

## Lanthanide *N,N*-Dimethylaminodiboranates: Highly Volatile Precursors for the Deposition of Lanthanide-Containing Thin Films

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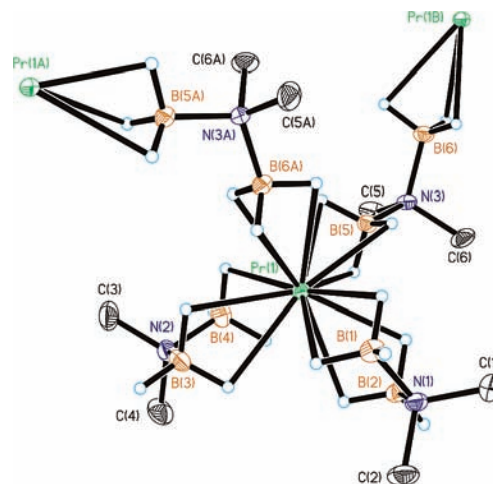
The development of improved lanthanide-containing precursors suitable for chemical vapor deposition (CVD) and atomic layer deposition (ALD) is a significant technological goal.<sup>1–3</sup> Lanthanide materials have optical,<sup>4–6</sup> electrical,<sup>7–9</sup> and magnetic<sup>9–11</sup> properties that make them useful in many applications such as phosphors in LEDs and lasers and as high- $\kappa$  dielectrics for microelectronic transistors. Ideal CVD and ALD precursors are highly volatile and deposit films cleanly and conformally (i.e., with uniform thickness) in trenches and vias with high aspect ratios (>5:1).<sup>12</sup>

Owing to their large radii and ionic nature, lanthanide(III) ions form volatile complexes only with certain ligand sets<sup>3,13–16</sup> able to encapsulate the metal ion and minimize intermolecular interactions.<sup>17</sup> Many volatile lanthanide complexes, however, are nonideal as CVD precursors because they deposit films that contain undesirable C, F, or Si impurities.<sup>17–19</sup>

Here we report the synthesis of highly volatile lanthanide complexes of a new ligand class, the aminodiboranates. The *N,N*-dimethylaminodiboranate ligand, H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub><sup>–</sup> (DMADB), can be considered as a multidentate (often chelating) borohydride ligand that binds to metal centers via M–H–B bridges.

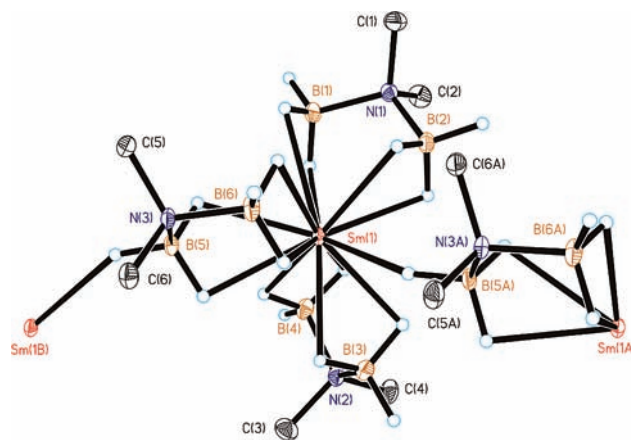
Treatment of anhydrous LnCl<sub>3</sub> salts with Na(DMADB)<sup>20,21</sup> in tetrahydrofuran (thf) affords monomeric complexes of stoichiometry Ln(H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>)<sub>3</sub>(thf) in good yields (51–71%). The synthesis is general for all of the commercially available lanthanides (including Y) except for La and Ce. When sublimed under a dynamic vacuum, these complexes lose thf to form the corresponding base-free Ln(H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>)<sub>3</sub> species. The sublimation yields are typically greater than 90% (Figure S1). The thf-free compounds, including those of La and Ce, can also be prepared by grinding the anhydrous LnCl<sub>3</sub> salt with solid Na(DMADB), followed by sublimation.

X-ray diffraction studies of the Ln(H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>)<sub>3</sub> complexes reveal that the solid state structure depends on the size of the lanthanide ion. For example, the Pr(H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>)<sub>3</sub> complex **1**, which contains a relatively large praseodymium(III) ion ( $r_{\text{ionic}} = 0.99 \text{ \AA}$ ),<sup>22</sup> forms a polymeric structure. Each Pr center is bound to two chelating DMADB ligands (in which each BH<sub>3</sub> group is  $\kappa^2H$ , i.e., forms two B–H–Pr interactions) and to two “ends” of two bridging ligands, Pr(H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>)Pr (in which each BH<sub>3</sub> group is  $\kappa^3H$ ).<sup>23</sup> Each Pr atom is therefore 14-coordinate (Figure 1). In the Sm(H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>)<sub>3</sub> complex **2**, which contains the smaller samarium(III) ion (0.96 Å),<sup>22</sup> all three DMADB ligands are chelating. The Sm atom is also coordinated to one hydrogen atom from an adjacent molecule, so that its



**Figure 1.** Structure of Pr(H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>)<sub>3</sub>, **1**. Ellipsoids are drawn at the 35% probability level, except for the hydrogen atoms, which are represented as arbitrarily sized spheres. Methyl hydrogen atoms have been deleted for clarity.

