Stable BH₃ Adducts to Rhodium Amide Bonds.

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Abstract

Rh(I) diolefin amides, [Rh(trop₂N)(L)] (trop₂N = bis(5*H*-dibenzo[*a,d*]cyclohepten-5-yl)amide), form the corresponding hydrido amine species, [RhH(trop₂NH)(L)], by reaction with Me₂HN-BH₃ (DMAB). Both amide and amine complexes are active dehydrocoupling catalysts, forming the monomer [Me₂N=BH₂], the linear [Me₂NHBH₂NMe₂BH₃] and the cyclic dimer [Me₂BNH₂]₂. Good catalytic activity was observed especially for complexes which contain a metal hydride unit, Rh–H, in a co-planar *cis*-arrangement with respect to the N–H unit and for those bearing an *N*-heterocyclic carbene ligand (IMe) in *trans*-position to the active basic site of the ligand. Four-membered Rh–N–B–H metallacycles [Rh{(μ-H)BH₂}(Ntrop₂)(L)] (L = PPh₃, IMe) were isolated by direct reaction of the amide complex with BH₃(THF). These stable species are not active in the dehydrogenation of DMAB. Their isolation and lack of reactivity gives some indication for a possible catalyst deactivation. This observation is consistent with a mechanism in which the unprotected amine or amide ligand is essential for N–H and B–H bond cleavage.

Keywords

B–H activation – N–H activation – cooperative ligand – Rhodium – olefin ligand

Introduction

Binding and activation of molecular hydrogen (H₂) by metal complexes leading to homolytic or heterolytic bond cleavage has been intensively investigated due to its relevance for catalytic hydrogenations.¹ The σ-coordination and activation of B–H bonds of boranes or borane-Lewis base adducts resemble closely the one of dihydrogen, and complexes with coordinated B–H bonds serve as models for the activation and functionalization of other X–H bonds (X = Si, C) in silanes and hydrocarbons, especially methane.² Furthermore, the activation of the B–H bond is relevant for catalytic processes including the borylation of hydrocarbons,³ the hydroboration of unsaturated organic molecules⁴ and dehydrogenation of boranes and borane adducts.⁵

Typically, coordination of the borane compound to a metal center precedes the activation process and many σ -borane complexes have been isolated.^{6, 7} In the activation step, the B–H bond is oxidatively added to the metal center under the formation of hydrido boryl intermediates.⁸ Alternatively, the activation of the B–H bond can be induced with the help of a basic ligand in an adjacent or remote position to the metal center. The heterolytic cleavage of the B–H bond (or σ -bond metathesis) depends on the nature of the metal center and the cooperative ligand (Scheme 1). Addition of a B–H bond across a metal oxygen bond is rather common.⁹ For example, a bifunctional pincer ligand with pendent hydroxyl groups coordinated to Ru(II) allowed the addition of H–BPin (pinacol borane) across a Ru(II)–O bond. This step is involved in the catalytic hydroboration of nitriles.¹⁰ Stradiotto¹¹ and Oestreich¹² showed that [Ru]–X (X = O or S) units interact with B–H bonds of borane esters. The addition of the B–H bond of boronic esters across the metal center and a basic site in a dearomatized pincer (PNP or PNN) ligand was reported by Milstein *et al.*¹³ Love *et al.* reported on rhodium phosphoramidate complexes where a B–H bond coordinates to a Rh–N or Ir–N bond. From these intermediates, a borane group can be transferred chemoselectively to organic substrates.¹⁴ An early example of B–H bond activation in a boron ester was reported by Fryzuk *et al.* who described the addition across a Ta–N bond leading to a complex with a functionalized N₂ ligand and a terminal hydride ligand as intermediate, which underwent spontaneous N–N bond cleavage.¹⁵ Other examples of B–H bond addition across M–N moieties concern the reversible interaction of boranes with non-innocent palladium or ruthenium pincer complexes, where the boron atom adds to the basic amine moiety.¹⁶

Scheme 1. Different coordination modes of B–H bonds ranging from σ -type complexes to oxidative addition. Top: Interaction of single metal centers with B–H bonds; bottom: Interaction of complexes showing metal ligand cooperativity, M–X, with B–H units.

The interaction of Lewis base–borane complexes with metal carbonyl fragments has been studied by Shimoi *et al* (Scheme 1).¹⁷ In σ -borane complexes (see Scheme 1 right), back-

donation of electron density from the metal into the unoccupied p orbital of boron is highly efficient. In contrast, in metal-complexes of Lewis-base borane-adducts, electron donation of the B–H σ -bond to the metal, with minor electron back-donation into the σ^* B–H orbital is involved in M–(B–H) bonding, which results in highly labile ligands. Significant efforts were made in order to investigate and understand the coordination and activation of amine boranes by metal complexes, which involve successive B–H and N–H bond activation.¹⁸ Mechanistic studies focused on the catalytic dehydropolymerization of $R_{3-x}H_xN-BH_3$.¹⁹ Subtle differences in the structure of the catalyst control the selectivity of these reactions and lead to drastic structural differences of the final products and the degree of dehydrogenation. Fagnou,²⁰ Schneider²¹ and Williams²² reported on different ruthenium-catalyzed amine borane dehydrogenation reactions that proceed through an outer-sphere hydrogen transfer mechanism involving a cooperative ligand. A concerted H^+/H^- transfer from an amine borane to a Ru-amide moiety under the release of $R_2N=BH_2$ and rate-determining H_2 elimination from the Ru hydrido amine complex was proposed. Furthermore, the catalyst deactivation by formation of a four-membered Ru–N–B–H metallacycle was observed spectroscopically.^{21b}

