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Coordinated Amine–Boranes

Coordination and Dehydrogenation of Amine–Boranes at Metal Centers

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amine–boranes · B–H activation · dehydrogenation ·
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There have been a number of approaches developed for the catalyzed dehydrogenation of amine–boranes as potential dihydrogen sources for hydrogen storage applications in recent years. Key advances in this area have been recently made thanks to catalytic and stoichiometric studies. In this Minireview, the fate of amine–boranes upon coordination to a metal center is discussed with a particular emphasis on B–H activation pathways. We focus on the few cases in which coordination of the resulting dehydrogenated product could be achieved, which includes the coordination of aminoborane, the simplest unit resulting from dihydrogen release of ammonia–borane.

1. Introduction

E–H bond activation by a metal center (E = H, C, Si, B) has been the subject of intense research activity for decades.[1] Two main motivations drive such an interest: the search for unusual bonding modes and the relevance to major catalytic processes. In this context, B–H bond activation is an extremely active area extending beyond the well-known metal-catalyzed hydroboration reaction.[2] In the last decade, two processes have been revealed that are both connected to major environmental concerns regarding energy sources: the borylation of alkanes or arenes, which mainly involves a B_{sp^2}–H bond activation,[3] and the dehydrogenative coupling of amine–boranes, which implicates adjacent B_{sp^3}–H and N–H bonds.[4] Promising applications can be expected in hydrogen storage, transfer hydrogenation, and synthesis of main-group polymeric materials. It is remarkable that the development of these two new processes is associated with the establishment of new bonding modes resulting from different stages of B–H bond activation.

Prior to the first unambiguous demonstration by Hartwig et al.[5] that a tricoordinated borane could be bonded to a metal center in a η^2 fashion (the so-called σ-borane complex, like the prototypical dihydrogen family), the chemistry of boron-attached compounds was dominated by borohydride species and boryl complexes resulting from oxidative addition of the B–H bond.[1c] Since the first work from Hartwig et al. in 1996, very few true σ-borane complexes have been isolated (Figure 1). To define a true σ-borane, the coordination of a tricoordinated boron substrate to a metal center has to be understood, as exemplified in several examples by the groups of Hartwig, Sabo-Etienne, Goldberg, and Heinekey.[6] Recently, we reported an unprecedented coordination mode of a tricoordinated borane by starting with a dihydroborane.[7] This led to the isolation of complexes in which the borane is bound to the metal by two geminal σ-B–H bonds. Such a coordination mode involves a 4-center, 4-electron mode and not the 5-center, 4-electron mode normally found in the rare cases of bis(σ-borane) complexes.[5,6h,8] In parallel to the chemistry of

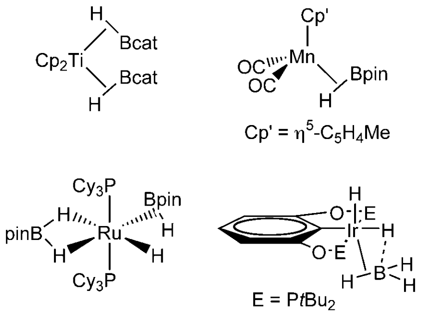

Figure 1. Representative examples of "true" σ-borane complexes.

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tricoordinated boron species, the chemistry of Lewis base–borane adducts was introduced in 1999 by Shimoi et al. and led to the isolation of a series of complexes of general formula $[L_nM(\eta^1\text{-}H_3B{\cdot}A)]$.[9] In the $H_3B{\cdot}A$ neutral borane adducts, A is a tertiary amine or phosphine.

Ammonia–borane (AB) has attracted considerable interest as a potential hydrogen source and storage material.[4] It now appears that the nature of the products resulting from metal-induced dehydrogenation of the amine–borane family $H_3B{-}NR_{3-n}H_n$ ($n = 1$–3) is strongly dependent on the nature of the transition metal precursors. Since the pioneering work of Manners and co-workers on the dehydrogenation of dimethylamine–borane (DMAB) using Wilkinson's catalyst or $[\{Rh(cod)(\mu\text{-}Cl)\}_2]$ (cod = 1,5-cyclooctadiene),[10] new catalytic systems for the dehydrogenation of AB have been blooming. A strong influence on the kinetics and the nature of the resulting polymeric or oligomeric materials was observed and tentatively rationalized with the help of theoretical approaches (see Section 3). Although the intricate mechanisms of these reactions are not completely elucidated, the recent works developed in this field by Weller et al. with rhodium,[11] and by Alcaraz and Sabo-Etienne with ruthenium,[12] took a step forward at the level of B–H activation and in the ability of a metal to retain a B–N unit along the elementary steps of the amine–borane dehydrogenation pathways. This latter aspect makes the tuning of free or metal-retained reactive aminoboranes particularly exciting.

Approaches to hydrogen storage by the use of ammonia–borane have been extensively reviewed elsewhere.[4,13] Herein, we describe significant progress made in the coordination of ammonia–borane and related amine–boranes to a metal center, and we discuss in more details the B–H bond-activation step in relation to the catalyzed dehydrogenation process.

2. Tertiary Amine–Boranes

2.1. η^1 Coordination of $H_3B{-}NMe_3$ and of $H_2BR{-}NMe_3$

Dehydrogenation of amine–boranes $H_3B{-}NR'_{3-n}H_n$ (R' = alkyl, $n = 1$–3) results from successive elementary steps involving B–H and N–H bond activation. Although the substitution pattern at the nitrogen atom in tertiary amine–borane adducts $H_3B{-}NR'_3$ prevents any dihydrogen release, it is worth mentioning that B–H bond activation can be achieved by complexation to a metallic center in an η^1 fashion. Best known as Shimoi-type complexes, these species have been mainly isolated with chromium, tungsten, manganese and ruthenium (Figure 2).[9,14]

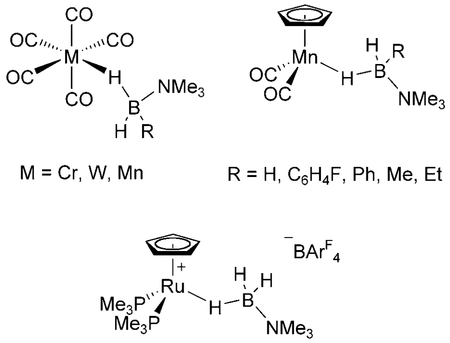

Figure 2. Shimoi-type complexes.

