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Facile Synthetic Method of Na[$BH_3(NH_2BH_2)_2H$] Based on the Reactions of Sodium Amidoborane ($NaNH_2BH_3$) with $NiBr_2$ or $CoCl_2$

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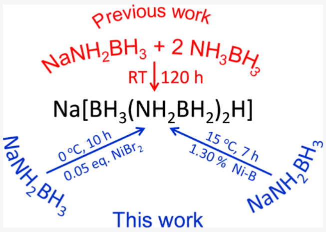
ABSTRACT: The reactions of sodium amidoborane ($NaNH_2BH_3$) with $NiBr_2$ have been investigated, and the results showed that black precipitate **1** including the $NiBNH_x$ composites could be obtained. From the aqueous solution of the precipitate **1**, the hydrolysis product Ni−B (**2**) was isolated and characterized. Both the in situ formed precipitate **1** and the hydrolysis product **2** can catalyze the formation of Na[$BH_3(NH_2BH_2)_2H$]. $CoCl_2$ showed comparable performance with $NiBr_2$. Based on these results, a facile method for the synthesis of Na[$BH_3(NH_2BH_2)_2H$] has been developed. This work provides insights into studying experimental methods for the synthesis of long B/N chain complexes and developing boron and nitrogen chemistry.



1. INTRODUCTION

Ammonia borane (NH_3BH_3) was synthesized for the first time by Shore and Parry in 1955.[1] Recently, the study on NH_3BH_3 has attracted more attention because it can release H_2 by thermolysis under mild conditions or by metal-catalyzed routes, both homogeneous and heterogeneous and promote both lower temperature release of H_2[2−8] and also the formation of increasingly well-defined B/N-polymeric materials, as reported by Manners.[2a,b] As a derivative of NH_3BH_3, $NaNH_2BH_3$ is also considered as a promising solid hydrogen storage material which can evolve 7.5 wt % hydrogen at lower temperature,[9] exhibiting significantly improved dehydrogenation properties in contrast to NH_3BH_3 such as increased dehydrogenation kinetics and decreased dehydrogenation temperature with no volatile byproduct borazine exhaust.[9,10]

$NaNH_2BH_3$ was first synthesized in 1938 by Schlesinger and Burg through the reaction of $(CH_3)_2OBH_3$ and Na in liquid ammonia.[11,12] In 2008, its structure was characterized,[9] and subsequently, two alternative synthetic approaches were developed through solid-state mechanical milling[9,13,14] and wet-chemistry synthesis.[10] Convenient synthetic methods facilitate further to explore its applications and reactivities.

Different types of reactions could take place on either $NaNH_2BH_3$ or amidoborane anion ($NH_2BH_3^-$) due to the lone pair electrons on the nitrogen atom and the active B−H bonding pair electrons.[15−17] It can act as a ligand,[18−20] a reducing reagent,[21−25] a Brønsted and Lewis base, or even an initiator for the dehydropolymerization of NH_3BH_3.[7] In 2010, Wolstenholme, McGrady, and co-workers have isolated a paramagnetic Ti(III) amidoborane complex, $Cp_2TiNH_2BH_3$, from the reaction of Cp_2TiCl_2 with 2 equiv. of $LiNH_2BH_3$.[26] Subsequently, Manners found that $Cp_2TiNMe_2BH_3$ and $Cp_2ZrNMe_2BH_3$ can also be formed by using $LiNMe_2BH_3$ instead of $LiNH_2BH_3$.[27] $Y(NH_2BH_3)_3$ was successfully synthesized by ball-milling YCl_3 with 3 equiv. of $LiNH_2BH_3$.[28] In 2012, Chen's group has examined the reduction of aromatic aldehydes by using $LiNH_2BH_3$ as a reductant.[29] They have also investigated the metathesis reaction of alkali-metal amidoborane with $FeCl_3$ in tetrahydrofuran (THF), indicating the formation of polymeric product $[Fe(HN{=}BH)_3]_n$.[30] In 2017, our group studied the reactivities of $NaNH_2BH_3$ as a Brønsted and Lewis base. We found that the $NaNH_2BH_3$ can react with different types of compounds such as acids, bases, amines, alcohols, and cyclopentadiene in which it acts as a proton acceptor and a hydride donor as well.[31,32] We also found that $NaNH_2BH_3$ plays an important role in the serial formation of B/N chain complexes Na[$BH_3NH_2BH_3$], Na[$BH_3(NH_2BH_2)_2H$], Na[$BH_3(NH_2BH_2)_3H$], and Na[$BH(NH_2BH_2)_3$].[33a] These five- or seven-membered B/N chain complexes were first reported by Sneddon in 2011 through the reactions of NH_3BH_3 with Verkade's base in which the $NH_2BH_3^-$ anion also plays an important role.[33b]

