

# Sequential Migrations between Boron and Rhodium Centres: A Cooperative Process between Rhodium and a Mono-Substituted Borohydride Unit

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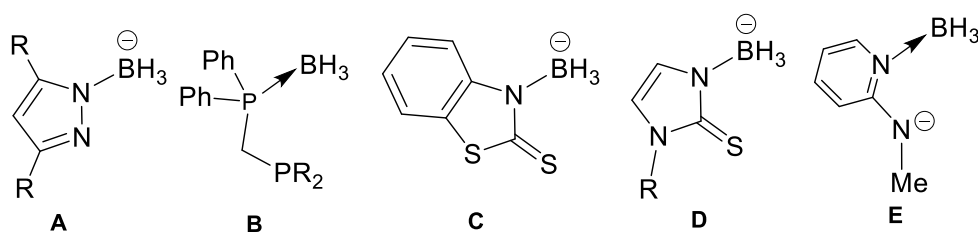
The sodium salt of a mono-substituted borohydride anion containing a 2-mercaptopyridyl unit (mp) is reported herein. This compound has been coordinated to a rhodium(I) center providing the complex,  $[\text{Rh}\{\kappa^3\text{-}H,H,S\text{-}H_3\text{B}(\text{mp})\}(\text{NBD})]$  (**1**) (where NBD = 2,5-norbornadiene) in which the boron based ligand is coordinated to the rhodium center via the thione donor and two of the B–H bonds of the  $\text{BH}_3$  unit. Reaction of complex **1** with carbon monoxide results in the activation of the complex leading to the product of a formal intramolecular hydroboration reaction where the NBD unit has, in effect, inserted into one of the B–H bonds. Three complexes have been prepared in which the newly formed norbornenyl unit (nbe) is located at the boron center,  $[\text{Rh}\{\kappa^3\text{-}H,H,S\text{-}H_2\text{B}(\text{nbe})(\text{mp})\}(\text{CO})_2]$  (**2**),  $[\text{Rh}\{\kappa^3\text{-}H,H,S\text{-}H_2\text{B}(\text{nbe})(\text{mp})\}(\text{CO})(\text{PCy}_3)]$  (**3**) and  $[\text{Rh}\{\kappa^3\text{-}H,H,S\text{-}H_2\text{B}(\text{nbe})(\text{mp})\}(\text{CO})(\text{PPh}_3)]$  (**4**). The identities of the three complexes have been confirmed by spectroscopic and analytical techniques. Further confirmation has been obtained via structural

characterization of **3**. Studies have confirmed that the reactivity occurs at the metal center. A metal-ligand cooperative mechanism, involving initial migration of hydride from boron to metal center, has been postulated for the formation of the new complexes based on previous investigations. The newly formed norbornenyl unit then migrates from metal center to boron.

## Introduction

The coordination of various substituted borohydride functional groups to transition metal centers has been of great interest for many years now.<sup>1</sup> There has been a focus on mono-substituted BH<sub>3</sub> units (Figure 1).<sup>2-8,9a,b</sup> Those bearing nitrogen substituents have attracted particular attention as a means of understanding the interactions necessary for transformations such as the catalytic dehydrogenation of hydrogen rich materials, e.g. amino-boranes.<sup>9</sup> As highlighted in Figure 1, several heterocycles and supporting units have been utilized in order to hold BH<sub>3</sub> units in close proximity to a given transition metal center. For example, mono-substituted pyrazolylborate ligands (**A**), the rare analogues of Trofimenko's ubiquitous polypyrazolylborate ligands,<sup>1c,d</sup> have been coordinated to group 11 transition metals providing a handful of examples where one of the B–H bonds of the BH<sub>3</sub> unit interacts with the metal center.<sup>10</sup> In 2001, Weller reported a neutral ligand system (**B**; where R = Ph) featuring a borane adduct with 1,1-bis(diphenylphosphino)methane. This phosphine-borane ligand was coordinated to a rhodium forming [Rh(COD){κ<sup>3</sup>-*H,H,P*-PPh<sub>2</sub>CH<sub>2</sub>P(BH<sub>3</sub>)Ph<sub>2</sub>}] [PF<sub>6</sub>].<sup>2</sup> In this case, the solid state structure revealed a dihydroborate (κ<sup>2</sup>-H<sub>2</sub>B) mode of coordination to the rhodium center. NMR spectroscopy confirmed rapid exchange of the three B–H bonds in solution. Jugé and Gouygou later reported a related system based on a phospholyl(phosphinoborane)methane.<sup>3</sup> Ghosh has reported a series of compounds featuring the benzothiazol-2-ylidene heterocycle (**C**).<sup>4</sup> Within these examples, there

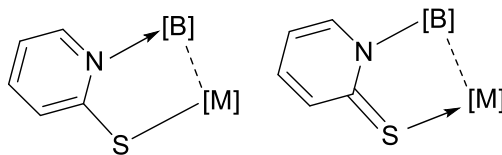
are complexes where the  $\text{BH}_3$  unit is bound with a  $\kappa^1\text{-HB}$  coordination mode and others with a  $\kappa^2\text{-H}_2\text{B}$  mode. Ghosh was the first to demonstrate hydroboration reactivity between a pre-coordinated  $\text{BH}_3$  group and alkynes.<sup>4f,g</sup> Such reactivity appears to occur via an intermolecular process rather than intramolecular. Santos also reported a similar ligand system based on the 2-mercapto-1-methylimidazolyl and related heterocycles (**D**).<sup>5</sup> Most recently, Cabeza reported the coordination of the anionic ligand formed via deprotonation of the adduct between 2-(methylamino)pyridine and borane (**E**) to rhodium(I) and iridium(I) metal centres.<sup>8</sup> Within the article, the ligand was described as a borane adduct of the 2-methylamidopyridine anion (as drawn in Figure 1; **E**).



**Figure 1.** Selected examples of heterocycles/supporting units which contain a donor atom capable of binding to a metal center thereby placing the  $\text{BH}_3$  group in close proximity to the metal. For the anionic examples, different descriptions are possible where the negative charge can be positioned either at boron or at the donor atom.

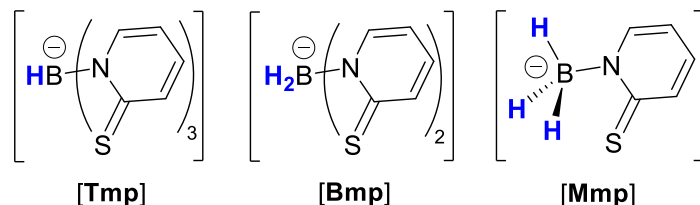
For some time now we have been interested in the 2-mercaptopyridine heterocycle as a supporting unit for complexes that contain metal–boron bonds.<sup>11-16</sup> One of the reasons why we have focused on this heterocycle is due to the potential for variation between the pyridine-2-thiolate and 2-thiopyridone forms as shown in Figure 2. Our studies have demonstrated that the dearomatized form is favored where the nitrogen binds to the boron center via an X-type

interaction. The corresponding aromatised form, would lead to an L-type interaction from pyridine to the boron center.



**Figure 2.** The respective L- and X-type interactions of the pyridine-2-thiolate and 2-thiopyridone forms with the boron center ([B] and [M] represent boron and metal centers containing other substituents which have been omitted for clarity).

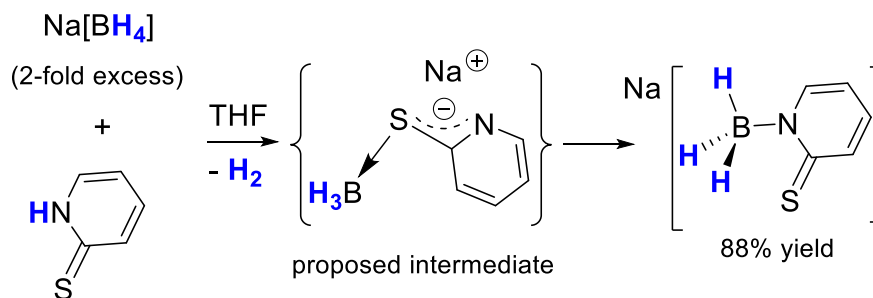
We previously reported the synthesis of borohydride salts substituted by two and three 2-mercaptopyridyl units (mp),  $\text{Na}[\text{H}_2\text{B}(\text{mp})_2]$  and  $\text{K}[\text{HB}(\text{mp})_3]$  (Figure 3).<sup>11,17</sup> The corresponding mono-substituted borohydride has not been reported. Indeed, such mono-substituted borohydrides which contain one tethered donor function unit are limited to the examples outlined in Figure 1. One reason for this is due to challenges in their synthesis. Targeting such ligands from borohydride salts can lead to overreaction resulting in multiple substitutions at boron. Despite this, we set out to synthesize this missing ligand and investigate its coordination to various metal centers with an aim to explore the reactivity of the primary substituted borohydride functional group. To the best of our knowledge, there have been no examples of a  $\text{BH}_3$  unit acting as a “hydride donor” to a transition metal center. During the course of our investigations we observed a novel transformation resulting from the formal intramolecular hydroboration of a norbornadiene unit to the borohydride unit. We therefore wish to report the synthesis of  $\text{Na}[\text{H}_3\text{B}(\text{mp})]$ , a series of complexes containing this borohydride based group and details of this novel transformation.