Complexation of an E–H bond and formation of the corresponding σ complex is reminiscent of the Chatt–Dewar–Duncanson model for the coordination of an olefin to a metal center. In dihydrogen complexes, the side-on (η^2) bonding results from electron donation from the $\sigma_{H\text{-}H}$ bonding orbital into a vacant metal orbital and back-donation from a filled metal d orbital to the $\sigma^*_{H\text{-}H}$ antibonding orbital. In the case of true σ-borane complexes, back-bonding into the $\sigma^*_{B\text{-}H}$ antibonding orbital is prevented owing to its high energy, but back-donation into the free p orbital of boron is highly efficient and responsible for the side-on (η^2) coordination mode. In contrast, in the Shimoi-type complexes, the M–H–B linkage results predominantly from electron donation of the B–H σ bond to the metal, with negligible back-donation into the $\sigma^*_{B\text{-}H}$ orbital.[9,14a] As a result, tertiary amine–boranes are highly labile ligands that adopt a bisectional geometry in the solid state, minimizing the steric hindrance with a tilted M–H–B bridge that is indicative of a 3-center, 2-electron bond coordinated in an end-on (η^1) fashion. ^{1}H NMR spectra at room temperature showed, in the hydride zone, an averaged signal for the BH_3 moiety, thus illustrating fluxional behavior

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Gilles Alcaraz received his PhD in 1995 in the group of Guy Bertrand at Toulouse University (LCC). After a postdoctoral position with Hansjörg Grützmacher at the ETHZ Zürich, he joined the CNRS in 1997 at Rennes University (Dr Michel Vaultier), working in the field of boron chemistry. In 2006, he joined Sylviane Sabo-Etienne's group at the LCC (Toulouse). His current research interests include organometallic boron chemistry and activation of boranes.

owing to a fast exchange between the bridging and terminal boron-attached hydrogen atoms.[9]

Further work concerning the interaction between a metal and tertiary amine–borane adducts has also been conducted by modifying the substitution pattern at the boron atom. The introduction of an electron-releasing substituent enables the stabilization of the M–H–B interaction by reinforcing the σ-donor character of the ligand without modifying the coordination mode.[15] A transition state involving an η^2 interaction between the metal and the $H_2BR\text{-}NMe_3$ ligand was postulated for the exchange between the B–H hydrogen atoms (Figure 3).

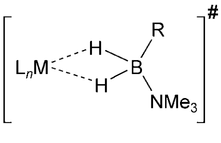
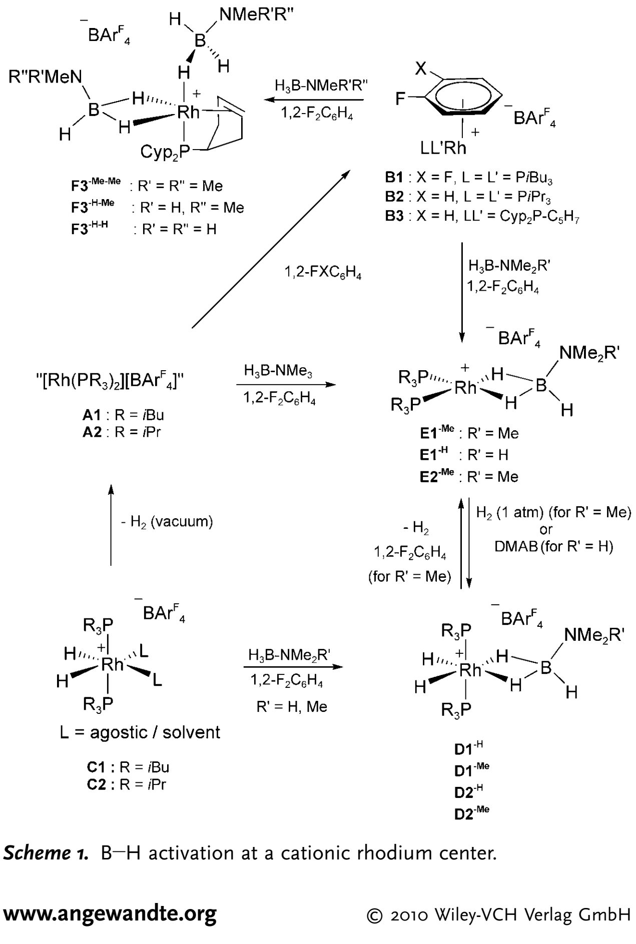


Figure 3. η^2 Shimoi-type transition state.

2.2. η^2 Coordination of $H_3B–NMe_3$

In a recent approach, Weller and co-workers used the potential of latent unsaturated cationic rhodium species to design amine–borane complexes with an η^2 coordination mode (Scheme 1).[16] In a first demonstration, they reacted the twelve-electron precursors **A1** or **A2** with $H_3B–NMe_3$ to produce the corresponding η^2-coordinated amine–borane species **E1**$^{\text{-Me}}$ or **E2**$^{\text{-Me}}$, respectively. **E**$^{\text{-Me}}$ were characterized by X-ray diffraction which confirmed the coordination of the amine–borane to a square-planar Rh^I center. In **E**$^{\text{-Me}}$, the η^2-amine–borane ligand is a σ donor only, in contrast to the situation in the geminal bis(σ-B–H) borane complexes disclosed by Alcaraz and Sabo-Etienne (see Section 3.3).[7,17] In earlier examples, thexyl borohydride was coordinated in a η^2 mode on one rhodium center in $[Rh(\eta^2\text{-}H_3B\text{-}CMe_2i\text{Pr})(i\text{Pr}_2PCH_2CH_2Pi\text{Pr}_2)]$ or as a bridging ligand in $[Rh_2(\mu\text{-}H)(\mu{:}\eta^1{:}\eta^1\text{-}H_3B\text{-}CMe_2i\text{Pr})(i\text{Pr}_2PCH_2CH_2Pi\text{Pr}_2)_2]$.[18]