We have previously described a rhodium(I) amide diolefin complex that splits molecular hydrogen heterolytically in a one-step process across the Rh–N bond resulting in the formation of the hydride species $[Rh(\eta^2-H)(trop_2NH)(PPh_3)]$ (**3a_{eq}**).²³ Both, the rhodium amide and the corresponding amine hydride species are active catalysts for the hydrogenation of ketones and imines. The complexes are also highly efficient catalysts for the dehydrogenative coupling (DHC) of alcohols to acids, esters and amides under mild conditions using a hydrogen acceptor.²⁴ The reversible formation of the hydride amine complex **3a_{eq}** is the key transformation in these catalytic processes. Herein, we report on the interaction of amine borane adducts, Me_2HN-BH_3 (DMAB) and $BH_3(THF)$, with rhodium(I) amide complexes and their catalytic activity in the dehydrogenative coupling of DMAB. Possible reasons for catalyst deactivation are suggested based on the isolation of two stable complexes in which a B–H bond coordinates across the Rh–N moiety. These complexes with a planar N–Rh–H–B cycle are remarkably stable and show no catalytic activity.

Results and Discussion

The complexes $[Rh(trop_2NH)(PPh_3)]$ (**2a**) and $[Rh(trop_2NH)(IMe)]$ (**2b**) ($trop_2N$ = bis(5-*H*-dibenzo[a,d]cyclohepten-5-yl)amide, IMe = 1,3,4,5-tetramethylimidazole-2-ylidene) are accessible by deprotonation of the amine precursors **1a** and **1b** with base [$tBuOK$ for **2a** or $Na[N(SiMe_3)_2]$ for **2b**].²⁵ An alternative and high-yielding synthesis of **2b** is a ligand exchange reaction whereby the PPh_3 ligand in the amide complex **2a** is displaced by addition of a *N*-heterocyclic carbene (Scheme 2).²⁶ These tetra-coordinated 16 electron rhodium(I) amido complexes **2** adopt a butterfly-type geometry (that is a trigonal bipyramidal structure with one missing ligand in the equatorial plane). The rhodium centers are coordinated to two olefinic units as π -acceptors in the equatorial positions and to an amido and phosphane or *N*-heterocyclic carbene as σ -donor groups placed mutually *trans* in the axial positions. The

corresponding amino hydride complexes **3a** or **3b** are formed by a rapid reaction of **2a** and **2b** with H_2 . In a similar manner, addition of 1.0 equivalents of $\text{Me}_2\text{HN}-\text{BH}_3$ (DMAB) to a green solution of $[\text{Rh}(\text{trop}_2\text{N})(\text{PPh}_3)]$ (**2a**) results in an immediate colour change to yellow. The formation of a mixture of hydride complexes $[\text{Rh}(\text{eq-H})(\text{trop}_2\text{NH})(\text{PPh}_3)]$ (**3a_{eq}**) and $[\text{Rh}(\text{ax-H})(\text{trop}_2\text{NH})(\text{PPh}_3)]$ (**3a_{ax}**) in a 10:1 ratio and the cyclic dimer $[\text{Me}_2\text{NBH}_2]_2$ is observed. The isomerization of the equatorial hydride complex to the complex with a hydride in axial position, which is 40 kcal mol^{-1} more stable, has been observed previously.²² This isomerisation reaction is catalyzed by base and/or accelerated thermally. In the reaction of the carbene analog **2b**, only the isomer with the hydride ligand in equatorial position (**3b_{eq}**) is formed. Complex **3b_{eq}** is stable and no conversion to its isomer **3b_{ax}** was observed even after prolonged reaction times. Reactions of amide complexes **2a,b** with the adduct $\text{BH}_3(\text{THF})$ proceed to completion after few minutes at room temperature to give the yellow complexes $[\text{Rh}\{(\mu\text{-H})\text{BH}_2\}(\text{Ntrop}_2)(\text{PPh}_3)]$ (**4a**) and $[\text{Rh}\{(\mu\text{-H})\text{BH}_2\}(\text{Ntrop}_2)(\text{IME})]$ (**4b**) which were isolated as single crystals in good yields.

Scheme 2. Synthesis of rhodium amides **2a** and **2b** and their reaction with amino boranes or BH_3 to **2a,b** and **3a,b**, respectively.

