

## Carbene-Stabilized Beryllium Borohydride

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**S** Supporting Information

**ABSTRACT:** The reaction of N-heterocyclic carbene, L:, with  $\text{BeCl}_2$  quantitatively yields  $\text{L}:\text{BeCl}_2$  **1** (L: =  $:\text{C}\{\text{N}(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)\text{CH}\}_2$ ). The carbene-stabilized beryllium borohydride monomer  $\text{L}:\text{Be}(\text{BH}_4)_2$  **2** is prepared by the reaction of **1** with  $\text{LiBH}_4$ . Compound **3**, prepared by the reaction of **2** with  $\text{Na}_2[\text{Fe}(\text{CO})_4]\cdot\text{dioxane}$ , represents an unusual “dual reduction” of the imidazole ring (i.e., hydroboration of the C=C backbone and hydrogenation of the C2 carbene center).

It has been more than seven decades since Burg and Schlesinger reported the synthesis of beryllium borohydride,  $\text{Be}(\text{BH}_4)_2$ .<sup>1</sup> In the intervening years, this obscure laboratory curiosity has evolved into an intriguing hydrogen storage candidate possessing the highest hydrogen capacity (20.8 wt %) of all metal borohydrides.<sup>2</sup> Although the original beryllium borohydride synthesis involved sequential borane addition to dimethylberyllium, reaction of beryllium chloride with alkali-metal borohydrides is an alternative preparative method.<sup>3</sup> The molecular structure of monomeric beryllium borohydride has, surprisingly, flummoxed chemists since the original 1940 synthetic report. Confusing and contradictory findings have fueled debate for decades.<sup>4</sup> Indeed, *both* bent and linear gas-phase structures for the B–Be–B fragment in  $\text{Be}(\text{BH}_4)_2$  have been suggested, while neither the number nor disposition of the bridging hydrogen atoms have been established with certainty.<sup>5</sup> The revelation that solid-state beryllium borohydride consists of helical polymers of  $-\text{BH}_4\text{Be}-$  and  $-\text{BH}_4-$  units situated about crystallographic screw axes<sup>6,7</sup> only augmented the structural ambiguities. Might there be a facile means to stabilize, and thus help characterize, the long-sought structure of the beryllium borohydride monomer? N-heterocyclic carbenes (NHCs) have recently been utilized to stabilize a variety of highly reactive main-group molecules.<sup>8,9</sup> Prominent examples from this laboratory include carbene-stabilized diborene,<sup>10,11</sup> disilicon,<sup>12</sup> diphosphorus,<sup>13</sup> diarsenic,<sup>14</sup> and the carbene-stabilized diphosphorus complexation of the  $\text{BH}_2^+$  cation.<sup>15</sup>

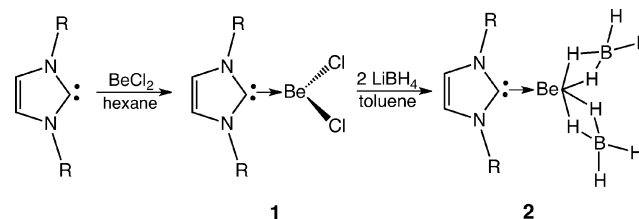
Herein we report the synthesis,<sup>16</sup> molecular structure,<sup>16</sup> and computations<sup>17</sup> of the carbene-stabilized beryllium borohydride monomer  $\text{L}:\text{Be}(\text{BH}_4)_2$  (**2**) (L: =  $:\text{C}\{\text{N}(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)\text{CH}\}_2$ ). Significantly, compound **2** represents the first experimental example of an unambiguously structurally characterized monomeric  $\text{Be}(\text{BH}_4)_2$  derivative. In addition, the unusual reducing capability of **2** is suggested by its reaction with

$\text{Na}_2[\text{Fe}(\text{CO})_4]\cdot\text{dioxane}$  to form **3**, an unusual imidazole ring “dual reduction” product.

