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Communication

Dehydrocoupling of boranes with amines using a scandium catalyst

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ABSTRACT

The scandocene alkyl complex $(C_5Me_5)_2ScCH_2SiMe_3$ was found to be an efficient catalyst for the dehydrocoupling of the non-cyclic boranes, dicyclohexylborane and thexylborane, with amines under mild conditions. The reactions afforded the corresponding aminoboranes in high yields with good functional group tolerance. The stoichiometric reaction of scandium alkyl with amine led to the isolation of a scandium amide complex, which was shown to be an active species during the catalysis. Although a borane-coordinated scandium hydride was also obtained from the stoichiometric experiment, it was not involved in the catalytic cycle. In addition, kinetic studies provided insight into this intermolecular dehydrogenation reaction.

Aminoboranes containing a B-N σ bond are an important class of compounds that are used to construct novel BN-based polymeric materials [1]. In organic synthetic chemistry, they also serve as efficient aminoboration reagents for a variety of unsaturated molecules, *e.g.*, isocyanates [2], carbodiimides [3], aldehydes [4], enones [5] and alkynes [6]. Primary aminoboranes have also been explored as ligand precursors to stabilize highly-reactive low-coordinated metal complexes by taking advantage of the π-interactions between the lone pair of electrons on nitrogen and the empty *p* orbital of boron [7]. Thus, the development of an efficient method to synthesize aminoboranes is of great significance.

In early reports, aminoboranes were obtained through cleavage of Si-N or Sn-N bonds by boranes or haloboranes [8]. Conventional salt elimination reactions of lithium amides with BCl_3 also provided the target compounds [9]. The selective hydroboration of imines provides an atom-economic pathway to obtain aminoboranes [10]. Recently, dehydrogenative coupling of amines and boranes to aminoboranes has emerged and drawn increasing attention because it employs readily-available starting materials and releases H_2 as the only side product. Although it was reported that the dehydrogenation of amines and boranes occasionally occurs under catalyst-free conditions [11], the reactions can be significantly promoted using a suitable catalytic system. Hill and coworkers disclosed that a β-diketiminato magnesium butyl complex **1** (Fig. 1) enabled the dehydrocoupling of pinacolborane (HBpin) or 9-borabicyclo[3.3.1]nonane (9-BBN) with a range of amines [12]. Roesky *et al.* prepared an aluminum dihydride **2** that catalyzed the dehydrocoupling of boranes and amines [13]. Alkali metal (Li, Na and K) hexamethyldisilazides **3** were also found to be active catalysts for such dehydrogenation reactions by Panda's group [14]. Power *et al.* used group 14 tin(II) methoxides **4** for catalytic dehydrocoupling reactions [15]. However, the substrate scope of boranes in all of the above dehydrogenation reactions was limited to cyclic secondary boranes, *i.e.*, HBcat (catechol borane), HBpin, and 9-BBN, and most of the above catalysts exhibited only low to moderate activities.

In our previous work, we demonstrated that the scandocene alkyl complex $Cp^*_2ScCH_2SiMe_3$ (**5**, $Cp^* = C_5Me_5$) [16] was a highly efficient catalyst for the dehydrogenation of dimethylamine-borane to cyclic borazine [17]. Mechanistic studies indicated that rapid β-H elimination to the corresponding scandium hydride played a crucial role in the catalytic reaction. Encouraged by this result, herein, we further investigated scandocene alkyl complex **5** for the intermolecular dehydrocoupling of boranes and amines. Gratifyingly, non-cyclic and primary boranes were successfully applied for the first time, affording a new family of aminoboranes under mild conditions. A plausible mechanism was also proposed based on the isolation and characterization of catalytic intermediates from the corresponding stoichiometric reactions.