The solid-state structures of complexes **4a** and **4b** were determined by single-crystal X-ray diffraction analyses (Figure 1, Table 1). Both complexes show a five-coordinated d^8 -Rh center coordinated to two olefinic units, the N atom of the trop ligand, the ligand $L = \text{PPh}_3$ or IMe , respectively and a hydride stemming from the BH_3 unit. The B1–N1 interatomic distances [1.551(3) Å for **4a** and 1.562(8) Å for **4b**] are comparable to the lengths of dative bonds in other $\text{R}_3\text{N}-\text{BH}_3$ metal complexes^{18a} and metal amidotrihydroborates (1.56 - 1.52 Å)^{27a} but significantly shorter than in free amine borane adducts (e.g. 1.617(4) in $\text{Me}_3\text{N}-\text{BH}_3$).^{27b} The coordination of BH_3 leads only to slight variations of the Rh–N1, coordinated $\text{C}=\text{C}_{\text{trop}}$, and Rh–L ($L = \text{P1}$ or C31) bond lengths with respect to the amides **2a,b** (Table 1).

Figure 1. Molecular structures derived from single crystal X-ray diffraction analysis. ORTEP plot of **4a** at 50% ellipsoid probability. Non-relevant H atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): A) Rh1–N1 2.085(1), Rh1–P 2.2730(6), N1–B1 1.551(3), Rh1–H1B 1.69(3), Rh1–ct 2.081(1), P1–Rh1–N1 165.08(5), B1–N1–Rh1 79.43(12). Complex **4b**: B) Rh1–N1 2.089(5), Rh1–C31 2.042(6), N1–B1 1.562(8), Rh1–H1 1.74(5), Rh1–ct 2.042(1), Rh1–ct 2.047(1), C31–Rh1–N1 170.65(19), B1–N1–Rh1 80.9(3).

Table 1. Comparison of bond distances and NMR chemical shifts of complexes **2**, **3** and **4**

Complex	Rh–N	Rh–ct	C=C _{trop}	Rh–X	B–N	$\delta(^{11}\text{B})$	$\delta(^{13}\text{C})\text{C}=\text{C}_{\text{trop}}$ (ppm)	$\delta(^1\text{H})\text{H}..M$ (ppm)
2a ^[a]	2.00	2.07	1.41	2.32	-	-	76.2, 84.5	-

		2.06	1.42					
2b	2.05	2.04	1.41	2.02	-	-	75.7, 81.3	-
3a_eq	2.18	2.06	1.44	2.23		-	57.8, 60.6	-8.15
3a_ax	-	-	-	-	-	-	57.1, 61.2	-21.37
3b_eq	-	-	-	-	-	-	52.3, 54.1	-6.30
4a	2.08	2.08	1.42	2.27	1.55	-0.4	65.2, 66.5	-6.96 (298 K)
4b	2.089	2.04, 2.05	1.43	2.04	1.56	-13.2	62.4, 62.5	-1.79 (298 K) -5.76 (193 K)

[a] The bond lengths of the $[\text{Rh}(\text{trop}_2\text{N})(\text{PR}_3)]$ complex with $\text{R} = 4\text{-Me-C}_6\text{H}_4$ are given²²

Differences in the binding of the BH_3 molecules in **4a** and **4b** are indicated by the NMR spectra in solution of both complexes. A solution of complex **4a** in d^8 -THF shows ^1H NMR resonances in accordance with the solid state structure. A broad resonance at $\delta = -6.96$ ppm (at 298 K) is assigned to the bridging hydrogen between the boron and rhodium center, while the terminal BH_2 group exhibits a chemical shift at higher frequencies (-0.55 ppm). In contrast, the ^1H NMR spectrum of complex **4b** exhibits only one broad resonance at -1.79 ppm at 298 K for the BH_3 group. At lower temperatures (< 193 K), this signal splits into one high-field resonance at -5.76 ppm and one at 0.22 ppm in approx. 1:2 intensity ratio corresponding to the hydride ligand and terminal BH_2 respectively (Figure 2). The bridging hydride and the terminal hydrides of the BH_2 group in **4b** undergo an exchange process, which formally can be described as a rotation of the BH_3 unit over the Rh-N bond. This phenomenon suggests a weaker coordination of the borane in the *N*-heterocyclic carbene complex **4b**. Temperature-dependent ^1H 1D selective gradient EXSY spectra were recorded for solutions of compound **4b** which allowed to estimate experimentally the barrier to rotation around the B-N bond as $E_{\text{rot}}^{\#} = (5.5 \pm 0.5)$ kcal/mol, which is about twice as high as in the adducts $\text{H}_3\text{N-BH}_3$ (2.04 kcal/mol)²⁸ or $\text{Me}_3\text{N-BH}_3$ (3.39 kcal/mol).²⁶

a)

b)

Figure 2. a) High field region of the ^1H NMR spectra (500 MHz, d^8 -THF) of complex **4b** as a function of temperature. b) Section of the IR spectra section of complexes **4a**, **4b**, $\text{Me}_3\text{N}-\text{BH}_3$ and $\text{K}[\text{Me}_2\text{N}-\text{BH}_3]$ showing the stretching vibrations of the B–H groups, $\nu(\text{B}-\text{H})$.

