Cobalt-Catalyzed Ammonia Borane Dehydrogenation: Mechanistic Insight and Isolation of a Cobalt Hydride-Amidoborane Complex

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ABSTRACT: A Co(I) complex featuring the electron-rich monoanionic bis(carbene) aryl pincer ligand (^{Mes}CCC) (^{Mes}CCC = bis(2,4,6-trimethylphenyl-benzimidazol-2-ylidene)phenyl), (^{Mes}CCC)Co-py (**1**), was found to catalytically dehydrogenate ammonia borane (NH₃BH₃, AB) in THF at 60 °C. This process releases 1.7 ± 0.1 equiv of H₂ per AB with simultaneous formation of both soluble (borazine and polyborazylene) and insoluble (poly(aminoborane)) BN-containing species. To help elucidate the Co species present under the catalytic conditions, **1** was reacted with a stoichiometric amount of AB in THF at room temperature, yielding (^{Mes}CCC)CoH(NH₂BH₃) (**2**), the first characterized hydride-amidoborane complex of a late transition metal. This complex was characterized by multinuclear (¹H, ¹¹B, and ¹³C) NMR and IR spectroscopies as well as X-ray crystallography. Formation of **2** via N–H activation of AB across the Co(I) center of **1** was confirmed by the reaction of **1** with the deuterated isotopologues of AB and was supported computationally by means of density functional theory (DFT) calculations. Isolated **2** was shown to catalyze AB dehydrogenation, forming BN-containing products similar to **1**, albeit at a slower rate. In both reactions starting with **1** or **2** as the catalyst, **2** is observed throughout the catalytic dehydrogenation of AB. DFT calculations revealed plausible pathways for the formation of aminoborane (NH₂BH₂) from **2**, the generation of soluble BN-containing products, as well as the on-metal oligomerization of AB to produce the insoluble polymeric species. The complexes reported herein represent rare examples of homogeneous cobalt catalysts for the dehydrogenation of AB.

INTRODUCTION

Amine boranes have been studied extensively for their ability to act as hydrogen storage materials.^{1,2} Ammonia borane (AB) has been of particular interest with the highest percentage of hydrogen (19.1 wt %) of all of the amine boranes. Researchers have sought to develop both homogeneous and heterogeneous systems to catalyze the release of H₂ from amine boranes under mild conditions.^{3,4} These compounds feature both hydridic (B–H) and protic (N–H) hydrogens which facilitate hydrogen release from these compounds; however, the varied modes of activation of these hydrogens yields mechanisms that vary widely with different experimental conditions and catalyst choice.⁵

Much progress has been made with second- and third-row transition metal catalysts toward understanding the complex homogeneous mechanisms,⁶ but insight on how first-row transition metals perform this dehydrogenation is still lacking.

First-row examples of Ni,^{7,8} Ti,^{9–14} Mn,¹⁵ Cr,^{16,17} and, increasingly, Fe^{18–25} complexes for homogeneous amine borane dehydrogenation have been demonstrated; however, for cobalt, there have only been a handful of published examples as depicted in Figure 1. These include a (PBP)Co pincer complex reported by Peters and Lin,²⁶ a Cp-based cobalt complex by Waterman and co-workers,²⁷ tripodal EP₃ (E = N and P) cobalt complexes by Rossin, Shubina, and co-workers,²⁸ a highly reduced diimine cobaltate complex by

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Figure 1. Examples of reported molecular cobalt catalysts for amine borane dehydrogenation.^{26–30}

44 Wangelin, Wolf, and co-workers,²⁹ and most recently a (PNP)
45 Co complex by Weller and co-workers.³⁰

Previously we have shown the low-valent (^{Dipp}CCC)Co and (^{Mes}CCC)Co pincer complexes (^{Dipp}CCC = bis(2,6-diisopropylphenyl-benzimidazol-2-ylidene)phenyl, ^{Mes}CCC = bis(mesityl-benzimidazol-2-ylidene)phenyl) to be competent for catalytic hydrosilylation,³¹ hydroboration,³² and (semi)-hydrogenation.^{33–35} The ability of these complexes to activate E–H bonds (E = Si, B, or H) in multiple hydrofunctionalization reactions prompted us to apply these cobalt complexes toward AB dehydrogenation. Herein we report the catalytic dehydrogenation of AB with (^{Mes}CCC)Co-py (1), resulting in the isolation of the first example of a hydride-amidoborane complex of a late transition metal. The insights gained from this well-defined species are expected to inspire more efficient cobalt pincer complexes for amine borane dehydrogenation.