Though MNH_2BH_3 (M = Li or Na) can react with lanthanide and metallocene salts by simple metathesis reactions, it is found that the reactions are complicated and hard to predict with transition metal salts. Therefore, we studied reactions of $NaNH_2BH_3$ with $NiBr_2$ and $CoCl_2$ in this work, and the results indicated that $NiBNH_x$ and $CoBNH_x$ composites were formed in situ, which catalyze the formation of Na[$BH_3(NH_2BH_2)_2H$], yet the simply metathetical formation of $Ni[NH_2BH_3]_2$ and $Co[NH_2BH_3]_2$ was not

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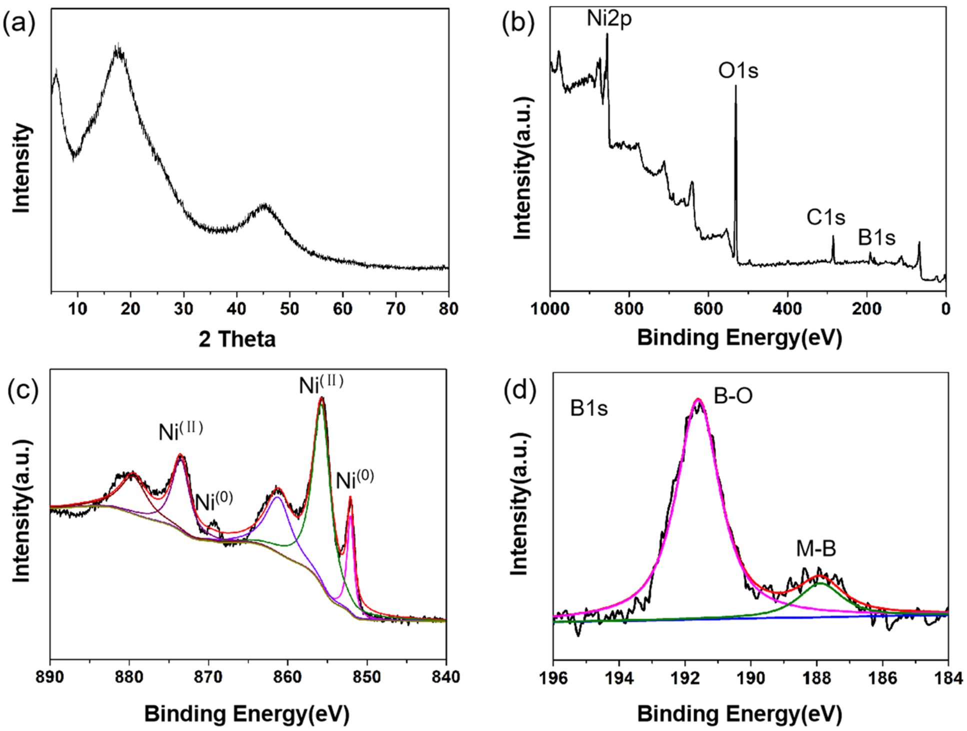

Figure 1. Characteristics of the hydrolysis product **2**: XRD pattern (a); XPS survey spectrum (b); Ni 2p XPS spectra (c); and B 1s XPS spectra (d).

observed. Based on this discovery, a facile method for the synthesis of $Na[BH_3(NH_2BH_2)_2H]$ has been developed.

2. RESULTS AND DISCUSSION

The reaction of $NaNH_2BH_3$ with $NiBr_2$ in a 2:1 ratio was carried out with anticipation of the synthesis of $Ni[NH_2BH_3]_2$. However, it was found that this reaction is not a simple metathesis reaction. When the THF solution of $NaNH_2BH_3$ was dropwise added into the solution of $NiBr_2$ with a rate of 0.1 mmol/min, only the NH_3BH_3 signal was observed in the ^{11}B NMR of the reaction mixture, indicating that NH_3BH_3 is the only boron-containing product in the solution in this case (Figure S1). At the same time, a large amount of black precipitate **1** was formed rapidly, which was isolated and characterized. X-ray diffraction (XRD) determination proved that the precipitate **1** contains NaBr (Figure S2), and Fourier transform infrared spectroscopy (FTIR) confirmed the existence of N−H, B−H, and B−N stretches (Figure S3).[30] Furthermore, the precipitate **1** was not soluble in polar organic solvents such as CH_3CN, dimethylformamide, and dimethyl sulfoxide, but partially soluble in water. The aqueous solution was monitored by ^{11}B NMR in which a single peak that appeared at δ 12.0 ppm could be assigned to borate (Figure S4). Thus, the precipitate **1** could be considered as a mixture of Ni(0), a complex of Ni(II) with BNH_x besides NaBr, noted as $NiBNH_x$. The formation of $NiBNH_x$ in this reaction is similar to the formation of $[Fe(NHBH)_3]_n$ in the reaction of $LiNH_2BH_3$ with $FeCl_3$.[30] The hydrolysis product **2** was isolated and characterized when the precipitate **1** was washed thoroughly with water. XRD of the hydrolysis product **2** showed a wide broad peak at $2\theta = 45°$ (Figure 1a), implying its amorphous structure.[34] The X-ray photoelectron spectroscopy (XPS) survey spectrum showing peaks of Ni 2p, B 1s, and O 1s (Figure 1b) and the Ni 2p and B 1s XPS spectra (Figure 1c,d) indicated that the hydrolysis product **2** contains nickel boride and nickel borate,[35] noted as Ni−B, which is formed in the hydrolysis of the formed $NiBNH_x$. This result indicated that the reaction of $NaNH_2BH_3$ with $NiBr_2$ is complicated in which $NiBNH_x$ and NH_3BH_3 are formed.

