Homogeneous Catalysis

DOI: 10.1002/ange.201108874

Dehydrogenation of Diamine–Monoboranes to Cyclic Diaminoboranes: Efficient Ruthenium-Catalyzed Dehydrogenative Cyclization**

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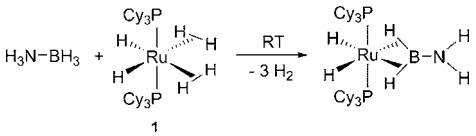
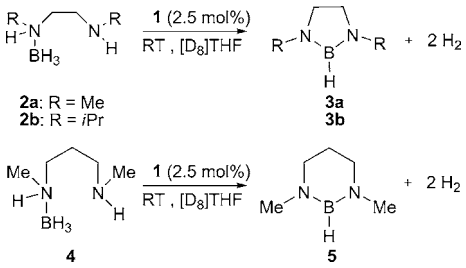
Ammonia–borane and the related amine–boranes (H_3B–$NR_{3-n}H_n$; $n=1,2$), as well as the corresponding dehydrogenated aminoboranes (H_2B–$NR_{2-n}H_n$; $n=1$–2), are the focus of intense interest as hydrogen storage or production materials,[1] and as building blocks for novel main-group-containing polymers.[2] In this context, transition metal catalyzed dehydrogenation of amine–boranes under homogeneous conditions is an active research area and a variety of catalytic systems have now been reported.[2c,3] Dehydrogenative coupling of amine–boranes involving adjacent B(sp^3)–H and N–H bonds is strongly dependent on the nature of the catalyst. The transition-metal catalyst precursor has an important impact on the kinetics of the reaction and on the nature of the resulting polymeric or oligomeric materials. Fine-tuning of controlled processes are closely associated with mechanistic investigations and the establishment of new bonding modes.[3a,j,k,4] By reaction of the bis(dihydrogen) complex [RuH_2-(η^2-H_2)$_2$(PCy_3)$_2$] (**1**) with amine-boranes, we showed the ability of the ruthenium center to retain a B–N unit during the elementary steps of amine–borane dehydrogenation. The recently disclosed bis(σ-BH) coordination mode[5] even enabled the trapping of the simplest and elusive prototypical aminoborane unit, H_2B–NH_2, in a stoichiometric process (Scheme 1).[6]

Herein, we report the catalyzed dehydrogenative cyclization (CDC) of diamine–monoboranes leading for the first time to the formation of 1,3,2-diazaborolidines upon reaction with the bis(dihydrogen) complex **1** as a catalyst precursor. Our study illustrates the striking influence on the reaction outcome of an additional remote NH moiety in the starting amine–borane. The addition, at room temperature, of a catalytic amount of **1** to a [D_8]THF solution of the diamine–monoboranes **2** yields a noticeable evolution of dihydrogen, and after stirring for a few hours the cyclic diaminoboranes **3** are cleanly produced as the sole products as determined by NMR analysis (Scheme 2). The diazaborolidines **3** were fully characterized by multinuclear NMR spectroscopy and the structures were ascertained by direct comparison with the authentic samples prepared from **2** under thermal conditions (see the Supporting Information).[7] The reaction is sensitive to steric bulk on the nitrogen atoms, with **2a** reacting much more rapidly (3 h) than the more sterically encumbered isopropyl derivative **2b** (8 h). In the latter case, the reaction was conveniently monitored by ^{1}H NMR spectroscopy, the results of which are illustrated in Figure 1 as the kinetic profile for the CDC obtained at 298 K.[8]



Scheme 1. Stoichiometric dehydrogenation of ammonia–borane and the synthesis of the corresponding bis(σ-BH) aminoborane ruthenium complex.



Scheme 2. CDC of **2** and **4**.

Rate constants for the consumption of **2b** were measured by ^{1}H NMR spectroscopy for a 2.5 mol % loading of **1** at four different temperatures (Figure 2), and for five different catalyst loadings at 298 K. The reaction appeared zero order in **2b** over a conversion range of 0–75 % (Figure 2) and first order in the ruthenium complex **1** by correlating the catalyst loading (1 to 10 %) with the change in k_{obs} (see Figures B and E–I in the Supporting Information).

