

Boryl-Mediated Reversible H₂ Activation at Cobalt: Catalytic Hydrogenation, Dehydrogenation, and Transfer Hydrogenation

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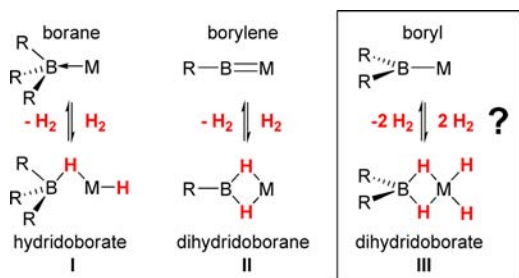
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S Supporting Information

ABSTRACT: We describe the synthesis of a cobalt(I)–N₂ complex (**2**) supported by a meridional bis-phosphino-boryl (PBP) ligand. Complex **2** undergoes a clean reaction with 2 equiv of dihydrogen to afford a dihydridoborato-cobalt dihydride (**3**). The ability of boron to switch between a boryl and a dihydridoborate conformation makes possible the reversible conversion of **2** and **3**. Complex **3** reacts with HMe₂N–BH₃ to give a hydrido-borane cobalt tetrahydridoborate complex. We explore this boryl–cobalt system in the context of catalytic olefin hydrogenation as well as amine–borane dehydrogenation/transfer hydrogenation.

Complexes bearing boron-centered ligands, namely boranes, boryls, and borylenes, have attracted considerable interest.¹ Among the versatile reactivity displayed by these complexes,^{1a} the reaction of boron–metal linkages with hydrogen offers a promising approach for catalysis (Chart 1).² Examples include borane complexes which split H₂

Chart 1. Reversible H₂ Activation Associated with Borane, Borylene, and Boryl Linkages with Metal



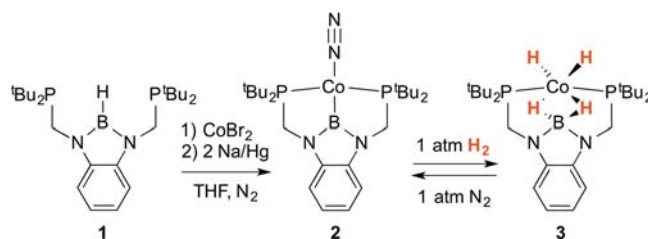
heterolytically (type I)^{2,3} and the insertion of H₂ into a borylene–metal bond (type II).⁴ The addition of H₂ can, in rare cases, be reversible.^{2b,c,3,4} These unusual reactions can be rationalized by (1) the formation of σ -borate/borane complexes upon hydrogenation and (2) the restoration of B–M bonds upon dehydrogenation.

Boryl complexes are often invoked as key intermediates in many important catalytic borylation processes,⁵ and their reactivity patterns have been extensively studied.⁶ Despite these advances, reaction of H₂ with boryl–metal linkages remains very uncommon, having been previously demonstrated irreversibly under forcing conditions.⁷ Herein, we report facile reversible addition of 2 equiv of H₂ across a Co–boryl bond

(type III) at room temperature. We further demonstrate that such Co–boryl species can be exploited in the context of rapid olefin hydrogenation and amine–borane dehydrocoupling/transfer hydrogenation under comparatively mild conditions. Co–boryls hence offer a promising strategy for mediating catalytic two-electron processes better known for the noble metals.⁸

To support the Co–boryl bond, we investigated Nozaki's bis-phosphino-hydridoborane ligand **1**⁹ and its complexation with cobalt. Reaction of **1** with CoBr₂ and sodium amalgam in THF under N₂ afforded **2** in modest yield (23%), isolated as a green solid (Scheme 1). Complex **2** is diamagnetic and features a ¹¹B

Scheme 1. Synthesis of 2 and 3



resonance at 46.6 ppm, consistent with a metalated three-coordinate boron center.⁶ A broad resonance centered at 110.1 ppm is observed in the ³¹P NMR spectrum of **2** (see Supporting Information (SI)). Additional characterization of **2** was obtained via IR spectroscopy and crystallographic analysis (Figure 1), confirming a terminal N₂ ligand ($\nu_{N-N} = 2013 \text{ cm}^{-1}$, Co–N3 1.7745(13) Å, N3–N4 1.119(2) Å). The

