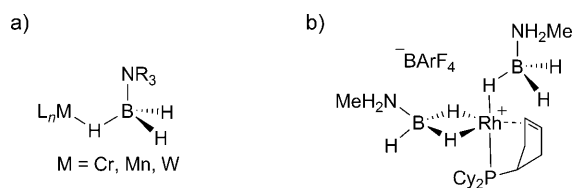


Ruthenium Bis(σ -B–H) Aminoborane Complexes from Dehydrogenation of Amine–Boranes: Trapping of $\text{H}_2\text{B–NH}_2^{**}$

Gilles Alcaraz,* Laure Vendier, Eric Clot, and Sylviane Sabo-Etienne*

Ammonia–borane has attracted considerable interest recently as a potential hydrogen source and storage material owing to its high hydrogen storage capacity.^[1] Homogeneous transition-metal-catalyzed dehydrogenation of ammonia–boranes leads to dihydrogen release; however, reversible storage from the resulting polymeric materials remains a major problem.^[2] The nature of the transition metal complex used to catalyze the dehydrogenation of the amine–borane family $\text{H}_3\text{B–NR}_{3-n}\text{H}_n$ ($n = 1–3$) (**I**) has a direct impact both on kinetics and dehydrocoupling routes.^[3] However, the successive elementary steps leading to dehydrocoupling are still not well understood, and the question of the BH/NH bond activation mechanism is a very active area of research.^[4]

B–H bond activation of a tertiary amine–borane adduct is achieved in the $\eta^1\text{-H}_3\text{B–NR}_3$ Shimoi-type complexes in the case of chromium, tungsten, and manganese (Scheme 1).^[5] In



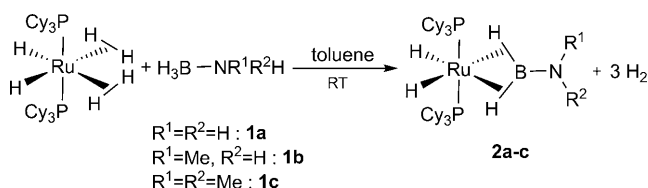
Scheme 1. Representative examples of a) $\eta^1\text{-H}_3\text{B–NR}_3$ Shimoi and b) η^1 - and η^2 -bis($\text{H}_3\text{B–NH}_2\text{Me}$) Weller complexes.

such a case, the substitution pattern at the nitrogen atom prevents further dihydrogen release. Thus, these complexes can be regarded as early intermediates in amine–borane B–H activation processes.^[6] Starting from precursors **I** that are likely to undergo dehydrogenation, known complexes retain-

ing a B–N unit are restricted to two cationic rhodium examples, as reported by Weller et al. They are amine–borane adducts with η^1 - and/or $\eta^2\text{-H}_3\text{B–NRR'H}$ bonding modes ($\text{R, R}' = \text{H, Me}$; Scheme 1).^[7,8]

With this work in mind, and following our recent findings on the isolation of bis(σ -B–H) complexes from the reaction of dihydrogenoboranes with the bis(dihydrogen) complex $[\text{RuH}_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2]$,^[9,10] we herein report the synthesis of the first “true” bis (σ -B–H) aminoborane ruthenium complexes.^[11] Stabilization of the simplest aminoborane units $\text{H}_2\text{B–NMe}_{n-2}\text{H}_n$ ($n = 1–2$) results from the stoichiometric dehydrogenation of the amine–borane precursors by the ruthenium complex.

Room-temperature reaction of $[\text{RuH}_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2]$ in toluene with the amine–boranes **1a–c** proceeds with gas evolution. After workup, the resulting solids, which analyzed as $[\text{RuH}_2(\eta^2\text{-H}_2)_2\text{B–NR}^1\text{R}^2](\text{PCy}_3)_2$ (**2**), were isolated as white powders (**2a**: 77 %, **2b**: 60 %, **2c**: 64 %; Scheme 2) and fully characterized by NMR and X-ray diffraction crystallography for **2a**.



Scheme 2. Synthesis of **2** by dehydrogenation of amine–boranes **1a–c**.

As a representative example, we will describe the NMR spectroscopic properties of **2a**, but similar features are observed for compounds **2b–c** and are reminiscent of the spectroscopic data reported for the ruthenium complexes $[\text{RuH}_2(\eta^2\text{-H}_2)_2\text{B–R}](\text{PCy}_3)_2$ ($\text{R} = t\text{Bu, Mes}$).^[9] The ^1H NMR spectrum of **2a** in the hydride region in C_6D_6 at 298 K exhibits a broad singlet at $\delta = -6.80$ ppm and a more shielded triplet ($J_{\text{PH}} = 24.8$ Hz) in a 1:1 integration ratio at $\delta = -11.85$ ppm. The triplet collapsed into a singlet upon phosphorus decoupling, whereas the singlet sharpened upon boron decoupling. A 1D TOCSY $^1\text{H}\{^1\text{B}\}$ experiment with a selective excitation at $\delta = -6.80$ ppm showed correlations with the triplet and a deshielded singlet at $\delta = 2.34$ ppm, which were assigned to the NH_2 protons (see the Supporting Information, Figure S1). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a sharp singlet at $\delta = 77.43$ ppm, and a broad signal is observed in the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum at $\delta = 46$ ppm. This ^{11}B signal is highly shifted from the resonance of the starting ammonia–borane ($\delta = -21.6$ ppm)^[12] and slightly downfield from those of free monomeric aminoboranes ($\text{H}_2\text{B–NR}_2$ $\delta = 35–36$ ppm).^[13]