It was further found that the products of the reaction are kinetically affected by the addition rate of $NaNH_2BH_3$. When $NaNH_2BH_3$ was introduced into the reaction at a higher rate (0.2 and 0.4 mmol/min, Figures S5 and S6) or directly mixed with $NiBr_2$ first and then the solvent was added (Figure S7), $Na[BH_3(NH_2BH_2)_2H]$ was obtained as the major product with a small amount of NH_3BH_3. We speculated that the slow increment of $NaNH_2BH_3$ concentration resulted in a $NaNH_2BH_3$-insufficient environment, allowing $NaNH_2BH_3$ to be converted into NH_3BH_3 and $NiBNH_x$ instantaneously by the excessive $NiBr_2$. On the other hand, when $NaNH_2BH_3$ was introduced into the reaction at a higher rate or two reactants were just directly mixed, excessive $NaNH_2BH_3$ continued to react with the formed NH_3BH_3 to produce $Na[BH_3(NH_2BH_2)_2H]$.

To verify this hypothesis, a series of reactions with different ratios of $NaNH_2BH_3$ and NH_3BH_3 in the presence of $NiBr_2$ were carried out (Figures S8−S10). It was found that both $NaNH_2BH_3$ and NH_3BH_3 could be consumed completely, and a sole product, $Na[BH_3(NH_2BH_2)_2H]$, was observed in ^{11}B NMR (Figure S10) when mixing $NaNH_2BH_3$ and NH_3BH_3 at a ratio of 2:1. Furthermore, an isotopic investigation was performed. When NH_3BD_3 was used to react with $NaNH_2BH_3$ at a 1:2 ratio, the deuterium atom appeared in the chemical shift of the BD_2 and BD_3 groups in $Na[BD_3(NH_2BD_2)_2D]$ in ^2H NMR (Figure 2), suggesting that $NaNH_2BH_3$ rapidly reacted with NH_3BD_3 under $NiBNH_x$ catalysis. When a reaction of NH_3BH_3 and $NaNH_2BD_3$ was conducted, similar results were obtained (Figures S11 and S12). This observation supports the hypothesis that the forming NH_3BH_3 would further react with $NaNH_2BH_3$ to form a five-membered B/N

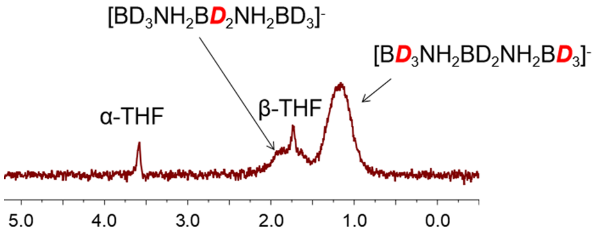

Figure 2. ^{2}H NMR spectrum of the solution mixture of $2NaNH_2BH_3 + NH_3BD_3 + 0.2NiBr_2$ in THF at room temperature.

chain in which the forming $NiBNH_x$ can in situ catalyze the dehydrocoupling between $NaNH_2BH_3$ and NH_3BH_3. The BH/BD exchange was observed, but the NH/BD exchange was not observed (Figure 2 and Figures S23−S27). These results are reminiscent of the formation of polymers by dehydropolymerization of amine boranes using transition metal catalysts, as reported by Ian Manners[36] and Weller[37,38] in which the BH/BD scrambling occurred during the dehydrocoupling reaction. However, the fact that the NH/BD scrambling is not observed in these cases is inconsistent with the formation mechanism of aminodiborane.[39] This observation implies that the formation of polymeric complexes and aminodiborane through dehydrocoupling reaction of amine borane underwent different mechanisms.

When $NaNH_2BH_3$ reacted with a catalytic amount of $NiBr_2$ (0.1 equiv.), $Na[BH_3(NH_2BH_2)_2H]$ was obtained in approximately 2 h, and no NH_3BH_3 was detected until $NaNH_2BH_3$ was consumed completely (Figure S13). However, once $NaNH_2BH_3$ was completely consumed (the signal of $NaNH_2BH_3$ was disappeared), the peak of NH_3BH_3 was observed in 30 min (Figure S14). This indicated that $Na[BH_3(NH_2BH_2)_2H]$ could decompose to form NH_3BH_3 under the catalysis of $NiBNH_x$. It is worthy to note that byproduct $Na[BH_3NH_2BH_3]$ (Figure S15) was detected in a large-scale reaction, probably due to the aggregated heat in large scale from its exothermic nature.[32]