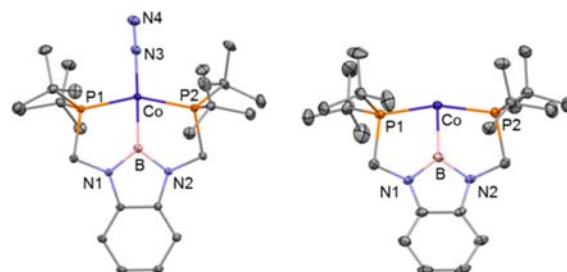


Figure 1. Solid-state structures of **2** (left) and **3** (right). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Co–B 1.9463(13) (**2**), Co–B 1.908 (**3**, av.).

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Co center in **2** adopts a pseudo-square-planar geometry as indicated by the P1–Co–P2 (156.260(14)°) and B–Co–N3 (178.62(6)°) angles, reminiscent of a previously structurally characterized (¹⁸PrPNP)Co(I)–N₂ complex (PNP = bisphosphino-amido).¹⁰ The B–Co bond distance in **2** (1.9463(13) Å) is comparable to that measured for (PMe₃)₄CoBcat (1.949(2) Å).¹¹

Exposure of **2** to 1 atm of H₂ in toluene-*d*₈ resulted in an immediate color change from blue to yellow. The quantitative formation of **3** (Scheme 1) is confirmed by multinuclear NMR spectroscopies including ³¹P (138.2 ppm) and ¹¹B (47.1 ppm). The ¹H NMR spectrum of **3** at 25 °C features a broad hydridic resonance (four H atoms) at –6.51 ppm (Figure 2). This

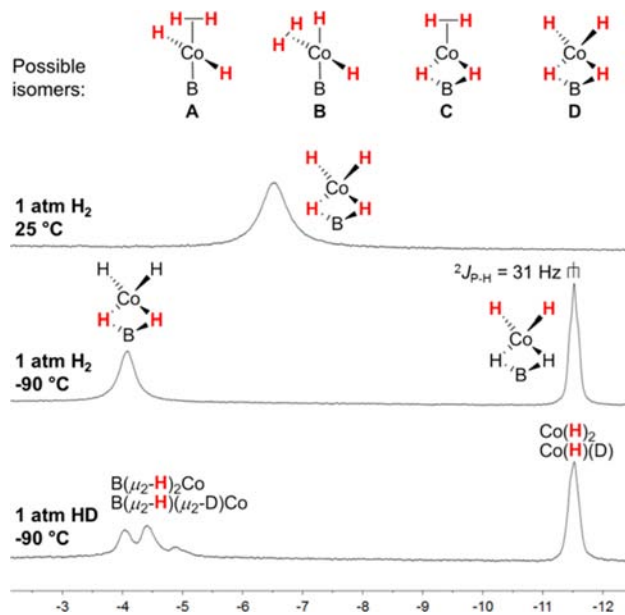


Figure 2. Top: Four possible isomers of **3**. Bottom: ¹H NMR spectra of **3** in toluene-*d*₈ under 1 atm H₂ at 25 °C, 1 atm H₂ at –90 °C, and 1 atm HD at –90 °C. The resonances are assigned to the H atoms highlighted in red.

observation led us to consider four possible products: boryl cobalt *trans*-dihydride dihydrogen (**A**), boryl cobalt *cis*-dihydride dihydrogen (**B**), dihydridoborato cobalt dihydrogen (**C**), and dihydridoborato cobalt dihydride (**D**).

