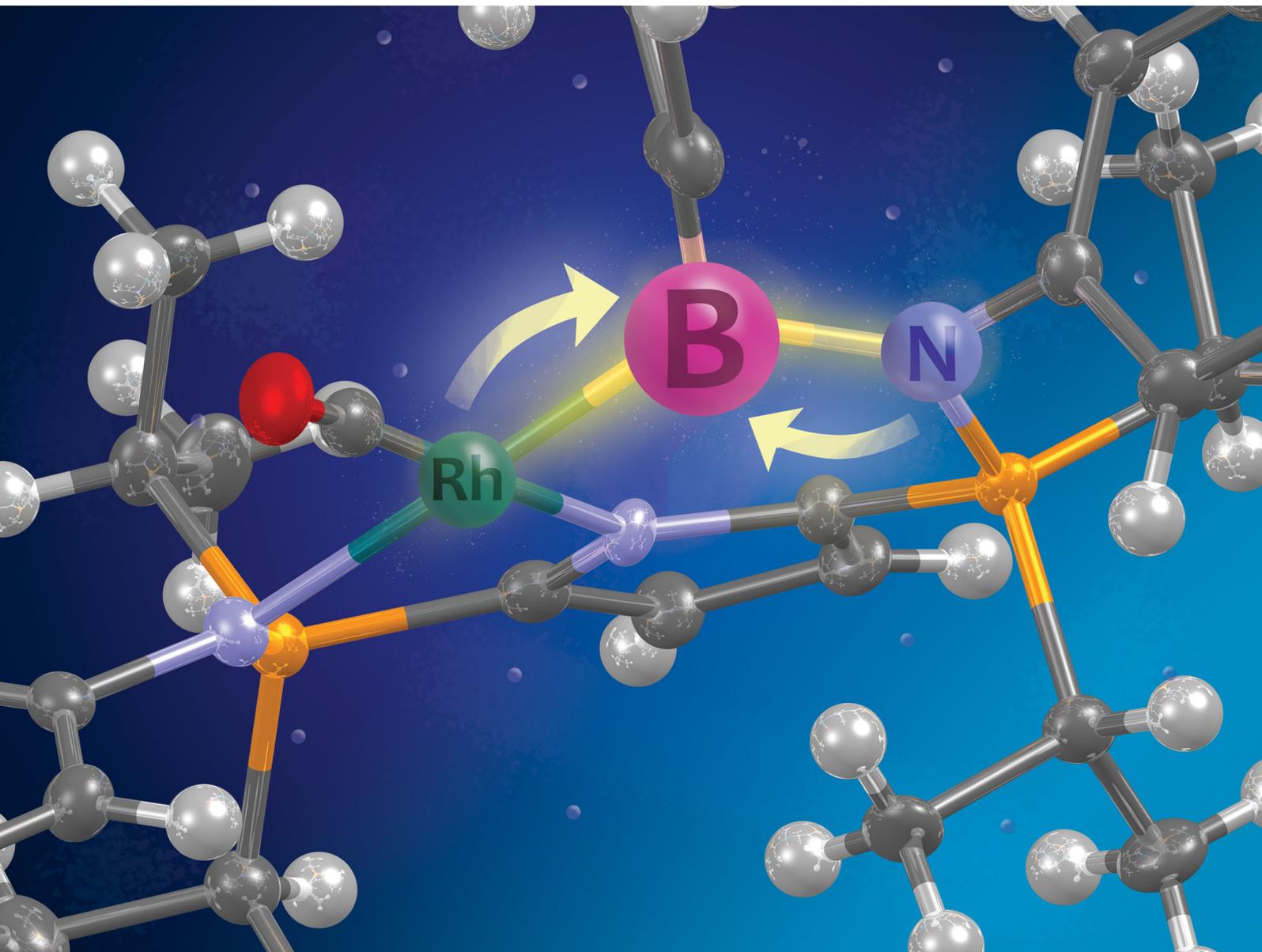


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Reversible dehydrogenation of a primary aryl borane†‡

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The consecutive activation of B–H bonds in mesitylborane (H_2BMe_3 ; Mes = 2,4,6- $(CH_3)_3C_6H_2$) by a 16-electron rhodium(i) monocarbonyl complex, $(iPrNNN)Rh(CO)$ (**1-CO**; $iPrNNN$ = 2,5- $[Pr_2P=N(4-*i*PrC_6H_4)]_2-N(C_4H_2)^-$) is described. Dehydrogenative extrusion of the {BMe₃} fragment led to the isolation of $(iPrNNN)(CO)RhBMe_3$ (**1-BMe₃**). Addition of H_2 gas to **1-BMe₃** regenerated **1-CO** and H_2BMe_3 , highlighting the ability of **1-CO** to facilitate interconversion of {BMe₃} with dihydrogen. Reactivity studies revealed that **1-BMe₃** promotes 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 .

