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Dehydrogenation of (Di)amine−Boranes by Highly Active Scandocene Alkyl Catalysts

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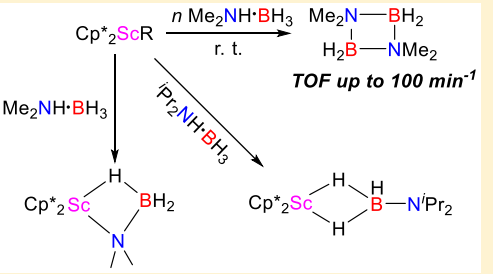
Supporting Information

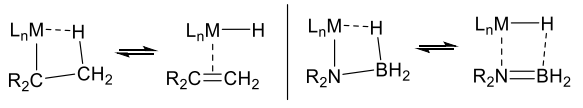
ABSTRACT: The scandocene alkyl complexes $(C_5Me_5)_2ScR$ (**1**, R = $CH(SiMe_3)_2$; **5**, R = CH_2SiMe_3) were found to be highly active catalysts for the dehydrogenation of dimethylamine−borane (DMAB), exhibiting turnover frequencies up to 100 min^{-1} at ambient temperature. The β-B-agostic scandium amidoborane intermediate **6** was isolated from a stoichiometric reaction of complex **5** with DMAB. In contrast, treatment of complex **5** with sterically bulky diisopropylamine−borane led to isolation of the aminoborane-coordinated scandocene hydride **7** via a complete β-H elimination. Scandium amidoborane complex **6** showed scandium hydride like reactivity toward dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP), affording DCC insertion product **8** and DMAP ortho-borylation product **9**, respectively. In addition, complexes **1** and **5** also showed remarkably high activity for the catalyzed dehydrogenative cyclization of diamine−boranes to give N-heterocyclic boranes.



INTRODUCTION

β-H elimination from metal alkyl complexes is a fundamental process in organometallic chemistry and plays an essential role in a variety of transition-metal-catalyzed reactions.[1] These transformations proceed via a β-agostic interaction[2] (e.g. **I**, Scheme 1). However, the resulting metal hydride alkene

Scheme 1. β-H Eliminations of β-Agostic Metal Alkyl and β-B-Agostic Metal Amidoborane[a]



[a] L_n, ligand; M, metal.

intermediate (**II**) is difficult to observe, especially for d^0 metal complexes because of weak alkene−metal π bonding and the tendency for further migratory insertion reactions to occur.[3] Amidoborane ligands $(NR_2\text{-}BH_3)^-$ are isoelectronic with alkyl ligands $(CR_2\text{-}CH_3)^-$, and so the β-B-agostic metal amidoborane (**III**, Scheme 1) is expected to exhibit chemical behavior similar to that of **I**.[4] However, the direct observation of metal hydride aminoborane intermediates (e.g. **IV**) that result from β-H elimination remains elusive.[5]

The catalytic dehydrogenation of amine−boranes has been explored extensively because of their potential for hydrogen storage and as precursors for BN-based ceramics and polymeric materials.[6] β-H elimination of a β-B-agostic metal amidoborane is thought to be a key step in many early-transition-metal- or main-group-metal-catalyzed dehydrocoupling of amine−boranes.[7] However, the isolation of key intermediates in the dehydrogenation reaction, particularly in highly active systems, is challenging and only a few active β-B-agostic metal amidoboranes have been characterized.[8] Herein, we have found that scandocene alkyls (Cp^*_2ScR; Cp^* = C_5Me_5, R = $CH(SiMe_3)_2$, CH_2SiMe_3) are remarkably active catalysts for the dehydrogenation of $Me_2NH{\cdot}BH_3$ (DMAB) and diamine−boranes, with a turnover frequency (TOF) of up to 100 min^{-1} at room temperature. Furthermore, a β-B-agostic scandium amidoborane intermediate was successfully isolated from the corresponding stoichiometric reaction.