**Figure 3.** The mono-substituted borohydride ligand, [Mmp]<sup>-</sup>, as the new addition to the family of ligand precursors based on 2-mercaptopyridine heterocycles.

### Results and Discussion

The synthesis of mono-substituted borohydrides, containing various nitrogen containing heterocycles, are notorious for being challenging since they tend to overreact forming mixtures of borohydride (the precursor), the target mono-substituted product and the corresponding bis-substituted product.<sup>5,18,19</sup> Such mixtures are difficult to separate, particularly as the two latter components tend to have similar solubility properties. Several conditions were tested in order to find the optimum conditions for the synthesis of Na[H<sub>3</sub>B(mp)]. It was found that the borohydride salt could be obtained in excellent yield when the reaction was carried out in a twofold excess of Na[BH<sub>4</sub>] with respect to the heterocycle (Scheme 1).

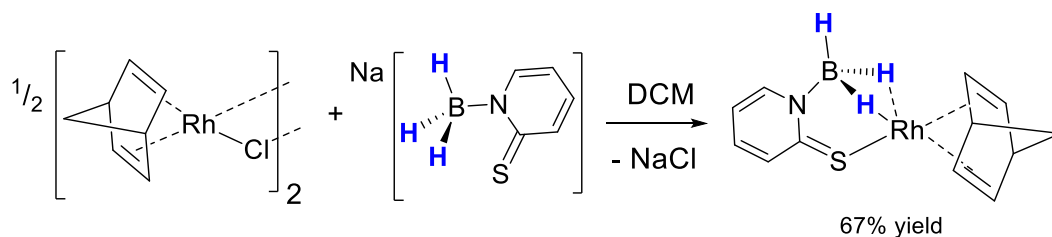


**Scheme 1.** Synthesis of Na[H<sub>3</sub>B(mp)], Na[Mmp]

In a typical reaction, the two solid reagents were placed in THF solvent at room temperature. It was evident that hydrogen gas was being generated as soon as the solvent was added to the mixture. The progress of the reaction was monitored by NMR spectroscopy. The  $^{11}\text{B}$  NMR spectrum of the mixture after 2 h indicated the presence of three boron containing species; unreacted  $[\text{BH}_4]^-$  ( $-43.4$  ppm, quintet), an intermediate species containing a  $[\text{BH}_3]^-$  group ( $-27.5$  ppm, quartet,  $^1J_{\text{BH}} = 93$  Hz) and the target product ( $-14.7$  ppm, quartet,  $^1J_{\text{BH}} = 93$  Hz), in a ratio of approximately 10%, 65%, and 25%, respectively. The corresponding  $^1\text{H}$  NMR spectrum at this time confirmed that all of the 2-mercaptopyridine had been consumed since the signal corresponding to the acidic proton at 12.8 ppm was absent. The  $^1\text{H}$  NMR spectrum also revealed the presence of two sets of signals corresponding to the aromatic protons of the mercaptopyridyl unit. The smaller set of signals (four chemical environments) was later confirmed as the target ligand,  $\text{Na}[\text{H}_3\text{B}(\text{mp})]$  (see experimental section). The larger set of signals corresponded to the intermediate species observed by  $^{11}\text{B}$  NMR. The intermediate species slowly converted into  $\text{Na}[\text{H}_3\text{B}(\text{mp})]$  over a total period of approximately 72 h. After this time only the excess borohydride and target ligand was observable in the NMR spectra of the reaction mixture. Despite the slow conversion, it was not possible to isolate the intermediate species. Based on spectroscopic evidence ( $^{11}\text{B}$  NMR;  $\delta -27.5$  ppm, quartet) obtained for the intermediate we believe that this species is as shown in Scheme 1 where the heterocycle has been deprotonated and the anionic form interacts with the sodium cation and the sulfur forms an adduct with the boron unit.<sup>20</sup> There are only a limited number of compounds featuring B–S bonds in which reported  $^{11}\text{B}$  NMR data is available. Those most closely related we found were,  $\text{Li}[\text{H}_3\text{B}(\text{SPh})]$  and  $\text{Na}[\text{H}_3\text{B}(\text{SPh})]$  which are reported as  $-26.8$  ppm and  $-22.5$  ppm, respectively.<sup>4d,21</sup> The target species, where the heterocycle is bound to the boron via the nitrogen

atom, was separated from the excess Na[BH<sub>4</sub>] via a standard work up procedure as an analytically and spectroscopically pure pale yellow solid in excellent yield.

Once the new ligand precursor was established, its coordination to rhodium(I) salts was investigated. The complex, [Rh{κ<sup>3</sup>-H,H,S-H<sub>3</sub>B(mp)}(NBD)] (**1**) (where NBD = 2,5-norbornadiene) was synthesized and characterized via established methods (Scheme 2).<sup>22</sup> A dichloromethane solution of [RhCl(NBD)]<sub>2</sub> was prepared and two equivalents of Na[H<sub>3</sub>B(mp)] were subsequently added. A <sup>11</sup>B NMR spectrum of the reaction mixture after 1 h confirmed the complete formation of the target complex. The product was isolated via removal of the reaction solvent and extraction into n-hexane.



**Scheme 2.** Synthesis of [Rh{κ<sup>3</sup>-H,H,S-H<sub>3</sub>B(mp)}(NBD)], (**1**)

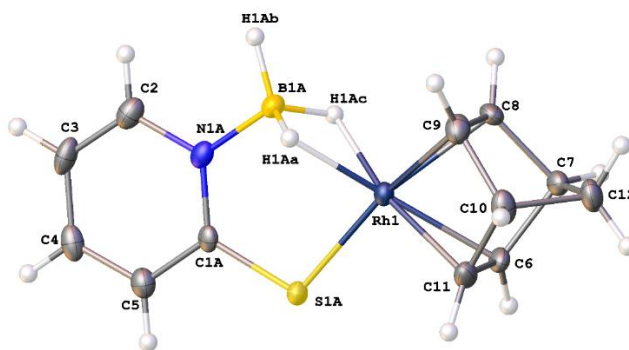
Complex **1** was isolated in good yield as a yellow powder. The isolated solid was fully characterized by NMR and IR spectroscopy, mass spectrometry and by elemental analysis. The <sup>11</sup>B{<sup>1</sup>H} NMR spectrum of **1** in CD<sub>3</sub>CN revealed a relatively sharp singlet at -7.8 ppm (half height width {h.h.w.} = 35 Hz), a downfield chemical shift relative to the free ligand. There was no apparent coupling between the boron and rhodium centers. The corresponding <sup>11</sup>B NMR spectrum exhibited a doublet of triplets resonance with <sup>1</sup>J<sub>BH</sub> coupling constants of 108 Hz and 79 Hz. The former coupling constant is larger than that of the free ligand (c.f. 93 Hz), and is therefore consistent with a terminal B-H unit, while the second coupling constant is consistent with a B-H

environment bridging to the rhodium center. As the smaller coupling constant is a triplet this suggests that the BH<sub>3</sub> unit is bridged to the rhodium center *via* two of the three B–H bonds, as indicated in Scheme 2. Furthermore, this mode of coordination of the borohydride unit is static in solution, at least of the NMR timescale. The reduction in the bridging <sup>1</sup>J<sub>BH</sub> constant relative to the free ligand and the static structure are suggestive of a relatively strong interaction between the BH<sub>2</sub> unit with the rhodium center. The <sup>1</sup>H NMR spectrum was also consistent with the formation of complex **1**. The spectrum revealed the expected pattern for the 2-mercaptopyridine ring protons, i.e. four chemical environments each integrating for one proton. It also confirmed the presence of the norbornadiene unit coordinated via both double bonds. The signal corresponding to these double bonds integrated for 4 protons and was broad, suggesting that the diene component of the molecule is fluxional in solution. The spectrum also exhibited two extremely broad signals which were difficult to observe in the standard <sup>1</sup>H NMR experiment, one centered at –2.72 ppm and the other at 2.89 ppm. Confirmation that these signals correspond to protons connected to the quadrupolar boron nuclei came from the corresponding <sup>1</sup>H{<sup>11</sup>B} NMR spectrum. This spectrum revealed more resolved signals at these two chemical shifts. These signals, however, were still too broad to resolve all coupling. The signal at –2.72 ppm resolved into a doublet which integrated for two protons relative to the other signals in the spectrum with a coupling constant 19.5 Hz. The chemical shift and the coupling is consistent with two of the three BH<sub>3</sub> protons interacting with the rhodium center (i.e. <sup>1</sup>J<sub>RhH</sub>). While, the signal at 2.89 ppm also sharpened significantly in the <sup>1</sup>H{<sup>11</sup>B} spectrum, it remained unresolved. As indicated above, a similar rhodium complex has previously been reported based on the 2-(methylamino)pyridine heterocycle and also contains 1,5-cyclooctadiene (COD).<sup>8</sup> In this complex, fluxional behavior was observed involving the rotation of both the BH<sub>3</sub> unit in addition to the exchanging positions of the double bonds of the COD ligand.



