboranate in diethyl ether followed by sublimation at 50 °C under vacuum. The hydrolysis/thermolysis product µ-(cis-2,6-dimethylpiperidinyl)diborane is, however, present in the sublimate due to similar volatility to the desired magnesium product. Synthesis of magnesium N,N-diisopropylaminodiboranate was attempted by ball milling MgBr₂ and sodium N,N-diisopropylaminodiboranate followed by sublimation at 65 °C. Interestingly, primarily decomposition products, N,N-dimethylimine and magnesium borohydride, Mg(BH₄)₂, were observed by ¹¹B NMR in the reaction mixture.

Static chemical vapor deposition (CVD) has been successfully used to deposit conformal thin films of hafnium diboride, HfB₂, and iron metal from hafnium borohydride, Hf(BH₄)₄, and iron pentacarbonyl, Fe(CO)₅, respectively. Microtrenches with aspect ratios greater than 10:1 were able to be completely infilled with HfB₂ or iron and macrotrenches were able to be coated with thin films of HfB₂ which has a 40% step coverage at an aspect ratio of 1000:1. Static CVD has been successfully used to infill a photonic crystal template, producing an inverse opal structure which may be used as the narrow band emitter of a thermophotovoltaic cell.⁶ HfB₂ thin films deposited by static CVD have a Hf:B ratio similar to films deposited using Hf(BH₄)₄ in an actively pumped, low pressure CVD system, although the relative hydrogen content of the film deposited by static CVD was greater. Iron thin films deposited by static CVD have an iron composition as high as 97% with approximately 1.5% carbon and oxygen each.

References