The higher degree of activation of the B–H unit in **4a** is also supported by the ^{11}B NMR spectrum, which shows a significant shift to higher frequency at $\delta(^{11}\text{B}) = -0.4$ ppm - the expected range for three-coordinate boron compounds compared to **4b** at $\delta(^{11}\text{B}) = -13.2$ ppm which is in the range of four-coordinated boron compounds. In both **4a** and **4b**, the hydride ligand in the pseudo-equatorial position provokes a shift of the olefinic ^{13}C NMR resonances to lower frequencies by about 15 ppm (average) as a consequence of σ -electron

donation of the hydride to the metal center which in turn induces higher electron back-donation into the π^* -orbitals of the coordinated $C=C_{trop}$ units. Note, however, that the corresponding resonances in the amino hydride complexes **3a_{eq}** and **3b_{eq}** are shifted by another 10 ppm to lower frequencies indicating a significantly stronger rhodium hydride interaction in these compounds.

The IR spectra of the borane complexes **4a** and **4b** together with the spectra of the potassium dimethylamidotrihydroborate $K[Me_2NBH_3]$ [$\nu(B-H) = 2192, 2120, \text{ and } 2052\text{ cm}^{-1}$] and of the amino borane Me_3N-BH_3 [$\nu(B-H) = 2350, 2310, 2282 \text{ and } 2263\text{ cm}^{-1}$] are shown in Figure 2b. The Rh-H stretching vibration in **3a_{eq}** is observed at 1727 cm^{-1} .^{29,30} In the IR spectra of **4a,b** there is no absorption band observed which can be associated with such a Rh-H stretching vibration. For complex **4a**, four absorptions at 2447, 2374, 2278 and 2213 cm^{-1} are recorded which are tentatively assigned to vibrations of the μ^2 -bridging B-H and BH_2 group. In complex **4b**, these stretching vibrations are observed at slightly higher wave numbers at 2457, 2428 and 2365 cm^{-1} . If one assumes that an increasing strength of the N→B donor-acceptor interaction is reflected in an increasing B-H bond length and a concomitant decrease of the wave numbers for the B-H stretching vibration, these results indicate a comparatively weaker N→B interaction in **4a,b**.³¹ That is the N→B bond strength decreases in the order $[Me_2N\rightarrow BH_3]^- > Me_3N\rightarrow BH_3 > Rh_{trop}N\rightarrow BH_3$ (**4a,b**), although this statement requires a detailed analysis which is beyond the scope of this work. In summary, the IR spectra in combination with the NMR spectra indicate that the borane adducts **4a,b** are best described as (metallo)amino borane adducts with a relatively weaker N→B bond and a weak but significant Rh-H interaction.

Next, we studied the catalytic dehydrocoupling of **DMAB** by complexes **2a-b**, **3a-b** and **4a-b** as catalysts (Table 2 and Figure 3). In an open system purged by a stream of argon, the addition of the rhodium amides **2a** or **2b** (0.2 mol%) to a toluene solution of DMAB at 50 °C results in. Analysis of the reaction mixtures revealed the formation of the linear and cyclic dimers (**C** and **D**) as **major** products. Moderate turnover frequencies (TOFs) of up to 185 h^{-1} were achieved. An increase in the catalyst loading of **2b** to 10 mol% resulted in a nearly complete conversion of DMAB (**A**) after 90 min (entry 3).

Table 2. Catalytic dehydrocoupling of Me₂HN–BH₃ (DMAB) by rhodium diolefin complexes^[a]

Entry	Catalyst	t _R (h)	Conversion (%)	B (%)	C (%)	D (%)	E (%)	F (%)
1 ^[b]	2a	3	33	<1	18	10	5	-
2 ^[b]	2b	3	37	<1	22	14	<1	-
3	2b	1.5	95	-	8	76	11	-
4 ^[c]	3a_{eq}	1.5	97	29	<1	52	15	<1
5	3b_{eq}	1.5	>99	-	12	76	12	-
6 ^[c]	3a_{ax}	1.5	48	-	2	39	4	2
7	4a	1.5	3	-	-	<1	2	<1
8	4b	1.5	0	-	-	-	-	-

^[a] Conditions: 10 mol% catalyst, Me₂HN–BH₃ (0.06 M) in *d*⁸-THF, open system to an argon stream.

^[b] Conditions: 0.2 mol% catalyst, Me₂HN–BH₃ (0.5 M) in toluene, open system to an argon stream.

^[c] Additional unidentified minor product also detected ¹¹B NMR δ = 27.1 ppm (d, J_{BH} = 140 Hz).

Figure 3. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of catalytic dehydrocoupling of $\text{Me}_2\text{HN-BH}_3$ (DMAB) by rhodium diolefin complexes at 50 °C after 90 min. **A:** $\text{Me}_2\text{HN-BH}_3$; **C:** $\text{Me}_2\text{HN-BH}_2\text{-NMe}_2\text{-BH}_3$; **D:** $[\text{Me}_2\text{NBH}_2]$; **E:** $(\text{Me}_2\text{N})_2\text{BH}$, **F:** $(\text{Me}_2\text{N})_3\text{B}$. Additional unidentified minor product (*) detected by ^{11}B NMR $\delta = 27.1$ ppm (d, $J_{\text{HB}} = 140$ Hz).