It appears that the barrier to rotation of the BH<sub>3</sub> unit is higher in complex **1** than that found for rhodium complex previously reported. In order to probe the fluxionality of the BH<sub>3</sub> unit as a function of temperature, solutions of **1** were heated in CD<sub>3</sub>CN at temperatures between 25 – 65 °C and their <sup>1</sup>H{<sup>11</sup>B} NMR spectra recorded (see supporting information). The signals at 2.89 and – 2.72 ppm began to broaden further as the temperature was increased. At around 55 °C these signals disappeared and an extremely broad signal was observed at approximately –1.75 ppm. This signal has been tentatively assigned to the BH<sub>3</sub> protons which are equivalent at this temperature. Unfortunately we were unable to heat the solution further as we were approaching the limit for the solvent and there were signs of decomposition within the tube.

Single crystals of **1** were obtained by allowing a saturated hexane solution stand at room temperature for 48 h. The molecular structure as determined by X-ray crystallography is shown in Figure 4. The structure was consistent with the spectroscopic data and supported the solution state assignment that the BH<sub>3</sub> unit was bound to the rhodium center via a bridging BH<sub>2</sub>Rh interaction. It also confirmed the pseudo square planar geometry of the rhodium(I) metal center. The structure revealed two complexes within the asymmetric unit both are additionally disordered in ratios, 56:44 and 89:11, respectively. The complexes have a mirror plane along the plane of the pyridine and an approximate mirror plane perpendicular to this through the rhodium atom and bisecting the pyridine. The disorder precluded a detailed discussion of the structure here. Despite this, the bond distances and angles are fully consistent with other closely related structures. Further details can be found in the supporting information.

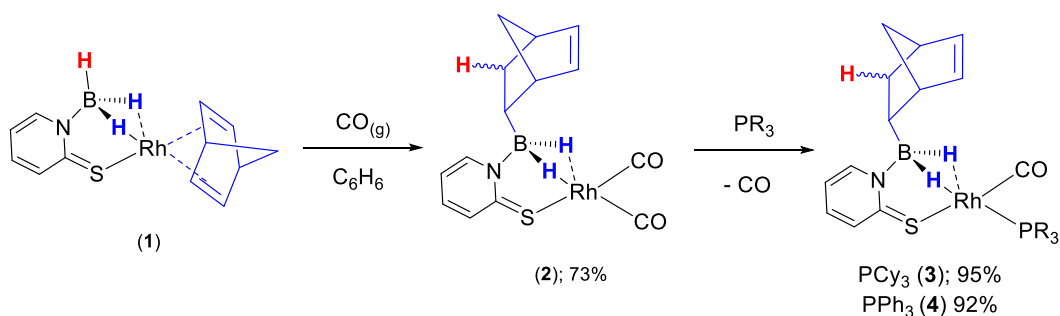


**Figure 4.** The molecular structure of complex **1**. Thermal ellipsoids drawn at 50% level. Selected bond distances (Å) and angles (°) for **1** can be found in the supporting information. Only the major disorder component of one of the two molecules in the crystallographic asymmetric unit is shown.

The ability of trisubstituted boron compounds to coordinate to transition metals has been of great interest for many years now.<sup>23-25</sup> Such compounds provide a fascinating array of bonding motifs and coordination modes. The nature of the metal–boron bond is distinctively impacted by the three other substituents around the boron center as very recently highlighted in an article by Langer.<sup>26</sup> A boron center with three groups around it can potentially act as any of the three ligand classes to a metal center, i.e. Z-type<sup>23-25</sup>, X-type<sup>27</sup> and L-type<sup>28</sup> depending on the three substituents. One strategy for installing metal–boron bonds is via activation of borohydride units. In many cases, migration of one of the hydride substituents at boron to the metal center has been observed.<sup>23-25</sup> Despite the diverse range of examples, to our knowledge, there are no reported examples of hydride migration involving a mono-substituted borohydride. We therefore set out to test for such reactivity. We have previously demonstrated that hydride migration could be triggered by addition of carbon monoxide to a COD complex.<sup>29</sup> A similar strategy was therefore undertaken with complex **1** in which CO was introduced into a solution of the complex in benzene. A test reaction

was initially conducted in a Young's NMR tube in  $C_6D_6$  (Scheme 3). The tube was degassed and closed under vacuum. A volume of CO gas was then introduced into the tube. The  $^{11}B$  NMR spectrum taken after 20 mins, revealed the presence of a new boron containing species as the only component at  $-5.3$  ppm. The mixture was therefore further analyzed. Where the starting material gave a triplet of doublets signal in the  $^{11}B$  spectrum, the new product complex **2** exhibited a triplet resonance ( $^1J_{BH} = 61$  Hz) suggesting that one of the hydrogen substituents at boron had been lost. This indicated that hydride migration had occurred from boron to rhodium center which has previously been observed in many cases.<sup>23b</sup> The corresponding  $^{11}B\{^1H\}$  NMR spectrum collapsed into a relatively sharp singlet resonance. There was no apparent coupling to rhodium which might have been expected if a Rh–B bond had been formed.<sup>30,31</sup> The  $^1H$  NMR spectrum of the mixture was then recorded. Four multiplet signals were observed in the aromatic region of the spectrum each integrating for one proton. Nine additional signals were also found, each integrating for one proton, confirming that a hydrogen atom had been incorporated into the former norbornadiene unit. Finally, two resonances with a ddd splitting pattern, each integrating for one proton, were observed at  $-0.90$  ppm ( $^1J_{RhH} = 20.6$  Hz,  $^2J_{HH} = 8.3$  Hz,  $^3J_{HH} = 2.7$  Hz),  $-2.86$  ppm (ddd,  $^1J_{RhH} = 24.3$  Hz,  $^2J_{HH} = 8.3$  Hz,  $^3J_{HH} = 3.7$  Hz), respectively. There was no indication of any other chemical environments in the spectrum and it was thus concluded that a hydrogen substituent had been lost from the  $BH_3$  unit and had been transferred to the norbornadiene unit.<sup>23b</sup> The corresponding  $^{13}C\{^1H\}$  NMR spectrum revealed six clear signals corresponding to the former norbornadiene unit. A closer examination of the baseline also revealed an additional signal as a very weak and broad signal. This accounted for the seven chemical environments expected for hydride migration and thus the formation of the norbornenyl fragment.<sup>32</sup> This carbon signal would be expected to appear as a doublet as a result of coupling to the rhodium centre.<sup>33</sup> The absence of this  $^1J_{RhB}$  coupling in

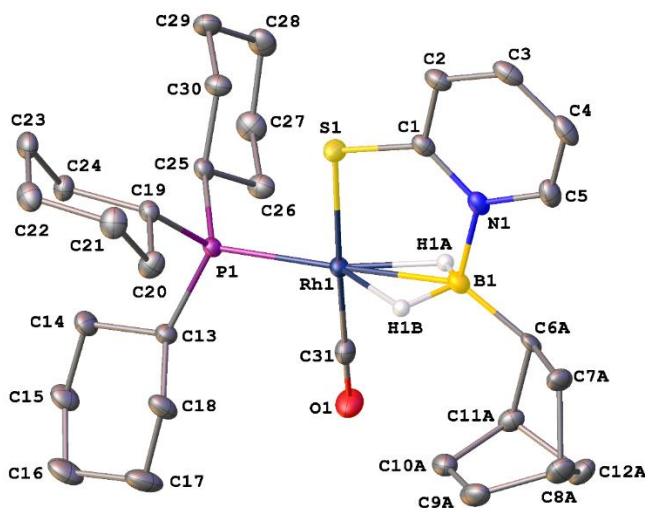
the  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum and the broad carbon signal in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum led us to believe that the norbornenyl fragment was bound to the boron centre. Based on the above evidence, complex **2** was assigned as  $[\text{Rh}\{\kappa^3\text{-}H,H,S\text{-}H_2\text{B}(\text{nbe})(\text{mp})\}(\text{CO})_2]$ . The reaction was repeated on a preparative scale and a solid was isolated in very good yield following a standard workup. The infrared spectrum of solid revealed very strong bands at 2062, 2010 and 1999  $\text{cm}^{-1}$  ( $\nu_{\text{CO}} + \nu_{\text{RhH}_2\text{B}}$ ). These values are consistent with a rhodium(I) center bearing carbonyl ligands bonded *cis* relative to each other<sup>34-36</sup> and  $\text{BH}_2\text{-Rh}$  motif.<sup>37</sup> Unfortunately, the solid sample of complex **2** degraded within a matter of hours as evidenced by a darkening of the solid. The solid turned quite black over the course of 48 h. In the absence of a CO atmosphere in solution, the complex degraded quite rapidly. For this reason, we were unable to obtain analytical data for this complex or grow single crystals suitable for X-ray crystallography. It is well known that bis-carbonyl rhodium complexes can readily lose CO and a strategy to provide a more stable compound is to replace one of the CO ligands with a phosphine ligand.<sup>34</sup> In order to achieve suitably stable complexes, and thereby gain further evidence, we carried out reactions in which phosphine ligands were added to mixtures containing complex **2**, prepared *in situ* (Scheme 3).