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The X-ray structure of **2a** was determined at 110 K (Figure 1 and Table 1). The quality of the measurement allows us to be confident on the location of the hydrogen atoms around the metal.^[14] The ruthenium atom is in a pseudo-octahedral environment with the phosphines in axial positions. The four hydrogen atoms (H1–4) surrounding the metal, the boron, the nitrogen, and the NH₂ hydrogen atoms are all located in the equatorial plane. The Ru–B distance (1.956(2) Å) is shorter than the sum of the covalent radii (2.09 Å) and similar to the distances previously reported for the bis(σ-B–H) borane ruthenium complexes.^[9,15] The most striking features are the shortening of the B–N distance (1.396(3) Å) with respect to that of ammonia–borane (1.58(2) Å as determined by neutron diffraction),^[16] and the

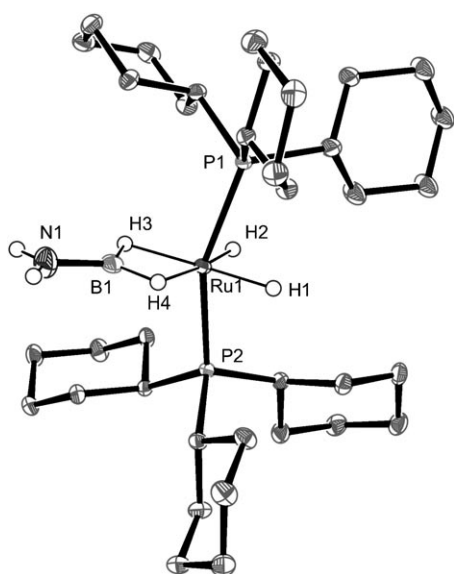


Figure 1. X-ray crystal structure of [RuH₂(η²:η²-H₂BNH₂)(PCy₃)₂] (**2a**). Ellipsoids set at 50% probability; phosphine hydrogen atoms omitted for clarity.

Table 1: Selected geometrical parameters for the experimental (**2a**, R = Cy) and calculated structures (**3a**, R = Me) of [RuH₂(η²:η²-H₂BNH₂)-(PR₃)₂] and the computed structure of H₂BNH₂.

	2a	3a	H ₂ B–NH ₂
Ru–B	1.956(2)	1.960	
Ru–P1	2.3215(5)	2.307	
Ru–P2	2.3131(5)	2.311	
B–N	1.396(3)	1.403	1.390
Ru–H1	1.54(2)	1.612	
Ru–H2	1.55(2)	1.612	
Ru–H3	1.71(2)	1.811	
Ru–H4	1.73(3)	1.811	
B–H3	1.25(2)	1.323	1.198
B–H4	1.22(3)	1.323	1.198
P1–Ru–P2	155.066(19)	156.76	
H3–B–H6	120.3(16)	127.01	121.9
P1–Ru–B	102.90(7)	100.60	
P2–Ru–B	102.03(7)	102.64	
Ru–B–N	179.4(2)	178.85	

[a] Distances in Å and angles in degrees.

increase of the B–H bond distances (1.25(2) and 1.22(3) Å) compared to 1.15(3) and 1.18(3) Å in H₃B–NH₃.^[16]

DFT(B3PW91) calculations on the model compound [Ru(H)₂(H₂BNH₂)(PMe₃)₂] (**3**) were carried out to characterize the mode of coordination of H₂BNH₂. Four different isomers were located on the potential energy surface (see the Supporting Information, Figure S3). The most stable isomer is the bis(σ-B–H) adduct **3a**, the model for **2a**. The π adducts of H₂BNH₂, **3c** and **3d**, are significantly less stable (ΔE = 19.0 kcal mol^{−1}, **3c**; ΔE = 14.3 kcal mol^{−1}, **3d**). The fourth isomer, **3b**, features both coordination of NH₂ and of a σ-B–H bond and lies 11.4 kcal mol^{−1} above **3a**. Therefore, the bis(σ-B–H) adduct **3a** corresponds to the most stable mode of coordination of aminoborane to [Ru(H)₂(PMe₃)₂]. Moreover, the calculated energy variations for the reaction [Ru(H)₂(H₂)₂(PMe₃)₂] + H₃BNH₃ → **2a** + 3H₂ are indicative of both an exothermic (ΔH = −2.5 kcal mol^{−1}) and an exergonic (ΔG = −15.7 kcal mol^{−1}) transformation. The σ-B–H bonds thus compete efficiently with H₂ for coordination to ruthenium and dissociation of three dihydrogen molecules entropically drives the reaction toward facile formation of **3a**.