RESULTS AND DISCUSSION

Stoichiometric Reactivity of 1 with AB: Isolation and Characterization of (^{Mes}CCC)CoH(NH₂BH₃) (2). Initial experiments sought to determine the reactivity of the reduced Co(I) species, 1, with AB in a stoichiometric fashion. The addition of AB (1.1 equiv) to 1 (Figure 2a) in THF at room temperature resulted in a color change from red to brown over the course of minutes and, upon workup, cleanly yielded a brown powder in excellent yield (93%). Crystallographic characterization of this complex revealed (^{Mes}CCC)CoH(NH₂BH₃) (2), seen in Figure 2b. This complex is best described as a hydride-amidoborane Co(III) species where the

Figure 2. (a) Synthesis of complex 2. (b) Crystal structure of 2 (ellipsoids at 50% probability, half of molecule symmetry generated). Hydrogen atoms on the ligand are omitted for clarity. Selected bond lengths [Å]: Co–H1, 1.53(4); Co–N5, 2.000(3); Co–B, 2.252(8); Co–H2, 1.85(4); B–N5, 1.547(6); Co–C1, 1.918(11); Co–C11, 1.865(3). (c) ¹H NMR spectrum of 2 in C₆D₆. (d) Overlaid ¹H NMR (black trace) and ¹H{¹¹B} NMR (teal trace) spectra of upfield resonances of 2.

N–H bond of AB has been oxidatively added across the Co(I) center of **1** to yield **2**. The amidoborane (NH_2BH_3^-) fragment of **2** is bound to the Co center through a Co–N bond and a Co–H–B bridging interaction with the hydride positioned trans to the bridging B–H moiety ($\text{H1–Co–H2} = 173.8(2.6)^\circ$).

The activation of the N–H bond over the B–H bond at the metal center is somewhat unsurprising given the BDE's of 95.5 and 102.0 kcal mol^{−1}, respectively.^{36–39} A cobalt amidoborane complex was suggested computationally by Shubina and co-workers upon N–H activation at a Co–H species followed by release of H₂;²⁸ however, the process presented herein does not occur in the presence of a hydride species. To our knowledge, only three other structurally characterized complexes containing the NH_2BH_3^- anion bound to a transition metal have been reported including the (Cp)₂ZrCl(NH₂BH₃) and (Cp)₂ZrH(NH₂BH₃) complexes synthesized from (Cp)₂ZrCl₂ with 1 and 2 equiv of AB and *n*BuLi respectively,⁴⁰ and (Cp)₂Ti(NH₂BH₃) synthesized by reacting (Cp)₂TiCl₂ with K(NH₂BH₃).⁴¹ Although the geometry and ligand fields are different in these cases, the structural parameters of **2** compare favorably to these examples when the contracted ionic radius of Co(III) is considered (see Figure S10).⁴² The formation of **2** represents a rare example of N–H activation to isolate an amidoborane species.

Recent examples by Manners and co-workers have found that Cp-based Ti-amidoborane complexes are active in amine borane dehydrocoupling. Specifically, Manners and co-workers reported the Cp₂Ti(Me₂NBH₃) complex as an active catalyst for the dehydrocoupling of dimethylamine borane (DMAB),^{10,14} and more recently, they have reported an analogous amidoborane complex, Cp^{*}₂Ti(MeNHBH₃), which was crystallographically characterized following the reaction of Cp^{*}₂Ti(CH₃) with MeNH₂BH₃.¹³ The latter isolated amidoborane was also found to be catalytically active when reintroduced to the reaction. Webster and co-workers have also suggested the participation of iron-amidoborane intermediates during the dehydrocoupling of DMAB with a (Nacnac)Fe complex and were able to isolate and crystallographically characterize the amidoborane intermediate with two monomer units.²⁵

Amidoborane complexes have also been studied and implicated in alkaline earth (AE) metal complexes for amine borane dehydrocoupling. Earlier work by Harder and co-workers reported the crystal structures of AE metals with the NH_2BH_3^- anion including (DⁱPPNacnac)Ca(NH₂BH₃)·(THF)₂,⁴³ and the Mg analogue (DⁱPPNacnac)Mg(NH₂BH₃)·(THF).⁴⁴ More recent work by Hill and co-workers has extended the study of the AE-amidoborane species and applied them in amine borane dehydrocoupling reactions^{45–47}

Characterization of **2** by ¹H NMR spectroscopy revealed a diamagnetic complex with three 6H resonances corresponding to the mesityl methyl groups, consistent with a C_s-symmetric complex (Figure 2c). The spectrum also contained upfield resonances at 0.12 (2H), −8.76 (1H), and −15.03 (1H) ppm. The assignment of these resonances was aided by collecting the ¹H{¹¹B} NMR spectrum of **2** (Figure 2d). Upon decoupling of the ¹¹B nucleus, the resonance at −8.76 ppm and a previously obscured broad resonance at 1.33 ppm changed peak shape to form sharper resonances. Due to the peak shape change upon decoupling of the ¹¹B nucleus and literature precedence for amidoborane moieties, the resonances at 1.33 and −8.76 ppm were assigned to BH₂(Terminal)

and BH(Bridging) protons, respectively, while the resonances at 0.14 and −14.97 ppm were assigned to the protons of NH₂ and Co–H, respectively.^{40,41} Complex **2** also featured a corresponding ¹¹B NMR resonance at −28.1 ppm assigned to the boron atom of the NH₂BH₃[−] fragment (Figure S3). Variable-temperature NMR experiments of **2** in toluene-*d*₈ revealed no fluxional character of this complex up to 80 °C.