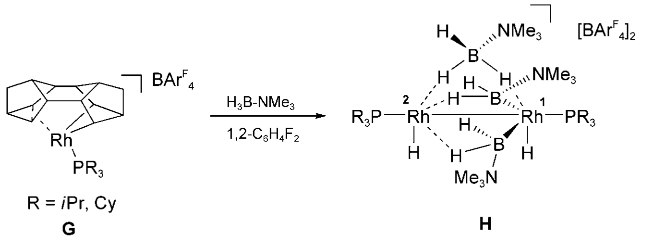
Scheme 1. B–H activation at a cationic rhodium center.

An alternate synthesis was also found from the dihydride rhodium(III) precursors **C**. In a first step, the authors obtained the corresponding dihydride amine–borane complexes **D**$^{\text{-Me}}$. With triisobutylphosphine ligands, **D1**$^{\text{-Me}}$ could only be characterized under a H_2 atmosphere, as it readily lost dihydrogen to form **E1**$^{\text{-Me}}$. In comparison, with bulkier triisopropylphosphine ligands, **D2**$^{\text{-Me}}$ was stable even under vacuum, and the solid-state structure showed a pseudo-octahedral rhodium(III) center with axial *trans* phosphines, equatorial *cis* hydrides, and an $\eta^2\text{-}H_3B–NMe_3$ ligand. However, in the presence of *tert*-butylethylene, **D2**$^{\text{-Me}}$ could be dehydrogenated to yield the rhodium(I) complex **E2**$^{\text{-Me}}$. They also used complexes **B1** and **B2**, which incorporate a labile fluorobenzene ligand, as latent unsaturated precursors. Their reaction with trimethylamine–borane resulted also in the formation of **E**$^{\text{-Me}}$.

The situation turned out to be very different when replacing $Pi\text{Bu}_3$ or $Pi\text{Pr}_3$ ligands by dicyclopentyl(cyclopentenyl)phosphine acting as a bidentate ligand in **B3**. For the first time, they could isolate a complex **F3**$^{\text{-Me-Me}}$, which incorporates two amine–borane ligands coordinated to the rhodium center with two different bonding modes, namely η^1 and η^2. This situation is reminiscent of the ruthenium complex $[RuH(\mu\text{-}H_2Bpin)(\eta^2\text{-}HBpin)(PCy_3)_2]$ (pin = pinacolato) incorporating two HBpin ligands with two different bonding modes: σ-borane and dihydroborate (Figure 1).[6e,f] The formation of **F3**$^{\text{-Me-Me}}$ and of its analogues obtained by reaction of DMAB or AB with **B3** shows the unique properties of the tricyclopentylphosphine ligands ($PCyp_3$), which upon partial dehydrogenation leads to a versatile reactivity, as illustrated by the groups of Weller and Sabo-Etienne.[19]

2.3. Unprecedented Activation Modes of $H_3B–NMe_3$

Amongst the many cationic rhodium complexes investigated by Weller and Chaplin, they also used the rhodium(III) complex **G** as a latent source of a $\{Rh(PR_3)\}^+$ fragment, which upon reaction with $H_3B{\cdot}NMe_3$ produced the dinuclear complex $[Rh_2(PR_3)_2(H)_2(\mu\text{-}\eta^1\text{-}H_2B–NMe_3)_2(\mu{:}\eta^1{:}\ \eta^1\text{-}H_3B–NMe_3)][(BAr^F_4)_2]$ (**H**; Scheme 2, R = Cy, *i*Pr).[11] The PCy_3 complex was characterized by X-ray crystallography. This complex has remarkable features owing to the coordination of $H_3B–NMe_3$ in two different stages of activation. For the first time, $H_3B–NMe_3$ acts as a bridging ligand with η^1-B–H bonds to each rhodium center. Furthermore, two other molecules of $H_3B–NMe_3$ have been further activated, resulting in oxidative addition at one rhodium center and formation of a hydrido diboryl rhodium fragment, with each boryl group stabilizing the second metal center through a η^1-B–H bond. The two different bonding modes are clearly shown by X-ray diffraction and NMR spectroscopy. The bridging ligand



Scheme 2. Formation of a base-stabilized boryl rhodium complex.

displays very long Rh–B bonds (2.747(5) Å and 2.757(5) Å). In contrast, the boryl groups are coordinated to Rh1, with Rh1–B bonds (2.086(4) Å and 2.086(4) Å) in the typical range for boryl compounds; the Rh2–B bonds (2.217(4) Å and 2.233(4) Å) are consistent with a η^1-B–H–Rh bond. Further support of these new bonding modes came from computational studies (optimized geometries and calculated bond orders). NMR spectroscopic data show that the structure is retained in solution. The two boron environments are characterized by two ^{11}B signals at $\delta = +37.3$ ppm and $\delta = -9.6$ ppm in a 2:1 ratio assigned to the boryl and the bridging amine–borane ligands, respectively. NMR and in-situ ESI-MS studies show that **H** results in a first step from the elimination of the hydrocarbon from **G** to produce an intermediate rhodium(I) complex $[Rh(PiPr_3)(\eta^2\text{-}(H_3B{-}NMe_3)(\eta^1\text{-}(H_3B{-}NMe_3)][(BAr^F_4)]$. Subsequent B–H activation is postulated to form a hydrido boryl species prior to dimerization, but no other intermediate could be detected.

Although similar bonding modes were previously disclosed for the silane class, it is worth noting that four coordinated base-stabilized boryl complexes are scarce. Only four trimethylphosphine-stabilized boryl complexes (with molybdenum, tungsten, manganese, and iron), which were produced by B–H activation of $Me_3P\text{-}BH_3$ in the presence of the corresponding methyl metal precursors, have been reported to date.[20] The reactions proceeded with loss of methane, which could only be achieved under photolytic conditions.