We initially examined the reaction of a non-cyclic secondary borane, dicyclohexylborane (**6**, $HBCy_2$), with aliphatic *n*-propylamine **7a** in C_6D_6 solution. The reaction rapidly generated a new resonance at δ −0.8 ppm in the ^{11}B NMR spectrum, indicating the formation of a Lewis acid-base adduct $Cy_2BH{\cdot}H_2N^nPr$ that did not undergo self-dehydrogenation for up to 24 h at room temper-

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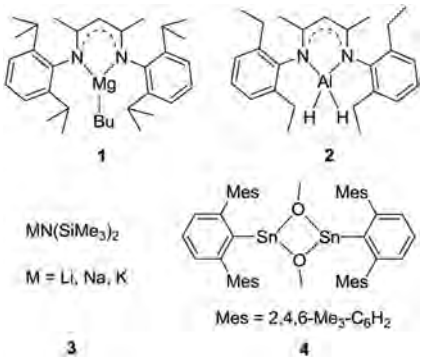
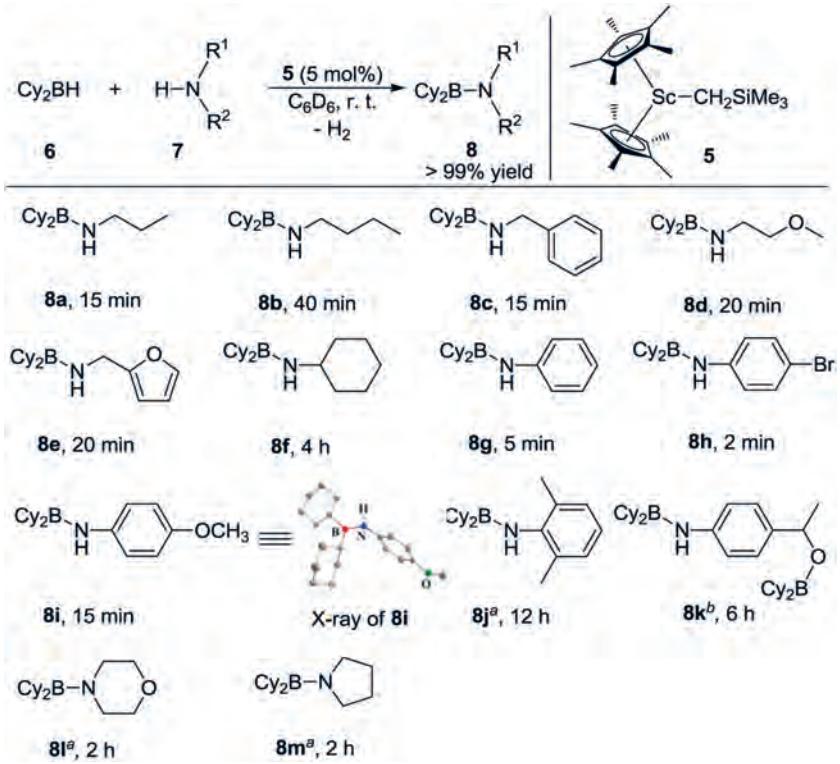


Fig. 1. Reported catalysts for the dehydrocoupling reactions of boranes and amines.

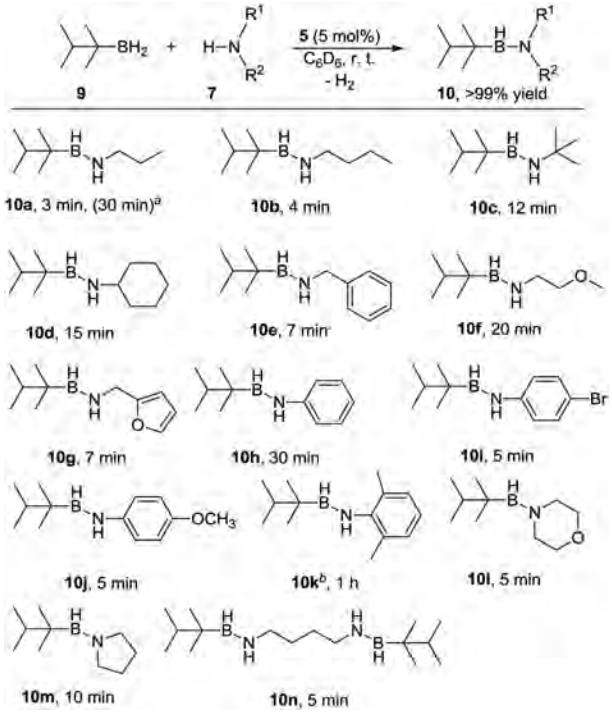
ature. Nevertheless, H_2 elimination readily occurred and was complete within 15 min at room temperature upon the addition of a catalytic amount of Sc complex **5** (5 mol%). The resulting aminoborane **8a** features a broad ^{11}B NMR signal at δ 45.6 ppm, which is significantly shifted to lower-field, indicating the presence of tricoordinate boron. In ^1H NMR spectrum, a signal for NH was observed at δ 3.67 ppm. The addition of an excess amount of $HBCy_2$ did not lead to further dehydrogenation even under relatively harsh conditions (10 h, 60 °C). Subsequently, reactions of $HBCy_2$ with a variety of amine substrates were investigated under such conditions (5 mol% **5, 6**/**7** = 1, in C_6D_6, room temperature; Scheme 1). Detailed isolations and characterizations of corresponding products were provided in Supporting information.