RESULTS AND DISCUSSION

Although a number of transition-metal and main-group catalysts have been investigated for the catalytic dehydrogenation of amine−boranes, examples using rare-earth (RE) catalysts are limited.[9] We have examined a series of well-known RE metallocene alkyl complexes[10] for the catalytic dehydrogenation of DMAB (Scheme 2). The dehydrogenation reaction was initially performed using 0.5 mol % $Cp^*_2ScCH(SiMe_3)_2$ (**1**) in C_6D_6 at room temperature (Table 1, entry 1). Remarkably, a vigorous evolution of H_2 gas was observed and subsequent analysis of the quenched reaction mixture using ^{11}B NMR spectroscopy indicated that the DMAB was completely consumed within 2 min. Thus, the TOF for the scandium complex **1** reached 100 min^{-1}, which is comparable to those of the most active catalyst for DMAB dehydrogenation.[11,12] After the reaction, the starting amine−borane was

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Scheme 2. Catalytic Dehydrogenation of DMAB with Complexes 1−5

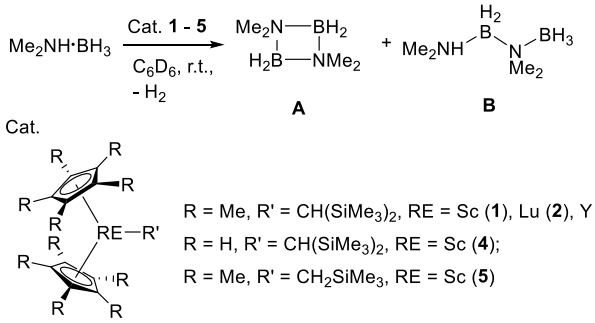


Table 1. Catalytic Dehydrogenation of DMAB with Rare-Earth Metallocene Alkyls 1−5[a]

entry	cat.	cat. loading (mol %)	time (min)	conversn (%)	A (%)	B (%)	TOF (min^{-1})
1	**1**	0.5	2	100	93	2	100
2	**1**	0.2	6	97	38	56	81
3	**2**	0.5	6	98	60	34	33
4	**3**	0.5	6	95	41	53	32
5	**4**	0.5	10	20	0	100	4
6	**5**	0.5	2	100	81	10	100

[a]Conditions: reactions were performed in C_6D_6 at room temperature in an unsealed vial. Conversion and product distribution were determined by integration of ^{11}B NMR spectra.

largely converted into the cyclic borazane $[Me_2N\text{-}BH_2]_2$ (**A**) (93%), along with trace amounts of other borane-containing species. Even with a very small catalyst loading (0.2 mol %), the reaction still achieved 97% conversion within 6 min. However, these reaction conditions resulted in the linear diborazane $Me_2NH{\cdot}BH_2{-}NMe_2{\cdot}BH_3$ (**B**) as the major product (Table 1, entry 2), presumably because the concentration of DMAB has a strong effect on the formation of different dehydrogenation products.[13] The effect of the metal ionic radius on the dehydrogenation of DMAB was examined by using larger RE metals, including lutetium and yttrium. Under the same reaction conditions, $Cp^*_2LuCH(SiMe_3)_2$ (**2**) and $Cp^*_2YCH(SiMe_3)_2$ (**3**) exhibited poor reaction selectivity and lower TOFs of 33 and 32 min^{-1}, respectively (Table 1, entries 3 and 4). Thus, the reaction activity decreased as the ionic radii of the central metal ion increased (Sc > Lu ≈ Y). The reactivity of RE metal complexes is highly dependent on the size of the ancillary ligand. The less sterically encumbered scandocene alkyl complex $Cp_2ScCH(SiMe_3)_2$ (Cp = C_5H_5; **4**) was prepared and used for the dehydrogenation reaction. Complex **4** exhibited dramatically lower activity, exclusively affording the linear borazane **B** when the reaction was performed using our standard conditions (Table 1, entry 5). Thus, it is plausible that the sterically bulky pentamethylcyclopentadienyl ligand might be crucial for achieving high catalytic activity. The influence of different alkyl initiating groups on the catalyst was also examined, with $Cp^*_2ScCH_2SiMe_3$ (**5**) that contained the less sterically hindered $-CH_2SiMe_3$ group showing reactivity similar to that of complex **1** (Table 1, entry 6).