We favor product **D** for the following reasons. Upon cooling, the ¹H NMR signal at –6.51 ppm gradually broadens and decoalesces to two peaks with a ratio of 1:1. The sharper peak observed as a triplet at –11.53 ppm (²J_{p–H} = 31 Hz; see SI for a better resolved spectrum) can be assigned to a terminal hydride resonance, whereas the broader peak at –4.09 ppm is consistent with bridging hydrides.¹² Hydride complexes with agostic interactions can exhibit large isotopic perturbations.¹³ Reaction of **2** with 1 atm of HD (or 1 atm of H₂/D₂ = 1:1) generated two additional resonances at –4.41 and –4.88 ppm with no H–D coupling. The two peaks can be attributed to the existence of two isomers of B(μ₂-H)(μ₂-D)Co as a result of unsymmetrical bridging hydrides, a point also reflected by the solid-state and DFT-optimized structures (*vide infra*).¹⁴ Accordingly, the IR spectrum of **3** under H₂ gas displayed a broad band at 1836 cm^{–1}, consistent with that observed for the B–H stretching frequencies in dihydridoborate complexes.^{12a}

Single crystals of **3** suitable for X-ray diffraction analysis were obtained by slowly concentrating a pentane solution of **3** under

H₂ (Figure 1). An important structural feature pertains to the position of Co, which deviates from the mean plane of the boron-containing five-membered ring by 0.56 Å and suggests the existence of unsymmetrical bridging hydrides.¹⁵ This argument is reinforced by the DFT-optimized structure of **3**, whose non-hydrogen framework is in excellent agreement with the solid-state structure (see SI), including an out-of-plane distance of 0.63 Å for Co. Geometry optimizations performed on the other isomers indicate that **A** and **B** are 1.51 and 6.51 kcal/mol, respectively, uphill in enthalpy from **D** (a global minimum could not be found for isomer **C**; see SI). Taken together with the NMR and IR spectroscopic data, these results confirm the identity of **3** as an η²:η²-dihydridoborato cobalt dihydride complex (**D**).

The bonding in dihydridoborate complexes can be illustrated on the basis of three different Lewis representations (Figure 3).¹⁶ Our studies indicate that **3** bears a significant contribution

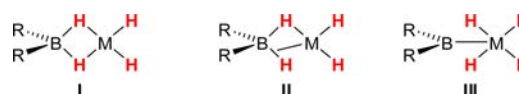


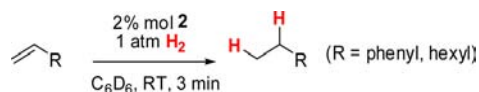
Figure 3. Three different valence bond descriptions for dihydridoborate complexes.

from form **II**. Indeed, the Co–B/B–H bond distances in **3** (Co–B(exp), 1.908(av.) Å; B–H(calc), 1.41, 1.58 Å) are significantly shorter/longer, respectively, than those observed for Co-(μ₂-H)₂-BH₂ complexes (form **I**: Co–B, 2.136–2.211 Å; B–(μ₂-H), 1.27–1.38 Å).¹⁷ Further, the Co–B distance in **3** is slightly shorter than for the Co–B distance in **2**, where no bridging hydrides are present. Perhaps conformational constraints of the phosphine ligand, combined with the difference between the terminal ligands in the two complexes, accounts for the small and unexpected direction of the difference.

While subjecting a solution of **3** to a few freeze–pump–thaw cycles did not induce a noticeable change in the ¹H NMR spectrum of **3**, exposure to 1 atm N₂ cleanly and rapidly regenerated **2**. The conversion from **3** to **2** can be conveniently monitored by NMR and IR spectroscopies (see SI). Reversible addition of 2 equiv of H₂ to a single Co site appears to be unique, highlighting the value of the Co–boryl subunit for H₂ activation chemistry. Heinekey recently obtained NMR/theoretical evidence for 2 equiv of H₂ ligating to a (POCOP)Co fragment under 75 psi H₂ at 190 K (POCOP = bisphosphino-phenyl).¹⁸ The product, (POCOP)Co(H)₂(H₂), decomposed above 220 K.