An Eyring plot for the CDC of **2b** over the temperature range of 293–308 K provided the activation parameters $\Delta H^{\ddagger} = 83 \pm 17$ kJ mol^{-1} and $\Delta S^{\ddagger} = -68 \pm 56$ J K^{-1} mol^{-1} with 95 % confidence limits (see Figure J in the Supporting Information,).

Remarkably, the catalyst was found to be durable. At room temperature and under the same reaction conditions,

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[**] We thank the CNRS and the ANR for support through the HyBoCat ANR-09-BLAN-0184 program. Johnson Matthey is gratefully acknowledged for a generous loan of $RuCl_3$ nH_2O.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201108874.

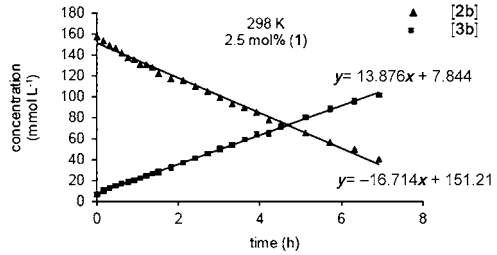


Figure 1. Kinetic profile of the CDC of **2b** at 298 K in the presence of 2.5 mol% of **1**.

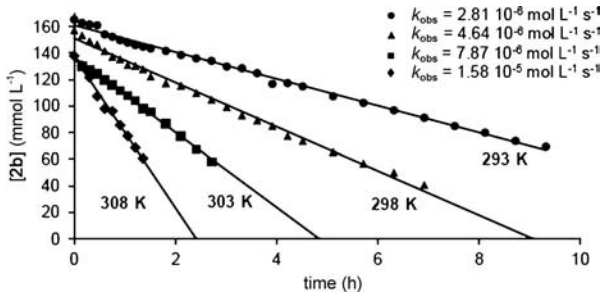
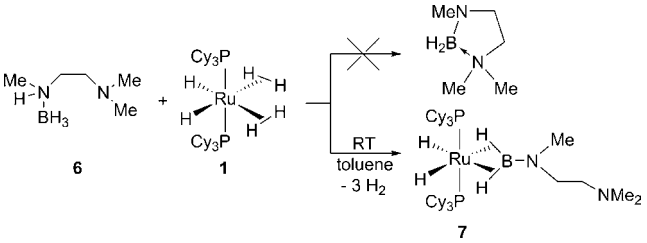


Figure 2. Zero-order plots of the decay of **2b** in the presence of 2.5 mol% of **1** at different temperatures.

addition of a second or third 80 equivalents of a [D_8]THF solution of **2b** to **1** gave again complete conversion within 24 hours, and **3b** was the sole product as determined by NMR spectroscopy. After 15 hours of a catalytic run performed at 298 K, the $^{31}P\{^1H\}$ NMR spectrum of the reaction taken in [D_8]THF showed the presence of an intense signal at $\delta =$ 76.4 ppm, corresponding to complex **1**, and an accompanying unidentified signal having a reduced intensity (see Figure K in Supporting Information). To identify a possible reaction intermediate, a stoichiometric reaction between **1** and **2b** was performed and monitored by multinuclear NMR spectroscopy. Under these conditions, the $^{31}P\{^1H\}$ NMR spectrum of the reaction in [D_8]THF at 293 K displays a similar set of signals with the major signal at $\delta = 76.3$ ppm corresponding to **1**. In addition to the prominent signal at $\delta = -8.30$ ppm, which is assigned to **1**, the ^1H NMR spectrum exhibits a well-resolved triplet at $\delta = -12.56$ ppm and a broad singlet at $\delta =$ -6.37 ppm in the hydride region; the triplet to singlet integration ratio was 2:1. Upon applying phosphorus decoupling the triplet ($J_{P\text{-}H} = 15$ Hz) collapsed into a singlet, and the singlet sharpened upon boron decoupling (see Figures L–M in the Supporting Information), which is reminiscent of a B–H bond ligated in a σ fashion to a [$RuH_2(PCy_3)_2$] fragment. It is worth mentioning that no coordination of **3b** to **1** was observed upon the use of a tenfold excess of **1**, even after 2 hours in [D_8]THF at room temperature.