To gain more insight into the reaction mechanism, a stoichiometric reaction between the scandocene complex **5** and an equimolar amount of DMAB was performed at −30 °C. Workup of the reaction mixture at low temperature resulted in the precipitation of pale yellow crystals that were identified as the β-B-agostic scandium amidoborane complex **6** by single-crystal X-ray diffraction (70% yield; Scheme 3 and Figure 1).

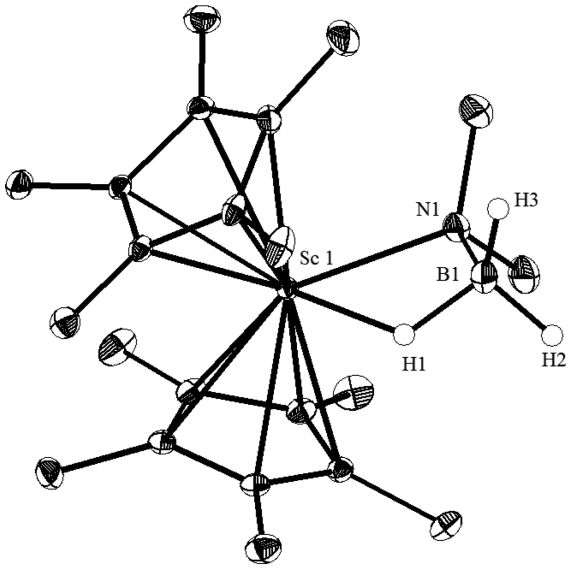
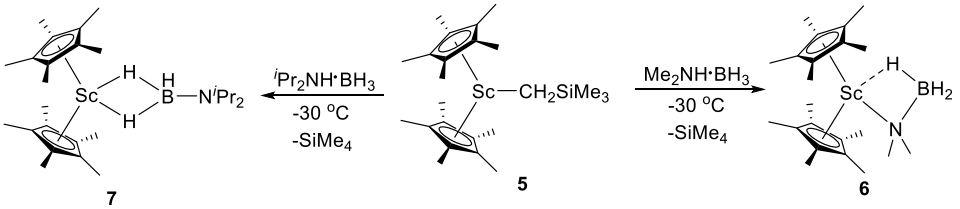


Figure 1. Molecular structure of complex **6**. Hydrogen atoms (except BH) are omitted for clarity, and ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Sc1−N1, 2.3116(17); Sc1−H1, 1.97(3); N1−B1, 1.577(3); B1−H1, 1.27(2); B1−H2, 1.15(2); B1−H3, 1.17(2); Sc1−N1−B1, 82.84(11); N1−B1−H1, 103.9(12); B1−H1−Sc1, 106.906(152); H1−Sc1−N1, 62.8(7).

The structure showed that the $[NMe_2BH_3]^-$ ligand was bound to the scandium metal center via a relatively long Sc−N (Sc1−N1 2.3116(17) Å) bond[9a,14] and an agostic Sc−H−B (Sc1−H1 1.97(3) Å, B1−H1 1.27(2) Å) interaction. The N1−B1 bond distance was 1.577(3) Å which was comparable to other well-defined main-group and transition-metal β-B-agostic amidoborane complexes.[4,5,8] Remarkably, the Sc−N−B bond angle (Sc1−N1−B1 82.84(11)°) in complex **6** was quite similar to those of the recently reported rare-earth β-agostic ethyl complexes (Cp^*_2YEt;[15] $Y{-}C_\alpha{-}C_\beta$ 82.6(2)°;

Scheme 3. Stoichiometric Reactions of Complex 5 with DMAB and $^iPr_2NH{\cdot}BH_3$



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Cp^*_2ScEt,[16] Sc−C_α−C_β 85.6(2)°). In addition, the IR spectrum of complex **6** contained bonds that were characteristic of terminal and bridging BH bonds at 2365 and 1688 cm^{-1}, respectively.[4a,8]