The highest conversion of the substrate was obtained with the equatorial hydride complexes **3a_{eq}** and **3b_{eq}**. However, the best selectivity with respect to the four-membered B₂N₂ heterocycle **D** was achieved with the carbene complex **2b** and the corresponding equatorial hydride complex **3b_{eq}** (entries 3 and 5). A small ratio of the dehydrogenated monomer Me₂N=BH₂ (**B**) $\delta = 33.1$ (d, J_{BH} 123 Hz) is typically observed when the reactions are carried out at room temperature. At 50 °C besides **C** and **D**, small amounts of other amine boranes like Me₂N–BH–NMe₂ (**E**) and B(NMe₂)₃ (**F**) are also detected (Figure 3). The formation of these products requires B–N bond cleavage and formation of free BH₃ in the reaction media.³² Because the reaction of the amido complexes **2a** and **2b** with BH₃ is fast and the borane complexes **4a** and **4b** show almost no activity, it is plausible that the dissociation of amine boranes in amine and BH₃ is responsible for the catalyst deactivation. This dissociation may occur either within the free amine borane or, even more likely, from [Rh{(μ-H)BH₂NMe₂H}(Ntrop₂)(L)] species where the amine boranes coordinate with a B–H bond to the Rh–N bond of **2a** or **2b**. These assumptions are bolstered by the observation that the reaction between **2a** and Me₃N–BH₃, which has no N–H bond, likewise gives the borane adduct **4a**.

Based on the results from this work in combination with our previously reported calculations,^{22,23} we propose the mechanism shown in Scheme 3. Me₂HN–BH₃ (**A**) is dehydrogenated by the rhodium amide **2** to the corresponding Me₂=BH₂ (**B**) and the amino hydride complex **3** is formed. Me₂N=BH₂ may either dimerize to cyclic **D** or react with **A** to give the linear dimer Me₂H–BH₂–MeN–BH₃ (**C**) which is likewise dehydrogenated by **2** to the cyclic product **D**.³³ We suggest that these dehydrogenation steps proceed via cyclic activated complexes at the transition states **TS1** as shown on the bottom of Scheme 3. Thus, the amide function in **2a,b** behaves as a cooperating ligand in this dehydrogenation step. However, while a hydrogen acceptor is necessary in the dehydrogenation reactions of alcohols in order to convert the amine hydride complex [RhH(trop₂NH)(L)] **3a,b** back to the amides **2a,b**, this is not a requirement in the catalytic dehydrogenation of DMAB. The amine hydride complexes **3a,b** readily react with DMAB to produce hydrogen. We propose the activated complex **TS2** as the transition state for this reaction as shown in Scheme 3. Two reactions were identified which can reduce the catalytic reactivity: i) If the free amino hydride complex **3a_{eq}** with L = PPh₃ is formed, this may rearrange to its isomer **3a_{ax}** with an axial hydride ligand. In this case, a much lower conversion of only 39% to the cyclic product (**D**) is observed (entry 6, Table 2). The mechanism by which the hydride complex **3a_{ax}** evolves hydrogen from aminoborane **A** remains speculative but may involve a slow re-isomerisation to **3a_{eq}** as the true catalyst. ii) The predominant deactivation reaction, however, is blocking the active Rh–N site by BH₃ in the complexes **4a** and **4b**. These latter species are remarkably stable and attempts to displace the BH₃ group by amides [NaN(TMS)₂] or amines (*N*-methylmorpholine, 2,6-dimethylpiperidine or NMe₃) added in excess gave no reaction. Additionally, transfer of the boron fragment to an unsaturated organic substrate (acetophenone) was also unsuccessful.

Scheme 3. A plausible simplified sketch of key-transformations in the catalyzed dehydrogenation of amino borane **A** by rhodium amide complexes **2**.

Conclusions

The rhodium amide complexes $[\text{Rh}(\text{trop}_2\text{N})(\text{L})]$ and their corresponding amine hydride complexes $[\text{RhH}(\text{trop}_2\text{NH})(\text{L})]$ catalyze the dehydrogenation of amine boranes. Likely this process proceeds via an outer-sphere hydrogen transfer mechanism which was also proposed for alcohol dehydrogenations. The best catalytic performance (given by the highest yield of 76% of the dehydrogenated cyclic azaboroethene **D** and concomitant formation of hydrogen) is achieved with the carbene complex $[\text{Rh}(\text{trop}_2\text{N})(\text{IMe})]$ **2b** and the corresponding amino hydride $[\text{RhH}(\text{trop}_2\text{NH})(\text{IMe})]$ **3b**. In the case of the hydride complex, the reaction proceeds with a slightly better overall conversion of the starting material but a higher amount of the linear dimer is formed. The performance is, however, magnitudes of order lower than the one observed with a paramagnetic $\text{Ni}(\text{I})$ complex carrying the same trop_2NH ligand.³⁴ Remarkably stable borane complexes $[\text{Rh}\{(\mu\text{-H})\text{BH}_2\}(\text{Ntrop}_2)(\text{L})]$ were isolated. In these species, a B–H bond binds to the Rh–N bond configuring a planar Rh–N–H–B metallacycle. This observation strongly bolsters calculations which indicate that H–H bond in dihydrogen is directly heterolytically cleaved via a comparable activated complex with a Rh–N–H–H ring and no σ -type H_2 bonded is formed as intermediate which is intra- or intermolecularly deprotonated.²²