Recently, NHCs have been employed to stabilize group 2 hydrides.<sup>18,19</sup> In particular,  $\text{L}:\text{Be}(\text{Me})(\mu\text{-H}_2)(\text{Me})\text{Be}:\text{L}$  was observed to undergo imidazole ring opening with insertion of a  $\text{BeH}_2$  unit into a C–N bond of an NHC ligand.<sup>19</sup>

NHC-complexed beryllium chloride,  $\text{L}:\text{BeCl}_2$  (**1**), was quantitatively prepared by the reaction of L: with  $\text{BeCl}_2$ . Lithium borohydride reacts with **1** to afford **2** (Scheme 1; R =

**Scheme 1. Synthesis of 1 and 2**

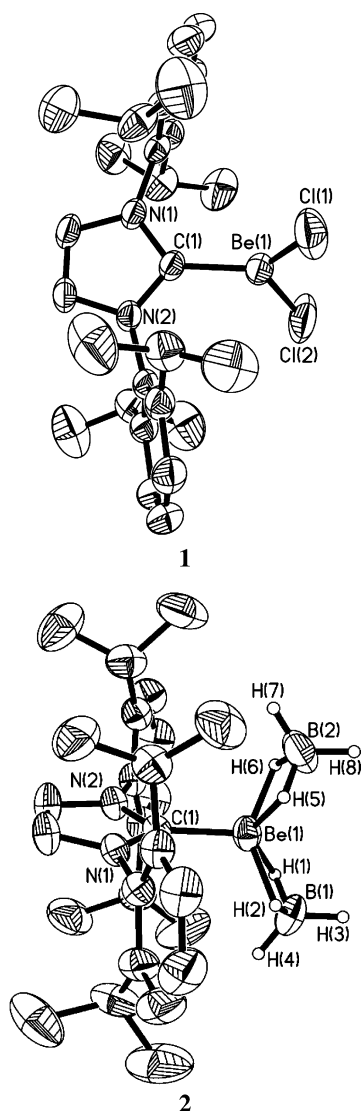


$2,6\text{-Pr}^i_2\text{C}_6\text{H}_3$ ) as colorless prism-shaped crystals (67.8% yield). Beryllium borohydride has been reported to be highly reactive (even explosive) upon exposure to air or moisture.<sup>20</sup> Indeed, the trimethylamine adduct of beryllium borohydride,  $(\text{CH}_3)_3\text{N}:\text{Be}(\text{BH}_4)_2$ , is pyrophoric.<sup>1</sup> In notable contrast, **2** survives in air for several days without decomposition. The  $^1\text{H}$  NMR imidazole resonances of **1** and **2** are at 6.39 and 6.42 ppm, respectively. The proton-coupled  $^{11}\text{B}$  NMR resonances of the  $[\text{BH}_4]^-$  units in **2** exhibit a broad quintet at  $-31.2$  ppm THF- $d_8$ , like those of other metal borohydrides  $[\text{Li}(\text{BH}_4)_2]$ ,  $-42.0$  ppm (THF- $d_8$ );<sup>21</sup> the corresponding  $^1\text{H}$  resonance can be assigned unambiguously as a singlet at 0.06 ppm THF- $d_8$  in the  $^1\text{H}\{^{11}\text{B}\}$  NMR spectrum.

While the three-coordinate beryllium atom in **1** resides in a trigonal planar geometry [the  $\text{CBeCl}_2$  plane is staggered relative to the imidazole ring with a  $\text{Cl}(1)-\text{Be}(1)-\text{C}(1)-\text{N}(1)$  torsion angle of  $76^\circ$ ], compound **2** features a five-coordinate beryllium atom in a distorted square-pyramidal geometry (Figure 1). The  $\text{Be}(1)-\text{C}(1)$  bond distance of 1.765(2) Å in **2** is comparable to the computed value of 1.797 Å for the simplified model compound  $\text{L}':\text{Be}(\text{BH}_4)_2$  (**2a**) (L': =  $:\text{C}\{\text{N}(\text{Ph})\text{CH}\}_2$ ) and the value of 1.773(5) Å in **1**. Each  $[\text{BH}_4]^-$  anion binds to the  $\text{Be}^{2+}$  center in a bidentate fashion through two bridging Be–H–B bonds. The  $\text{Be}\cdots\text{B}$  distances in **2** (1.947 and 1.959 Å) are

