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Conformational control of nonplanar free base porphyrins: towards bifunctional catalysts of tunable basicity

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COMMUNICATION

Reversible dehydrogenation of a primary aryl borane†‡

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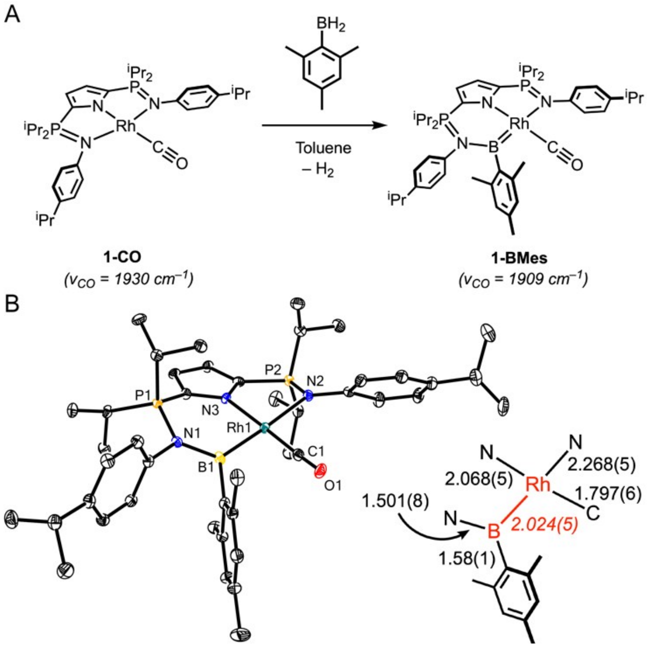
The consecutive activation of B–H bonds in mesitylborane (H_2BMes; Mes = 2,4,6-$(CH_3)_3C_6H_2$) by a 16-electron rhodium(I) monocarbonyl complex, (^{iPr}NNN)Rh(CO) (1-CO; ^{iPr}NNN = 2,5-[$^{i}Pr_2P{=}N(4\text{-}^{i}PrC_6H_4)]_2N(C_4H_2)^-$) is described. Dehydrogenative extrusion of the {BMes} fragment led to the isolation of (^{iPr}NNN)(CO)RhBMes (1-BMes). Addition of H_2 gas to 1-BMes regenerated 1-CO and H_2BMes, highlighting the ability of 1-CO to faciliate interconversion of {BMes} with dihydrogen. Reactivity studies revealed that 1-BMes is capable of promoting formal group transfer and that {BAr} fragments accessed by dehydrogenation are reactive entities.

Metal-catalyzed hydroboration and C–H borylation are powerful methods for the conversion of feedstock hydrocarbons into value-added chemicals.[1] Oxidative addition of a borane B–H bond to an electron-rich metal centre is well-precedented for a variety of secondary boron electrophiles (*e.g.* 9-borabicyclo[3.3.1]nonane, pinacol-, catechol-, and dialkylboranes).[2] Conversely, reactions between transition metal complexes and dihydroboranes (H_2BR) wherein consecutive B–H activation removes both hydrogen atoms from boron are exceedingly rare.[3] To this end, aryl dihydroboranes (H_2BAr) have been leveraged in the isolation of terminal borylene complexes following a dehydrogenative pathway described by Alcaraz and Sabo-Etienne.[4] Aldridge and co-workers have shown that amino-boryl complexes (*e.g.* $L_nM\{B(H)NR_2\}$; R = ^{i}Pr, Cy), formed by B–H oxidative addition of aminodihydroboranes (H_2BNR_2), can undergo boron-to-metal α-hydride migration to produce metal borylenes.[5]

An inherent challenge involved in removing dihydrogen from dihydroboranes using well-defined transition metal complexes is the potential for hydride ligands to interact with boron, thereby stabilizing the resulting borylene fragment.[4e] Borylene extrusion by reversible and consecutive B–H activation is therefore complicated by the fidelity of B···H interactions in transition metal systems that contain hydride ligands.[6] The development of thermal- and photo-driven intermetallic borylene transfer from $[(CO)_5M{=}B{=}N(SiMe_3)_2]$ (M = Cr, Mo, W) to metal carbonyl complexes (*e.g.* $CpM(CO)_n$; M = V, Re, Co, Rh, and Ir) overcomes the issues involved in consecutive B–H activation of dihydroboranes.[7] Thus, complementary routes that leverage reversible dehydrogenation in the formation of unsupported metal–boron bonds are of interest, as such species provide access to reactive alkyl and aryl {BR} fragments sourced directly from H_2BR.