Experimental Section

General methods

All reactions were carried out under an inert atmosphere using standard vacuum Schlenk line techniques or in a MBraun glovebox. THF and *n*-hexane were dried over sodium, CH₂Cl₂ was purified using an Innovative Technologies PureSolv system. Starting materials were obtained from Sigma Aldrich or Johnson Matthey or synthesized according to the literature, [Rh(COD)Cl]₂,³⁵ [Rh(trop₂NH)Cl]₂,²⁹ [RhCl(trop₂NH)PPh₃],²⁴ [Rh(trop₂N)(PPh₃)],²² [Rh(trop₂N)(IME)]²⁵ and IME.³⁶ NMR spectra were recorded on Bruker instruments at 300 or 500 MHz. For ¹H and ¹³C NMR spectra, SiMe₄, for ¹¹B NMR spectra BF₃(OEt₂), for ³¹P NMR spectra H₃PO₄ and for ¹⁰³Rh NMR spectra Rh(acac)₃ was used as an external standard. Data collections for single-crystal X-ray diffractions were performed using a Bruker APEX I or Bruker VENTURE diffractometer (MoK_α, λ = 0.71073 Å). The structures were solved with direct methods using SHELX-97³⁷ or SHELXT³⁸ software and refined via full-matrix least-squares methods³⁹.

Synthesis of [Rh(trop₂N)(PPh₃)] (2a)

To a solution of **1a** (150 mg, 0.19 mmol, 1.0 equiv) in THF (2 ml) was added KOtBu (21.1 mg, 0.19 mmol, 1 equiv). After stirring for 1h at room temperature, the solvent was removed. The dark green residue was dissolved in THF (2 ml) and filtered over Celite. The solution was concentrated under vacuum and layered with toluene (1ml) and *n*-hexane (5mL). The product was obtained as dark green microcrystals (110 mg, 0.144 mmol, 77%).

¹H NMR (300 MHz, *d*⁸-THF) δ = 4.82 (d, ⁴J_{PH} = 13.5 Hz, 2H, CH_{benzyl}), 5.17 (s, 4H, CH_{olefin}), 6.72-6.84 (m, 12H, CH_{arom}), 7.00-7.02 (m, 4H, CH_{arom}), 7.49-7.51 (m, 9H, CH_{arom}), 7.61-7.68 (m, 6H, CH_{arom}) ppm.

Synthesis of [Rh(*eq*-H)(trop₂NH)(PPh₃)] (3a_{eq})

To a solution of **2a** (24.0 mg, 0.03 mmol, 1.0 equiv) in *d*⁸-THF (2 ml) was added Me₂NN-BH₃ (1.8 mg, 0.03 mmol, 1.0 equiv). After stirring at room temperature for 10 min, the resulting yellow solution was analysed and used for the catalytic experiments.

¹H NMR (300 MHz, *d*⁸-THF) δ = -8.29 (t, ¹J_{RhH} = 23.1 Hz, 1H, RhH), 3.54 (s, 2H, CH_{olefin}), 3.86-3.90 (m, 2H, CH_{olefin}), 4.45 (d, ⁴J_{PH} = 8.1 Hz, CH_{benzyl}), 5.04 (d, ³J_{PH} = 4.6 Hz, 1H, NH), 6.16-7.81 (m, 31H, CH_{arom}) ppm.

Synthesis of [Rh(*ax*-H)(trop₂NH)(PPh₃)] (3a_{ax})

A solution of **3a_{eq}** (0.004 mmol) in *d*⁸-THF (0.6 mL) was heated to 50°C for 16 h. Complete isomerization was observed as indicated by the NMR spectrum.

^1H NMR (300 MHz, d^8 -THF) δ = -21.52 (t, $^1J_{\text{RhH}}$ = 17.7 Hz, 1H, RhH), 0.89 (s, 1H, NH), 4.12 (s, 2H, $\text{CH}_{\text{benzyl}}$), 4.43 (t, $^3J_{\text{HH}}$ = 8.5 Hz, 2H, $\text{CH}_{\text{olefin}}$), 5.15-5.19 (m, 2H, $\text{CH}_{\text{olefin}}$), 6.20-7.47 (m, 31H, CH_{arom}) ppm.