Complex **6** was dissolved in toluene-d_8 at room temperature for NMR analysis. Two singlets at 2.57 ppm (NMe_2) and 1.92 ppm (Cp*) were present in the ^1H NMR spectrum. Peaks from BH_3 or Sc*H* were not observed clearly, likely because of quadrupole broadening and/or the rapid exchange of hydrides.[17,18] However, the ^{11}B NMR spectrum showed two broad signals at 5.2 and −8.7 ppm (Figure S10), which indicated that two species existed in the solution state. The scandium amidoborane complex **6** may have caused the signal at −8.7 ppm, which would be consistent with other metal amidoborane complexes that have been reported.[4a,5,9a,9c] We have tentatively assigned the peak at 5.2 ppm, which has considerable sp^2 character,[19] to another borane unit from the β-H elimination product that contains a $Me_2N{=}BH_2$ coordinated scandocene hydride (**6′**). Unfortunately, attempt to isolate complex **6′** failed because it slowly converted to the cyclic borazane **A** and other unidentified species in solution at ambient temperature. Thus, the structure of **6′** currently remains undetermined. Variable-temperature NMR experiments of the sample were investigated and showed a decoalescence of the ^1H resonances at 253 K. Notably, the ratio of complex **6** in the mixture increased as the temperature was decreased (for details, see the Supporting Information).

To elucidate the structure of **6′**, we performed a controlled reaction of scandocene alkyl **5** with 1 equiv of $^iPr_2NH{\cdot}BH_3$, which contained a sterically bulky amino group. Following the reaction, an $^iPr_2N{=}BH_2$ coordinated scandium hydride (**7**; Scheme 3) was obtained in 75% yield. Therefore, it is likely that a similar β-B-agostic scandium amidoborane intermediate formed initially, which was followed by a rapid β-H elimination to afford the final product. The crystal structure of complex **7** (Figure 2) revealed that the B−N bond (1.491(3) Å) was considerably shorter than that in complex **6** (1.577(3) Å). The solution ^{11}B NMR spectrum of complex **7** featured a broad signal at 23.3 ppm, which was significantly shifted to lower field in comparison with the signal from complex **6** (−8.7 ppm). Variable-temperature NMR spectroscopy of complex **7** showed that it was the product of an irreversible β-H elimination product, with the reinsertion reaction most likely hampered by the sterically hindered N atom.[20]

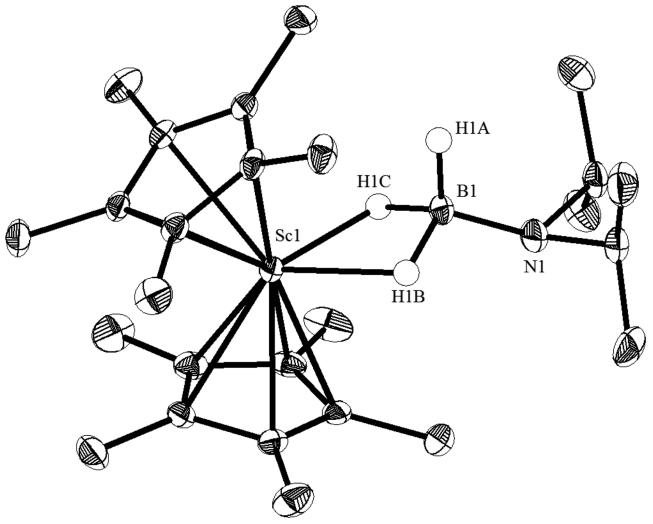

Figure 2. Molecular structure of complex **7**. Hydrogen atoms (except BH) are omitted for clarity, and ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Sc1−H1B, 2.02(2);Sc1−H1C, 1.95(2); B1−H1A, 1.18(2); B1−H1B, 1.22(3); B1−H1C, 1.22(3); B1−N1, 1.491(3); H1B−Sc1−H1C, 53.4(11); H1B−B1−H1C, 94.4(17).