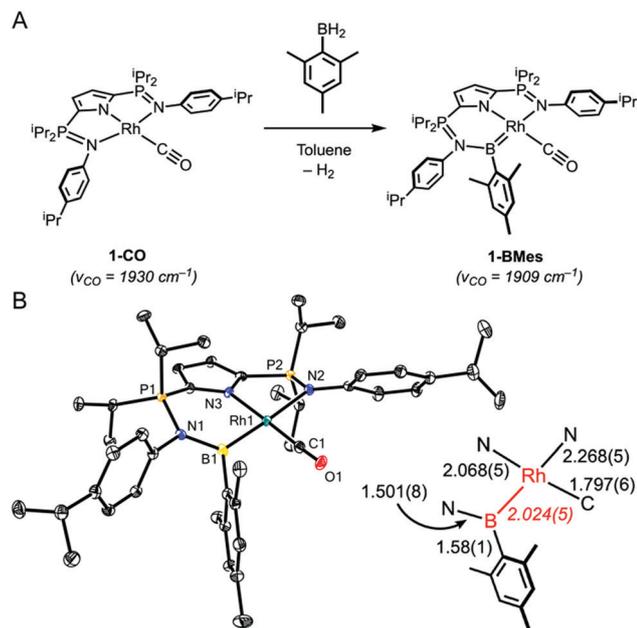
Using strongly-donating phosphinimine ligands, our group has demonstrated straightforward dehydrogenation of primary and secondary silanes at a mononuclear rhodium(i) centre leading to the isolation of stable rhodium(i) silylenes $(iPrNNN)(CO)RhSiRPh$ (R = H, Ph).⁸ Encouraged by these results, we sought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

Analysis by 1H and ^{31}P NMR spectra revealed that treatment of **1-CO** with 1 equivalent of mesitylborane (H_2BMe_3) 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 ($(iPrNNN)(CO)RhBMe_3$, **1-BMe₃**) in 22% yield. X-ray diffraction studies on single crystals of **1-BMe₃** revealed a 4-coordinate rhodium centre bearing a {BMe₃} fragment stabilized by a phosphinimine nitrogen (Scheme 1B). The geometry at the 3-coordinate boron centre ($\Sigma_{angles} = 359.8^\circ$) is trigonal planar with mesityl *o*-CH₃ 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-BMe₃** is $[2.024(5) \text{ \AA}]$. In benzene- d_6 , **1-BMe₃** 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

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† Dedicated to the memory of Prof. Suning Wang.

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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.

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 pseudo-potentials for Rh (see ESI,† for details). Metrical parameters were reproduced in good agreement with experiment (see ESI,† 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 (Fig. S26, ESI,†) 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 [$(\eta^5\text{-C}_5\text{H}_5)(\text{L})(\text{M}=\text{BNX}_2)$; L = CO, PMe_3 , X = Me, SiH_3 , SiMe_3] ($0.97\text{--}1.33$).¹² Second order perturbation analysis indicated strong delocalization of the Lewis-type nitrogen lone pair donor orbital, $\text{N}(\text{lp})$, into a vacant acceptor orbital on boron, $\text{B}(\text{p})$ (Fig. 1). Notably, the $\text{N}(\text{lp}) \rightarrow \text{B}(\text{p})$ interaction [$E^{(2)}: 35.2\text{ kcal mol}^{-1}$] is greater than the donor–acceptor π -interaction between rhodium and boron [$E^{(2)}: 10.3\text{ kcal mol}^{-1}$]. 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 (Fig. 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_2BMe_2 . To better understand the reversibility of this process, a 1:1 mixture of H_2BMe_2 and D_2BMe_2 (1 total equivalent of borane) was combined with **1-CO** in benzene- d_6 . Monitoring product speciation by ^{31}P NMR spectroscopy revealed **1-CO**, **1-BMes**, and an unsymmetrical intermediate (*vide infra*). Both H_2 and HD gas were identified in the ^1H NMR spectrum (Fig. S18, ESI,†). 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_2BMe_2 and D_2BMe_2 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_2BMe_2 by variable temperature NMR spectroscopy in toluene- d_8 at $-40\text{ }^\circ\text{C}$ led to the observation of ^{31}P resonances at $\delta 50.4$ and $\delta 47.8$, resembling the intermediate observed in reactions between **1-CO** and $\text{H}_2\text{BMe}_2/\text{D}_2\text{BMe}_2$ (*vide supra*). The accompanying ^1H NMR spectrum revealed a broad resonance centered at $\delta -2.7$. Upon warming