Synthesis of $[\text{Rh}(\text{eq-H})(\text{trop}_2\text{NH})(\text{IMe})]$ (**3b_{eq}**)

To a solution of **2b** (18.7 mg, 0.03 mmol, 1.0 equiv) in d^8 -THF (2 ml) was added $\text{Me}_2\text{HN-BH}_3$ (1.8 mg, 0.03 mmol, 1.0 equiv). After stirring at room temperature for 10 min, the resulting yellow solution was analysed and used for the catalytic experiments

^1H NMR (300 MHz, d^8 -THF) δ = -6.00 (br, 1H, RhH), 2.13 (s, 3H, CH_3), 2.16 (s, 3H, CH_3), 3.32 (d, $^3J_{\text{HH}}$ = 9.2 Hz, 2H, $\text{CH}_{\text{olefin}}$), 3.84 (d, $^3J_{\text{HH}}$ = 9.2 Hz, 2H, $\text{CH}_{\text{olefin}}$), 3.93 (s, 3H, CH_3), 4.12 (s, 3H, CH_3), 4.32 (s, 2H, $\text{CH}_{\text{benzyl}}$), 6.58-7.16 (m, 16H, CH_{arom}) ppm.

Synthesis of $[\text{Rh}\{(\mu\text{-H})\text{BH}_2\}(\text{Ntrop}_2)(\text{PPh}_3)]$ (**4a**)

To a solution of $[\text{Rh}(\text{trop}_2\text{N})(\text{PPh}_3)]$ (25 mg, 0.0328 mmol, 1.0 equiv) in THF (1 mL) was added $\text{BH}_3(\text{THF})$ (360 μL of 1M in THF, 0.0361 mmol, 1.1 equiv). The green solution immediately turned yellow forming $[\text{Rh}\{(\mu\text{-H})\text{BH}_2\}(\text{Ntrop}_2)(\text{PPh}_3)]$ as only product. The complex was recrystallized from DCM/*n*-hexane. Yield: 87%, 22 mg.

^1H -NMR (300 MHz, d^8 -THF): δ = -6.96 (br, 1H, BH_2H), -0.55 (br, 2H, BH_2H), 4.03 (d, $^3J_{\text{HH}}$ = 10.9 Hz, 2H, $\text{CH}_{\text{olefin}}$), 4.59 (d, $^4J_{\text{PH}}$ = 8.8 Hz, 2H, $\text{CH}_{\text{benzyl}}$), 4.78 (d, $^3J_{\text{HH}}$ = 10.9 Hz, 2H, $\text{CH}_{\text{olefin}}$), 6.54-7.79 (m, 31H, CH_{arom}) ppm. $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, CD_2Cl_2): δ = 65.3 (d, $^1J_{\text{RhC}}$ = 10.4 Hz, 2C, C_{olefin}), 66.5 (d, $^1J_{\text{RhC}}$ = 8.2 Hz, 2C, C_{olefin}), 77.0 (d, $^2J_{\text{RhC}}$ = 2.4 Hz, 2C, C_{benzyl}), 125.1-139.9 (C_{arom}) ppm. $^{31}\text{P}\{^1\text{H}\}$ -NMR (121 MHz, d^8 -THF): δ = 56.5 (d, $^1J_{\text{RhP}}$ = 136.1 Hz) ppm. $^{11}\text{B}\{^1\text{H}\}$ -NMR (96 MHz, d^8 -THF) δ = -0.4 ppm (br). $^1\text{H}^{103}\text{Rh}$ (18.8 MHz, CD_2Cl_2): δ = -8078 ppm.

Synthesis of $[\text{Rh}\{(\mu\text{-H})\text{BH}_2\}(\text{Ntrop}_2)(\text{IMe})]$ (**4b**)

To a cooled solution of $[\text{Rh}(\text{trop}_2\text{N})\text{PPh}_3]$ (54 mg, 0.071 mmol, 1 equiv) in THF (2 ml) at -30°C was added a solution of IMe (8.8 mg, 0.071 mmol, 1 equiv) in THF (2 ml). After stirring the resulting green solution for 10 min at rt, $\text{BH}_3(\text{THF})$ (0.2 ml of 0.5M in THF, 0.1 mmol, 1.4 equiv) was added. The green solution turns immediately yellow. After removing the solvent *in vacuo*, the residue was recrystallized from DCM/*n*-hexane. The product was obtained as pale yellow plates (30 mg, 0.047 mmol, 66%).