Several aliphatic primary amines were applicable for the dehydrogenation and completely transformed into the expected aminoboranes **8b**-**8e** within a short time (15–40 min). Amines containing oxygen atoms were compatible with the catalyst system. Cyclohexylamine required a long time (4 h) to achieve full conversion to the corresponding aminoborane **8f**. Dehydrocoupling reactions were greatly facilitated when using aromatic amines as the substrates, *e.g.,* the production of **8g**-**8i**. Notably, reaction of *para*-bromoaniline with $HBCy_2$ gave **8h** in quantitative yield in only 2 min. The molecular structure of compound **8i** was further confirmed by single-crystal X-ray diffraction and showed a planar tricoordinate geometry at boron (for details, see Supporting information). 2,6-Dimethylaniline was completely converted into the corresponding dehydrogenated product **8j** in a prolonged reaction time (12 h) under heating (80 °C), presumably due to severe steric hindrance. When using *para*-acetylaniline as the substrate, hydroboration of the carbonyl group was preferred. Nevertheless, the dehydrocoupling product **8k** was obtained by adding 2 equiv. borane **6**. Secondary amines, *e.g.,* morpholine and tetrahydropyrrole, were also suitable for this reaction, affording **8l** and **8m**, respectively, albeit under relatively harsh conditions (2 h, 80 °C). No dehydrogenation product was observed when treatment of sterically hindered $(Me_3Si)_2NH$ with $HBCy_2$ under the same conditions.

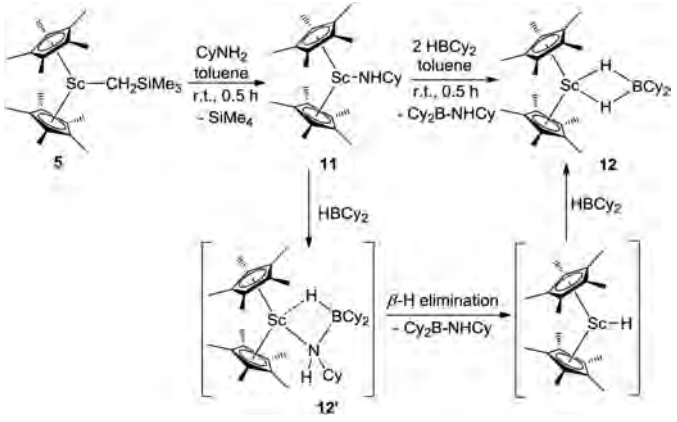
Reactions of primary thexylborane **9** with a wide range of amines were also investigated under the optimized conditions (5 mol% **5, 9**/**7** = 1, in C_6D_6, room temperature; Scheme 2). Again, a control reaction of thexylborane with *n*-propylamine **7a** afforded a Lewis acid-base adduct, which did not decompose within 12 h at 60 °C. In the presence of scandium catalyst **5**, the resultant adduct rapidly underwent dehydrogenation to form aminoborane **10a**. Further dehydrogenation of **10a** to form a B=N double bond was not observed, even when reacted overnight at 60 °C. Compound **10a** showed a typical tricoordinate borane resonance at δ 44.8 ppm in the ^{11}B NMR spectrum as a doublet with a $^1J_{HB}$ coupling constant of 126.5 Hz. Increasing the amount of either borane or amine did not alter the reaction outcome. A series of aliphatic



Scheme 1. Dehydrocoupling of $HBCy_2$ and amines catalyzed by Sc complex **5**. Conditions: [**6**] = 0.1 mmol, [**7**] = 0.1 mmol, 5 mol% **5**. Reactions were performed in C_6D_6 at room temperature in an unsealed vial. Yields were determined by ^1H NMR using ferrocene as an internal standard. [a]Reaction was conducted at 80 °C. [b]0.2 mmol **6** was used.