Hence, the reaction of $NaNH_2BH_3$ with $NiBr_2$ is believed to follow three steps. First, $NaNH_2BH_3$ reacted with $NiBr_2$ to form $NiBNH_x$ (in which Ni(0) may be included as the black precipitate) as well as NH_3BH_3 (Eq. 1). Second, the formed $NiBNH_x$ in situ catalyze excessive $NaNH_2BH_3$ to react with the first-step-product NH_3BH_3 to form $Na[BH_3(NH_2BH_2)_2H]$ (Eq. 2). Finally, $NiBNH_x$ catalyzed the second-step-product $Na[BH_3(NH_2BH_2)_2H]$, which decomposed to form NH_3BH_3 and other unknown species in the absence of $NaNH_2BH_3$ (Eq. 3). On the other hand, alternative pathways should be considered. For example, the reaction of $NaNH_2BH_3$ with $NiBr_2$ seems to be violent (step 1) in which step (2) and (3) may be involved as the elementary steps. Only when the concentration of $NiBr_2$ is low, the reaction will be ceased after step (2), and the products of the step (2) were obtained. Therefore, these interesting observations and possible mechanisms inspired us to develop a facile synthetic method of $Na[BH_3(NH_2BH_2)_2H]$ based on this catalytic reaction.

$$\begin{aligned}&NaNH_2BH_3 + NiBr_2\\&\quad \rightarrow NiBNH_x(s) + NH_3BH_3 + NaBr(s) + H_2(g)\end{aligned} \tag{1}$$

$$\begin{aligned}&NaNH_2BH_3 + 2NH_3BH_3 \xrightarrow{NiBNH_x} Na[BH_3(NH_2BH_2)_2H]\\&\quad + NH_3\,(g) + H_2(g)\end{aligned} \tag{2}$$

$$Na[BH_3(NH_2BH_2)_2H] \xrightarrow{NiBNH_x} NH_3BH_3 + \text{unknown species} \tag{3}$$

In our previous work,[32] it took five days to obtain $Na[BH_3(NH_2BH_2)_2H]$ from the reaction of $NaNH_2BH_3$ with 2 equiv. of NH_3BH_3. Inspired by the fast reaction between $NaNH_2BH_3$ and $NiBr_2$, we inferred that the in situ formed precipitate **1** acts as a catalyst to facilitate the formation of $Na[BH_3(NH_2BH_2)_2H]$. Therefore, the precipitate **1** was recycled from the reaction mixture by a simple filtration manipulation and could be reused for as many as 4 times without compromising its catalytic performance (Figure S16). To further prove the catalytic role of $NiBNH_x$ rather than NaBr, we have conducted the experiment of $NaNH_2BH_3$ and NH_3BH_3 with NaBr (Figure S17). The results show that NaBr cannot catalyze this reaction. These results indirectly prove the catalytic role of $NiBNH_x$. The reaction of pure $NaNH_2BH_3$ in THF solution can generate a small amount of $Na[BH_3(NH_2BH_2)_2H]$, but the process is very slow (Figure S18). Based on this inference, we tried to develop a rapid synthetic method of $Na[BH_3(NH_2BH_2)_2H]$ by optimizing the reaction conditions. Results show that the reaction of $NaNH_2BH_3$ with 0.05 equiv. of $NiBr_2$ at 0 °C could produce $Na[BH_3(NH_2BH_2)_2H]$ (Figure 3) in 10 h with 60% yield, which is comparable with the yield obtained using the method reported in the literature, which took five days.[32]

It is worth to note that $NiBNH_x$ and the hydrolysis product **2** were characterized by NMR, IR, XRD, and XPS, but their compositions are not exactly determined. Hence, the catalytic mechanism of this reaction is not clear. Considering the catalytic effect of the hydrolysis product **2** in the hydrolysis of $NaBH_4$,[40] we further examined the catalytic behavior of the hydrolysis product **2**. When the catalytic amount of the hydrolysis product **2** was used in the reaction, the formation of $Na[BH_3(NH_2BH_2)_2H]$ was confirmed in 68% yield (Figure S19). It was found that the hydrolysis product **2** could also

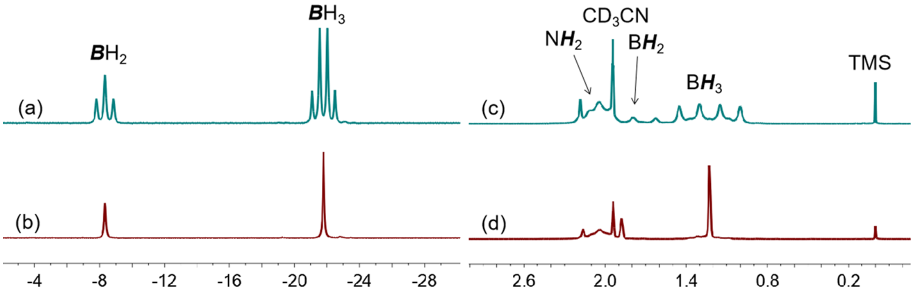

Figure 3. ^{11}B NMR (a), ^{11}B{^{1}H} NMR (b), ^{1}H NMR (c), and ^{1}H{^{11}B} NMR (d) spectra of the prepared $Na[BH_3(NH_2BH_2)_2H]$ in CD_3CN.

catalyze the conversion of $Na[BH_3(NH_2BH_2)_2H]$ into NH_3BH_3 (Figure S20). In general, it is proved that the in situ formed $NiBNH_x$ and the hydrolysis product **2** have the similar catalytic behavior for this reaction.