To further support the proposed N–H oxidative addition pathway to form **2**, we turned to the deuterated isotopologues of AB. To this end, NH₃BD₃ and ND₃BH₃ were synthesized and reacted with **1** at room temperature in THF to form (Mes₃CCC)CoH(NH₂BD₃) (**2-BD**) and (Mes₃CCC)CoD(ND₂BH₃) (**2-ND**), respectively (Scheme 1).²⁹ Consistent

Scheme 1. Reaction of **1** with Deuterated Isotopologues of AB

with the N–H oxidative addition pathway, the resulting ¹H NMR spectrum of the reaction of **2-BD** lacked the resonances previously assigned to the BH₂(Terminal) and BH(Bridging) protons and maintained the resonances assigned to the Co–H and NH₂ protons (Figure S5). The ²H NMR spectrum of **2-BD** showed the inverse picture with the corresponding BD₂(Terminal) and BD(Bridging) resonances present. In a similar fashion, **2-ND** showed the enrichment of the ND₂ and Co–D resonances in the ²H NMR spectrum (Figure S6). The ¹H NMR spectrum of **2-ND** revealed the expected BH₂(Terminal) and BH(Bridging) resonances; however, the spectrum also contained a significant amount of Co–H (1.00:2.18 integration ratio of Co–H/BH(Bridging)). Some of the Co–H in this case is not only the likely result of incomplete enrichment of the ND₃BH₃ (ca. 90% enriched by ¹H NMR integration) but also suggests that some exchange with the hydride is possible. The difference in integration between the NH₂ (0.2) and Co–H (1.0) resonances is also notable because in theory the ratio should be 2:1 if the difference came from the starting material. The Co–H/D mixture of the product also results in the splitting of the BH(Bridging) resonance in the ¹H NMR spectrum. A report studying the IR and Raman spectra of d⁶ trans-dihydride complexes found the substitution of a hydride for deuteride resulted in changes in the charge gradient and density in these species.⁴⁸ An effect of this sort may explain the differing influence of a hydride or deuteride trans to the BH(Bridging) on the chemical shift of this proton; however, more analogous examples would be needed to support this hypothesis. Both isotopic enrichment experiments are consistent with N–H/D

Figure 3. IR spectra (KBr) of **2** (green), $(^{\text{Mes}}\text{CCC})\text{CoD}(\text{ND}_2\text{BH}_3)$ (blue), and $(^{\text{Mes}}\text{CCC})\text{CoH}(\text{NH}_2\text{BD}_3)$ (orange). Asterisks mark new stretching frequencies corresponding to the deuterated species.

Scheme 2. Independent Synthesis of **2** from **3**

177 activation of the AB substrates and further support the peak
178 assignments in the ^1H NMR spectrum.

179 Analysis of **2** by IR spectroscopy (Figure 3, green trace)
180 revealed stretching frequencies at 3434 cm^{-1} (NH_2), 2415 and
181 2344 cm^{-1} ($\text{BH}_{2(\text{Terminal})}$), and 1862 cm^{-1} (Co-H) which were
182 consistent with those reported for other amidoborane^{40,41} and
183 Co-H species.³³ As with the NMR spectra of the deuterated
184 isotopologues of **2**, the IR spectra were consistent with these
185 assignments as evidenced by the shift of the deuterated
186 positions' stretching frequencies in the corresponding IR
187 spectra. The IR spectrum of **2-ND** (Figure 3, blue trace)
188 revealed a shift of the NH_2 stretching frequency at ca. 3400 –
189 2567 cm^{-1} consistent with the reduced mass calculation for
190 ND_2 (calcd 2513 cm^{-1}). This spectrum also lacked a

significant peak at ca. 1860 cm^{-1} which is consistent with an
isotopically shifted Co-D frequency. The resulting Co-D
stretch could not be unambiguously assigned as it was lost in
the fingerprint region. The IR spectrum for **2-BD** (Figure 3,
orange trace) featured a small peak at ca. 2375
 cm^{-1} ($\text{BH}_{2(\text{Terminal})}$) resulting from incomplete deuteration of
the B-H bonds and a peak at 1752 cm^{-1} , which was consistent
with the shifted $\text{BD}_{2(\text{Terminal})}$ stretching frequency (calcd 1753
 cm^{-1}). The spectrum maintained the Co-H peak at ca. 1860
 cm^{-1} and NH_2 stretching frequency at ca. 3400 cm^{-1} . Both
isotopically labeled samples help support the assignment of the
stretching frequencies in the IR spectra and are consistent with
the corresponding ^1H NMR resonances.