The ability of **2** to serve as an olefin hydrogenation catalyst was tested as follows. Introducing 1 atm H₂ by one freeze–pump–thaw cycle to a C₆D₆ solution of 1-octene (or styrene) and **2** (5% mol) led to an immediate color change from blue to yellow. The ¹H NMR spectrum of the resulting solution indicated the formation of **3** and octane (or ethylbenzene). The catalysis can be achieved with 2% mol loading of **2** over a period of 3 min, corresponding to a turnover frequency (TOF) of 1000/h (Scheme 2). The quantitative formation of octane

Scheme 2. Catalytic Olefin Hydrogenation



(97%) and ethylbenzene (100%) was established by ^1H and ^{13}C NMR spectroscopies as well as GC analyses (see SI). These reactions proceeded similarly in the presence of elemental Hg.

Homogenous olefin hydrogenation catalysts are rare for Co.¹⁹ Hanson recently showed the hydrogenation of styrene by ($^{\text{Cy}}\text{PNP}$)CoR (R = CH_2SiMe_3)^{19d} under similar conditions (TOF = 25/h, Table 1). By comparison, complex **2** operates at

Table 1. Hydrogenation of Styrene with H_2

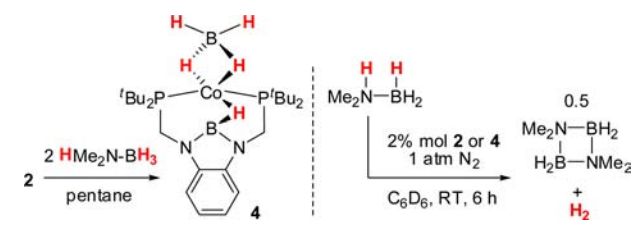
catalyst	TOF (h^{-1})	catalyst	TOF (h^{-1})
2	1000 ^b	($^{\text{Mes}}\text{DPB}^{\text{Ph}}$)Ni	20 ^d
($^{\text{Cy}}\text{PNP}$)CoR	25 ^b	($^{\text{iPr}}\text{TPB}$)Fe(N_2)	0.27 ^c
($^{\text{iPr}}\text{PDI}$)Fe(N_2) ₂	1344 ^a	(PPh_3) ₃ RhCl	100 ^b

Conditions: RT, 1 atm H_2 , organic solvents. Catalyst loading: ^a0.3% mol; ^b2% mol; ^c3.3% mol; ^d5% mol. PNP = bis-phosphino-amido; PDI = pyridyl-diimine; DPB = bis-phosphino-borane; TPB = tris-phosphino-borane.

a higher rate. Unlike Hanson's systems,^{19d,e} however, **2** cannot catalyze the hydrogenation of internal olefins such as *cis*-cyclooctene, presumably due to the presence of bulkier phosphorus substituents in **2**. For styrene hydrogenation (Table 1), **2** is also faster than (PPh_3)₃RhCl (see SI), ($^{\text{Mes}}\text{DPB}^{\text{Ph}}$)Ni,^{2b} ($^{\text{iPr}}\text{TPB}$)Fe(N_2),^{2c} and is similar to ($^{\text{iPr}}\text{PDI}$)Fe(N_2)₂,²⁰ which features a redox active ligand.

Amine-boranes have attracted much attention as hydrogen storage/transfer materials.²¹ However, homogeneous dehydrocoupling reactions of amine-boranes catalyzed by earth-abundant first-row metals are limited (Ti,²² Fe,²³ and Ni²⁴). Reaction of **2** with $\text{HMe}_2\text{N}-\text{BH}_3$ in a 1:2 stoichiometry resulted in the quantitative formation of a hydridoborane cobalt tetrahydridoborate complex (**4**) (Scheme 3). Complex **4** is

Scheme 3. Synthesis of **4 and Catalytic Amine-Borane Dehydrogenation**



characterized by a ^{31}P resonance at 103.3 ppm as well as two ^{11}B resonances at 40.4 and 5.7 ppm in a 1:1 ratio. The presence of a bridging hydride and an $\eta^2\text{-BH}_4$ ligand is established by ^1H , $^1\text{H}\{^{11}\text{B}\}$, and $^1\text{H}-^1\text{H}$ NOESY NMR spectra (see SI). Consequently, the IR spectrum of **4** exhibits bands corresponding to B-H stretches (2422, 2342, 1959, 1901, and 1786 cm^{-1}). The structure of **4** was confirmed by X-ray crystallography (Figure 4) and DFT calculations, revealing short Co-B1 (exp 1.9077(15) Å vs calc 1.921 Å) and long Co-B2 contacts (exp 2.1308(17) Å vs calc 2.130 Å).