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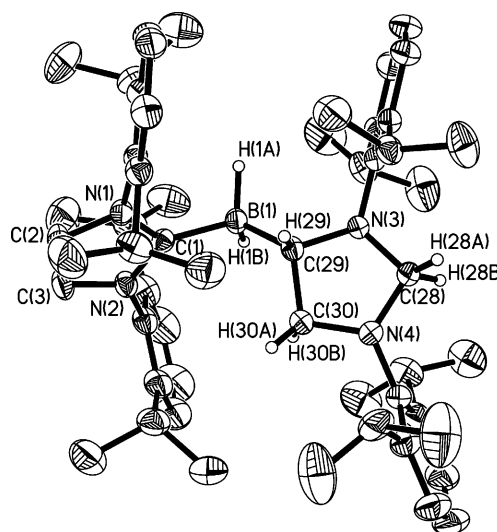
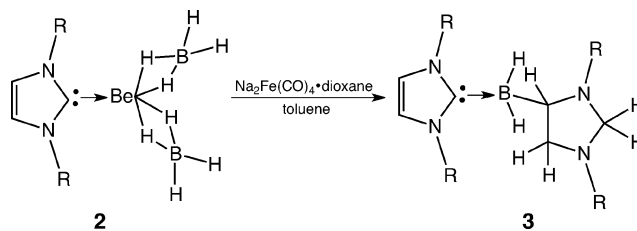


**Figure 1.** Molecular structures of **1** and **2**. Thermal ellipsoids represent 30% probability. Some H atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): For **1**: Be(1)–C(1), 1.773(5); Be(1)–Cl(1), 1.881(6); Be(1)–Cl(2), 1.884(9). For **2**: Be(1)–C(1), 1.765(2); Be(1)–H(1), 1.586(14); Be(1)–H(2), 1.549(19); Be(1)–H(5), 1.530(15); Be(1)–H(6), 1.571(19); B(1)–H(1), 1.03(2); B(1)–H(2), 1.07(2); B(1)–H(3), 1.045(17); B(1)–H(4), 1.057(17); B(2)–H(5), 1.19(2); B(2)–H(6), 1.12(2); B(2)–H(7), 1.04(2); B(2)–H(8), 1.048(18); Be(1)–H(1)–B(1), 94.6(12); Be(1)–H(2)–B(1), 94.9(14); Be(1)–H(5)–B(2), 90.6(11); Be(1)–H(6)–B(2), 91.1(13).

similar to those in polymeric  $\text{Be}(\text{BH}_4)_2$  [1.918(4)–2.001(4) Å].<sup>7</sup> Moreover, the B(1)–Be(1)–B(2) angle in **2** (121.7°) approaches those in  $\text{Be}(\text{BH}_4)_2$  (123.5–124.8°).<sup>7</sup> The average B–H bond distance (1.08 Å) in the  $[\text{BH}_4]^-$  units of **2** is comparable to that in polymeric  $\text{Be}(\text{BH}_4)_2$  (1.13 Å). The Wiberg bond indices (WBIs) of the B–H bonds in the  $[\text{BH}_4]^-$  units range from 0.87 to 0.99. In contrast, the very low WBIs of the Be–C (0.22) and Be–H bonds (0.07–0.08) in **2** suggest significant ionic bonding character. Indeed, NBO analysis showed that while the sum of the natural atomic charges for each  $\text{BH}_4$  unit is –0.83, the natural charge of the beryllium atom, +1.53, is consistent with dicationic character.