To test the catalytic competence of **1** toward AB dehydrogenation, 10 mol % **1** was reacted with AB at 60 °C in THF and tracked by ¹¹B NMR spectroscopy over time (Figure 4). The primary soluble products formed at the

The BN products (mainly PB and borazine) observed by ^{11}B NMR spectroscopy during catalytic dehydrogenation with **1** are suggestive of a mechanism which involves the formation of NH_2BH_2 followed by the release of this species from the cobalt center. Because of its reactivity, NH_2BH_2 is not practically observed in solution; however, addition of cyclohexene to the reaction allows for the trapping of the hydroborated cyclohexene product ($\text{C}_6\text{H}_9\text{BNH}_2$).⁵⁷ Running this trapping experi-

Type I - Formation of oligomeric species

$$[M] + AB \xrightarrow{-H_2} \text{Oligomer} + \text{Polyaminoborane (PAB)}$$

Type II - Release of NH_2BH_2 from metal

$$[M] + H_2 \xrightarrow{+ 2 AB, - 2 H_2} \text{BCDB} \xrightarrow{- 3 H_2} \text{Borazine} \xrightarrow{- 3 H_2} \text{Polyborazylene (PB)}$$

Figure 5. Top: calculated Gibbs energy profile in THF at 298 K and 1 atm for the formation of **2** starting from **1** and further release of NH_2BH_2 from **2**. Bottom: optimized transition state structures with the relevant bond distances (in Å).

ment under the catalytic conditions resulted in the formation of the Cy_2BNH_2 species as confirmed by ^{11}B NMR spectroscopy (Figure S11). Both the soluble BN-containing species observed in the catalytic dehydrogenation of AB and the trapping of NH_2BH_2 suggest that **1** is acting as a Type II catalyst (Scheme 3). However, under small-scale catalytic runs, a non-negligible amount of precipitate was formed. Upon scaling up of the reaction, characterization of this precipitate by IR spectroscopy suggested the formation of poly(aminoborane) (PAB) (Figure S12).^{58,59} The formation of PAB suggests that **1** is acting as both a Type I and II catalyst under these conditions. The amount of H_2 per AB was determined to be 1.7 ± 0.1 equiv with an inverted buret apparatus (see Supporting Information). The amount of H_2 released is consistent with **1** acting as both types of AB dehydrogenation catalyst.

Monitoring catalytic reactions utilizing **1** by ^1H and ^{11}B NMR spectroscopy reveals that **2** is formed within minutes in THF and remains the primary observable cobalt species in solution. To ensure that **2** was not simply a stable, off-pathway product from the catalytic reaction, isolated **2** was employed in the catalytic dehydrogenation of AB. Reacting 10 mol % **2** with AB at 60 °C in THF at the same concentration for reactions with **1** resulted in conversion of AB to form a similar soluble product distribution (Figure S13), albeit at a slower rate (ca. 24 vs 48 h for full conversion). The isolation of PAB was not achieved when starting from **2**, which may rely on a sufficient concentration of NH_2BH_2 to be competitive (*vide infra*). These results suggest that **2** is either one of the active species

or goes on to form one of the active species in solution. Heating **2** at 60 °C in the absence of AB in THF- d_8 revealed no appreciable conversion of **2** to other complexes. This suggests that β -hydride elimination directly from **2** is not a likely pathway for the release of NH_2BH_2 from the cobalt center in the absence of additional AB.

The competing pathways for AB dehydrogenation under the catalytic conditions frustrated efforts to perform kinetic analyses on this system. Hence, we turned our attention to DFT to try and provide insight into possible pathways starting from **2** that would match experimental observations.

DFT Studies: Formation of **2** and Further Reactivity of **2** with AB.

DFT studies at the wb97xD level sought to provide further insight on the reaction mechanism for the initial N–H activation process of AB onto **1** to form **2**. The lowest Gibbs energy pathway obtained for this process is presented in Figure 5. The reaction begins with the dissociation of the pyridine ligand from **1** to form intermediate **I1**, followed by the association of AB through an η^2 B–H interaction to afford **I2**. This latter complex, which lies 12.2 kcal mol^{−1} above the separate reactants, subsequently undergoes rearrangement to form η^1 species **I3**, which is ready for N–H activation. The N–H activation step across the Co center is achieved through TS1 and results in structurally characterized hydride-amidoborane complex **2**. The calculated barrier for the overall process is 24.0 kcal mol^{−1} in THF, which is consistent with the reaction proceeding at room temperature. DFT calculations also predict the formation of **2** to be exergonic by −11.0 kcal mol^{−1}, which is in line with the

stability of the hydride-amidoborane complex formed. Other reaction pathways considered for the formation of **2** included the activation of the N–H bond from **1** (with the pyridine coordinated to Co) and the B–H activation of AB from **I3** (see Figures S21 and S22 respectively). Both alternative paths were discarded based on their significantly high energy barriers (50.1 and 35.2 kcal mol^{−1}, respectively). Notably, the fact that the B–H activation of AB was 11.2 kcal mol^{−1} higher in energy than the N–H activation via **TS1** is in good agreement with the deuteration studies.