Additional experiments were carried out to provide further information for the β-H elimination of complex **6** in solution. The stoichiometric reaction of **6** with an equimolar amount of dicyclohexylcarbodiimide (DCC) was examined because of its tendency to undergo insertion reactions into RE−H bonds.[21] As expected, the reaction clearly gave DCC insertion product **8** in 76% isolated yield with the concomitant formation of the cyclic borazane **A** (Scheme 4 and Figure 3; for details, see the Experimental Section and Supporting Information). The scandocene hydride is also reported to react with heterocyclic compounds (e.g. pyridine) to afford the ortho C−H activation product with the release of H_2.[18] Thus, the reaction of **6** with 4-dimethylaminopyridine (DMAP) was also investigated. The evolution of H_2 gas was observed during the reaction, which was confirmed by in situ ^1H NMR spectroscopy. Workup of the reaction mixture gave complex **9** as a yellow crystalline solid in 79% yield. The molecular structure of complex **9** determined by single-crystal X-ray diffraction is depicted in Figure 3. It has a contact ion pairing framework in which the cationic scandium center is coordinated by both B−*H* and *N* atoms of the former DMAP ring. We propose that the formation of complex **9** resulted from ortho C−H activation of DMAP followed by an alkide abstraction by a borane Lewis acid (for details, see Scheme S6 in the Supporting Information).[22,23] Both of the reactions that have been described may represent typical scandocene hydride like behavior and possibly indicate the existence of a β-H elimination product in solution.

As both scandocene alkyls **1** and **5** exhibited excellent performances in dehydrogenation of DMAB, we examined their use in the catalytic dehydrogenation of diamine−borane substrates to form cyclic diaminoboranes, which are nitrogen-containing analogues of widely used pinacol− or catechol−borane reagents. To date, there have only been three other catalysts that were reported to be active for such a transformation, each having a low activity (TOF < 0.4 min^{-1}) even at elevated temperatures.[24] Using complex **1** as the catalyst (2 mol %), the diamine−borane substrate **10a** was converted to the corresponding cyclic product **11a** in 92% yield in 20 min at room temperature (Table 2, entry 1). When complex **5** was used as the catalyst, a significantly higher activity was observed in transforming **10a** into **11a** (95% yield within 5 min, TOF = 9.5 min^{-1}; Table 2, entry 2). Scandocene alkyl **5** also showed high activity for the dehydrogenative cyclization of other challenging diamine−borane substrates such as **10b**,**c**. This resulted in the five-membered N-heterocyclic borane **11b** (TOF = 9.7 min^{-1}) and the six-membered N-heterocyclic borane **11c** (TOF = 4.9 min^{-1}), respectively (Table 2, entries 3 and 4).

CONCLUSION

In summary, a series of rare-earth metallocene alkyls were examined for the catalytic dehydrogenation of DMAB. The catalytic activity was found to be dependent on both the metal ion and the surrounding ligands. The scandocene alkyls **1** and **5** showed extremely high activity, affording TOFs of up to 100

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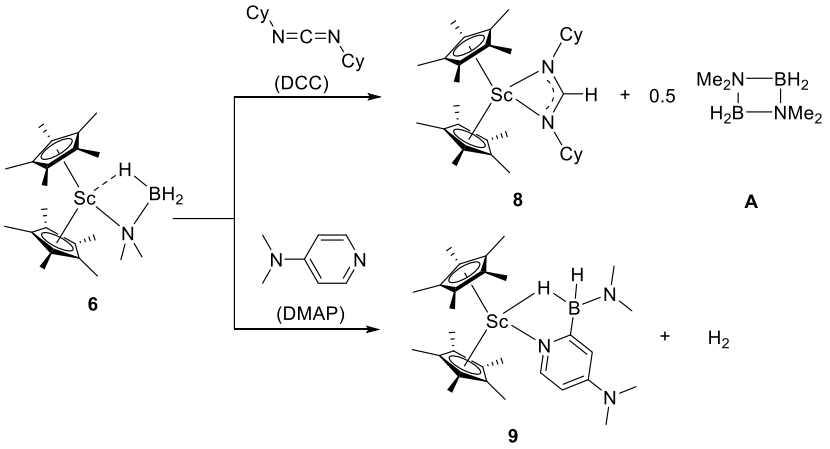
Scheme 4. Stoichiometric Reactions of Complex 6 with DCC and DMAP