We also studied the reactions of $NaNH_2BH_3$ with $CoCl_2$ under the same conditions. The similar results with the reaction of $NaNH_2BH_3$ with $NiBr_2$ were obtained, but yields were lower (Figures S28−S41).

3. CONCLUSIONS

In this work, we systematically studied the reactions of $NaNH_2BH_3$ with $NiBr_2$ and $CoCl_2$ in different conditions. The reaction is complicated, and it is likely a catalytic reaction rather than a simple metathesis reaction. It was found that $NiBNH_x$ and $CoBNH_x$ composites were first formed from the reactions of $NaNH_2BH_3$ with $NiBr_2$ and $CoCl_2$, and their catalytic behavior on $Na[BH_3(NH_2BH_2)_2H]$ and $NaNH_2BH_3$ was investigated, for example, catalyzing the formation of $Na[BH_3(NH_2BH_2)_2H]$ from $NaNH_2BH_3$ and the decomposition of $Na[BH_3(NH_2BH_2)_2H]$ into NH_3BH_3 in the absence of $NaNH_2BH_3$. Based on these results, further optimization was carried out and a rapid synthetic method of $Na[BH_3(NH_2BH_2)_2H]$ was developed. The Ni−B and Co−B composites were isolated and characterized by XRD and XPS. Investigation showed that their catalytic behavior is similar to those of the in situ formed $NiBNH_x$ and $CoBNH_x$ composites.

4. EXPERIMENTAL SECTION

4.1. General Procedures. All manipulations were carried out by using Schlenk-line techniques or in a glovebox filled with high-purity nitrogen. ^{11}B NMR spectra were obtained at 193 MHz and externally referenced to $BF_3 \cdot OEt_2$ in C_6D_6 ($\delta = 0.00$ ppm). FTIR spectra were measured by a Spectrum 400F. XRD data were collected on a Rigaku D/max 2500 diffractometer by using Cu-K α radiation ($\lambda = 0.1542$ nm, 45 kV, 40 mA). XPS patterns were studied by X-ray Photoelectron Spectrometer Microprobe (150 W, 5 kV at 1486.6 eV, monochromatic Al Kα radiation). THF was dried over sodium/benzophenone and freshly distilled prior to use. The metal salts used were stored under a nitrogen atmosphere or in a desiccator. $NaNH_2BH_3$ was synthesized according to the literature.[32]

4.2. Reaction of $NaNH_2BH_3$ with $NiBr_2$ (2:1). In a glovebox, a 25 mL flask was charged with $NiBr_2$ (0.219 g, 1.0 mmol), and then the flask was connected to a vacuum line and 5 mL of THF was condensed into it. The suspension of $NaNH_2BH_3$ (0.106 g, 2.0 mmol) in THF was dropwise added (the drop rate is 0.1 mmol/min) to the flask at room temperature, and the reaction was rapidly initiated. A large amount of ammonia and H_2 was released (Figure S21), and a black precipitate was observed. The reaction solution was monitored by ^{11}B NMR in which a quartet peak appeared at δ −22.3 ppm, assigned to NH_3BH_3 (Figure S1). The black precipitate was filtered, noted as precipitate **1**, and then dried under vacuum. XRD determination of the precipitate **1** indicated that it contains NaBr (Figure S2), and FTIR confirmed the existence of N−H, B−H, and B−N stretches (Figure S3). The solvent of the filtration was removed to give a white NH_3BH_3 powder. ^{11}B NMR (193 MHz, THF), δ −22.3 ppm (*q*, $J_{B-H} = 96.5$ Hz) (Figure S1). ^1H NMR (600 MHz, C_6D_6): δ 4.47 ppm (*s*, H_2) (Figure S21). FTIR (cm^{-1}): 3400 (s), 3230 (s), 2400 (w), 1629 (w), 1410 (s), 1187(w), 1037(w), 710(w) (Figure S3).

A similar procedure was repeated with the drop rate increased to 0.2 mmol/min (Figure S5) and 0.4 mmol/min (Figure S6), or the two solid reactants were directly mixed (Figure S7) and then 10 mL of THF was added to the flask. All afforded $Na[BH_3(NH_2BH_2)_2H]$ as the major product with a small amount of NH_3BH_3.

The black precipitate **1** partially dissolved in water showed a single peak in ^{11}B NMR assigned to borate (Figure S4). The hydrolysis product **2** was isolated, dried under vacuum, and then characterized by XRD. A broad peak appeared at $2\theta = 45°$ (Figure 1a).