The vibrational modes of the optimized structure of **2** were calculated and can be found in Figure S23. The Co–H stretching frequency was calculated to be 1968 cm^{−1}, which is in reasonably good agreement with the reported experimental peak at ca. 1860 cm^{−1}. The calculated BH₂ stretching frequencies are 2506 and 2554 cm^{−1} which also match moderately well to the experimental BH₂ stretching frequencies at ca. 2400 cm^{−1}. The asymmetric and symmetric NH₂ stretching frequencies were calculated to be 3709 and 3624 cm^{−1} respectively, compared to the experimental stretching frequencies of 3434 and 3364 cm^{−1}. The Co–BH_(Bridging) stretching frequency was calculated to be 1713 cm^{−1}; however, this peak could not be definitively assigned in the experimental spectra (*vide supra*).

In order to shed light on the nature of the bonding of the amidoborane fragment in **2**, natural bond orbital (NBO) and second-order perturbation theory (SOPT) analyses were performed to ascertain the main donor–acceptor interactions involved in the Co–N, Co–H(B), and B–N bonds (Figure 6). These analyses revealed that the most important interaction

between Co and the N from amidoborane arises from the electron donation from a N 2p orbital to an empty sd–sp hybrid orbital constituted by Co and the aryl C atom of the ligand and from the donation from a hybrid sd–s orbital from the Co–H bond to an empty sp orbital from N. The interaction between Co and H(B) was found to be mostly governed by the electron donation from the hybrid sp³ orbital of the B–H bond to the antibonding sd–s hybrid orbital from Co–H, and the backdonation from the above s bonding orbital from Co–H to an empty sp orbital from B. Finally, the main donor–acceptor interactions within the amidoborane fragment correspond to the electron donation from the bonding sp–s orbital of B–H to the above empty sp orbital from N, and the backdonation from the above filled N-2p orbital to the sp–s antibonding orbital of B–H. For details of the exact composition of the NBOs involved in these donor–acceptor interactions, see Table S1.

Because employing both **1** and **2** as a catalyst showed **2** as the primary observable cobalt species, we next sought to use DFT to elucidate a plausible reaction mechanism for NH₂BH₂ release from **2** to form the products consistent with a Type II catalyst. To this end, DFT calculations of the reaction of **2** with AB were conducted, obtaining the reaction pathway summarized in Figure 5. Interestingly, the release of NH₂BH₂ from **2** proved to be energetically unfavorable unless an AB molecule was in proximity to the Co center to assist the process. This is consistent with the fact that no elimination of NH₂BH₂ is observed when **2** is heated in the absence of AB. Calculations also show that when AB is present the release of NH₂BH₂ takes place via **TS2** with an activation energy of 34.4 kcal mol^{−1}, in line with catalytic turnover occurring at 60 °C in THF. During **TS2**, both Co–N and B–H_(Bridging) bonds (3.097 and 1.513 Å, respectively) are cleaved to release NH₂BH₂ with the concomitant coordination of the nearby AB (Co–B: 3.455 Å) to yield **I5**.

Upon elimination of NH₂BH₂ from **I4**, the more stable (9.1 kcal mol^{−1} lower than **I4**) *trans*-dihydride species with an η¹ B–H interaction (**I5**) is formed. This species subsequently undergoes a *trans*-to-*cis* isomerization through **TS3** where the BH₂NH₃ moiety is transferred to one of the hydrides to yield **I6**. This step requires a relative energy barrier of 18.2 kcal mol^{−1} and is slightly endergonic by 1.8 kcal mol^{−1}. From **I6**, the reductive elimination of H₂ occurs via **TS4** with a relative energy barrier of only 5.2 kcal mol^{−1}. The result of this last transformation is **I3** which can again undergo N–H activation to yield **2**. The highest energy point of the diagram is **TS3** at 37.6 kcal/mol from **2**, which is consistent with catalytic turnover occurring at 60 °C in THF. Overall, the mechanism depicted in Figure 5 accounts for the release of 1 equiv of H₂ and NH₂BH₂ from **2**, which was confirmed by trapping experiments using cyclohexene. A process in which the NH₂BH₃[−] fragment of **2** stays intact with reactivity occurring solely at the hydride is also a possibility but was not found computationally.

Finally, DFT calculations were performed to propose a plausible mechanism for the oligomerization of AB starting from **2** (Figure 7). Starting from this species, the association of NH₂BH₂ previously formed to yield **I7** was found to be slightly endergonic (by ca. 1 kcal mol^{−1}). This complex can then undergo N–B bond formation and B–H bond formation with the existing B–H_(Bridging) of the amidoborane fragment in a concerted process via **TS5** leading to on-metal oligomeric species **I8**. Overall, the oligomerization of AB requires an

Figure 6. NBO representation (isovalue = 0.08 e[−]/bohr³) of the main donor–acceptor interactions involved in the Co–N, Co–H(B), and B–N bonds obtained from SOPT. The energy computed for each of these interactions, E_{SOPT} , is shown in kcal/mol. Orange arrows indicate the electron flow from the donor to the acceptor NBO. The mesityl flanking groups have been omitted for clarity. The color code is the same as that in Figure 5.