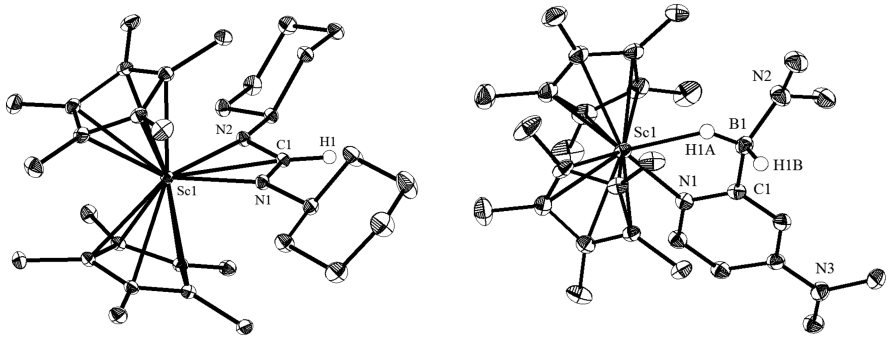
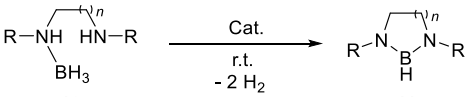


Figure 3. Molecular structures of complexes **8** (left) and **9** (right). Hydrogen atoms (except BH) are omitted for clarity, and ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg) for **8**: N1−C1, 1.324(3); N2−C1, 1.324(3); N1−Sc1, 2.2268(17); N2−Sc1, 2.2424(18); C1−N1−C2, 115.40(17); C1−N1−Sc1, 88.99(13); C2−N1−Sc1, 153.72(14); C1−N2−Sc1, 88.32(12). Selected bond lengths (Å) and angles (deg) for **9**: Sc1−N1, 2.228(2); B1−N2, 1.506(4); B1−C1, 1.620(4); N2−B1−C1, 116.0(2); C1−N1−Sc1, 110.17(16); N1−C1−B1, 118.2(2).

Table 2. Catalyzed Dehydrogenative Cyclization of Diamine−Boranes by Scandocene Alkyls[a]



10 **11**

entry	substrate	cat.	time (min)	yield (%)	TOF (min^{-1})
1	**10a** (n = 1, R = Me)	**1**	20	92	2.3
2	**10a** (n = 1, R = Me)	**5**	5	95	9.5
3	**10b** (n = 1, R = ^{i}Pr)	**5**	5	97	9.7
4	**10c** (n = 2, R = Me)	**5**	10	98	4.9

[a]Conditions: reactions were performed in C_6D_6 with 2 mol % catalyst loading at room temperature in an unsealed vial. Yields were determined by ^{1}H NMR using hexamethylbenzene as an internal standard.

min^{-1} at room temperature. The stoichiometric reaction of complex **5** with DMAB led to the isolation of the scandocene β-B-agostic amidoborane complex **6**, which probably underwent a β-H elimination in solution to react with DCC and DMAP. However, the reaction of scandocene alkyl **5** with ^{i}Pr$_2$NH·BH$_3$ gave an aminoborane-coordinated scandocene hydride through a complete β-H elimination process. In addition, complexes **1** and **5** also exhibited very high activities for the catalyzed dehydrogenative cyclization of diamine−boranes to give N-heterocyclic boranes. This work shows that scandocene alkyls are highly active catalysts for the dehydrogenation of (di)amine−boranes and gives a deeper understanding of the β-H elimination of β-agostic metal complexes.

EXPERIMENTAL SECTION

For general information and the characterization data of the new compounds see the Supporting Information.

Preparation of Complex 4. LiCH(SiMe$_3$)$_2$ (118 mg, 0.71 mmol, in 2 mL of toluene) was added to a solution of [Cp$_2$ScCl]$_2$ (150 mg, 0.36 mmol) in toluene (2 mL). The reaction mixture was stirred at room temperature for 1 h. After filtration, the volatiles were removed under vacuum and the residue was dissolved in hexane. After standing at −30 °C overnight, a large amount of pale yellow crystalline solid was formed, which was collected and washed with hexane (2 × 0.5 mL) to finally give complex **4** (152 mg, 64%).

General Procedure for Dehydrogenation of DMAB. A 20 mL oven-dried glass reactor was charged with rare-earth-metal complex (3.0×10^{-3} mmol) inside the glovebox. DMAB was dissolved in the solvent (0.5 mL) and added to the catalyst at room temperature. A vigorous evolution of H$_2$ gas was immediately observed. The mixture was allowed to react uncapped and unstirred. After the measured time interval, a 0.2 mL aliquot was taken out and quickly quenched into a 4 mL vial containing 0.5 mL of undried "wet" C_6D_6. The quenched reaction mixture was immediately frozen in liquid N$_2$ and was defrosted just before NMR analysis.