To get more insight in the reaction, studies with structurally modified diamine–boranes were also performed. Lengthening the diamine alkyl chain does not modify the outcome of the reaction. When starting from the *N*,*N*′-dimethyl-1,3-propanediamine–monoborane adduct (**4**), the CDC proceeds with a complete conversion of **4** after 3 hours in [D_8]THF at room temperature, and the corresponding *N*,*N*′-dimethyl-1,3,2-diazaborinane (**5**) is observed as the sole product as determined by NMR spectroscopy (Scheme 2). In contrast, the modification of the substitution pattern at the remote amino group in the starting diamine–borane had a strong impact on the reaction. The reaction of **1** with the NMe_2-substituted analogue **6** (1 equiv or excess) was carried out in toluene at room temperature and only affords the ruthenium complex [$RuH_2((\eta^2{:}\eta^2{:}H_2BN(Me)CH_2CH_2NMe_2)(PCy_3)_2$] (**7**; Scheme 3). No dehydrogenated cyclized amine–borane



Scheme 3. Synthesis of the bis(σ-BH) complex **7**.

adduct could be detected in the $^{11}B\{^1H\}$ NMR spectrum of the crude reaction mixture (see Figures N–O in the Supporting Information). Complex **7** was fully characterized by NMR spectroscopy and X-ray diffraction crystallography. The X-ray structure of **7** was determined at 110 K. The ruthenium atom is in a pseudo-octahedral environment with the phosphines in axial positions (Figure 3). The four hydrogen atoms (H1–H4) surrounding the metal, the boron, and the nitrogen are all located in the equatorial plane. The Ru-B distance (1.967(2) Å) and the B-N bond length (1.399(2) Å) are similar to the distances previously reported for the bis(σ-BH) aminoborane ruthenium complex [$RuH_2(H_2BNH_2)$-$(PCy_3)_2$] (Ru-B 1.956(2) Å; B-N 1.396(3 Å)[6] and related analogues.[9] The diamine backbone in **7** adopts a linear conformation without any interaction between the nitrogen atom of the pendant NMe_2 moiety and the boron atom ligated to the metal center (Figure 3).

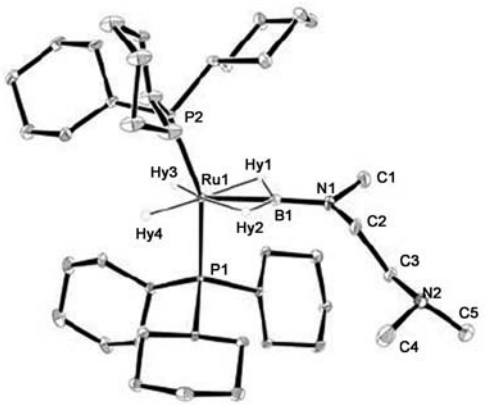


Figure 3. X-ray structure of complex **7**. The hydrogen atoms not associated with the metal are omitted for clarity. Ellipsoids are shown at 30% probability.

In conclusion, we report herein an unprecedented catalyzed dehydrogenative cyclization of diamine–monoboranes leading to cyclic diaminoboranes. This outcome is in sharp contrast to the results obtained in the dehydrogenation of classical amine–boranes by the ruthenium complex **1**. In the latter case case, the dehydrogenation stopped at the stoichiometric level, and the corresponding bis(σ-BH) ruthenium complexes were isolated (Scheme 1).[6] The cyclization described herein is strongly dependent on the nature of the remote amino moiety and requires the presence of a secondary amine group to go to completion. Complex **1** serves as precatalyst and resting state, and is regenerated as a result of concomitant evolution of dihydrogen during the CDC process. Additional investigations, including theoretical studies, are on going to better understand the factors controlling the cyclization, and to extend the scope of the CDC reaction.

CCDC 858963 (**7**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: December 16, 2011
Published online: February 15, 2012

Keywords: boranes · cyclizations · hydrogen · ruthenium · synthetic methods

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[8] The very slight lag behind the rate of consumption of **2b** and the rate of production of **3b** (see Figures A–D in the supporting Information) can be attributed to the evaporation of the relatively volatile diaminoborane as a result of hydrogen evolution during the course of the reaction performed in an open system.

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