3. Amine–Boranes $H_3B{-}NR_{3-n}H_n$ (n = 1–3)

In comparison to the relatively simple previous case involving $H_3B{-}NMe_3$ with only hydridic atoms, the reactivity of primary and secondary amine–boranes, and more importantly of ammonia–borane, is rendered complicated by the presence of hydridic B–H and protic N–H bonds that are likely to undergo dihydrogen loss. In the presence of transition metal complexes, dehydrogenation can be achieved under mild conditions, and the products of the reaction formally result from the association of aminoborane units $H_2BNR_{3-n}H_{n-1}$ ($n = 1$–3) and loss of dihydrogen through B–H and N–H bond-breaking. It is now recognized that the formation of well-defined polyaminoboranes is both dependent on the substitution pattern at the nitrogen atom of the starting substrate and on the nature of the catalytic metal precursor.[4a]

3.1. Catalytic Dehydrogenation

When starting from secondary amine–boranes $H_3B{-}NR_2H$ and more particularly from the prototypical $H_3B{-}NMe_2H$ adduct (DMAB), catalyzed dehydrogenation produces specifically the cyclic dimer $(H_2BNMe_2)_2$.[10] With sterically demanding substituents on the nitrogen atom, the formation of monomeric species H_2BNR_2 could be achieved upon simple thermal dehydrogenation of the corresponding borane adducts of secondary amines.[21] Manners et al. demonstrated that the dehydrogenation of DMAB could be promoted by a variety of late-transition-metal catalysts. The authors showed that the process, which was mostly studied on rhodium species, took place under heterogeneous conditions involving small metallic clusters as active catalysts.[10b,c,22] Further studies contributing to the growth of interest in this field have extended the scope of this reaction to early- (Ti, Zr),[23] middle- (Cr, Mo, W, Re),[24] and late- (Ru, Rh)[11,16a–c,25] transition-metal-containing catalysts under homogeneous conditions, including the hydrogenation of olefins in a tandem procedure.[26]

In contrast to DMAB, the fate of ammonia–borane (AB) or primary amine–boranes during the dehydrogenation process is highly dependent on the nature of the metal precursor catalyst. For example, borazines $(HB{=}NR)_3$ (R = H, alkyl) can be obtained by a two-step dehydrogenation process involving a cyclic trimer $(H_2BRNH)_3$ along with the production of oligomeric and polymeric B–N-containing species $(BH_2NHR)_n$ (R = H, alkyl).[27] Produced in variable amounts, these polyborazane materials are characterized in ^{11}B NMR spectroscopy by broad upfield signals in the range $\delta = +5$ to -25 ppm.[10b] Further dehydrogenation leads to B–N cross-linked borazine materials that exhibit broad downfield signals at $\delta = +40$ to $+20$ ppm.[10b,28] A significant contribution in this field arose in 2006 with the use of Brookhart's iridium catalyst $[IrH_2(POCOP)]$ (POCOP = η^3-1,3-$(OPtBu_2)_2C_6H_3$). First reported by Goldberg and Heinekey with ammonia–borane[29] and later by Manners with primary amine–boranes,[30] dehydrogenation occurs under homogeneous conditions with a strong impact on the kinetics and the distribution of the reaction products with respect to previously reported catalysts. In a dilute THF solution, fast release of one equivalent of dihydrogen was observed from ammonia–borane and primary-amine–boranes with production of the insoluble pentamer $(H_2BNH_2)_5$ and soluble polyalkylaminoboranes, respectively. The dehydrogenation of AB catalyzed by 0.5 mol % of $[IrH_2(POCOP)]$ was complete within 14 min at room temperature. Polymeric aminoborane species were obtained in both cases with higher precursor concentrations.

Similar results were obtained by Fagnou et al. using $[RuCl_2(R_2PCH_2CH_2NH_2)_2]$ precatalysts and activation by KO*t*Bu.[31] In the case of methylamine–borane, $H_3B{-}NMeH_2$, the release of one equivalent of dihydrogen led first to poly(*N*-methylaminoborane) in less than 10 s, followed by a slower release of a second equivalent of H_2 in 10 min and the formation of B–N cross-linked borazine materials. Very efficient dehydrogenation of AB into $[H_2BNH_2]_n$ was also achieved by Schneider et al. by using a hydrido-

(amido)ruthenium complex stabilized by a PNP pincer ligand (turnover number = 8300 at 0.01 mol% of catalyst).[32] Polyborazilene materials were also reported by Baker et al. from AB in the presence of nickel–NHC-based catalysts.[33] Recently, Kawano and Shimoi reported the dehydrogenation of a series of borane adducts of secondary or primary amines by $[M(CO)_6]$ upon irradiation. The cyclic aminoborane dimer or borazine materials were obtained in good yields.[24b]

3.2. Insights into the Mechanism

Despite the number of organometallic complexes that are able to induce the dehydrogenation of amine–borane adducts, the identification of key active species for a better understanding of the activation step is still an ongoing challenge. On the basis of kinetic studies, by characterizing organometallic resting states ex situ or by using operando techniques, several reaction pathways have been suggested and tentatively rationalized by theoretical calculations.

The mechanism of the titanocene-catalyzed dehydrogenation of dimethylamine–borane[23] was analyzed in a DFT/B3LYP study by Luo and Ohno.[34] They proposed an intramolecular stepwise mechanism consisting of 1) the coordination of DMAB to the titanium center through an η^1-B−H bond to form $[Cp_2Ti(\eta^1\text{-}H_3B{-}NHMe_2)]$, 2) N−H activation to generate a hydride species, 3) B−H activation to form a second hydride with release of H_2BNMe_2, which can dimerize, and finally, 4) reductive elimination of H_2 from the $[Cp_2TiH_2]$ species and regeneration of $[Cp_2Ti(\eta^1\text{-}H_3B{-}NHMe_2)]$ upon DMAB coordination.