Scheme 1 (A) Formation of **1-BMes**. (B) Solid state molecular structure of **1-BMes** with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity; selected metrical data shown.

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†Dedicated to the memory of Prof. Suning Wang.

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Using strongly-donating phosphinimine ligands, our group has demonstrated straightforward dehydrogenation of primary and secondary silanes at a mononuclear rhodium(I) centre leading to the isolation of stable rhodium(I) silylenes (^{iPr}NNN)(CO)RhSiRPh (R = H, Ph).[8] Encouraged by these results, we sought to extend this reactivity in a conceptually-diagonal approach that combined an electron-rich rhodium(I) complex (^{iPr}NNN)Rh(CO) (**1-CO**) with primary aryl boranes to promote similar dehydrogenative reactivity.

Analysis by ^{1}H and ^{31}P NMR spectra revealed that treatment of **1-CO** with 1 equivalent of mesitylborane (H_2BMes) in benzene-d_6 gave a mixture of unreacted **1-CO**, hydrogen gas, and a new, unsymmetrical product (Scheme 1A). When the reaction was carried out in toluene, recrystallization from Et_2O at –35 °C provided a bright yellow crystalline solid ((^{iPr}NNN)(CO)RhBMes, **1-BMes**) in 22% yield. X-ray diffraction studies on single crystals of **1-BMes** revealed a 4-coordinate rhodium centre bearing a {BMes} fragment stabilized by a phosphinimine nitrogen (Scheme 1B). The geometry at the 3-coordinate boron centre (Σ_{angles} = 359.8 °) is trigonal planar with mesityl *o*-CH_3 groups occupying the axial space above and below the equatorial plane defined by the phosphinimine nitrogen, mesityl *ipso*-carbon, and rhodium centre. The rhodium-boron distance in **1-BMes** is 2.024(5) Å]. In benzene-d_6, **1-BMes** features a broad ^{11}B resonance at δ 32.6 ($\omega_{1/2}$ = 457 Hz), upfield compared to known rhodium aminoborylene complexes (δ 75 to 120),[9,10] suggesting that π-donation from nitrogen to boron in **1-BMes** effectively shields the ^{11}B nucleus. Moreover, the chemical shift in **1-BMes** closely resembles those reported for platinum iminoboryl complexes.[11]

The gas-phase structure of **1-BMes** was optimized at the B3LYP/aug-cc-pVDZ level of theory with associated pseudopotentials for Rh (see SI for details). Metrical parameters were reproduced in good agreement with experiment (see SI for details). Natural bond orbital (NBO) analysis was performed on the optimized structure of **1-BMes** to better guide our understanding of the orbital interactions between rhodium, boron, and nitrogen. The B–Rh σ-bonding NBO (Figure S26) is slightly polarized toward boron, suggesting a bonding model in which boron-to-rhodium σ-donation is the predominant interaction. Infrared (IR) spectroscopic analysis of **1-CO** (1930 cm^{-1}) and **1-BMes** (1909 cm^{-1}) revealed a redshift of the ν_{CO} stretch as a result of borylene formation, emphasizing the σ-donor ability of borylene relative to phosphinimine. The B–Rh Wiberg bond index (WBI) of 0.93 falls slightly below the range established for terminal neutral borylene complexes of Co, Rh, and Ir [(η^5-C_5H_5)(L)M=BNX_2); L = CO, PMe$_3$, X = Me, SiH$_3$, SiMe$_3$] (0.97-1.33).[12] Second order perturbation analysis indicated strong delocalization of the Lewis-type nitrogen lone pair donor orbital, N(lp), into a vacant acceptor orbital on boron, B(p) (Figure 1B). Notably, the N(lp)→B(p) interaction [$E^{(2)}$: 35.2 kcal mol^{-1}] is greater than the donor-acceptor π-interaction between rhodium and boron [$E^{(2)}$: 10.3 kcal mol^{-1}]. These data imply that both phosphinimine π-donation, along with Rh-backdonation, are important in stabilizing the acceptor p-type orbital on boron, and that **1-BMes** has characteristics of both a rhodium borylene and iminoboryl, with the former representation drawn for clarity (Figure 1).