**Scheme 3.** Reaction of complex **1** with CO to form bis-carbonyl complex **2**. This complex was also prepared *in situ* and further reacted with phosphine ligands to form complexes **3** and **4**.

In a typical reaction, complex **1** was dissolved in benzene solvent after which an atmosphere of CO was introduced into a degassed solution. The mixture was left to stir for 1 h, the flask was then opened to a nitrogen atmosphere and one equivalent of either tricyclohexylphosphine or triphenylphosphine was added. In both cases, an immediate release of gas was observed upon addition. The mixtures were left for a further 1 h and subsequently worked up by a standard procedure. Both reactions revealed clean transformations and gave new phosphine containing complexes (complex **3**: PCy<sub>3</sub> and complex **4**: PPh<sub>3</sub>) in excellent yields and with good stabilities. This enabled complexes **3** and **4** to be fully characterized by spectroscopic and analytical techniques. Furthermore, we were able to grow single crystals of complex **3**. X-ray crystallography studies allowed us to unambiguously confirm the identity of the structure of this complex. As shown in Figure 5, the location of the norbornenyl unit is indeed located at the boron center. In most aspects, the spectroscopic data for complexes **3** and **4** are similar to that described above for those components they have in common with complex **2**. As with complex **2**, there is no <sup>1</sup>J<sub>RhB</sub> coupling observed in complexes **3** and **4**. Furthermore, the α-carbon signals on the norbornenyl fragment are either absent or very poorly resolved in their <sup>13</sup>C{<sup>1</sup>H} NMR spectra.<sup>32</sup> The spectroscopic data for complexes **3** and **4** confirmed the presence of the phosphine ligand within the coordination spheres of the complexes. The identity of complexes **3** and **4** were confirmed as [Rh{κ<sup>3</sup>-H,H,S-H<sub>2</sub>B(nbe)(mp)}(CO)(PCy<sub>3</sub>)] (**3**) and [Rh{κ<sup>3</sup>-H,H,S-H<sub>2</sub>B(nbe)(mp)}(CO)(PPh<sub>3</sub>)] (**4**). There were some differences in the chemical environments of the BH<sub>2</sub> unit in complex **2** compared with those of **3** and **4**. For complex **2**, there were two distinct hydrogen environments as confirmed by two ddd signals at -0.90 and -2.86, respectively in the <sup>1</sup>H{<sup>11</sup>B} NMR spectrum. The <sup>1</sup>J<sub>RhH</sub> coupling constant is larger in the more upfield shifted environment confirming that one of the two hydrogen atoms has a slightly stronger interaction with the metal center than the other

in solution. The coupling in this complex was well resolved. In addition to the  $^1J_{\text{RhH}}$  coupling, the geminal coupling is also observed between the  $\text{BH}_2$  hydrogens and the  $\alpha$ -hydrogen on the norbornenyl fragment. This latter evidence provided even further support of the fact that the organic fragment is boron bound. The situation is slightly different in the case of the phosphine containing compounds. Here, one broad signal is observed corresponding to both  $\text{BH}_2$  hydrogens at a chemical shift close to the midpoint between those found in **2** (i.e.  $-2.16$  ppm for **3** and  $-2.11$  ppm for **4**). In these latter two complexes, it appears that the hydrogens are exchanging their positions rapidly on the NMR timescales whereas for **2** these protons are static.



**Figure 5.** The molecular structure of complex **3**. Thermal ellipsoids drawn at 50% level. Hydrogen atoms, with the exception of H(1A) and H(1B) (which were located in the difference map) and the minor disorder component of the norbornenyl fragment have been omitted for clarity. Selected bond distances (Å) and angles (°); Rh(1)-B(1) 2.3733(19), Rh(1)-S(1) 2.3348(4), Rh(1)-C(31) 1.8322(18), Rh(1)-P(1) 2.2737(4), B(1)-N(1) 1.576(2), B(1)-H(1A) 1.18(2), B(1)-H(1B) 1.17(2), B(1)-C(6) 1.593(7), C(1)-S(1) 1.7209(16), C(31)-O(1) 1.149(2), B(1)-Rh(1)-S(1) 81.22(5), B(1)-

Rh(1)-C(31) 100.67(7), S(1)-Rh(1)-P(1) 90.001(15), S(1)-Rh(1)-P(1) 89.23(5). The  $\Sigma$  of all angles at the rhodium centre = 361.1.

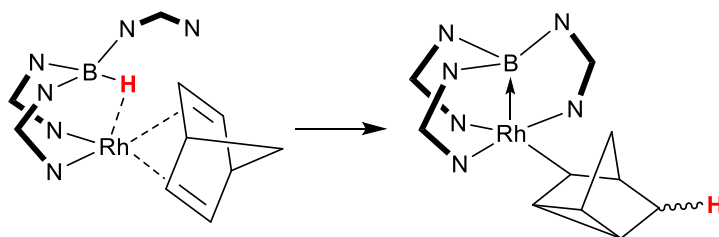
As indicated above, the position of the norbornenyl unit in complex **3** was unambiguously established by X-ray single crystal diffraction studies (Figure 5). Crystals suitable for X-ray diffraction were obtained by allowing an ether solution to stand and slightly concentrate overnight. The crystalline material of complex **3** contained a single complex in the asymmetric unit. The norbornenyl unit is disordered over two positions in an approximate ratio of 84:16. The rhodium center in **3** contains a tricyclohexylphosphine ligand and a carbon monoxide ligand which are positioned *cis* to each other. It also contains the anionic H<sub>2</sub>B(nbe)(mp) ligand which is linked to the metal center via the thione donor and the BH<sub>2</sub> unit. The latter linkage to the rhodium center can be considered in two ways, either as two separate B–H agostic type interactions or as a three centered dihydroborate interaction. If the complex is considered to be a distorted square planar structure, as expected from a Rh(I) center, then one of the B–H bonds appears to be closer to the idealized fourth coordination site with respect to the other three ligands. The rhodium center adopts a distorted square planar geometry (when considering the boron center as occupying the fourth coordination site) with *cis*-inter ligand angles in the range 81.22(5) – 100.67(7)°. The rhodium center is essentially planar, the sum of all angles at this center is 361.1°. The rhodium-boron distance in **3** is 2.3733(19) Å which is longer than the sum of the covalent radii of the two elements = 2.26 Å.<sup>38</sup> This distance however is consistent with other structurally characterized rhodium complexes containing a coordinating BH<sub>2</sub> group.<sup>39,40</sup>

The pathway leading to the boron bound norbornenyl complexes was intriguing to us since we were initially expecting the organic moiety to remain at the metal center. It is plausible that the

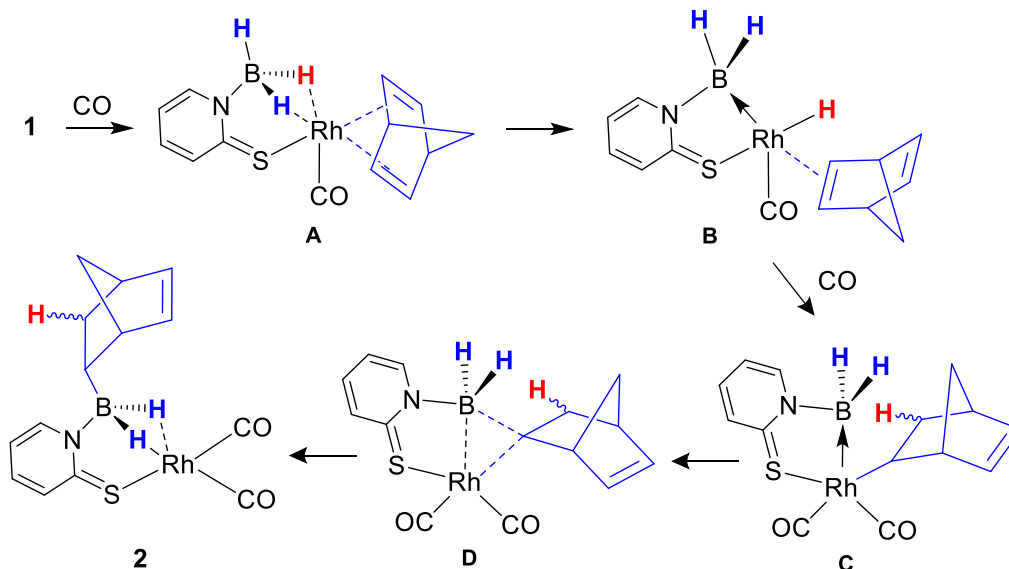
norbornadiene could be eliminated from the rhodium center to form  $[\text{Rh}\{\kappa^3\text{-}H,H,S\text{-}H_3\text{B}(\text{mp})\}(\text{CO})_2]$  (**5**).<sup>41</sup> Then, the free diene would react externally via a direct addition across one of the B–H bonds, *i.e.* an intermolecular hydroboration. In order to rule this reactivity out, an excess of norbornadiene was added to a mixture containing **5**. No reactivity was observed even when the mixture was heated to 60 °C. This provided evidence that the reaction was indeed occurring at the metal center. During the reaction from **2** to **3**, we did not observe any intermediate species by NMR spectroscopy. We looked for signals in the hydride region of <sup>1</sup>H NMR spectra and for new signals in the <sup>11</sup>B spectra however only starting complex and the final product were observed. We previously reported the related reactions involving the reactivity of  $[\text{Rh}\{\kappa^3\text{-}N,N,H\text{-}HB(7\text{-azaindolyl})_3(\text{NBD})\}]$  which converts to the metallaboratrane complex  $[\text{Rh}\{\kappa^4\text{-}N,N,B,N\text{-}B(\text{azaindolyl})_3\}(\text{nortricyclyl})]$  over time (Figure 6).<sup>30</sup> There are also many reported complexes where hydride migration has led to the formation of a transition metal–hydride complex.<sup>12,14,29,42</sup> Furthermore, there are many examples where an organic group has transferred from a metal center to boron, albeit not in the case of a primary substituted borohydride unit.<sup>43</sup> Based on these observations, we propose the pathway for the reaction of complex **1** to the bis-carbonyl complex **2** shown in Scheme 4. The 16 valence electron complex **1** would first be expected to react with one equivalent of carbon monoxide to form species **A**. This would destabilize the coordination of the norboradiene unit so that it is coordinated via only one of the two double bonds. Hydride migration from boron to metal center can then take place forming an intermediate species **B**. As this species is not observed, a spontaneous migratory insertion reaction between the rhodium–hydride and norboradiene unit would occur facilitated by the addition of a second CO ligand forming species **C**. This was the complex we initially expected. Species **C** might have been expected to be stable despite being a square based pyramidal structure. Indeed there are many