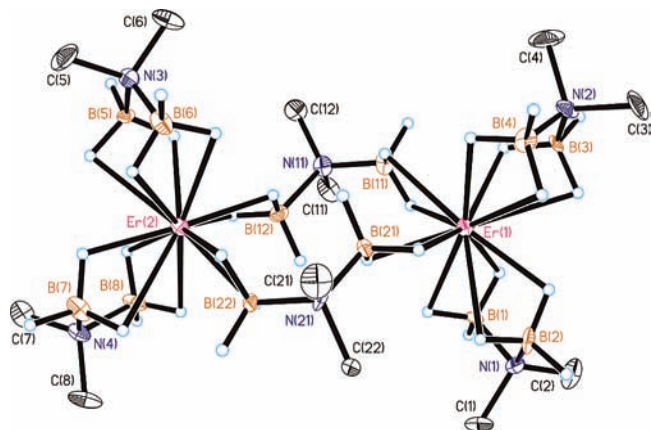
coordination number is 13 (Figure 2). The intermolecular Sm–H distance of 2.50 Å is comparable to the average intramolecular Sm–H distances of 2.44 Å.<sup>24</sup> The Er(H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>)<sub>3</sub> complex **3**, which contains the even smaller erbium(III) ion (0.89 Å),<sup>22</sup> adopts a dinuclear structure in which each metal center is bound to two chelating DMADB ligands and to two bridging ligands



**Figure 2.** Structure of Sm(H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>)<sub>3</sub>, **2**. Ellipsoids are drawn at the 30% probability level, except for the hydrogen atoms, which are represented as arbitrarily sized spheres. Methyl hydrogen atoms have been deleted for clarity.

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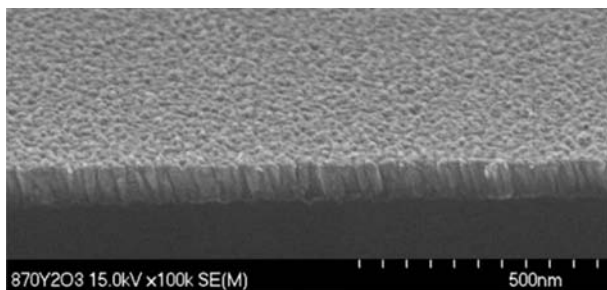


**Figure 3.** Structure of  $\text{Er}(\text{H}_3\text{BNMe}_2\text{BH}_3)_3$ , **3**. Ellipsoids are drawn at the 35% probability level, except for the hydrogen atoms, which are represented as arbitrarily sized spheres. Methyl hydrogen atoms have been deleted for clarity.

each bound in an  $\text{Er}(\kappa^2\text{H}-\text{H}_3\text{BNMe}_2\text{BH}_3-\kappa^2\text{H})\text{Er}$  fashion. The coordination number is 12 (Figure 3).

Lanthanide complexes of  $\text{BH}_4^-$  and  $\text{B}_3\text{H}_8^-$  are poorly volatile;<sup>25–29</sup> in contrast, the  $\text{Ln}(\text{H}_3\text{BNMe}_2\text{BH}_3)_3$  complexes exhibit high volatility, despite the fact that some of them are polymeric, and their sublimation temperatures at  $10^{-2}$  Torr decrease steadily across the period, from 120 °C (La) to 65 °C (Lu). Quantitative comparisons are difficult, but the  $\text{Ln}(\text{H}_3\text{BNMe}_2\text{BH}_3)_3$  compounds appear to be more volatile than lanthanide complexes of tetramethylheptanediolate,<sup>30</sup> guanidates,<sup>31</sup> amidinates,<sup>32</sup> and cyclopentadienyls.<sup>33</sup> The sublimation temperatures are as low as (or lower than) those reported for certain lanthanide silylamides (72–102 °C at  $10^{-4}$  Torr),<sup>34</sup> ether-functionalized  $\beta$ -ketoiminates (80–110 °C at  $10^{-4}$  Torr),<sup>15</sup> and methylborohydrides (100 °C *in vacuo*).<sup>35</sup> Lanthanide hexafluoroacetylacetonato complexes also sublime at similar temperatures (75–110 °C at  $10^{-3}$  Torr), but these precursors afford films that tend to retain fluoride.<sup>19</sup> Evidently, for those  $\text{Ln}(\text{H}_3\text{BNMe}_2\text{BH}_3)_3$  complexes that are polymers in the solid state, the barrier for ligand rearrangement to volatile monomers (or dimers) must be small. Similar behavior has been noted for  $\text{U}(\text{BH}_4)_4$ , which also forms a polymeric structure in the solid state but nevertheless is highly volatile.<sup>36,37</sup>

Preliminary CVD results reveal that  $\text{Y}_2\text{O}_3$  can be deposited on silicon at 300 °C using  $\text{Y}(\text{H}_3\text{BNMe}_2\text{BH}_3)_3$  and water as a secondary reactant (Figure 4). Auger spectroscopy reveals that the films contain no carbon, nitrogen, or boron impurities, within the limits of detection (Figure S2). These precursors, which are also able to deposit clean oxide films under ALD conditions,<sup>38</sup> are promising new precursors for the deposition of lanthanide-containing phases.



**Figure 4.** Cross-sectional SEM images of the  $\text{Y}_2\text{O}_3$  film deposited on silicon substrates at 300 °C from  $\text{Y}_2(\text{H}_3\text{BNMe}_2\text{BH}_3)_6$  and  $\text{H}_2\text{O}$ .

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**Supporting Information Available:** Experimental details, spectroscopic data, representative TGA traces, and X-ray crystallographic data (CIF format). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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