Preparation of Complex 6. DMAB (22 mg, 0.37 mmol, in 1 mL of toluene) was added to a solution of complex **5** (150 mg, 0.37 mmol) in hexane (1 mL) at −30 °C. The volatiles were immediately removed under vacuum, and the residue was dissolved in cold hexane.

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After standing at −30 °C overnight, a large amount of pale yellow crystalline solid was formed, which was collected and washed with cold hexane (0.5 mL) to finally give complex **6** (97 mg, 70%). Crystals suitable for a single-crystal X-ray structure analysis were grown from a solution of **6** in hexane at −30 °C. In solution, complex **6** was partially converted to complex **6′** (molar ratio of **6**:**6′** = ca. 0.85:1, Tol-d_8, 253 K). Note: complexes **6** and **6′** are not stable at room temperature in solution and will slowly convert to the cyclic borazane **A** and other undefined species.

X-ray Crystal Structure Analysis of Complex 6: formula $C_{22}H_{39}BNSc$, M_r = 373.31 g mol^{-1}, colorless, 0.20 × 0.15 × 0.05 mm, triclinic, space group $P\bar{1}$, a = 8.4624(17) Å, b = 9.2052(18) Å, c = 14.534(3) Å, β = 89.9975(121)°, V = 1083.3(4) Å^3, ρ_{calc} = 1.145 g cm^{-3}, μ = 0.344 mm^{-1}, empirical absorption correction (0.8197 ≤ T ≤ 1.0000), Z = 2, λ = 0.71073 Å, T = 123.1500 K, 10529 reflections collected (−10 ≤ h ≤ 10, −11 ≤ k ≤ 11, −18 ≤ l ≤ 17), 4854 independent (R_{int} = 0.0377) and 3794 observed reflections (I > 2σ(I)), 250 refined parameters, final R1 = 0.0459 (I > 2σ(I)), final wR2 = 0.1175 (all data), maximum (minimum) residual electron density 0.427 (−0.345) e Å^{-3}. Hydrogen atoms were placed in calculated positions and refined using a riding model.

Preparation of Complex 7. Following the procedure described for **6**, reaction of complex **5** (100 mg, 0.25 mmol) with ^{i}Pr$_2$NH·BH$_3$ (29 mg, 0.25 mmol) gave **7** as orange crystals (81 mg, 75%). Crystals suitable for an X-ray single crystal structure analysis were grown from a solution of **7** in hexane at −30 °C.

X-ray Crystal Structure Analysis of Complex 7: formula $C_{26}H_{47}BNSc$, M_r = 429.41 g mol^{-1}, yellow, 0.25 × 0.16 × 0.12 mm, monoclinic, space group $P1_21/c1$, a = 14.6104(11) Å, b = 11.8168(8) Å, c = 15.3319(12) Å, β = 100.813(2)°, V = 2600.0(3) Å^3, ρ_{calc} = 1.097 g cm^{-3}, μ = 0.295 mm^{-1}, empirical absorption correction (0.4789 ≤ T ≤ 0.7456), Z = 4, λ = 0.71073 Å, T = 120 K, 46380 reflections collected (−17 ≤ h ≤ 17, −14 ≤ k ≤ 14, −18 ≤ l ≤ 18), 4839 independent (R_{int} = 0.1072) and 3448 observed reflections (I > 2σ(I)), 345 refined parameters, final R1 = 0.0524 (I > 2σ(I)) final wR2 was 0.1690 (all data), maximum (minimum) residual electron density 0.479 (−0.509) e Å^{-3}. Hydrogen atoms were placed in calculated positions and refined using a riding model.

Preparation of Complex 8. Dicyclohexylcarbodiimide (DCC; 37 mg, 0.18 mmol, in 0.5 mL of toluene) was added to a solution of complex **6** (67 mg, 0.18 mmol) in toluene (0.5 mL) at room temperature. The reaction mixture stood at room temperature for 30 min. The volatiles were removed under vacuum, and the residue was dissolved in hexane. After standing at −30 °C overnight, a large amount of colorless crystalline solid was formed which was collected and washed with hexane (2 × 0.5 mL) to finally give complex **8** (72 mg, 77%). Crystals suitable for an X-ray single-crystal structure analysis were grown from a solution of **8** in hexane at −30 °C.