examples of metal–borane complexes which are stable with this geometry.<sup>23b,c</sup> In this case however, it appears that species **C** reacts further whereby the newly formed norbornenyl fragment migrates from the rhodium to the boron center. There is rotation of the N–B bond to allow the two remaining B–H bonds to bind to the rhodium. In such a scenario, the formation of the square planar rhodium(I) complex (considering the BH<sub>2</sub> unit as occupying one coordination site) or the formation of a strong Lewis acid-Lewis complex, *i.e.* an alkyl borate, appear to be possible driving forces for the formation of complex **2**. An alternative pathway in which there is an equilibrium mixture formed in solution between complex **1** and a hydride migration product is also feasible where the equilibrium lies in favor of complex **1**. In this case, addition of CO could, in principle, act as a driving force to lead the reaction to the final product. The reaction outlined in Figure 6 indicates that this could be a possibility. We heated complex **1** for 20 h at 100 °C in toluene. We also added trialkyl- and triaryl-phosphines to complex **1** as potential ligands. In both these scenarios, we observed no evidence of hydride migration. It is therefore most likely that CO is necessary to trigger the B–H activation.<sup>29</sup>



**Figure 6.** The transfer of hydride from boron to rhodium center and finally to the organic fragment (N—N represents the three atom bridging unit, 7-azaindolyl).



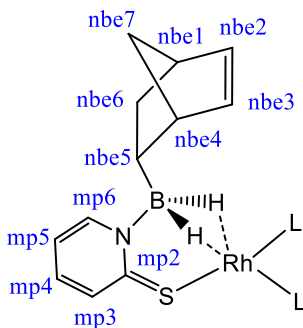
**Scheme 4.** Postulated reaction pathway following the addition of CO to a solution of complex **1**.

## Conclusions

In summary, the synthesis and characterization of the novel mono-substituted borohydride ligand, Na[H<sub>3</sub>B(mp)] has been reported. This adds to the family of ligands containing the 2-mercaptopyridine moiety. The first complexes of this ligand have been synthesized and fully characterized. Furthermore, a crystallographic study has been undertaken of complex **1**. While there are a small number of transition metal complexes containing mono-substituted borohydride ligands known, their further reactivity has not previously been explored. This is the first time that an intramolecular hydroboration has been observed in complexes of this type. Based on previously investigations by ourselves and others, we have postulated that such reactivity occurs via a hydride migration step and the formation of an intermediate *Z*-class borane species (**C**). If this is indeed the case, this would be the first observed example of hydride migration within a mono-substituted borohydride ligand. The implications of such reactivity, and the cooperation between the boron and the metal centers, are currently under investigation.

## Experimental Section

**General remarks.** All manipulations were conducted under inert atmosphere using standard Schlenk line techniques. Solvents were supplied extra dry from Acros Organics and were stored over 4 Å molecular sieves. CD<sub>3</sub>CN and C<sub>6</sub>D<sub>6</sub> NMR solvents were stored in a Young's ampules under N<sub>2</sub>, over 4 Å molecular sieves and were degassed through three freeze-pump-thaw cycles prior to use. All reagents were used as purchased from commercial sources. The rhodium bimetallic precursor [RhCl(NBD)]<sub>2</sub> was synthesized according to the published procedure.<sup>44</sup> All NMR experiments were conducted on a Bruker 400 MHz Ascend™ 400 spectrometer. Proton (<sup>1</sup>H) and carbon (<sup>13</sup>C) assignments (Figure 7) were supported by HSQC, HMBC and COSY NMR experiments. Infrared spectra were recorded on a Perkin-Elmer Spectrum Two ATR FT-IR spectrometer. Mass spectra were recorded by the EPSRC NMSF at Swansea University. Elemental analysis was performed at London Metropolitan University by their elemental analysis service.



**Figure 7.** Numbering scheme used for assignments of NMR spectra

**Synthesis of Na[H<sub>3</sub>B(mp)].** A Schlenk flask was charged with freshly ground NaBH<sub>4</sub> (340.3 mg, 8.996 mmol) and 2-mercaptopyridine (500 mg, 4.498 mmol). Dry degassed THF (50 mL) was added and the reaction mixture was stirred continuously for 72 hours. After this time the reaction mixture was filtered into a new flask and the solvent volume was reduced to approximately 10 mL

before hexane (10 mL) was added to precipitate a small amount of a white solid. The reaction mixture was filtered again and the resulting filtrate was reduced to a few milliliters under reduced pressure. The solid product was obtained as a fine off-white powder upon addition of hexane. The supernatant liquid was removed *via* cannula filtration and the solid dried under dynamic vacuum. Yield: 582.6 mg, 3.96 mmol, 88%.  $^1\text{H}$  NMR  $\delta$  ( $\text{CD}_3\text{CN}$ ): 6.51 ( $\tau\text{d}$ ,  $^3\text{J}_{\text{HH}} = 6.6$  Hz,  $^4\text{J}_{\text{HH}} = 1.5$  Hz, 1H,  $^{\text{mp}5}\text{CH}$ ), 7.07 ( $\tau\text{d}$ ,  $^3\text{J}_{\text{HH}} = 7.7$  Hz,  $^4\text{J}_{\text{HH}} = 1.9$  Hz, 1H,  $^{\text{mp}4}\text{CH}$ ), 7.38 (d,  $^3\text{J}_{\text{HH}} = 8.3$  Hz, 1H,  $^{\text{mp}3}\text{CH}$ ), 8.19 (dd,  $^3\text{J}_{\text{HH}} = 6.3$  Hz,  $^4\text{J}_{\text{HH}} = 1.6$  Hz, 1H,  $^{\text{mp}6}\text{CH}$ ).  $^1\text{H}\{^{11}\text{B}\}$  NMR  $\delta$  ( $\text{CD}_3\text{CN}$ ): 2.11 (s, 3H,  $\text{BH}_3$ ).  $^{11}\text{B}$  NMR  $\delta$  ( $\text{CD}_3\text{CN}$ ): -14.1 (q,  $^1\text{J}_{\text{BH}} = 93$  Hz,  $\text{BH}_3$ ).  $^{11}\text{B}\{^1\text{H}\}$  NMR  $\delta$  ( $\text{CD}_3\text{CN}$ ): -14.1 (s, h.h.w. = 44 Hz,  $\text{BH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\delta$  ( $\text{CD}_3\text{CN}$ ): 113.5 (s,  $^{\text{mp}5}\text{C}$ ), 134.0 (s,  $^{\text{mp}4}\text{C}$ ), 134.7 (s,  $^{\text{mp}3}\text{C}$ ), 147.8 (s,  $^{\text{mp}6}\text{C}$ ), 181.3 (s,  $^{\text{mp}2}\text{C}$ ). IR ( $\text{cm}^{-1}$ , ATR powder film) 2307 s (B-H). FTMS -p:  $m/z$  124.0 [ $\text{M} - \text{H}$ ] $^-$ . Anal. [Found (calc)] for  $\text{C}_5\text{H}_7\text{NBNaS}$ : C 40.69% (40.86%), H 4.88% (4.80%), N 9.44% (9.53%).