Scheme 2. Dehydrocoupling of thexylborane and amines catalyzed by Sc complex **5**. Conditions: [**9**] = 0.1 mmol, [**7**] = 0.1 mmol, 5 mol% **5**. Reactions were performed in C_6D_6 at room temperature in an unsealed vial. Yields were determined by ^{1}H NMR using ferrocene as an internal standard. [a]Reaction was conducted in the presence of 2.5 mol% **5**. [b]Reaction was conducted at 60 °C.



Scheme 3. Preparation of complexes **11** and **12**.

and aromatic primary amines was involved and gave the corresponding aminoboranes **10b**-**10k** in a short time. It is noteworthy that cyclic secondary amines generated dehydrogenation products **10l** and **10m** under mild conditions (5–10 min, room temperature), in sharp contrast to the reactions of $HBCy_2$ with secondary amines. A double dehydrogenation product **10n** could be obtained when treatment of 1,4-diaminobutane with 2 equiv. thexylborane.

To gain further insight into the Sc-catalyzed dehydrocoupling reactions, several stoichiometric reactions were conducted. The reaction of Sc alkyl complex **5** with an equimolar amount of amine $CyNH_2$ gave the expected Sc amide complex **11** in 92% yield (Scheme 3) with the release of $SiMe_4$. Complex **11** was comprehensively characterized by NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction (Fig. 2). The bond length of Sc1-N1 was found to be 2.0112(16) Å, which was comparable to those

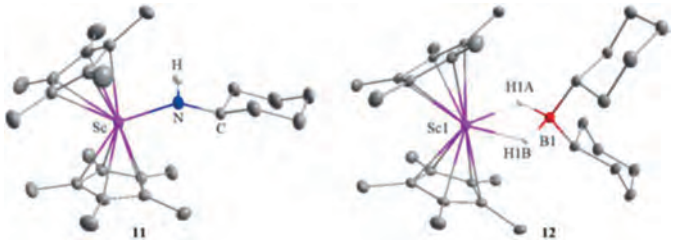


Fig. 2. Molecular structures of complexes **11** and **12**. Hydrogen atoms (except NH and BH) are omitted for clarity, and ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): **11**: Sc-N, 2.0112(16); N–C, 1.453(2); Sc-N-C, 147.42(14); **12**: Sc1-H1A, 2.02(1); Sc1-H1B, 1.97(1); B1-H1A, 1.24(1); B1-H1B, 1.28(9); H1A-Sc1-H1B, 53.8(8); H1A-B1-H1B, 91.6(13).

of previously-reported complexes containing Sc-NHR moieties [18]. Further reaction of complex **11** with 1 equiv. of $HBCy_2$ rapidly yielded the dehydrocoupling product **8f** and a new species with a ^{11}B NMR signal at δ 8.0 ppm. In addition, the unreacted complex **11** was also detected in a 1:1 ratio with **8f** in the reaction mixture, suggesting that 2 equiv. of $HBCy_2$ were required for this reaction. The new species was finally isolated in 65% yield and identified as the $HBCy_2$ coordinated scandium hydride **12** (Scheme 3) by single-crystal X-ray diffraction. The molecular structure of complex **12** was shown in Fig. 2. Hydride atoms were located in a Fourier difference map and refined with isotropic displacement parameters. Two hydride ligands were bound to the metal center with bond lengths of 1.97(1) Å and 2.02(1) Å, respectively. The Sc···B distance was found to be 2.634(2) Å, which is significantly longer than those in previously-reported scandium tetrahydridoborate complexes [19]. It is noted that the three-component reaction of scandium alkyl complex **5**, $CyNH_2$, and $HBCy_2$ also led to identical results. Therefore, it is likely that the scandium amidoborane intermediate **12′** was formed initially as in our previous case [17], which underwent rapid β-H elimination to afford scandocene hydride and aminoborane. The resultant metal hydride was highly reactive and thus immediately trapped by hydroborane. Unsuccessful isolation of complex **12′** presumably resulted from the sterically bulky amino group.