X-ray Crystal Structure Analysis of Complex 8: formula $C_{33}H_{53}N_2Sc$, M_r = 522.73 g mol^{-1}, colorless, 0.26 × 0.15 × 0.12 mm, tetragonal, space group $I4_1/a$, a = 35.6027(14) Å, b = 35.6027(14) Å, c = 9.9827(4) Å, β = 90°, V = 12653.6(11) Å^3, ρ_{calc} = 1.098 g cm^{-3}, μ = 0.254 mm^{-1}, empirical absorption correction (0.5617 ≤ T ≤ 0.7456), Z = 16, λ = 0.71073 Å, T = 120(2) K, 102778 reflections collected (−46 ≤ h ≤ 46, −46 ≤ k ≤ 45, −12 ≤ l ≤ 12), 7275 independent (R_{int} = 0.1168) and 5448 observed reflections (I > 2σ(I)), 339 refined parameters, final R1 = 0.0485 (I > 2σ(I)) and final wR2 = 0.1639 (all data), maximum (minimum) residual electron density 0.306 (−0.518) e Å^{-3}. Hydrogen atoms were placed in calculated positions and refined using a riding model.

Preparation of Complex 9. 4-Dimethylaminopyridine (DMAP; 35 mg, 0.29 mmol, in 0.5 mL of toluene) was added to a solution of complex **6** (108 mg, 0.29 mmol) in toluene (0.5 mL) at room temperature. Vigorous evolution of H_2 gas was immediately observed, and the reaction mixture stood at room temperature for 30 min. The volatiles were removed under vacuum, and the residue was dissolved in hexane. After standing at −30 °C overnight, a large amount of pale yellow crystalline solid was formed which was collected and washed with hexane (2 × 0.5 mL) to finally give complex **9** (113 mg, 79%). Crystals suitable for an X-ray single-crystal structure analysis were grown from a solution of **9** in hexane at −30 °C.

X-ray Crystal Structure Analysis of Complex 9: formula $C_{29}H_{47}BN_3Sc$, M_r = 493.47 g mol^{-1}, yellow, 0.25 × 0.18 × 0.15 mm, monoclinic, space group $P2_1/c$, a = 10.0262(5) Å, b = 17.7978(8) Å, c = 31.4224(13) Å, β = 94.5270(10)°, V = 5589.7(4) Å^3, ρ_{calc} = 1.173 g cm^{-3}, μ = 0.285 mm^{-1}, empirical absorption correction (0.6624 ≤ T ≤ 0.7460), Z = 8, λ = 0.71073 Å, T = 120(2) K, 93919 reflections collected (−14 ≤ h ≤ 14, −25 ≤ k ≤ 25, −43 ≤ l ≤ 44), 16397 independent (R_{int} = 0.1084) and 9797 observed reflections (I > 2σ(I)), 641 refined parameters, final R1 = 0.0616 (I > 2σ(I)) and final wR2 = 0.2048 (all data), maximum (minimum) residual electron density 0.598 (−0.629) e Å^{-3}. Hydrogen atoms were placed in calculated positions and refined using a riding model.

General Procedure for Dehydrogenation of Diamine−Borane. A 20 mL oven-dried glass reactor was charged with rare-earth-metal complex (2.5 × 10^{-3} mmol) inside the glovebox. Diamine−borane and hexamethylbenzene (internal standard) were dissolved in the solvent (0.5 mL) and added to the catalyst at room temperature. A vigorous evolution of H_2 gas was immediately observed. The mixture was allowed to react uncapped and unstirred. After the measured time interval, a 0.2 mL aliquot was taken out and quickly quenched into a 4 mL vial containing 0.5 mL of undried "wet" C_6D_6. The quenched reaction mixture was immediately frozen in liquid N_2 and was defrosted just before NMR analysis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00461.

General procedures, characterization data, and NMR spectra of the compounds (PDF)

Accession Codes

CCDC 1915434−1915437 contain the supplementary crystallographic data for this paper. 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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The authors declare no competing financial interest.

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