**Intermediate species observed during reaction of  $\text{Na}[\text{BH}_4]$  with 2-mercaptopyridine** (see main text for details)

$^1\text{H}$  NMR  $\delta$  ( $\text{CD}_3\text{CN}$ ): 6.74 (ddd,  $^3\text{J}_{\text{HH}} = 6.9$  Hz,  $^3\text{J}_{\text{HH}} = 5.0$  Hz,  $^4\text{J}_{\text{HH}} = 1.5$  Hz, 1H,  $^{\text{mp}5}\text{CH}$ ), 7.32 ( $\tau\text{d}$ ,  $^3\text{J}_{\text{HH}} = \text{unresolved}$ , 1H,  $^{\text{mp}4}\text{CH}$ ), 7.35 (d,  $^3\text{J}_{\text{HH}} = \text{unresolved}$ , 1H,  $^{\text{mp}3}\text{CH}$ ), 8.14 (ddd,  $^3\text{J}_{\text{HH}} = 5.0$  Hz,  $^4\text{J}_{\text{HH}} = 1.9$  Hz,  $^5\text{J}_{\text{HH}} = 1.0$  Hz 1H,  $^{\text{mp}6}\text{CH}$ ).  $^1\text{H}\{^{11}\text{B}\}$  NMR  $\delta$  ( $\text{CD}_3\text{CN}$ ): 1.39 (s, 3H,  $\text{BH}_3$ ).  $^{11}\text{B}$  NMR  $\delta$  ( $\text{CD}_3\text{CN}$ ): -26.7 (q,  $^1\text{J}_{\text{BH}} = 98$  Hz,  $\text{BH}_3$ ).  $^{11}\text{B}\{^1\text{H}\}$  NMR  $\delta$  ( $\text{CD}_3\text{CN}$ ): -26.7 (s, h.h.w. = 40 Hz,  $\text{BH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\delta$  ( $\text{CD}_3\text{CN}$ ): 116.5 (s,  $^{\text{mp}5}\text{C}$ ), 124.5 (s,  $^{\text{mp}4}\text{C}$ ), 135.4 (s,  $^{\text{mp}3}\text{C}$ ), 149.0 (s,  $^{\text{mp}6}\text{C}$ ), 172.3 (s,  $^{\text{mp}2}\text{C}$ ).

**Synthesis of  $[\text{Rh}\{\kappa^3\text{-H,H,S-H}_3\text{B}(\text{mp})\}(\text{NBD})]$  - Complex 1.** A Schlenk flask was charged with  $[\text{RhCl}(\text{NBD})]_2$  (100 mg, 2.17 mmol) which was fully dissolved in 20 mL of DCM.  $\text{Na}[\text{H}_3\text{B}(\text{mp})]$  (79.7 mg, 5.42 mmol) was added to the solution. The reaction mixture was continuously stirred and allowed to react for 1 h before the solvent was removed under reduced pressure. The product

was then extracted from the resulting solid with 3 × 20 mL portions of n-hexane. This was separated from the remaining solid *via* cannula filtration. The hexane was removed under reduced pressure and the solid product was dried under dynamic vacuum. Yield: 92.9 mg, 2.92 mmol, 67%. <sup>1</sup>H NMR δ (CD<sub>3</sub>CN): -2.72 (br. q, 2H, HBH<sub>2</sub>Rh), 1.41 (t, <sup>3</sup>J<sub>HH</sub> = 1.6 Hz, 2H, <sup>NBD</sup>CH<sub>2</sub>), 2.89 (br. q, <sup>1</sup>J<sub>BH</sub> = 120 Hz, 1H, HBH<sub>2</sub>Rh), 3.65 (m, 2H, <sup>NBD</sup>CH), 4.01 (br., 4H, <sup>NBD</sup>CH), 6.95 (τd, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, <sup>4</sup>J<sub>HH</sub> = 1.3 Hz, 1H, <sup>mp5</sup>CH), 7.49 (τd, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, <sup>4</sup>J<sub>HH</sub> = 1.4 Hz, 1H, <sup>mp4</sup>CH), 7.75 (d, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, 1H, <sup>mp3</sup>CH), 8.45 (d, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, 1H, <sup>mp6</sup>CH). <sup>1</sup>H{<sup>11</sup>B} NMR δ (CD<sub>3</sub>CN): -2.72 (d, <sup>1</sup>J<sub>RhH</sub> = 19.5 Hz, 2H, HBH<sub>2</sub>Rh), 2.89 (br., 1H, HBH<sub>2</sub>Rh). <sup>11</sup>B NMR δ (CD<sub>3</sub>CN): -7.8 (dt, <sup>1</sup>J<sub>BH terminal</sub> = 108 Hz, <sup>1</sup>J<sub>BH2Rh</sub> = 79 Hz). <sup>11</sup>B{<sup>1</sup>H} NMR δ (CD<sub>3</sub>CN): -7.8 (s, h.h.w. = 35 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR δ (CD<sub>3</sub>CN): 41.4 (v. br. <sup>NBD</sup>CH<sub>2</sub>=CH<sub>2</sub>),<sup>45</sup> 49.6 (d, <sup>2</sup>J<sub>RhC</sub> = 2.5 Hz, <sup>NBD</sup>CH), 55.8 (v. br. <sup>NBD</sup>CH<sub>2</sub>=CH<sub>2</sub>),<sup>45</sup> 62.9 (d, <sup>3</sup>J<sub>RhC</sub> = 5.3 Hz, <sup>NBD</sup>CH<sub>2</sub>), 116.9 (s, <sup>mp5</sup>C), 128.8 (d, <sup>3</sup>J<sub>CP</sub> = 1.6 Hz, <sup>mp3</sup>C), 135.3 (s, <sup>mp4</sup>C), 147.3 (s, <sup>mp6</sup>C), 175.1 (d, <sup>2</sup>J<sub>CP</sub> = 1.3 Hz, <sup>mp2</sup>C). IR (cm<sup>-1</sup>, ATR powder film) 2439 w (B-H). TOF MS ASAP<sup>+</sup>: *m/z* 317.9 [M - H]<sup>+</sup>. Anal. [Found (calc)] for C<sub>12</sub>H<sub>15</sub>NBRhS: C 45.12% (45.18%), H 4.83% (4.74%), N 4.25% (4.39%).

**Synthesis of [Rh{κ<sup>2</sup>-*H,H,S*-H<sub>2</sub>B(nbe)(mp)}(CO)<sub>2</sub>] – Complex 2.** A Schlenk flask was charged with [Rh{κ<sup>3</sup>-*H,H,S*-H<sub>3</sub>B(mp)}(NBD)] (50 mg, 1.57 mmol) which was fully dissolved in 15 mL of hexane. The solution was then degassed through three consecutive freeze-pump-thaw cycles and left under a partial vacuum. The headspace above the solution was subsequently filled with CO and the solution was stirred continuously for 2 hours. After this time the solvent was removed under reduced pressure and the resulting solid dried under dynamic vacuum. Yield: 43.2 mg, 1.15 mmol, 73%. <sup>1</sup>H NMR δ (C<sub>6</sub>D<sub>6</sub>): 0.95 (m, 1H, <sup>nbe6</sup>CH<sub>2</sub>), 1.35 (m, 1H, <sup>nbe7</sup>CH<sub>2</sub>), 1.69 (m, 1H, <sup>nbe7</sup>CH<sub>2</sub>), 1.78 (br. m, 1H, <sup>nbe5</sup>CH), 2.10 (τd, <sup>3</sup>J<sub>HH</sub> = 11.3 Hz, 1H, <sup>nbe6</sup>CH<sub>2</sub>), 2.87 (s, 1H, <sup>nbe1</sup>CH), 2.92 (s, 1H, <sup>nbe4</sup>CH), 6.03 (τd, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, <sup>4</sup>J<sub>HH</sub> = 1.3 Hz, 1H, <sup>mp5</sup>CH), 6.08 (dd, <sup>3</sup>J<sub>HH</sub> = 5.7 Hz,

$^3J_{\text{HH}} = 3.0$  Hz 1H,  $^{\text{nbe}3}\text{CH}$ ), 6.19 (dd,  $^3J_{\text{HH}} = 5.7$  Hz,  $^3J_{\text{HH}} = 3.1$  Hz, 1H,  $^{\text{nbe}2}\text{CH}$ ), 6.37 ( $\tau$ d,  $^3J_{\text{HH}} = 7.6$  Hz, 1H,  $^{\text{mp}4}\text{CH}$ ), 7.35 (d,  $^3J_{\text{HH}} = 8.4$  Hz, 1H,  $^{\text{mp}3}\text{CH}$ ), 8.01 (d,  $^3J_{\text{HH}} = 6.4$  Hz, 1H,  $^{\text{mp}6}\text{CH}$ ).  $^1\text{H}\{^{11}\text{B}\}$  NMR  $\delta$  ( $\text{C}_6\text{D}_6$ ): -0.90 (ddd,  $^1J_{\text{RhH}} = 20.6$  Hz,  $^2J_{\text{HH}} = 8.3$  Hz,  $^3J_{\text{HH}} = 2.7$  Hz, 1H,  $\text{BH}_2\text{Rh}$ ), -2.86 (ddd,  $^1J_{\text{RhH}} = 24.3$  Hz,  $^2J_{\text{HH}} = 8.3$  Hz,  $^3J_{\text{HH}} = 3.7$  Hz, 1H,  $\text{BH}_2\text{Rh}$ ).  $^{11}\text{B}$  NMR  $\delta$  ( $\text{C}_6\text{D}_6$ ): -5.3 (t,  $^1J_{\text{BH}} = 61$  Hz, h.h.w. = 180 Hz).  $^{11}\text{B}\{^1\text{H}\}$  NMR  $\delta$  ( $\text{C}_6\text{D}_6$ ): -5.3 (s, h.h.w. = 70 Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\delta$  ( $\text{C}_6\text{D}_6$ ): 28.5 (br,  $^{\text{nbe}5}\text{C}$ ),<sup>32</sup> 33.4 (s,  $^{\text{nbe}6}\text{C}$ ), 43.1 (s,  $^{\text{nbe}1}\text{C}$ ), 45.7 (s,  $^{\text{nbe}4}\text{C}$ ), 52.0 (s,  $^{\text{nbe}7}\text{C}$ ), 116.0 (s,  $^{\text{mp}5}\text{C}$ ), 129.1 (s,  $^{\text{mp}3}\text{C}$ ), 133.1 (s,  $^{\text{mp}4}\text{C}$ ), 134.5 (s,  $^{\text{nbe}3}\text{C}$ ), 136.1 (s,  $^{\text{nbe}2}\text{C}$ ), 143.7 (s,  $^{\text{mp}6}\text{C}$ ), 172.5 (s,  $^{\text{mp}2}\text{C}$ ). IR ( $\text{cm}^{-1}$ , ATR powder film) 1988, 2010, 2062.