Figure 7. Calculated Gibbs energy profile in THF at 298 K and 1 atm for the oligomerization of AB on 2.

energy barrier of $24.0 \text{ kcal mol}^{-1}$ and is exergonic by ca. $4.3 \text{ kcal mol}^{-1}$. Further oligomerization steps are postulated to involve the insertion of additional NH_2BH_2 molecules into the growing oligomeric chain. Although isolation of PAB was not possible when starting from 2, this suggested oligomerization process relies on a sufficient concentration of NH_2BH_2 in solution.⁶⁰ Given the higher activity when employing 1, it is possible that this results in a higher concentration of NH_2BH_2 in solution which can react with 2.

CONCLUSION

Co(I) pincer complex 1 reported herein represents a rare example of a homogeneous catalyst for the dehydrogenation of AB. The formation of soluble (borazine and polyborazylene) and insoluble (poly(aminoborane)) BN-containing products suggests the existence of competing mechanisms for the dehydrogenation/dehydropolymerization of AB on 1. Reaction of 1 with AB yielded complex 2, the first characterized hydride-amidoborane complex on a late transition metal. Isotopic labeling and DFT studies revealed that 2 was formed via an N–H activation process of AB at the Co center of 1. In addition, computational studies outline likely pathways of activation for 2 to produce the experimentally observed BN-containing species. The knowledge generated herein is expected to inspire the design of well-defined cobalt pincer complexes to provide further insights into the dehydrogenation and dehydropolymerization of AB and other amine boranes.

EXPERIMENTAL SECTION

General Considerations. All manipulations of air- and moisture-sensitive compounds were carried out in the absence of water and dioxygen in an MBraun inert atmosphere drybox under a dinitrogen atmosphere except where specified otherwise. The MBraun drybox was equipped with a -35°C freezer for cooling samples and crystallizations. All glassware was oven-dried for a minimum of 8 h and cooled in an evacuated antechamber prior to use in the drybox. Solvents for sensitive manipulations were dried and deoxygenated on a Glass Contour System (SG Water USA, Nashua, NH) and stored over $4 \text{ \AA}$ molecular sieves purchased from Strem following literature procedure prior to use.⁶¹ NMR solvents (C_6D_6 and $\text{THF}-d_8$) were purchased from Cambridge Isotope Laboratories and were degassed and stored over $4 \text{ \AA}$ molecular sieves prior to use. Celite 545 (J. T. Baker) was dried in a Schlenk flask for 24 h under dynamic vacuum while heating to at least 150°C prior to use in a glovebox. Ammonia borane was purchased from Sigma and filtered through Celite with THF before use. Dimethylamine borane (DMAB) was purchased

from Sigma and used as received. The deuterated isotopologues NH_3BD_3 and ND_3BH_3 were synthesized according to a literature procedure.²⁹ ($^{\text{Mes}}\text{CCC})\text{Co-py}$ (1),³⁵ ($^{\text{Mes}}\text{CCC})\text{CoHClPMe}_3$ (3),³³ methylamine borane,⁶² and KNH_2BH_3 ⁶³ were synthesized according to literature procedures.

^1H , ^{13}C , and ^{11}B NMR spectra were recorded at room temperature on a Varian spectrometer operating at 500 MHz (^1H NMR), 126 MHz (^{13}C NMR), and 128 MHz (^{11}B NMR) and referenced to the residual solvent peaks and $\text{BF}_3\cdot\text{Et}_2\text{O}$ (δ 0 ppm) for ^{11}B . Solid-state infrared spectra were recorded using a PerkinElmer Frontier FT-IR spectrophotometer equipped with a KRSS thallium bromide/iodide universal attenuated total reflectance accessory. Electrospray ionization mass spectrometry (ESI) was recorded on a Water Q-TOF Ultima ESI instrument in the Mass Spectrometry Laboratory at the University of Illinois at Urbana–Champaign (UIUC).

Crystallography. X-ray crystallography was performed at the George L. Clark X-ray Facility at UIUC. Single-crystal X-ray diffraction data were collected with the use of multimirror monochromatized Mo $K\alpha$ radiation ($0.71073 \text{ \AA}$) at 100 K on a Bruker D8 Venture diffractometer equipped with a Photon 100 detector. Combinations of $0.5^\circ \varphi$ and ω scans were used to collect the data. The collection, cell refinement, and integration of intensity data were carried out with the APEX2 software.⁶⁴ A multiscan absorption correction was performed using SADABS.⁶⁵ The structure was solved with XT⁶⁶ and refined with the full-matrix least-squares SHELXL⁶⁷ program within the Olex2⁶⁸ refinement GUI. Metrical parameters are available in Table S1.