Shimoi systems were investigated in particular by DFT/PBE0 in the case of the chromium-catalyzed dehydrogenation of DMAB, and under photolytic conditions. A mechanism involving a scenario similar to the titanium case but through a concerted pathway was discarded. As an alternative, they proposed initial in-situ generation of the unsaturated $\{Cr(CO)_4\}$ species that could then react with DMAB in a stepwise intramolecular pathway involving prior coordination of B−H and N−H linkages to the metal in a κ^2-$[H,H']$ mode.[24b]

In the nickel–NHC ammonia–borane dehydrogenation system, Baker et al. measured kinetic isotope effects (KIE), which indicate the intermediacy of the N−H and B−H bonds in the rate-determining step(s).[33] An initial unusual mechanism was computed in which the first key step implied a proton N−H transfer from AB to the metal-bound carbene ligand.[35] More recently, Musgrave et al. conducted an in-depth theoretical study supporting the experimental KIE.[36] The main feature was the displacement of one carbene ligand by AB. Two key intermediates were proposed to play a major role in the dehydrogenation process. Initially, a β-agostic amidoborane nickel hydride monocarbene complex would be formed, although no Ni−H signal could be detected by ^{1}H NMR spectroscopy.[33] The recent isolation of β-agostic amidoborane zirconocene complexes, however, supports the involvement of such an intermediate.[37] By loss of dihydrogen, this nickel species would generate an active nickel(0) species $[Ni(NHC)(NH_2BH_2)]$ in which the aminoborane bonding would be similar to ethylene binding to nickel centers.

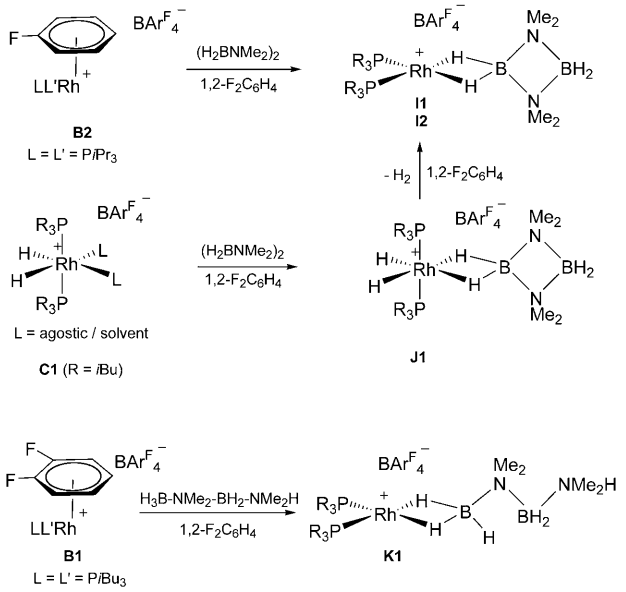
The computed catalyzed dehydrogenation of AB by the iridium–POCOP pincer complex was predicted to initially involve a η^1-coordinated AB molecule to the iridium center.[38] Among several possible routes, the authors proposed an iridium(III)/iridium(V) concerted mechanism (B−H hydrogen transfer to the metal and N−H hydrogen transfer to one hydride) through a six-membered transition state.[29] The release of aminoborane would then afford an iridium tetrahydride intermediate, which was experimentally observed (this species was very recently formulated as a dihydride(dihydrogen) complex[39]). Subsequent loss of dihydrogen would regenerate the starting dihydride complex.

Based on the knowledge that ruthenium-catalyzed alcohol oxidation can operate through an outer-sphere hydrogen transfer mechanism involving an amido ligand, Fagnou et al. performed DFT calculations with an amido hydride species as a starting point.[31] They proposed that AB reacts with that species through $N{-}H^{(AB)}$ to $N^{(ligand)}$ amidophosphine proton transfer and formation of an η^1-amidoborane metal species. Subsequent elimination of H_2BNH_2 would produce a dihydride complex, and the starting active species could be regenerated through elimination of dihydrogen from a *trans* hydrido(dihydrogen) complex by proton transfer from the aminophosphine ligand.

A similar strategy was followed by Schneider et al.[25,32] who prepared the PNP amido pincer ruthenium complex $[Ru(H)(NPP)(PMe_3)]$ ($NPP = N(CH_2CH_2PiPr_2)_2$) and used it as a bifunctional catalyst for the dehydrogenation of AB and DMAB into polymeric $(BH_2{-}NH_2)_n$ and dimeric $(H_2B{-}NMe_2)_2$ species, respectively (the head-to-tail dehydrocoupling product was detected during the course of the reaction). Kinetic isotope effects even larger than in Baker's system were reported. This is consistent with a concerted mechanism in which the N−H and B−H bond cleavages are in the rate-determining step(s). Four-membered Ru−N−B−H metallacycles $[Ru(H)\{(\mu\text{-}H)BH(NR_2)(NPP)\}(PMe_3)]$ (R = Me, H) were isolated by direct reaction of the pincer complex with the amine–boranes, with concomitant dihydrogen evolution.[25] These species, which appeared not to be active in the fast-dehydrogenation AB regime, might play a role in the slow dehydrogenation DMAB regime. Their isolation from AB gives some indication of the stability of H_2BNH_2 when coordinated to a N−Ru fragment.

Rhodium-induced dehydrogenation has been extensively investigated. Several studies combining operando techniques and ab-initio molecular dynamics were performed to better understand the role of rhodium-containing catalyst in the dehydrocoupling of amine–boranes.[40] For example, by exposing $[\{Rh(cod)Cl\}_2]$ to DMAB, tetrahedral clusters of four rhodium atoms stabilized by dimethylaminoborane ligands ($[Rh_4(H_2BNMe_2)_8]^{2+}$) are proposed to be the resting state of the catalyst.[40b] After dissociation of one H_2BNMe_2 ligand, η^1-coordination of DMAB to the vacant site was computed to be strongly exothermic. The mechanism would then proceed stepwise by N−H-to-Rh hydrogen transfer and H_2 release. The B−H-to-Rh hydrogen transfer was calculated to have a negligible energy barrier and would proceed rapidly.