Recognizing that the synthesis of **1-BMes** via dehydrogenation resulted in poor yields, we reasoned that the product could react with evolved hydrogen gas to establish an equilibrium mixture with **1-CO** and H_2BMes. To better understand the reversibility of this process, a 1:1 mixture of H_2BMes and D_2BMes (1 total equivalent of borane) was combined with **1-CO** in benzene-d_6. Monitoring product speciation by ^{31}P NMR spectroscopy after short reaction times revealed **1-CO**, **1-BMes**, and an unsymmetrical intermediate (*vide infra*). Both H_2 and HD gas were identified in the ^{1}H NMR spectrum (Figure S18). Isotope mixing supports the presence of a reactive boryl hydride species,[5,13] capable of rapid Rh–H(D) and B–D(H) exchange at a rate that is competitive with the formation of **1-BMes**. The reaction between H_2BMes and D_2BMes in the absence of **1-CO** showed no sign of H/D scrambling or evolution of HD gas.

Monitoring the reaction of **1-CO** and H_2BMes by variable temperature NMR spectroscopy in toluene-d_8 at –40 °C led to the observation of ^{31}P resonances at δ 50.4 and δ 47.8, resembling the intermediate observed in reactions between **1-CO** and H_2BMes/D_2BMes (*vide supra*). The accompanying ^{1}H NMR spectrum revealed a broad resonance centered at δ –2.7.

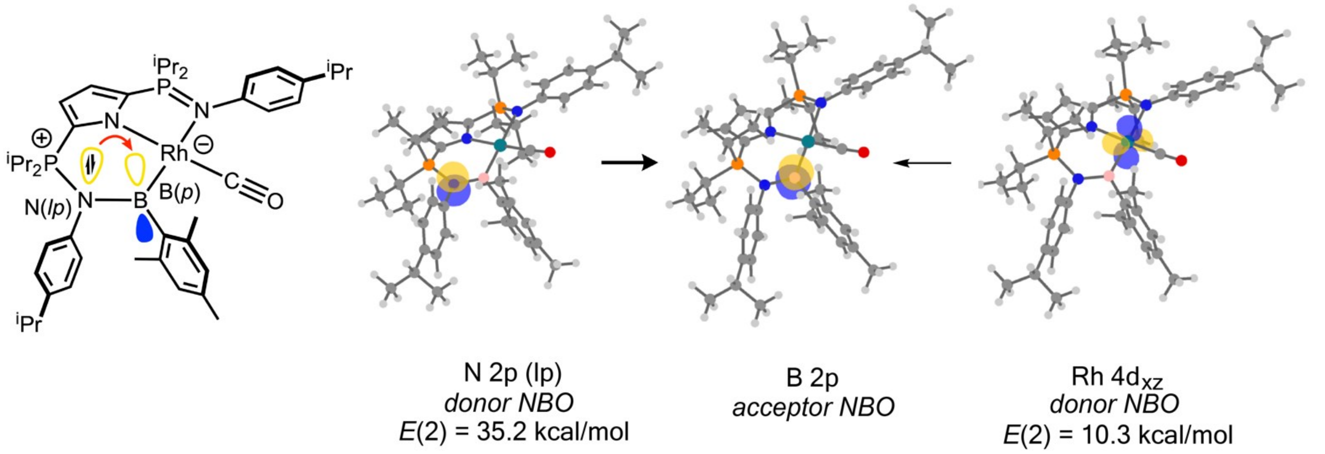

Fig. 1 Orbital interactions in **1-BMes** illustrating the extent of delocalization from N lone-pair and Rh-based donors toward the boron p-type acceptor NBO. Orbital surfaces plotted with an Isovalue of 0.08.