Preparation of ($^{\text{Mes}}\text{CCC})\text{CoH}(\text{NH}_2\text{BH}_3)$ (2). In the glovebox, a 20 mL scintillation vial was charged with ($^{\text{Mes}}\text{CCC})\text{Co-py}$ (20.5 mg, 0.03 mmol, 1.0 equiv), a magnetic stir bar, and ca. 3 mL of THF. To this stirring solution, NH_3BH_3 (1.0 mg, 0.033 mmol, 1.1 equiv) was added with ca. 3 mL of THF resulting in a color change from dark red/brown to amber within minutes. This solution was allowed to stir for 2 h, and then volatiles were removed. The brown residue was washed with hexanes ($4 \times 2 \text{ mL}$) dissolved in benzene, and then filtered through Celite. This solution was frozen, and then volatiles were removed to yield ($^{\text{Mes}}\text{CCC})\text{CoH}(\text{NH}_2\text{BH}_3)$ as a light brown powder (17.8 mg, 93%). Crystals suitable for X-ray diffraction were grown from the diffusion of pentane into a solution of 2. ^1H NMR (500 MHz, C_6D_6) δ 7.77 (d, $J = 8.1 \text{ Hz}$, 2H), 7.59 (d, $J = 7.8 \text{ Hz}$, 2H), 7.42 (t, $J = 7.7 \text{ Hz}$, 1H), 7.05 (t, $J = 7.7 \text{ Hz}$, 2H), 6.87 (t, $J = 7.7 \text{ Hz}$, 2H), 6.69 (s, 2H), 6.56 (s, 2H), 6.52 (d, $J = 8.0 \text{ Hz}$, 2H), 2.20 (s, 6H), 2.01 (s, 6H), 1.90 (s, 6H), 1.33 (br s, 2H, Co–BH_(Terminal)) 0.12 (s, 2H, Co–NH₂), -8.76 (s, 1H, Co–BH_(Bridging)), -15.03 (s, 1H, Co–H). ^{13}C NMR (126 MHz, C_6D_6) δ 208.27 (Co–C_{NHC}), 172.99 (Co–C_{Aryl}), 148.24, 139.20, 138.17, 137.20, 136.61, 132.17, 131.70, 130.00, 129.37, 123.03, 122.39, 121.80, 111.01, 109.75, 107.81, 20.94, 18.68, 18.66. ^{11}B NMR (128 MHz, C_6D_6) δ -28.1 . IR (KBr): $\nu(\text{cm}^{-1}) = 3434$ (m, NH), 3364 (w, NH), 3100–2800 (m, CH), 2415 (m, BH_(Terminal)), 2344 (m, BH_(Terminal)), 1862 (m, Co–H). HRMS (ESI), calcd for $\text{C}_{38}\text{H}_{34}\text{CoN}_4[\text{M} - \text{NH}_2\text{BH}_3]^+$: 605.2115. Found 605.2112.

Formation of Deuterated Analogues of 2. In the glovebox, a 20 mL scintillation vial was charged with ($^{\text{Mes}}\text{CCC})\text{Co-py}$ (1) (10.2 mg, 0.015 mmol, 1.0 equiv), a magnetic stir bar, and ca. 2 mL of THF. To this stirring solution, the deuterated analogue (NH_3BD_3 or ND_3BH_3 , 0.0165 mmol, 1.1 equiv) was added with ca. 2 mL of THF resulting in a color change from dark red/brown to amber within minutes. This solution was allowed to stir for 2 h and then volatiles were removed. The brown residue was washed with hexanes ($3 \times 1 \text{ mL}$), dissolved in benzene, and then filtered through Celite. This solution was frozen, and then volatiles were removed to yield ($^{\text{Mes}}\text{CCC})\text{CoH}(\text{NH}_2\text{BD}_3)$ and ($^{\text{Mes}}\text{CCC})\text{CoD}(\text{ND}_2\text{BH}_3)$ as light brown powders in ca. 90% yield.

Catalytic Dehydrogenation Reactions. In the glovebox, a quartz J. Young NMR tube was charged with ($^{\text{Mes}}\text{CCC})\text{Co-py}$ (2.0 mg, 0.003 mmol, 0.10 equiv) or ($^{\text{Mes}}\text{CCC})\text{CoH}(\text{NH}_2\text{BH}_3)$ (1.9 mg, 0.003, 0.10 equiv) and 600 μL of THF of a 0.05 M AB solution (0.9 mg, 0.03 mmol, 1.0 equiv). The tube was sealed and then brought out of the glovebox to heat in a 60°C oil bath. The progress of the reaction was tracked over time by ^{11}B NMR.