4.3. Reaction of $NaNH_2BH_3$ with NH_3BH_3 and $NiBr_2$ (1:1:0.1). $NaNH_2BH_3$ (0.106 g, 2.0 mmol) and NH_3BH_3 (0.062 g, 2.0 mmol) were charged in a two-necked 25 mL flask with a magnetic stir bar, and THF (10 mL) was injected into the flask. Then, the mixture was added to the THF solution of $NiBr_2$ (0.043 g, 0.2 mmol) at room temperature. A black precipitate was formed immediately. After 1.5 h, $NaNH_2BH_3$ was completely converted to $Na[BH_3(NH_2BH_2)_2H]$ and mixed with unreacted NH_3BH_3 (Figure S8).

4.4. Reaction of $NaNH_2BH_3$ with NH_3BH_3 and $NiBr_2$ (1:2:0.1). $NaNH_2BH_3$ (0.053 g, 1.0 mmol) and NH_3BH_3 (0.062 g, 2.0 mmol) were charged in a two-necked 25 mL flask with a magnetic stir bar, and THF (10 mL) was injected into the flask. Then, the mixture was added to the THF solution of $NiBr_2$ (0.043 g, 0.2 mmol) at room temperature. A black precipitate was formed immediately. After 1.5 h, $NaNH_2BH_3$ was completely converted to $Na[BH_3(NH_2BH_2)_2H]$ and mixed with unreacted NH_3BH_3 (Figure S9).

4.5. Reaction of $NaNH_2BH_3$ with NH_3BH_3 and $NiBr_2$ (2:1:0.1). $NaNH_2BH_3$ (0.106 g, 2.0 mmol) and NH_3BH_3 (0.031 g, 1.0 mmol) were charged in a two-necked 25 mL flask with a magnetic stir bar, and THF (10 mL) was injected into the flask. Then, the mixture was added to the THF solution of $NiBr_2$ (0.043 g, 0.2 mmol) at room temperature. A black precipitate was formed immediately. After 1.5 h, both $NaNH_2BH_3$ and NH_3BH_3 were consumed completely and pure $Na[BH_3(NH_2BH_2)_2H]$ was obtained (Figure S10).

4.6. Reaction of $NaNH_2BD_3$ with NH_3BH_3 and $NiBr_2$ (2:1:0.1). $NaNH_2BD_3$ was prepared by the reaction of NH_3BD_3 with NaH in THF. ^2H NMR (ppm; THF) δ 1.46 (*br*, BD_3) (Figure S11).

$NaNH_2BD_3$ (0.112 g, 2.0 mmol) and NH_3BH_3 (0.031 g, 1.0 mmol) were charged in a two-necked 25 mL flask with a magnetic stir bar, and THF (5 mL) was injected into the flask at room temperature. Then, the mixture was added to the THF solution of $NiBr_2$ at room temperature. A black precipitate was formed immediately. After 1.5 h, deuterium signals were determined by ^2H NMR and assigned to BD_2 and BD_3 groups of $Na[BD_3(NH_2BD_2)_2D]$ (Figure S12).

4.7. Reaction of $NaNH_2BH_3$ with $NiBr_2$ (10:1). $NaNH_2BH_3$ (0.106 g, 2.0 mmol) and $NiBr_2$ (0.044 g, 0.2 mmol) were placed in a two-necked 25 mL flask with a magnetic stir bar, and THF (10 mL) was injected into the flask at room temperature. This reaction mixture was stirred for 3 h and monitored by ^{11}B NMR (Figures S13 and S14).

4.8. Cycle Reaction of $NaNH_2BH_3$ with $NiBr_2$. $NaNH_2BH_3$ (0.106 g, 2.0 mmol) and $NiBr_2$ (0.044 g, 0.2 mmol) were placed in a two-necked 25 mL flask with a magnetic stir bar, and THF (10 mL) was injected into the flask at room temperature. After 2 h, $NaNH_2BH_3$ converted to $Na[BH_3(NH_2BH_2)_2H]$ completely. The filtrate was filtered, the precipitate was washed with THF, and then the THF solution of $NaNH_2BH_3$ (0.106 g, 2.0 mmol) was added to the precipitate again. The same process was repeated five times (Figure S16).

4.9. Reaction of $NaNH_2BH_3$ with NH_3BH_3 and NaBr. $NaNH_2BH_3$ (0.106 g, 2.0 mmol) and NH_3BH_3 (0.031 g, 1.0 mmol) were charged in a two-necked 25 mL flask with a magnetic stir bar, and THF (5 mL) was injected into the flask. Then, the mixture was added to the THF solution of NaBr (0.0206 g, 0.2 mmol) at room temperature. The reaction solution was monitored by ^{11}B NMR (Figure S17).

4.10. Reaction of $NaNH_2BH_3$ in THF. $NaNH_2BH_3$ (0.053 g, 1.0 mmol) was charged in a two-necked 10 mL flask with a magnetic stir bar, and THF (3 mL) was injected into the flask at room temperature. The reaction solution was monitored by ^{11}B NMR (Figure S18).