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Upon warming to 22 °C, ^{1}H and ^{31}P peaks corresponding to the intermediate species were consumed while those attributed to **1-BMes** grew in intensity. Notably, H_2 gas (δ 4.56) was visible in solution throughout the reaction. We propose that the intermediate species forms by dissociation of phosphinimine from rhodium, followed by coordination to the aryl dihydroborane to afford B–H agostic complex **1-CO·H$_2$BMes**. A B–H bond then undergoes oxidative addition, producing the Rh(III) boryl hydride species (^{iPr}NNN)(CO)Rh(H)(BHMes). Finally, H_2 loss presumably occurs *via* either a 4-centred transition state involving Rh–H (δ+) and hydridic B–H (δ–), or a Brønsted pathway mediated by a free phosphinimine group.[8]

In an effort to corroborate the reversibility of **1-BMes** formation, a J. Young NMR tube containing **1-BMes** in benzene-*d*$_6$ was pressurized with 4 atmospheres of H_2 and monitored by ^{1}H and ^{31}P NMR spectroscopy. Rapid regeneration of mesitylborane and formation of **1-CO** (>80% in 10 minutes) was confirmed by comparing the product of the reaction to authentic samples (Scheme 2). Examination of the ^{31}P NMR spectrum after 1 week showed that the equilibrium of **1-CO** + H_2BMes and **1-BMes** + H_2 was maintained under H_2 pressure (**1-BMes**:**1-CO** = 9:1). Hence, it was concluded that the poor yields obtained for reactions conducted at ambient temperature were likely the result of rapid hydrogen uptake by **1-BMes**, even under reduced pressure. Altering the original procedure by carrying out the reaction at low temperature (see SI for details) allowed the isolation of analytically pure **1-BMes** in substantially improved (53%) yield.[14] Rapid back-reactivity of **1-BMes** with dihydrogen encouraged us to explore other means of {BMes} group transfer. Addition of pinacol to a benzene-*d*$_6$ solution of **1-BMes** resulted in gradual formation of the boronate ester MesBpin and **1-CO**, along with H_2 gas. This proof-of-principle reaction demonstrates that a {BMes} fragment obtained through dehydrogenation of H_2BMes can undergo formal borylene transfer.[7]

The generality of aryl borane dehydrogenation was studied by reducing the steric profile about boron and altering the electronics of the aryl group. The trifluoromethylated borane H_2BAr^F (Ar^F = 3,5-$(CF_3)_2C_6H_3$) was combined with **1-CO** in benzene-*d*$_6$ leading to new ^{31}P NMR resonances at δ 51.2 and δ 48.8, which closely resemble the intermediate observed in the low temperature reactions between **1-CO** and mesitylborane (δ 50.4 and δ 47.8, *vide supra*), as well as those in the H/D scrambling experiments. In benzene-*d*$_6$, the ^{11}B NMR spectrum exhibits a single peak at δ –5.92 ($\omega_{1/2}$ = 11.1 Hz). In anticipation of unproductive back-reaction with H_2, the experiment was repeated at –30 °C in diethylether. A gradual colour change from orange to dark-yellow was accompanied by formation of a crystalline yellow solid which was isolated in 80% yield. Single crystals suitable for X-ray diffraction analysis were grown from a concentrated pentane/benzene (5:1) solution. The solid-state structure of the isolated product **1-CO·H$_2$BAr^F** was confirmed as a B–H agostic complex between **1-CO** and H_2BAr^F, stabilized by phosphinimine coordination to boron [N1–B1 = 1.558(2) Å] and a B–H agostic interaction [H1–Rh1 = 1.61(2) Å] with the Rh(I) centre (Figure 2A). Notably, **1-CO·H$_2$BAr^F** is a model complex for initiating dehydrogenation of aryl dihydroboranes at **1-CO**.