Both isolated complexes **11** and **12** were employed as catalysts for the reaction of $HBCy_2$ with $CyNH_2$ under our typical conditions. Scandium amide complex **11** showed comparable activity to that of parent complex **5**. In contrast, the catalytic activity drastically decreased when using complex **12** as a catalyst, indicating that **12** should not be included in the catalytic cycle of Sc-catalyzed dehydrocoupling reaction. In addition, the reaction of $HBCy_2$ with $CyNH_2$ in a 10:1 molar ratio catalyzed by scandocene alkyl complex **5** did not yield any dehydrocoupling product under the same conditions, suggesting that excess borane inhibited the reaction. These experimental results were consistent with those observed in main-group metal Mg-catalyzed dehydrocoupling of boranes with amines [12].

Kinetic studies of the dehydrocoupling reaction of $HBCy_2$ with $CyNH_2$ were also conducted by varying the catalyst loading from 3 mol% to 9 mol% and monitored by NMR spectra (for details, see Supporting information). As shown in Fig. 3, plots of the substrate conversion *versus* reaction time for all trials generated straight lines, indicating a zero-order kinetic behavior. Based on these results, a first-order dependence on catalyst **5** was observed (Fig. 3). Replacement of $HBCy_2$ with deuterated $DBCy_2$ resulted in a significant kinetic isotope effect (KIE) of 4.0 (Fig. S88 in Supporting information). In contrast, deuterated amine only afforded a KIE of 1.2. These results suggested that B-H bond cleavage might be involved in the rate-determining step.

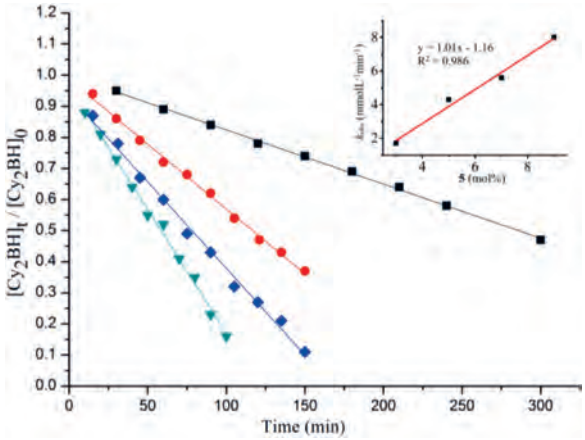


Fig. 3. Plot of $[Cy_2BH]_t$ /$[Cy_2BH]_0$ *versus* time at various catalyst loadings. Standard substrate concentration (0.67 mol/L): 3 mol% **5** (black squares, $y = -0.0017x + 0.998$, $R^2 = 0.998$); 5 mol% **5** (red dots, $y = -0.0043x + 0.992$, $R^2 = 0.997$); 7 mol% **5** (blue diamonds, $y = -0.0056x + 0.934$, $R^2 = 0.994$); 9 mol% **5** (green triangles, $y = -0.0080x + 0.967$, $R^2 = 0.995$). Inset: first-order plot for [**5**].

Based on the above observations and previous literature reports, a plausible mechanistic framework for the Sc-catalyzed dehydrocoupling of boranes and amines is shown in Supporting information (Fig. S89 in Supporting information). The reaction of Sc alkyl complex **5** with an amine gave a Sc amide complex with the release of $SiMe_4$, which easily reacted with borane through N-B and Sc-H interactions to form a Sc amidoborane intermediate. Rapid β-H elimination then occurred to produce the aminoborane product and Sc hydride. Finally, the dehydrogenation of Cp^*_2ScH with an amine produced Sc amide to complete the catalytic cycle. Alternatively, Sc hydride species could be also trapped by hydroborane.

In summary, the catalytic dehydrocoupling of non-cyclic boranes, *i.e.*, dicyclohexylborane and thexylborane, with a wide range of amines has been achieved for the first time by using a scandocene alkyl complex under mild conditions. The reactions provided a new family of aminoboranes with a high atom economy and broad substrate scope. Mechanistic studies, including stoichiometric and kinetics experiments, indicated that a scandium hydride derived from the β-H elimination of the corresponding metal amidoborane played a critical role in catalysis. Exploration of the applications of such aminoboranes in synthetic chemistry is in progress.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2021.05.041.

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