4.11. Reaction of $NaNH_2BH_3$ with Ni−B. The hydrolysis product **2** was separated from the black precipitate **1**. The black precipitate **1** was washed with ethanol and water, and then the residue material was dried in vacuum at 100 °C for 6 h to obtain the hydrolysis product **2**. In a glovebox, a 200 mL flask was charged with a magnetic stir bar and the hydrolysis product **2** (0.056 g), and then the flask was connected to a vacuum line and ca. THF (15 mL) was condensed into it. The suspension of $NaNH_2BH_3$ (0.424 g, 8.0

mmol) in THF was injected into the flask, and the reaction mixture was vigorously stirred for 7 h at 15 °C. Pure $Na[BH_3(NH_2BH_2)_2H]$ was isolated through the same method as described above (Figure S19). The yield was 68%.

4.12. Reaction of $Na[BH_3(NH_2BH_2)_2H]$ with Ni−B. $Na[BH_3(NH_2BH_2)_2H]$ (0.096 g, 1.0 mmol) and Ni−B (0.014 g) were placed in a two-necked 25 mL flask with a magnetic stir bar, and THF (10 mL) was injected into the flask at room temperature. After stirring for 1 h, the reaction mixture was monitored by ^{11}B NMR (Figure S20).

4.13. Reaction of $NaNH_2BH_3$ with NH_3BD_3 and $NiBr_2$ (2:1:0.1). NH_3BD_3 was prepared by a method reported in the literature.[41] ^{11}B NMR (193 MHz, D_8-THF): δ −22.28 ppm (*br s*, BD_3) (Figure S22a). $^{11}B\{^1H\}$ NMR (193 MHz, D_8-THF): δ −22.28 ppm (*br s*, BD_3) (Figure S22b). ^1H NMR (600 MHz, D_8-THF): δ 3.94 (*t*, 3 H of NH_3, J_{N-H} = 42 Hz) (Figure S23a). $^1H\{^{11}B\}$ NMR (600 MHz, D_8-THF): δ 3.94 (*t*, 3 H of NH_3, J_{N-H} = 42 Hz) (Figure S23b). ^2H NMR (ppm; THF) δ 1.40 (*br*, BD_3) (Figure S24). We also characterized NH_3BD_3 in CD_3CN, and it shows a multiplet in ^{11}B NMR (Figure S25a).

$NaNH_2BH_3$ (0.106 g, 2.0 mmol) and NH_3BD_3 (0.034 g, 1.0 mmol) were charged in a two-necked 25 mL flask with a magnetic stir bar, and THF (5 mL) was injected into the flask at room temperature. Then, the mixture was added to the THF solution of $NiBr_2$ at room temperature. A black precipitate was formed immediately. After 1.5 h, deuterium signals were determined by ^2H NMR and assigned to BD_2 and BD_3 groups of $Na[BD_3(NH_2BD_2)_2D]$ (Figure 2). ^{11}B NMR and ^1H NMR showed that the BD_2 and BD_3 groups are only partially deuterated (Figures S26 and S27).

4.14. Reaction of $NaNH_2BH_3$ with $NiBr_2$ (20:1). In a glovebox, a 200 mL flask was charged with $NiBr_2$ (0.109 g, 0.5 mmol), and then the flask was connected to a vacuum line and ca. 15 mL THF was condensed into it. Another flask was charged with $NaNH_2BH_3$ (0.530 g, 10.0 mmol), and ca. 50 mL THF was condensed into it. Then, the THF solution of $NaNH_2BH_3$ was added to the THF solution of $NiBr_2$ at 0 °C. After 10 h, the black precipitate was filtered, and then, 120 mL of *n*-hexane was added to the filtrate. A large amount of white solid precipitate was formed. The mixture was filtered again, and the white solid was dried under vacuum to give a white power product $Na[BH_3(NH_2BH_2)_2H]$ (0.191 g, 60%). ^{11}B NMR (193 MHz, CD_3CN): δ −8.3 (*t*, J_{B-H} = 100 Hz, BH_2), −21.8 ppm (*q*, J_{B-H} = 91 Hz, BH_3) (Figure 3a). $^{11}B\{^1H\}$ NMR (193 MHz, CD_3CN): δ −8.3 (*s*, BH_2), −21.8 ppm (*s*, BH_3) (Figure 3b). ^1H NMR (600 MHz, CD_3CN): δ 2.04 (*br t*, 4 H of 2 NH_2, J_{N-H} = 33 Hz), 1.87 (*q*, 2 H of BH_2, J_{B-H} = 98 Hz), 1.23 (*q*, 6 H of 2 BH_3, J_{B-H} = 91 Hz) ppm (Figure 3c). $^1H\{^{11}B\}$ NMR (600 MHz, CD_3CN): δ 2.04 (*br t*, 4 H of 2 NH_2, J_{N-H} = 33 Hz), 1.87 (*q*, 2 H of BH_2, J_{B-H} = 4 Hz), 1.23 (*br t*, 6 H of 2 BH_3, J_{B-H} = 82 Hz) ppm (Figure 3d).