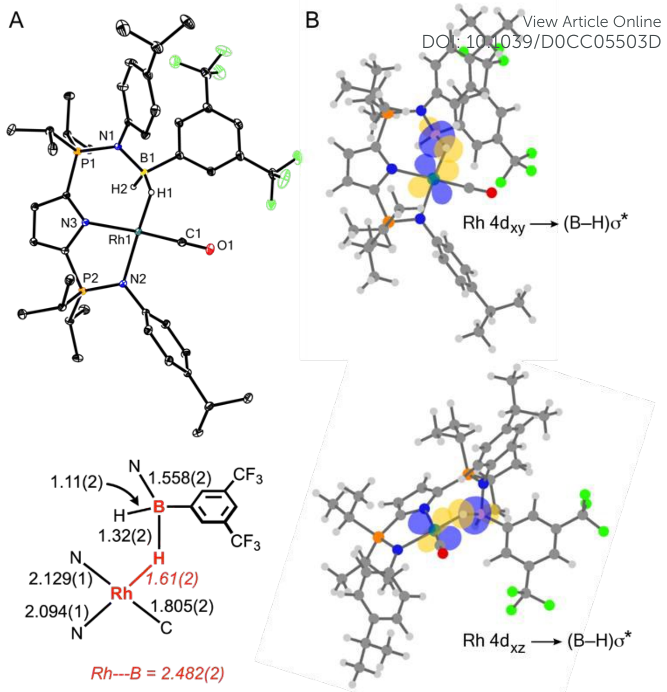
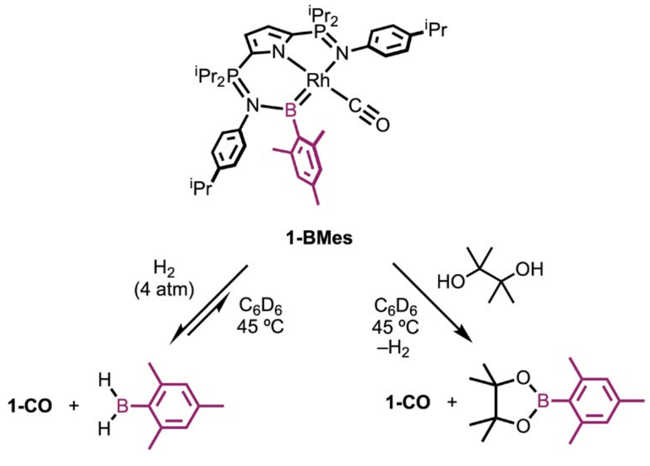


Fig. 2 (A) Molecular structure of **1-CO·H$_2$BAr^F** at 30% probability ellipsoids with H-atoms (except for *H*$_2$BAr^F) omitted for clarity. Principle metrical parameters shown. (B) Orbital interactions (NBOs) derived from second-order perturbation theory analysis. Orbital surfaces plotted with an isovalue of 0.08.



Scheme 2 Reactivity of **1-BMes** with H_2 and pinacol.

Second-order perturbation analysis of **1-CO·H$_2$BAr^F** show delocalization interactions between Rh 4d$_{xy}$/4d$_{xz}$ and (B–H)σ* orbitals (Figure 2B). Back-donation from Rh to B through the B–H agostic bridge is consistent with the IR spectroscopic data that shows a strong ν_{CO} stretching frequency (1950 cm^{-1}), blue-shifted in the order **1-CO·H$_2$BAr^F** > **1-CO** > **1-BMes**. These data are consistent with Nakazawa's report that strong delocalization of electron density from Rh to B is facilitated by a Rh···H–B linkage.[15] At 23 °C, the ^{1}H NMR spectrum of **1-CO·H$_2$BAr^F** contains a broad resonance at δ –3.8, tentatively assigned to the two rapidly exchanging B*H*$_2$. Upon cooling a toluene-*d*$_8$ solution of **1-CO·H$_2$BAr^F** to –80 °C distinct resonances at δ 3.9 (B–*H*) and δ –9.8 (Rh–*H*–B) were observed. The two signals coalesce at –25 °C ($\Delta G^\ddagger$ = 9.9(4) kcal mol^{-1}), reappearing as the original broad resonance (δ –3.8) near 0 °C (Figure S21).