The systems developed by Weller et al. from unsaturated cationic rhodium species provide key information on the nature of the intermediates generated during the dehydrogenation of amine–borane adducts.[16a–c] All the rhodium precursors **A**–**C** (Scheme 1) can induce catalytic dehydrogenation of DMAB to ultimately afford the cyclic dimer. Upon reaction with a stoichiometric amount or excess of DMAB, the corresponding complexes **D**–**F** were isolated, or characterized in situ by NMR spectroscopy when they were short-lived species. Their ability to induce dehydrogenation was also demonstrated. Their properties are very similar to those of the analogous $H_3B{-}NMe_3$ complexes (see Section 2.2 above) with a η^2 coordination mode of DMAB in particular to the rhodium center. This η^2 coordination mode is also adopted by the cyclic dimer upon coordination to the metal. Indeed, addition of $(H_2BNMe_2)_2$ to **B2** led to the isolation of $[Rh(P\textit{i}Pr_3)_2\{\eta^2\text{-}(H_2BNMe_2)_2\}][BAr^F_4]$ (**I2**), or alternatively, the corresponding $P\textit{i}Bu_3$ complex **I1** could be obtained from **C1** and loss of H_2 (Scheme 3). Despite its high instability, they were able to characterize the intermediate dihydride complex $[Rh(P\textit{i}Bu_3)_2(H)_2\{\eta^2\text{-}(H_2BNMe_2)_2\}][BAr^F_4]$ (**J1**) by X-ray diffraction.



Scheme 3. Coordination of the cyclic and linear dimer amine–boranes at rhodium.

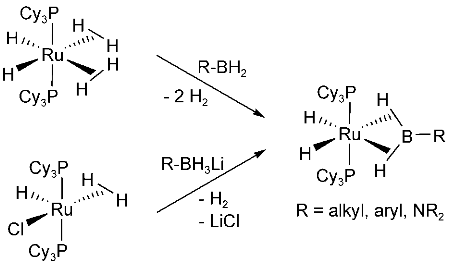
Weller's group also managed to isolate and fully characterize the complex $[Rh(P\textit{i}Bu_3)_2(\eta^2\text{-}H_3BNMe_2BH_2NMe_2H)][BAr^F_4]$ (**K1**) with a linear amine–borane dimer (Scheme 3).[16b] This result is particularly remarkable as by using **A2** or **B2** as catalyst precursors, formation of the linear head-to-tail dimer $Me_2NH\text{-}BH_2\text{-}NMe_2\text{-}BH_3$ was observed as an intermediate during the catalytic dehydrocoupling leading to the cyclic dimer.[16a,c] **K1**, which was independently prepared by adding the linear dimer to **B1**, displays also a η^2-coordination mode of the linear head-to-tail dimer to the rhodium center, as confirmed by NMR spectroscopy and X-ray diffraction. In solution, **K1** is stable and does not give the cyclic dimer through an intramolecular dehydrocoupling. In contrast, when reacting **A1** with two equivalents of the linear head-to-tail dimer they observed a mixture of $\mathbf{D1^{-H}}$, **K1** and a species formulated as the dihydride $[Rh(H)_2(\eta^2\text{-}H_3B{-}NMe_2BH_2NMe_2H)(P\textit{i}Bu_3)_2][BAr^F_4]$ (**L1**) in a 10:50:40 ratio. A change in composition was observed after 2 h, resulting in a 65:0:35 ratio, along with the formation of the cyclic dimer. The increase of $\mathbf{D1^{-H}}$ under these conditions indicates B–N dissociation during the dehydrocoupling process, which in any case remains complex. Finally, the DFT study on the dehydrogenation of DMAB into cyclic dimethylaminoborane by these rhodium species suggests 1) initial η^2 coordination of the substrate to the metal and stepwise activation by B–H oxidative addition/N–H-to-rhodium hydrogen transfer or a N–H/B–H transfer sequence, and 2) sequential H_2/H_2BNMe_2 loss or the reverse.

3.3. Bis(σ-B–H) Coordination of Aminoboranes

The mechanism of metal-induced dehydrogenation of amine–borane adducts $H_3B{-}NR_{3-n}H_n$ ($n = 1$–3) involves protic N–H and hydridic B–H bonds. Until now, a number of possibilities concerning their activation have been proposed on the basis of experimental observations and theoretical calculations. In contrast to DMAB, which leads solely to the cyclic dimer $(H_2BNMe_2)_2$, the situation with AB appears to be somewhat different. Depending on the nature of the catalyst and the experimental conditions, a diverse range of products can be obtained, as nicely illustrated in the case of the iridium catalyst $[IrH_2(POCOP)]$.[29–30] At this point, the simplest elementary unit has to be considered, which results from the direct loss of one equivalent of H_2 from AB: the aminoborane H_2BNH_2.[41] The intermediacy of this molecule during the metal-assisted dehydrogenation process remains puzzling and its fate has received little attention. Its implication in B–N bond formation during chain propagation has been discussed to rationalize the formation of cyclic oligomers versus linear polymers.[42] A more general question deals with the importance of aminoborane $H_2BNR_{2-n}H_n$ ($n = 0$–2) binding to a metal center in determining product selectivity. The necessity of better understanding the fate of the substrate in the coordination sphere of the metal is thus crucial.

Baker et al. have conducted a series of useful experiments to bring some information on this specific problem. Using $[\{Rh(cod)Cl\}_2]$ as a precatalyst, they showed that dehydrogenation of AB at 25 °C, but carried out in the presence of a large excess of cyclohexene, resulted in the formation of the amino(dicyclohexyl)borane (Cy_2BNH_2) instead of the expected borazine and polyborazylene products. Thus, it can be assumed that hydroboration of the alkene occurred thanks to double B–H activation from H_2BNH_2 released in the media.[41a] In contrast, the use of $[IrH_2(POCOP)]$ under the same conditions afforded the cyclic pentamer $(H_2BNH_2)_5$ as the sole product, despite the presence of cyclohexene. However, at 60 °C, a mixture of amino(dicyclohexyl)borane and cyclic pentamer was observed. By keeping the temperature at 60 °C, but in the absence of cyclohexene, significant amounts of borazine along with cyclic pentamer were produced. It thus appears that NH_2BH_2 binding is stronger at the iridium center. Indeed, the search for catalysts allowing efficient release of aminoborane will be important for the future.