4.15. Reaction of $NaNH_2BH_3$ with $CoCl_2$ (2:1). A similar reaction was observed in the reaction of $NaNH_2BH_3$ with $CoCl_2$. When the suspension of $NaNH_2BH_3$ (0.106 g, 2.0 mmol) in THF was dropwise added (the drop rate is about 0.1 mmol/min) to the flask filled with $CoCl_2$ (0.129 g, 1.0 mmol) at room temperature, a rapid reaction was initiated and the black precipitate was observed. A pungent smelling gas was also released during the reaction which was determined as ammonia and H_2 (Figure S28). The reaction solution was monitored by the ^{11}B NMR in which a quartet peak appeared at δ −22.6 ppm, assigned to NH_3BH_3 (Figure S29). The black precipitate was filtered, noted as the precipitate **3**, and then dried under vacuum. XRD determination of the precipitate **3** indicated that it contains NaCl (Figure S30), and FTIR confirmed the existence of N−H, B−H, and B−N stretches (Figure S31). The solvent of the filtration was removed to give a white NH_3BH_3 powder. ^{11}B NMR (193 MHz, THF), δ −22.6 ppm (*q*, J_{B-H} = 96.5 Hz) (Figure S29). ^1H NMR (600 MHz, C_6D_6,): δ 4.47 ppm (*s*, H_2) (Figure S28). FTIR (cm^{-1}): 3410 (s), 3220 (s), 2440 (w), 1630 (w), 1410 (s), 1190(w), 1030(w), 696 (w) (Figure S31).

A similar procedure was repeated with the drop rate increased to 0.2 mmol/min (Figure S32) and 0.4 mmol/min (Figure S33) or the two solid reactants were directly mixed (Figure S34) and then 10 mL of THF was added to the flask. All afforded $Na[BH_3(NH_2BH_2)_2H]$ as the major product with a small amount of NH_3BH_3.

The black precipitate **3** dissolved in water showed a single peak at δ 12.8 ppm in ^{11}B NMR, assigned to borate (Figure S35). Some insoluble black precipitates were isolated and then dried under vacuum, noted as Co−B (**4**), which were characterized by XRD (Figure S36) and XPS (Figures S37 and 38).[42]

4.16. Reaction of $NaNH_2BH_3$ with $CoCl_2$ (20:1). In a glovebox, a 200 mL flask was charged with $CoCl_2$ (0.065 g, 0.5 mmol), and then the flask was connected to a vacuum line and ca. THF (15 mL) was condensed into it. Another flask was charged with $NaNH_2BH_3$ (0.530 g, 10.0 mmol), and ca. 50 mL of THF was condensed into it. Then, the THF solution of $NaNH_2BH_3$ was added to the THF solution of $CoCl_2$ at 0 °C. After 8 h, the black precipitate was filtered, and then, 120 mL of *n*-hexane was added to the filtrate. A large amount of white solid precipitate was formed. The mixture was filtered again, and the white solid was dried under vacuum to give a white power product $Na[BH_3(NH_2BH_2)_2H]$ (0.131 g, 41%) (Figure S39).

4.17. Reaction of $NaNH_2BH_3$ with Co−B. The hydrolysis product **4** was separated from the black precipitate **3**. The black precipitate **3** was washed with ethanol and water, and then, the insoluble material was dried in vacuum at 100 °C for 6 h to obtain the hydrolysis product **4**. In a glovebox, a 200 mL flask was charged with a magnetic stir bar and the hydrolysis product **4** (0.112 g), and then the flask was connected to a vacuum line and ca. THF (15 mL) was condensed into it. The suspension of $NaNH_2BH_3$ (0.424 g, 8.0 mmol) in THF was injected into the flask, and the reaction mixture was vigorously stirred for 15 h at 15 °C. This reaction was monitored by ^{11}B NMR. Pure $Na[BH_3(NH_2BH_2)_2H]$ was isolated through the same method as mentioned above. The yield was 32% (Figure S40).

4.18. Cycle Reaction of $NaNH_2BH_3$ + $CoCl_2$. $NaNH_2BH_3$ (0.106 g, 2.0 mmol) and $CoCl_2$ (0.026 g, 0.2 mmol) were placed in a two-necked 25 mL flask with a magnetic stir bar, and THF (10 mL) was injected into the flask at room temperature. After 2 h, $NaNH_2BH_3$ was converted to $Na[BH_3(NH_2BH_2)_2H]$ completely. The filtrate was filtered, the precipitate was washed with THF, and then the THF solution of $NaNH_2BH_3$ (0.106 g, 2.0 mmol) was added to the precipitate again. The same process was repeated five times (Figure S41).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00071.

NMR, PXRD, FTIR, XPS, and additional catalytic experiments (PDF)

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Notes

The authors declare no competing financial interest.

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