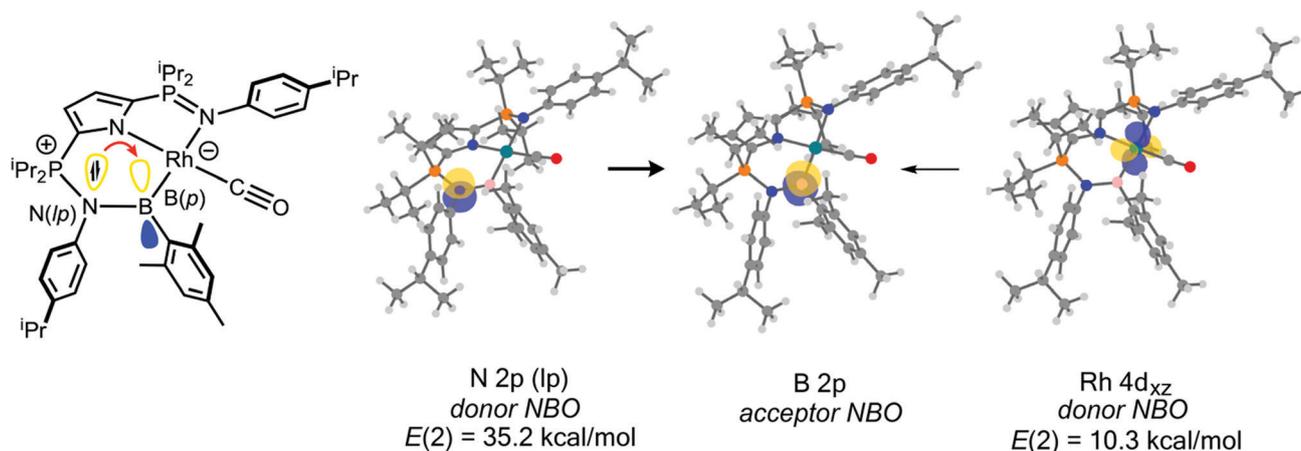
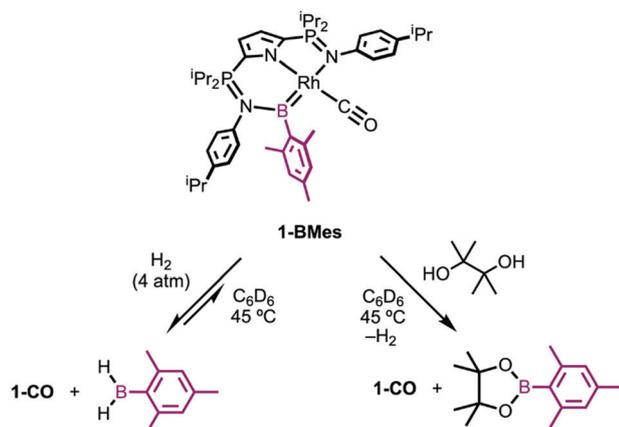


Fig. 1 Orbital interactions in **1-BMes** illustrating the extent of delocalization from N lone-pair and Rh-based donors toward the boron p-type acceptor NBO. Orbital surfaces plotted with an isovalue of 0.08.

to 22 °C, ^1H 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 phosphininime from rhodium, followed by coordination to the aryl dihydroborane to afford B–H agostic complex **1-CO-H₂BMes**. A B–H bond then undergoes oxidative addition, producing the Rh(III) boryl hydride species ($^{\text{iPr}}\text{NNN}$)(-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 phosphininime 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 ^1H 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 ESI† 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 $\text{H}_2\text{BAR}^{\text{F}}$ ($\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$) was combined with **1-CO** in benzene- d_6 leading to new ^{31}P NMR resonances at δ 51.2 and



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

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-H₂BAR^F** was confirmed as a B–H agostic complex between **1-CO** and $\text{H}_2\text{BAR}^{\text{F}}$, stabilized by phosphininime 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 (Fig. 2A). Notably, **1-CO-H₂BAR^F** is a model complex for initiating dehydrogenation of aryl dihydroboranes at **1-CO**.