In the course of our studies on borane activation by ruthenium complexes,[6e,f,43] we investigated monosubstituted boranes RBH_2. These boranes deserve special attention in connection with the topic discussed herein: they can coordinate to a ruthenium center in a 4-center, 4-electron coordination mode[7,17,44] or produce a borylene complex upon reversible dihydrogen release.[45] The new bis(σ-B–H)-borane complexes $[RuH_2(\eta^2{:}\eta^2\text{-}H_2BR)(PCy_3)_2]$ were isolated in high yields by reaction of $[RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]$ or $[Ru(H)Cl(\eta^2\text{-}H_2)(PCy_3)_2]$ with RBH_2 or RBH_3Li (R = Mes, *t*Bu), respectively (Scheme 4).[7,17] Our strategy is quite general as we have now isolated a series of bis(σ-B–H)-borane complexes with various borane substituents (R = alkyl, aryl, NR_2).[46]



Scheme 4. Synthesis of bis(σ-B–H) borane ruthenium complexes.

The borane bonding is the result of σ donation from the two geminal B–H bonds into the low-lying vacant orbitals of the metal fragment reinforced by π back-donation from one ruthenium atom lone pair into the vacant p orbital on boron (Figure 4). Very recently, we showed that the bis(dihydrogen) complex $[RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]$ was able to dehydrogenate amine–boranes $H_3B\text{–}NR_{3-n}H_n$ ($n = 1\text{–}3$) in stoichiometric reactions at ambient temperature. In the presence of DMAB, MAB, or AB, the reaction takes place with loss of dihydrogen and the corresponding bis(σ-B–H) borane complexes $[RuH_2(\eta^2{:}\eta^2\text{-}H_2BNR^1R^2)(PCy_3)_2]$ (R^1, R^2 = H, Me) are isolated in high yields (Scheme 5).[12]

The NMR spectra of these complexes all have similar features. As a representative example, the simplest aminoborane complex $[RuH_2(\eta^2{:}\eta^2\text{-}H_2BNH_2)(PCy_3)_2]$ has a characteristic broad singlet in the ^{1}H NMR spectrum at $\delta = -6.80$ ppm (B–H) and a more shielded sharp triplet at $\delta = -11.85$ ppm ($J_{PH} = 24.8$ Hz, Ru–H) in a 1:1 ratio. The $^{31}P\{^1H\}$ NMR spectrum shows a sharp singlet at $\delta = 77.43$ ppm, and a broad signal is observed at $\delta = 46$ ppm in the $^{11}B\{^1H\}$ NMR spectrum. From the X-ray structure determination, the ruthenium atom is in a pseudo-octahedral environment with phosphine ligands in the axial positions (Figure 5).

The four hydrogen atoms surrounding the metal, the boron, the nitrogen, and the NH_2 hydrogen atoms are all located in the equatorial plane. The Ru–B bond (1.956(2) Å) is shorter than the sum of the covalent radii (2.09 Å) and is similar in length to the bonds previously reported for bis(σ-B–H) ruthenium complexes.[7,17,44] The loss of H_2 from the starting AB is confirmed, and the shortening of the B–N bond (1.396(3) Å) and the lengthening of the B–H bond (1.25(2) and 1.22(3) Å) relative to that of AB (B–N 1.58(2) Å, B–H 1.15(3) and 1.18(3) Å)[47] reflect the $N_{sp^2}\text{–}B_{sp^2}$ multiple-bond character and the bis(σ-B–H) coordination mode of the aminoborane H_2BNH_2, as ascertained by theoretical calculations.

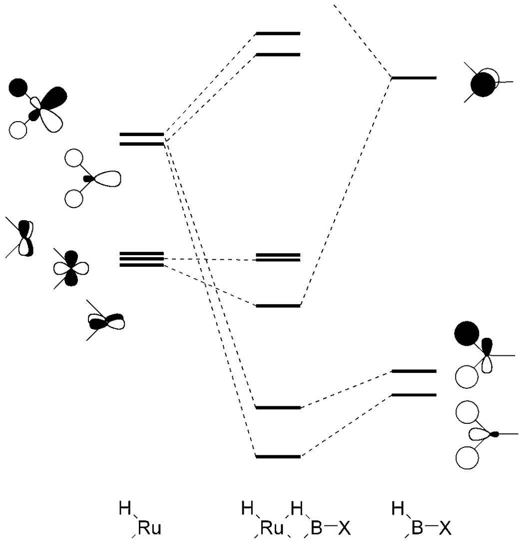
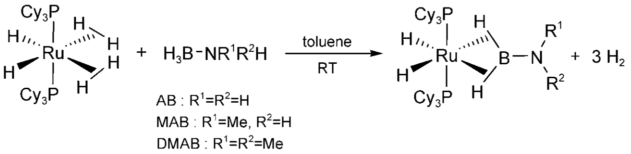


Figure 4. Simplified diagram showing the bonding interaction between a $\{RuH_2\}$ fragment and a borane ligand.



Scheme 5. Bis(σ-B–H) aminoborane ruthenium complexes.

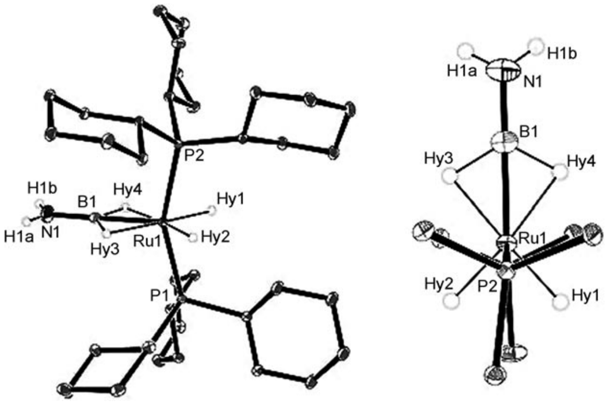


Figure 5. X-ray structure of $[RuH_2(\eta^2{:}\eta^2\text{-}H_2BNH_2)(PCy_3)_2]$ (left) and a view of the equatorial plane (right; cyclohexyl groups omitted for clarity).