Encouraged by these results and the equilibrium that exists between **2** and **4** in the presence of excess Et_3N (see SI), $\text{HMe}_2\text{N}-\text{BH}_3$ was allowed to stir in C_6D_6 with 2% mol of **2** or **4** under N_2 (Scheme 3). As evidenced by the ^{11}B NMR spectra (see SI), $\text{HMe}_2\text{N}-\text{BH}_3$ was initially dehydrogenated to form a linear product ($\text{HMe}_2\text{N}-\text{BH}_2-\text{Me}_2\text{N}-\text{BH}_3$), then fully converted into ($\text{Me}_2\text{N}-\text{BH}_2$)₂ in 6 h (TOF \approx 8/h, Figure 4).²⁵ The reaction was again not inhibited by Hg. Complex **2**

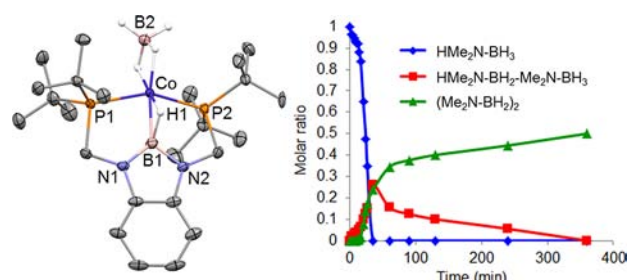


Figure 4. Left: Solid-state structure of **4**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except for the boron-bound hydrides, are omitted for clarity. Selected bond lengths (Å): Co-B1 1.9077(15), Co-B2 2.1308(17). Right: Plot of molar ratio against reaction time for $\text{HMe}_2\text{N}-\text{BH}_3$ dehydrogenation.

constitutes a rare example of a homogeneous Co catalyst for amine-borane dehydrogenation.²⁶ Based on the observation that **2** can catalyze both olefin hydrogenation and amine-borane dehydrogenation, we examined the possibility of a transfer hydrogenation reaction.^{21b} To this end, equal amounts of styrene and $\text{HMe}_2\text{N}-\text{BH}_3$ were stirred in C_6D_6 at 25 °C with 2 mol% of **2** under N_2 . After 24 h, styrene was hydrogenated to ethylbenzene quantitatively, alongside the dehydrogenation of $\text{HMe}_2\text{N}-\text{BH}_3$ to ($\text{Me}_2\text{N}-\text{BH}_2$)₂ (see SI). Control experiments carried out in the absence of **2** showed no reactivity.

In conclusion, we have demonstrated reversible double H_2 addition across a cobalt-boryl linkage. An unusual facet of the present system originates from the ability of the cobalt-boryl subunit to take up and release hydrogen atoms by accommodating cobalt-boryl (**2**), -dihydridoborate (**3**), and -hydridoborane (**4**) configurations. In turn, this enables the cobalt-boryl subunit to promote multielectron catalysis. This has been demonstrated in the present study via (1) efficient catalytic olefin hydrogenation and (2) amine-borane dehydrogenation/transfer hydrogenation catalysis.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental procedures, characterizations, crystallographic analyses, and computational data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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(14) These studies also indicate that the hydride ligands are rapidly exchanging with free H₂. The peak corresponding to free H₂ is only observed below –50 °C. Higher pressure VT-NMR experiments (4 atm H₂ or HD) produced similar results (see SI).

(15) Complex **3** crystallizes in P₂₁2₁2₁ space group with four independent molecules in an asymmetric unit (see SI). Although the exact positions of the hydrogen atoms cannot be reliably located on the difference map, residual positive electron density around Co can be observed.

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