Second-order perturbation analysis of **1-CO-H₂BAR^F** show delocalization interactions between Rh $4d_{xy}/4d_{xz}$ and (B–H) σ^* orbitals (Fig. 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-H₂BAR^F** > **1-CO** > **1-BMes**. These data are consistent with Nakazawa's report that delocalization of electron density from Rh to B is facilitated by a Rh...H–B linkage.¹⁵ At 23 °C, the ^1H NMR spectrum of **1-CO-H₂BAR^F** contains a broad resonance at δ -3.8, tentatively assigned to

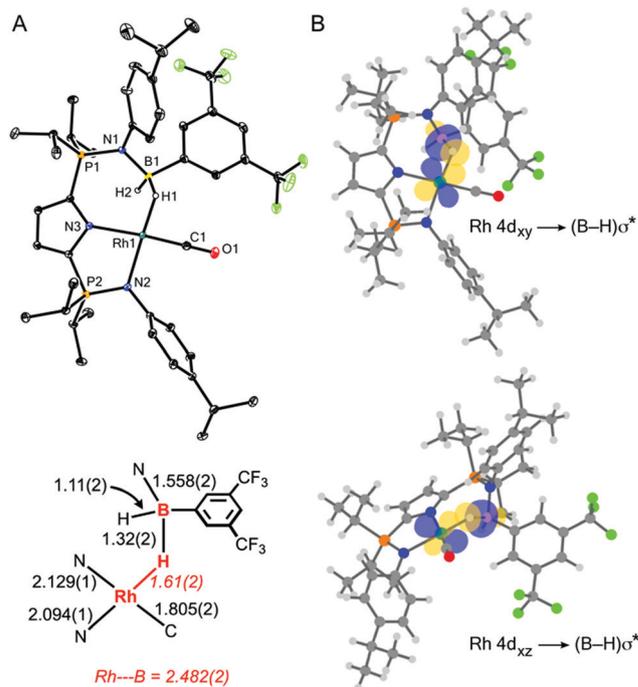


Fig. 2 (A) Molecular structure of **1-CO-H₂BAR^F** at 30% probability ellipsoids with H-atoms (except for $\text{H}_2\text{BAR}^{\text{F}}$) omitted for clarity. Principle metrical parameters shown. (B) Orbital interactions (NBOs) derived from second-order perturbation theory analysis. Orbital surfaces plotted with an isovalue of 0.08.

the two rapidly exchanging BH_2 . Upon cooling a toluene- d_8 solution of $1-CO-H_2BAR^F$ to $-80\text{ }^\circ\text{C}$ distinct resonances at δ 3.9 (B-H) and δ -9.8 (Rh-H-B) were observed. The two signals coalesce at $-25\text{ }^\circ\text{C}$ ($\Delta G^\ddagger = 9.9(4)\text{ kcal mol}^{-1}$), reappearing as the original broad resonance (δ -3.8) near $0\text{ }^\circ\text{C}$ (Fig. S21, ESI ‡).

Despite the attenuated steric profile of H_2BAR^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 $1-CO-H_2BAR^F$. These observations are in line with a recent contribution from Braunschweig detailing the steric and electronic parameters associated with dehydrogenative borylene formation from $Ru(PCy_3)_2HCl(H_2)$ and various dihydroboranes.¹⁶ For spontaneous dehydrogenation, 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 $1-CO-H_2BAR^F$. When a sample of $1-CO-H_2BAR^F$ was left at $23\text{ }^\circ\text{C}$ 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 $1-^{13}\text{CO-H}_2BAR^F$ was prepared using $1-^{13}\text{CO}$. The ^{13}C NMR spectrum of $1-^{13}\text{CO-H}_2BAR^F$ in benzene- d_6 exhibited a doublet ($J_{CRh} = 73.4\text{ Hz}$) centered at δ 190.6 which disappeared after 12 h at $23\text{ }^\circ\text{C}$. The ^{13}C label was not identified in any by-products, so it is reasonable to conclude that direct ^{13}CO elimination from $1-^{13}\text{CO-H}_2BAR^F$ 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_2BMe_3 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 $H_2B(3,5-(CF_3)_2C_6H_3)$ 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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