The bis(σ-B−H) aminoborane ruthenium complex is the closest inorganic analogue of ethylene, but it is licoordinated to the metal in an end-on fashion. DFT calculations show that three other isomers could be located on the potential energy surface. They are significantly less stable than the isolated aminoborane bis(σ-B−H) ruthenium complex: the β-agostic σ-B−H complex and two aminoborane lateral π adducts are similar to the intermediates calculated by Musgrave et al. with nickel[36] and Rousseau et al. with rhodium.[40b]

Very recently, the bis(σ-B−H) coordination mode of dimethylaminoborane was identified using NMR spectroscopy by Weller et al. in the rhodium-induced dehydrogenation of DMAB; DFT calculations showed that it is a major thermodynamically favored product. The corresponding dicyclohexylaminoborane version could also be prepared.[16b] Following Weller's work, Aldridge et al. isolated analogous cationic η²-coordinated diisopropylaminoborane rhodium and iridium complexes with IMes ligands (IMes = *N*,*N*-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) in place of the phosphines. The dicyclohexylaminoborane analogue was also obtained in the rhodium case.[48]

4. Summary and Outlook

Metal-induced dehydrogenation of amine–boranes results from a sequence of elementary steps that include B−H and N−H bond activation. Despite the number of studies reported in the literature, the mechanism of this process remains complex and is highly dependent on the nature of the organometallic catalyst. In this context, the series of results recently reported by Weller et al. is remarkable in many aspects. Tuning the starting precursor to generate a latent source of highly unsaturated species proved to be a very efficient strategy to gain access to complexes that not only show unprecedented amine–borane activation steps, but also act as catalysts in the dehydrogenation process. Mostly based on his work and that of Shimoi concerning the isolation of electron-deficient metal-ligated amine–boranes, B−H bond activation by η¹ or η² coordination modes seems to be the common denominator for an early stage of activation in which the metal fragment retains the full structural integrity of the substrate around its coordination sphere (Figure 6). This finding is well-corroborated by DFT calculations, which show that the initial η¹ interaction between the amine–borane and the metal is barrierless and energetically favored. The isolation by Weller et al. of a dinuclear rhodium complex incorporating activated $H_3B{-}NMe_3$ molecules in different advanced stages of activation was particularly informative regarding possible activation pathways for the dehydrogenation process of amine–boranes. In such a system, activation is observed until the loss of the structural integrity of the substrate and B−H bond oxidative addition to the metal was achieved, with formation of a base-stabilized boryl complex (Figure 6). In contrast, little is precisely understood about the N−H activation step and the subsequent or concomitant proton transfer in the coordination sphere of the metal.

Baker et al. pointed out that the intermediacy of "free" or metal-bound reactive aminoboranes had a strong impact on the selectivity of the dehydrogenation process. The ability of a metal to retain a B−N unit along the elementary steps of amine–borane dehydrogenation pathways (and even until the very last stage) should be crucial in selecting a catalyst precursor. Thus, the isolation by Alcaraz and Sabo-Etienne of the complex $[RuH_2(\eta^2{:}\eta^2\text{-}H_2BNH_2)(PCy_3)_2]$, which is the first example of the elusive aminoborane $H_2B\text{-}NH_2$ coordinating in a bis(σ-B−H) mode, is clearly a key step (Figure 6). Its synthesis was achieved thanks to a stoichiometric dehydrogenation process. The release step of aminoborane and its impact on the distribution products are currently being investigated in our group. Future research to control the release of highly reactive key units from the coordination sphere of the metal will be valuable for the design of more efficient and selective catalysts.

The discovery of dihydrogen coordination to a metal center has led to unimaginable development both in fundamental knowledge and in catalysis.[1b] We do hope that such a success story will also be seen for the chemistry of σ-amine–borane species.

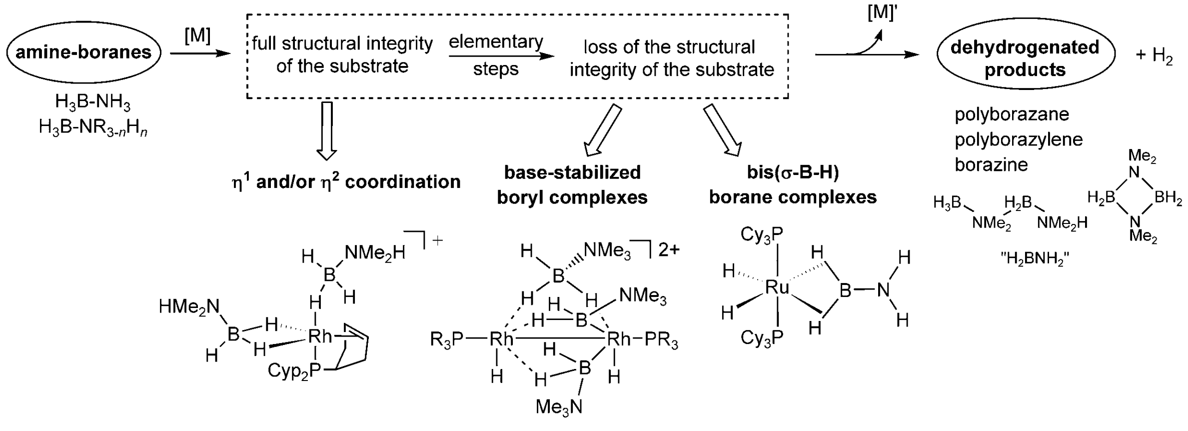


Figure 6. Activation step in the dehydrogenation of amine–boranes.

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