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Despite the attenuated steric profile of H$_2$BAr^F, no evidence for borylene formation was observed. The product of oxidative addition, a Rh(III) boryl hydride, is likely unstable to reductive elimination and reformation of **1-CO$\cdot$H$_2$BAr^F**. These observations are in line with a recent contribution from Braunschweig detailing the steric and electronic parameters associated with dehydrogenative borylene formation from Ru(PCy$_3$)$_2$HCl(H$_2$) and various dihydroboranes.[16] For spontaneous dehydrogenation to occur, aryl groups bearing *ortho*-substituents were required.

Without a viable pathway for release of H$_2$, and consequently, borylene formation, reaction progress appears to stall at **1-CO$\cdot$H$_2$BAr^F**. When a sample of **1-CO$\cdot$H$_2$BAr^F** was left at 23 °C in benzene-d_6 for 48 h, a gradual change in the ^{31}P NMR spectrum revealed a new unsymmetrical product with peaks located at δ 52.0 and δ 10.6. The latter resonance is diagnostic of a dissociated phosphinimine,[8] implying that the product features a κ^2-bound ^{iPr}NNN ligand scaffold. Examination of the corresponding IR spectrum revealed no distinguishable ν_{CO} stretching frequencies. Accordingly, the ^{13}C-labelled complex **1-^{13}CO$\cdot$H$_2$BAr^F** was prepared using **1-^{13}CO**. The ^{13}C NMR spectrum of **1-^{13}CO$\cdot$H$_2$BAr^F** in benzene-d_6 exhibited a doublet ($^1J_{CRh}$ = 73.4 Hz) centered at δ 190.6 which disappeared after 12 h at 23 °C. The ^{13}C label was not identified in any by-products, so it is reasonable to conclude that direct ^{13}CO elimination from **1-^{13}CO$\cdot$H$_2$BAr^F** occurred. While spontaneous CO elimination from square-planar Rh(I) is rare, Nakazawa showed that a B–H–Rh linkage can destabilize π-back-donation from Rh(I) to CO.[15]

For the first time the reversible dehydrogenation of an aryl dihydroborane has been observed at rhodium. Complexation of H$_2$BMes by a hemilabile phosphinimine led to spontaneous H$_2$ loss, highlighting the importance of the ^{iPr}NNN ligand in promoting cooperative reactivity. Group transfer of the {BMes} fragment was observed in reactions with H$_2$ and pinacol, where the latter generated the boronate ester MesBpin, along with H$_2$ gas. Entrapment of the electron-deficient borane H$_2$B(3,5-(CF$_3$)$_2$C$_6$H$_3$) by **1-CO** highlights that subtle steric and electronic factors are involved in spontaneous dehydrogenation. Ultimately, with the demonstration of formal borylene transfer, these results provide a method for interconversion of boranes and borylenes with hydrogen, from which new and more efficient routes to organoboranes are being explored.

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Conflicts of interest

There are no conflicts to declare.

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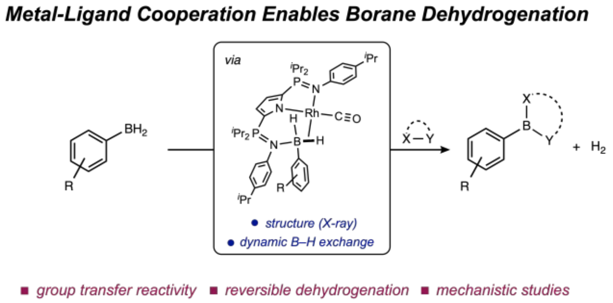

A rhodium carbonyl complex facilitates the reversible dehydrogenation of a primary aryl borane leading to a reactive rhodium borylene capable of engaging in group transfer reactivity.