**Synthesis of  $[\text{Rh}\{\kappa^3\text{-}H,H,S\text{-H}_2\text{B}(\text{nbe})(\text{mp})\}(\text{CO})(\text{PCy}_3)]$  – Complex 3.** A Schlenk flask was charged with  $[\text{Rh}\{\kappa^3\text{-}H,H,S\text{-H}_3\text{B}(\text{mp})\}(\text{NBD})]$  (100 mg, 3.15 mmol) and was fully dissolved in 10 mL of benzene. The resulting solution was then freeze-pump-thaw degassed and the headspace was filled with CO. The solution was continuously stirred for 1 hour after which time  $\text{PCy}_3$  (88.2 mg, 3.15 mmol) dissolved in 10 mL of benzene was added. After another 1 hour of continuous stirring the solvent volume was minimized under reduced pressure and 20 mL of hexane was added. The hexane was subsequently removed under reduced pressure to yield an orange solid. This was then washed with cool pentane and the resulting solid was dried under dynamic vacuum. Yield: 186.5 mg, 2.97 mmol, 95%.  $^1\text{H}$  NMR  $\delta$  ( $\text{C}_6\text{D}_6$ ): 1.15 (m, 3H,  $^{\text{Cy}}\text{CH}_2$ ), 1.26 (m, 6H,  $^{\text{Cy}}\text{CH}_2$ ), 1.45 (m, 1H,  $^{\text{nbe}6}\text{CH}_2$ ), 1.51 (m, 1H,  $^{\text{nbe}7}\text{CH}_2$ ), 1.60 (m, 3H,  $^{\text{Cy}}\text{CH}_2$ ), 1.68 (m, 6H,  $^{\text{Cy}}\text{CH}_2$ ), 1.74 (m, 6H,  $^{\text{Cy}}\text{CH}_2$ ), 1.81 (m, 1H,  $^{\text{nbe}7}\text{CH}_2$ ), 2.12 (br. m, 1H,  $^{\text{nbe}5}\text{CH}$ ), 2.18 (m, 6H,  $^{\text{Cy}}\text{CH}_2$ ), 2.28 (m, 3H,  $^{\text{Cy}}\text{CH}$ ), 2.29 (m, 1H,  $^{\text{nbe}6}\text{CH}_2$ ), 3.03 (s, 1H,  $^{\text{nbe}1}\text{CH}$ ), 3.31 (s, 1H,  $^{\text{nbe}4}\text{CH}$ ), 6.08 ( $\tau$ d,  $^3J_{\text{HH}} = 6.7$  Hz,  $^4J_{\text{HH}} = 1.4$  Hz, 1H,  $^{\text{mp}5}\text{CH}$ ), 6.41 (dd,  $^3J_{\text{HH}}$  unresolved, 1H,  $^{\text{nbe}2}\text{CH}$ ), 6.43 ( $\tau$ d,  $^3J_{\text{HH}}$  unresolved, 1H,  $^{\text{mp}4}\text{CH}$ ), 6.53 (dd,  $^3J_{\text{HH}} = 5.6$  Hz,  $^3J_{\text{HH}} = 2.9$  Hz, 1H,  $^{\text{nbe}3}\text{CH}$ ), 7.60 (d,  $^3J_{\text{HH}} = 8.4$  Hz, 1H,  $^{\text{mp}3}\text{CH}$ ), 8.33 (d,  $^3J_{\text{HH}} = 6.5$  Hz, 1H,  $^{\text{mp}6}\text{CH}$ ).  $^1\text{H}\{^{11}\text{B}\}$  NMR  $\delta$  ( $\text{C}_6\text{D}_6$ ): -2.16 (dd,  $^1J_{\text{RhH}}$  and  $^2J_{\text{HH}} = 37.2$  Hz

and 23.2 Hz, 2H,  $\text{BH}_2\text{Rh}$ ).  $^{11}\text{B}$  NMR  $\delta$  ( $\text{C}_6\text{D}_6$ ):  $-5.0$  (br.  $^1\text{J}_{\text{BH}}$  not observed, h.h.w. = 320 Hz).  $^{11}\text{B}\{^1\text{H}\}$  NMR  $\delta$  ( $\text{C}_6\text{D}_6$ ):  $-5.0$  (s, h.h.w. = 270 Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR  $\delta$  ( $\text{C}_6\text{D}_6$ ):  $53.1$  (d,  $^1\text{J}_{\text{RHP}} = 162$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\delta$  ( $\text{C}_6\text{D}_6$ ):<sup>32</sup>  $26.9$  (s,  $^{\text{Cy}}\text{CH}_2$ ),  $28.0$  (dd,  $^{\text{Cy}}\text{CH}_2$ ),  $30.7$  (d,  $\text{J}_{\text{PC}} = 5.3$  Hz,  $^{\text{Cy}}\text{CH}_2$ ),  $33.1$  (s,  $^{\text{nbe}6}\text{C}$ ),  $36.4$  (d,  $^1\text{J}_{\text{PC}} = 23.4$  Hz,  $^{\text{Cy}}\text{CH}$ ),  $43.5$  (s,  $^{\text{nbe}4}\text{C}$ ),  $46.5$  (s,  $^{\text{nbe}1}\text{C}$ ),  $51.9$  (s,  $^{\text{nbe}7}\text{C}$ ),  $115.0$  (s,  $^{\text{mp}5}\text{C}$ ),  $129.8$  (s,  $^{\text{mp}3}\text{C}$ ),  $131.8$  (s,  $^{\text{mp}4}\text{C}$ ),  $135.2$  (s,  $^{\text{nbe}2}\text{C}$ ),  $135.4$  (s,  $^{\text{nbe}3}\text{C}$ ),  $143.8$  (s,  $^{\text{mp}6}\text{C}$ ),  $174.4$  (d,  $^2\text{J}_{\text{RhC}} = 5.3$  Hz,  $^{\text{mp}2}\text{C}$ ),  $192.7$  (poorly resolved signal, CO). IR ( $\text{cm}^{-1}$ , ATR powder film) 1961, 2850, 2924. MS  $\text{EI}^+$  :  $m/z$  627.2 [ $\text{M}$ ] $^+$ , 599.2 [ $\text{M} - \text{CO}$ ] $^+$ , 281.2 [ $\text{PCy}_3$ ] $^+$ . Anal. [Found (calc)] for  $\text{C}_{31}\text{H}_{48}\text{BNOPRhS}$ : C 59.02% (59.15%), H 7.98% (8.01%), N 2.31% (2.23%).