^1H -NMR (500 MHz, CD_2Cl_2 , 298 K): δ = -1.79 (s, br, 3H, BH_3), 2.14 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 3.73 (s, 3H, NCH_3), 4.00 (dd, $^3J_{\text{HH}}$ = 9.3 Hz, $^2J_{\text{RhH}}$ = 1.5 Hz, 2H, $\text{CH}_{\text{olefin}}$), 4.05 (s, 3H, NCH_3), 4.44 (s, 2H, $\text{CH}_{\text{benzyl}}$), 5.17 (dd, $^3J_{\text{HH}}$ = 9.3 Hz, $^2J_{\text{RhH}}$ = 2.4 Hz, 2H, $\text{CH}_{\text{olefin}}$), 6.70-6.76 (m, 6H, CH_{arom}), 6.92-7.10 (m, 10H, CH_{arom}) ppm. $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, CD_2Cl_2): δ = 10.0 (s, 1C, CH_3), 10.4 (s, 1C, CH_3), 36.1 (s, 1C, CH_3), 38.4 (s, 1C, CH_3), 62.42 (d, $^1J_{\text{RhC}}$ = 1.3 Hz, 2C, $\text{CH}_{\text{olefin}}$), 62.55

(d, $^1J_{\text{RhC}} = 2.5$ Hz, 2C, CH_{olefin}), 76.6 (s, 2C, CH_{benzylic}), 124.4 (s, 2C, C_{aroma}), 125.1 (s, 2C, C_{arom}), 125.5 (s, 1C, C_{quart}), 125.7 (s, 1C, C_{quart}), 126.9 (s, 2C, C_{arom}), 127.0 (s, 2C, C_{arom}), 127.4 (s, 2C, C_{arom}), 127.8 (s, 2C, C_{arom}), 128.1 (s, 2C, C_{arom}), 130.0 (s, 2C, C_{arom}), 137.3 (d, $^1J_{\text{RhC}} = 1.4$ Hz, 1C, C_{quart}), 138.3 (s, 1C, C_{quart}), 139.4 (s, 1C, C_{quart}), 139.5 (s, 1C, C_{quart}), 173.1 (d, $^1J_{\text{RhC}} = 49.8$ Hz, 1C, C_{quart}) ppm. $^{11}\text{B}\{^1\text{H}\}$ -NMR (160.50 MHz, CD₂Cl₂): $\delta = -13.22$ ppm (br). $^1\text{H}^{103}\text{Rh}$ (18.8 MHz, CD₂Cl₂): $\delta = -7915$ ppm.

General procedure for catalytic dehydrogenation of DMAB

A solution of the catalyst (0.004 mmol, 1 equiv) in THF (0.6 mL) was added to Me₂HN-BH₃ (0.04 mmol, 2.7 mg, 10 equiv). The reaction solution was warmed to 50 °C in an open system connected to an argon stream. After 90 min the conversion was determined via ^{11}B NMR spectroscopy.

Table 3. Crystallographic data for complex **4a**.

Empirical formula	C ₅₀ H ₄₄ BCl ₄ NPRh
Formula weight	945.35
Temperature/K	100(2)
Crystal system	Orthorhombic
Space group	Pnma
a/Å	25.9576(15)
b/Å	13.4699(8)
c/Å	11.9483(7)
$\alpha/^\circ$	90.00
$\beta/^\circ$	90.00
$\gamma/^\circ$	90.00
Volume/Å ³	4177.7(4)
Z	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.503
μ/mm^{-1}	0.741
F(000)	1936.0
Crystal size/mm ³	0.50 × 0.36 × 0.32
Radiation	MoK α ($\lambda = 0.71073$)
2 θ range for data collection/ $^\circ$	3.14 to 56.64
Index ranges	-34 ≤ h ≤ 34, -17 ≤ k ≤ 17, -15 ≤ l ≤ 15
Reflections collected	41959
Independent reflections	5392 [$R_{\text{int}} = 0.0429$, $R_{\text{sigma}} = 0.0257$]
Data/restraints/parameters	5392/0/370
Goodness-of-fit on F ²	1.059
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0285$, $wR_2 = 0.0717$
Final R indexes [all data]	$R_1 = 0.0333$, $wR_2 = 0.0735$
Largest diff. peak/hole / e Å ⁻³	1.06/-0.99

Table 4. Crystallographic data for complex **4b**.

Empirical formula	C ₃₉ H ₄₁ BCl ₄ N ₃ Rh
Formula weight	807.27
Temperature/K	103.4
Crystal system	triclinic
Space group	P-1
a/Å	11.0484(11)
b/Å	11.6239(10)
c/Å	14.3834(15)
α/°	76.298(4)
β/°	87.498(5)
γ/°	82.833(4)
Volume/Å ³	1780.4(3)
Z	2
ρ _{calc} /g/cm ³	1.506
μ/mm ⁻¹	0.813
F(000)	828.0
Crystal size/mm ³	0.22 × 0.04 × 0.04
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.69 to 49.59
Index ranges	-13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -16 ≤ l ≤ 16
Reflections collected	33958
Independent reflections	6105 [R _{int} = 0.1663, R _{sigma} = 0.1090]
Data/restraints/parameters	6105/0/407
Goodness-of-fit on F ²	1.011
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0556, wR ₂ = 0.1111
Final R indexes [all data]	R ₁ = 0.1041, wR ₂ = 0.1292
Largest diff. peak/hole / e Å ⁻³	0.69/-1.08

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Supplementary data

The crystallographic data is deposited free of charge at the Cambridge Crystallographic Data Centre (CCDC-1451490 (**4a**), 1450882 (**4b**) via <https://summary.ccdc.cam.ac.uk/structure-summary-form>).

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