Mercury Drop Test Reaction. In the glovebox, a quartz J. Young NMR tube was charged with (^{Mes}CCC)Co-py (2.0 mg, 0.003 mmol, 0.10 equiv), and 600 μL of THF of a 0.05 M AB solution (0.9 mg, 0.03 mmol, 1.0 equiv). One drop of Hg(0) was added to the tube, and the tube was then sealed before being brought out of the glovebox to heat in a 60 °C oil bath. The reaction was agitated about every hour to ensure contact of possible nanoparticles with Hg(0). The progress of the reaction was tracked over time by ¹¹B NMR.

Cyclohexene Trapping Experiment. In the glovebox, a quartz J. Young NMR tube was charged with (^{Mes}CCC)Co-py (2.0 mg, 0.003 mmol, 0.10 equiv), 600 μL of THF of a 0.05 M AB solution (0.9 mg, 0.03 mmol, 1.0 equiv), and cyclohexene (49.3 mg, 0.6 mmol, 20 equiv). The tube was sealed and then brought out of the glovebox to heat in a 60 °C oil bath. The progress of the reaction was tracked over time by ¹¹B NMR spectroscopy.

Gas Evolution Reaction. In the glovebox, a 20 mL storage vessel was charged with (^{Mes}CCC)Co-py (6.8 mg, 0.01 mmol, 0.05 equiv), AB (6.2 mg, 0.20 mmol, 1.0 equiv), and 4.0 mL of THF. The vessel was sealed, removed from the glovebox, attached to the gas evolution setup as seen in Figure S17, and heated at 60 °C in a heating block. The reaction was run in triplicate to determine 1.7 ± 0.1 equiv of H₂ was released per AB.

Reaction of (^{Mes}CCC)CoHClPMe₃ (3) with KNH₂BH₃. In the glovebox, a 20 mL scintillation vial was charged with (^{Mes}CCC)-CoHClPMe₃ (10.0 mg, 0.014 mmol, 1.0 equiv), KNH₂BH₃ (1.0 mg, 0.014 mmol, 1.0 equiv), a magnetic stir bar, and ca. 5 mL of THF. This solution was stirred at ambient temperature for ca. 15 min, and then volatiles were removed. This residue was dissolved in C₆D₆ and then eluted through Celite into an NMR tube.

Reaction of (^{Mes}CCC)CoH(NH₂BH₃) (2) with KNH₂BH₃. In the glovebox, a 20 mL scintillation vial was charged with (^{Mes}CCC)-CoH(NH₂BH₃) (9.5 mg, 0.015 mmol, 1.0 equiv), PMe₃ (1 M in THF, 10 equiv), a magnetic stir bar, and ca. 5 mL of THF. After stirring for 5 min, KNH₂BH₃ (1.0 mg, 0.014 mmol, 10.0 equiv) was transferred to the reaction vial with THF (ca. 1 mL) and stirred at ambient temperature for an additional 30 min. Volatiles were removed, and then the residue was dissolved in C₆D₆ and eluted through Celite into an NMR tube.

Computational Details. DFT calculations were carried out using the dispersion-corrected hybrid exchange-correlation functional wB97XD⁶⁹ and the Gaussian09 software.⁷⁰ To describe the electrons of B, C, and H atoms, the 6-31G(d,p) basis set with polarization functions was employed, while the same basis set with added diffuse functions, i.e., 6-31+G(d,p), was used in the description of the more electronegative N atoms. In contrast, Co electrons were represented with the Stuttgart/Dresden effective core potential with added *f*-polarization functions (exponent: 2.780).⁷¹ The geometry of the stationary points was optimized in vacuum without imposing any constraint. The nature of these points was further assessed by means of vibrational frequency calculations, which confirmed that energy minima had only real frequencies, while transition states had only one single imaginary frequency. In addition, the latter were confirmed to connect the expected reaction intermediates by relaxing the transition state geometry following the eigenvector associated to the imaginary frequency.

The effect of the solvent employed in experiments (THF, $\epsilon = 7.52$) was introduced by performing single-point calculations on the optimized geometries in vacuum using the SMD solvation model.⁷² Gibbs energies in THF were calculated by adding to the potential energies in solution the Gibbs energy corrections calculated in vacuum at the experimental temperature of 298 K and 1 atm.

NBO and SOPT analyses on selected donor–acceptor interactions in intermediate **2** were performed using the software NBO 6.0.⁷³

NMR and IR spectra of **2** and deuterated analogues, comparison of **2** with other amidoborane complexes, catalytic dehydrogenation of AB and other amine boranes, gas evolution experiments, reaction of Co(III) complexes with KNH₂BH₃, DFT data, crystallographic parameters (PDF)

Accession Codes

CCDC 1999728 contain the supplementary crystallographic data for complex **2**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

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Notes

The authors declare no competing financial interest. All the DFT data underlying this work, including the Cartesian coordinates of the modeled structures and energies, are available at the following ioChem-BD online data set: <https://iochem-bd.bsc.es/browse/review-collection/100/194393/072224b9999729ba5ccea358>.

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.0c00459>.

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