The reaction of **2** with  $\text{Na}_2[\text{Fe}(\text{CO})_4]\cdot\text{dioxane}$  affords compound **3** (64.3% yield) (Scheme 2). The structure of **3**

### Scheme 2. Synthesis of **3**



**Figure 2.** Molecular structure of **3**. Thermal ellipsoids represent 30% probability. Some H atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): B(1)–C(1), 1.615(2); B(1)–C(29), 1.614(2); C(2)–C(3), 1.327(2); C(1)–N(1), 1.3550(16); C(1)–N(2), 1.3792(18); C(28)–N(4), 1.448(2); C(28)–N(3), 1.454(2); C(1)–B(1)–C(29), 113.97(11); B(1)–C(29)–N(3), 112.28(11); B(1)–C(1)–N(2), 126.98(12).

(Figure 2) indicates that the imidazole ring in an NHC ligand is reduced both by hydroboration of the C=C backbone and by hydrogenation of the C2 carbon. Notably, lithium aluminum hydride has been used to reduce the C2 carbon atoms of imidazolium salts.<sup>22</sup> Bertrand has reported the reduction of the carbene center of an (alkyl)(amino)carbene with  $\text{H}_2$ .<sup>23</sup> Moreover,  $\text{Mg}(\text{BH}_4)_2\cdot(\text{pyrazine})_2$  has been observed to undergo facile arene hydroboration.<sup>24</sup> Indeed, a mixture of sodium borohydride and an osmium–carbonyl compound has been shown to reduce imidazole to imidazolidine.<sup>25</sup> However, **3** is the first example of the “dual reduction” of both the C=C backbone and the C2 carbene center of an NHC ligand. Although the mechanism is unclear, our studies suggests that the combination of **2** and  $\text{Na}_2[\text{Fe}(\text{CO})_4]\cdot\text{dioxane}$  is a prerequisite for the formation of **3**.

The X-ray structure of **3** reveals a  $\text{BH}_2$  fragment bridged between C(1) of a non-reduced NHC ligand and C(29) of a reduced NHC moiety. The B(1)–C(1) bond distance of 1.615(2) Å is marginally longer than those in anionic N-heterocyclic dicarbene (NHDC)– $\text{BH}_3$  binuclear complexes [1.588(7)–1.602(7) Å].<sup>26</sup> In contrast to the C(2)=C(3)

double bond [1.327(2) Å], the elongated C(29)–C(30) bond [1.507(2) Å] corresponds to a C–C single bond. Moreover, C(28) is bound to two hydrogens. The hydrogen at C(29) and all of the geminal hydrogen pairs at B(1), C(28), and C(30) were located in the difference Fourier map.

The  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra of **3** support the “dual reduction” of the imidazole ring. Two resonances at 4.08 and 4.22 ppm are assigned to the two diastereotopic hydrogens at the C2 carbon of the imidazole ring [C(28)], in accord with the C2 proton resonances of similar saturated imidazolidines (4.29 and 4.59 ppm).<sup>22</sup> The  $\text{BH}_2$  moiety is not evident in the  $^1\text{H}$  NMR spectrum of **3**. However, the proton-coupled  $^{11}\text{B}$  NMR spectrum of **3** contains a broad singlet with shoulders at  $-25.5$  ppm, suggesting the presence of the  $\text{BH}_2$  unit in **3**.

The versatile N-heterocyclic carbene L: reacts with  $\text{BeCl}_2$  to form  $\text{L}:\text{BeCl}_2$ , **1**. The reaction of **1** with  $\text{LiBH}_4$  affords **2**, a carbene-stabilized analogue of the elusive beryllium borohydride monomer. Compound **2** exhibits unusual reactivity with  $\text{Na}_2[\text{Fe}(\text{CO})_4]\cdot\text{dioxane}$  by dual reduction of an imidazole ring, affording **3**.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Full details concerning the syntheses, computations, and X-ray crystal structure determinations, including CIF files for **1–3**, and complete ref 17. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### ■ Notes

The authors declare no competing financial interest.

**Caution:** Beryllium and its compounds are extremely toxic. Manipulation of the substances described herein requires special precautions.

## ■ ACKNOWLEDGMENTS

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