As can be seen from Table 1, the optimized geometry (DFT/B3PW91) is in excellent agreement with the experimental structure, and comparison with the free computed H₂BNH₂ compound shows an elongation of the B–H bonds as expected. The trigonal planar geometry of both boron and nitrogen atoms and the B–N distance reflect the expected multiple N_{sp2}–B_{sp2} bond character in monomeric aminoboranes owing to the π donation of the nitrogen lone pair into the vacant p atomic orbital on boron. It is worth noting that the B–N and B–H distances are very similar to those found in two agostic complexes [Cr{HBN(SiMe₃)₂CH=CHCMe₃}(CO)₄] and [RuH₂{η²-H–B(NiPr₂)CH₂PPh₂}(PCy₃)₂] as reported recently by Braunschweig and our group (B–N/B–H: 1.4034(16) Å/1.257 Å,^[17] and 1.404(9) Å/1.23(7) Å,^[18] respectively). All these features are in full agreement with the trapping of H₂B–NH₂,^[19] the first formal elementary step of dehydrogenation of ammonia–borane [Eq. (1)].



In conclusion, compounds **2a–c** are the first examples of “true” bis(σ-B–H) monomeric aminoborane complexes. They result from the simple metal-assisted dehydrogenation of amine–boranes and can be regarded as intermediates in the dehydrogenation process generally leading to polyaminoboranes. Remarkably, the bis-σ coordination mode enables the stabilization of monomeric aminoboranes in the coordination sphere of a metal, including the simplest and elusive prototypical H₂B–NH₂ elementary unit.

Experimental Section

2a–c: Two to four equivalents of amine–boranes **1a–c** were added to a toluene solution of [RuH₂(η²-H₂)₂(PCy₃)₂] (typically 300 mg) at room temperature, and the reaction was monitored by ³¹P NMR spectroscopy until consumption of all the starting ruthenium complex was observed. After removal of the solvent, the residue was dried under vacuum, dissolved in pentane, and filtered. After evaporation of the solvent, compounds **2a–c** were isolated as air-sensitive white solids

(**2a**: 77%, **2b**: 60%, **2c**: 64%). In the case of **1a**, the resulting toluene solution was filtered after reaction before evaporation of the solvent.

Selected data for **2a–c**: **2a**: $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 161.975 MHz): $\delta = 77.44$ ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 128.377 MHz): $\delta = 46$ ppm (br). ^1H NMR (C_6D_6 , 298 K, 400.130 MHz): $\delta = 1.2$ – 2.5 (m, 68H, $\text{NH}_2 + \text{Cy}$), -6.80 (br s, 2H, BH_2), -11.85 ppm (t, 2H, $J_{\text{PH}} = 24.8$ Hz, RuH_2). IR (Nujol): $\tilde{\nu} = 3484$ and 3394 (s, NH_{as}), 1971 and 1923 (m br, RuH), 1833 and 1785 (m br, RuHB), 1583 cm^{-1} (s, NH_{bend}). Elemental analysis (%) calcd for $\text{C}_{36}\text{H}_{72}\text{BNP}_2\text{Ru}$: C 62.41; H 10.48; N 2.02; found: C 62.80; H 10.34; N 2.05.

2b: $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 202.537 MHz): $\delta = 78.50$ ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 160.525 MHz): $\delta = 45.7$ ppm. ^1H NMR (C_6D_6 , 298 K, 500.330 MHz): $\delta = 2.675$ (d, 3H, $^3J_{\text{HH}} = 5$ Hz, CH_3), 2.48 (br, 1H, NH), 1.2 – 2.4 (m, 66H, Cy), -6.80 (br s, 2H, BH_2), -11.99 ppm (t, 2H, $J_{\text{PH}} = 24.4$ Hz, RuH_2). Elemental analysis (%) calcd for $\text{C}_{37}\text{H}_{74}\text{BNP}_2\text{Ru}$: C 62.87; H 10.55; N 1.98; found: C 63.04; H 9.49; N 2.11.

2c: $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 161.975 MHz): $\delta = 79.34$ ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 128.377 MHz): $\delta = 47.7$ ppm (br). ^1H NMR (C_6D_6 , 298 K, 400.127 MHz): $\delta = 2.80$ (s, 6H, NMe_2), 1.2 – 2.5 (m, 66H, Cy), -6.89 (br s, 2H, BH_2), -12.17 (t, 2H, $J_{\text{PH}} = 24.6$ Hz, RuH_2). Elemental analysis (%) calcd for $\text{C}_{38}\text{H}_{76}\text{BNP}_2\text{Ru}$: C 63.32; H 10.63; N 1.94; found: C 63.69; H 9.63; N 1.75.

CCDC 751581 (**2a**) 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.

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