**Synthesis of  $[\text{Rh}\{\kappa^3\text{-}H,H,S\text{-H}_2\text{B}(\text{nbe})(\text{mp})\}(\text{CO})(\text{PPh}_3)]$  – Complex 4.** A Schlenk flask was charged with  $[\text{Rh}\{\kappa^3\text{-}H,H,S\text{-H}_3\text{B}(\text{mp})\}(\text{NBD})]$  (100 mg, 3.15 mmol) and was fully dissolved in 10 mL of benzene. The resulting solution was then freeze-pump-thaw degassed and the headspace was filled with CO. The solution was continuously stirred for 1 hour before  $\text{PPh}_3$  (82.5 mg, 3.15 mmol) dissolved in 10 mL of benzene was added. After another 1 hour of continuous stirring the solvent volume was minimized under reduced pressure and 20 mL of hexane was added. The hexane was subsequently removed under reduced pressure to yield an orange solid. This was then washed with cool pentane and the resulting solid was dried under dynamic vacuum. Yield: 175.8 mg, 2.89 mmol, 92%.  $^1\text{H}$  NMR  $\delta$  ( $\text{C}_6\text{D}_6$ ): 1.46 (m, 1H,  $^{\text{nbe}6}\text{CH}_2$ ), 1.49 (m, 1H,  $^{\text{nbe}7}\text{CH}_2$ ), 1.78 (m, 1H,  $^{\text{nbe}7}\text{CH}_2$ ), 2.12 (br, 1H,  $^{\text{nbe}5}\text{CH}$ ), 2.31 (m, 1H,  $^{\text{nbe}6}\text{CH}_2$ ), 3.00 (s, 1H,  $^{\text{nbe}1}\text{CH}$ ), 3.26 (s, 1H,  $^{\text{nbe}4}\text{CH}$ ), 6.05 ( $\tau\text{d}$ ,  $^3\text{J}_{\text{HH}} = 6.7$  Hz,  $^4\text{J}_{\text{HH}} = 1.4$  Hz, 1H,  $^{\text{mp}5}\text{CH}$ ), 6.33 ( $\tau\text{d}$ ,  $^3\text{J}_{\text{HH}} = 7.6$  Hz, 1H,  $^{\text{mp}4}\text{CH}$ ), 6.35 (dd,  $^3\text{J}_{\text{HH}}$  unresolved, 1H,  $^{\text{nbe}2}\text{CH}$ ), 6.46 (dd,  $^3\text{J}_{\text{HH}} = 5.6$  Hz,  $^3\text{J}_{\text{HH}} = 2.9$  Hz, 1H,  $^{\text{nbe}3}\text{CH}$ ), 7.02 (m, 9H,  $m/p\text{-PPh}_3$ ), 7.30 (d,  $^3\text{J}_{\text{HH}} = 8.5$  Hz, 1H,  $^{\text{mp}3}\text{CH}$ ), 7.87 (m, 6H,  $o\text{-PPh}_3$ ), 8.33 (d,  $^3\text{J}_{\text{HH}} = 6.5$  Hz, 1H,  $^{\text{mp}6}\text{CH}$ ).  $^1\text{H}\{^{11}\text{B}\}$  NMR  $\delta$  ( $\text{C}_6\text{D}_6$ ):  $-2.11$  (dd,  $^1\text{J}_{\text{RhH}}$  and  $^2\text{J}_{\text{HH}} = 40.5$  Hz and 23.8 Hz, 2H,  $\text{BH}_2\text{Rh}$ ).  $^{11}\text{B}$  NMR  $\delta$  ( $\text{C}_6\text{D}_6$ ):  $-5.5$  (br. no  $^1\text{J}_{\text{BH}}$  coupling observed, h.h.w. = 320 Hz).  $^{11}\text{B}\{^1\text{H}\}$

NMR  $\delta$  ( $C_6D_6$ ): -5.5 (s, h.h.w. = 230 Hz).  $^{31}P\{^1H\}$  NMR  $\delta$  ( $C_6D_6$ ): 42.8 (d,  $^1J_{RhP}$  = 172 Hz).  $^{13}C\{^1H\}$  NMR  $\delta$  ( $C_6D_6$ ): 30.0 (br,  $^{nbe5}C$ ),<sup>32</sup> 33.1 (s,  $^{nbe6}C$ ), 43.4 (s,  $^{nbe1}C$ ), 46.2 (s,  $^{nbe4}C$ ), 52.0 (s,  $^{nbe7}C$ ), 115.1 (s,  $^{mp5}C$ ), 128.3 [*m*-P( $C_6H_5$ )<sub>3</sub>],<sup>46</sup> 129.5 (s,  $^{mp3}C$ ), 130.2 [d,  $^4J_{PC}$  = 2.2 Hz, *p*-P( $C_6H_5$ )<sub>3</sub>], 131.8 (s,  $^{mp4}C$ ), 135.1 (s,  $^{nbe2}C$ ), the signal for *i*-P( $C_6H_5$ )<sub>3</sub> was not observed, 135.5 (s,  $^{nbe3}C$ ), 143.7 (s,  $^{mp6}C$ ), 173.9 (s,  $^{mp2}C$ )<sup>47</sup>, 191.5 (poorly resolved signal, CO). IR ( $cm^{-1}$ , ATR powder film) 1976, 2860, 2946, 3055. MS EI<sup>+</sup> : *m/z* 515.3 [*M* - nbe - H]<sup>+</sup>.

### X-ray Crystallography

Single-crystal X-ray diffraction studies of complexes **1** and **3** were carried out at the UK National Crystallography Service at the University of Southampton.<sup>48</sup> Single crystals of **1** were obtained by allowing a saturated hexane solution stand at room temperature for 48 h. Single crystals of complex **3** were obtained by allowing an ether solution to stand and slightly concentrate overnight. The samples were mounted on a MITIGEN holder in perfluoroether oil on a Rigaku FRE+ equipped with HF Varimax confocal mirrors and an AFC12 goniometer and HG Saturn 724+ detector. The crystals were kept at *T* = 100(2) K during data collection. Data were collected and processed and empirical absorption corrections were carried out using CrysAlisPro<sup>49</sup> The structures were solved by Intrinsic Phasing using the ShelXT structure solution program<sup>50</sup> and refined on  $F_o^2$  by full-matrix least squares refinement with versions 2014/7 and 2016/6, for **1** and **3** respectively, of ShelXL<sup>51</sup> as implemented in Olex2,<sup>52</sup> For complex **1**, the structure contained two independent complexes in the asymmetric unit, each of which contained disorder of the [**Mmp**]<sup>-</sup> ligand occupying both respective sites *trans* to the double bonds of the NBD ligand, in ratios of 56:44 and 89:11, respectively. Only, the complex which was found as the major component is shown in Figure 4. All hydrogen atoms at boron were located in the difference map except those located on the minor disorder component of the second molecule of the asymmetric unit. These and all other



hydrogen atom positions were calculated geometrically and refined using the riding model. Crystal Data:  $C_{12}H_{15}BNSRh$ ,  $M_r = 319.03$ , monoclinic,  $P2_1/n$  (No. 14),  $a = 6.58930(10) \text{ \AA}$ ,  $b = 30.0229(4) \text{ \AA}$ ,  $c = 12.2379(2) \text{ \AA}$ ,  $\beta = 91.7550(10)^\circ$ ,  $\alpha = \gamma = 90^\circ$ ,  $V = 2419.89(6) \text{ \AA}^3$ ,  $T = 100(2) \text{ K}$ ,  $Z = 8$ ,  $Z' = 2$ ,  $\mu(\text{MoK}\alpha) = 1.552$ , 22354 reflections measured, 5542 unique ( $R_{int} = 0.0327$ ) which were used in all calculations. The final  $wR_2$  was 0.0558 (all data) and  $R_I$  was 0.0287 ( $I > 2(I)$ ). For complex **3**, the hydrogen atoms at boron were located in the difference map and all other hydrogen atom positions were calculated geometrically and refined using the riding model. The norbornenyl moiety is disordered over two positions with an approximate ratio of 84:16. Only the major component is shown in Figure 5. Crystal Data:  $C_{31}H_{48}BNOPRhS$ ,  $M_r = 627.45$ , monoclinic,  $C2/c$  (No. 15),  $a = 26.0508(6) \text{ \AA}$ ,  $b = 9.3936(2) \text{ \AA}$ ,  $c = 24.6207(4) \text{ \AA}$ ,  $\beta = 94.141(2)^\circ$ ,  $\alpha = \gamma = 90^\circ$ ,  $V = 6009.2(2) \text{ \AA}^3$ ,  $T = 100(2) \text{ K}$ ,  $Z = 8$ ,  $Z' = 1$ ,  $\mu(\text{MoK}\alpha) = 0.716$ , 28571 reflections measured, 6853 unique ( $R_{int} = 0.0466$ ) which were used in all calculations. The final  $wR_2$  was 0.0646 (all data) and  $R_I$  was 0.0261 ( $I > 2(I)$ ). A summary of the crystallographic data collection parameters and refinement details for the two complexes are presented in the supporting information. Anisotropic parameters, bond lengths and (torsion) angles for these structures are available from the CIF files which have been deposited with the Cambridge Crystallographic Data Centre and given the following deposition numbers, 1567561 (**1**) and 1567562 (**3**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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## ASSOCIATED CONTENT

The following files are available free of charge.

Crystallographic parameters, selected distances and angles for the two crystal structures in addition to selected spectroscopic data are provided in the Electronic Supporting Information.

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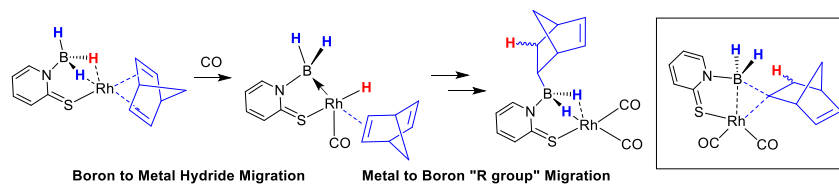
### **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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## Graphical Abstract



The reactivity of a mono-substituted borohydride unit is presented in which a hydride is first transferred to the metal, a migratory insertion step occurs and then the newly formed organic fragment is returned back to boron. The boron and metal centre work in cooperation to furnish an intramolecular hydroboration of a pre-coordinated norbornadiene.