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Unravelling the Mechanism of Phosphine-Borane Dehydrocoupling for the Synthesis to Order of Valuable New Materials

DEHYDROCOUPLE

Unravelling the Mechanism of Phosphine-Borane Dehydrocoupling for the Synthesis to Order of Valuable New Materials

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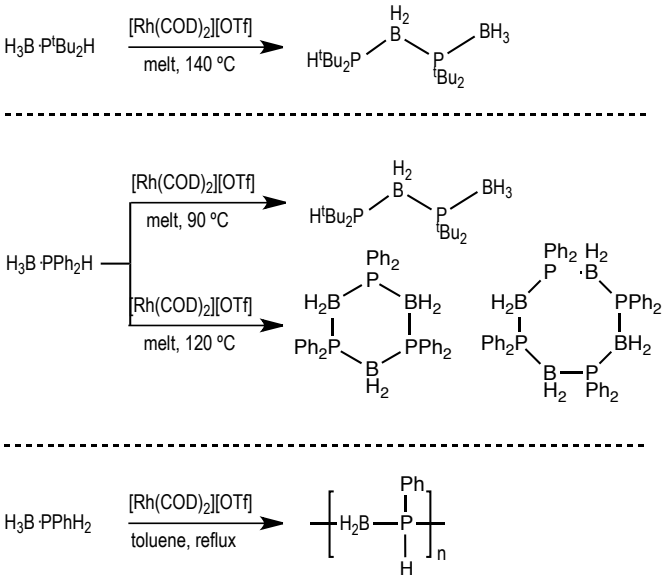
INTRODUCTION

The synthesis of polymeric materials based in the skeleton of alternating phosphorous and boron atoms, poly-(phosphino-boranes), received significant attention in 1950s and 1960s as such materials seemed likely candidates for accessing valuable, high-performance such as high-temperature stability and flame retardancy.[1] However, these materials have not been developed due to the lack of reliable methods for their synthesis. Recently rhodium (I)-catalyzed dehydrocoupling has been described as a route to these materials, as well as the synthesis of dimers, oligomers and polymeric derivatives of $H_3B{\cdot}PPhH_2$, $H_3B{\cdot}P^tBu_2H$ and $H_3B{\cdot}PPh_2H$ (Scheme 1).[2] However, the mechanism for this process is unknown, apart from the fact that it is homogeneous, rather than heterogeneous, process. In this project I am developing well defined catalyst for this process and determining the catalytic cycle.



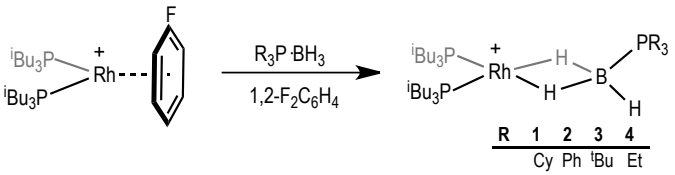
Scheme1. Catalytic dehydrocoupling of phosphine-boranes.

RESULTS

Synthesis of σ-complexes of $H_3B{\cdot}PR_3$

The research group of Weller (host) has recently reported the synthesis of $[Rh(PR_3)(\eta^2\text{-}H_3B{\cdot}NMe_3)][BAr^F{}_4]$, $[RhH_2(PR_2)(\eta^2\text{-}H_3B{\cdot}NMe_3)][BAr^F{}_4]$ and $[Rh(Ph_2P(CH_2)_nPPh_2)(\eta^2\text{-}H_3B{\cdot}NMe_3)][BAr^F{}_4]$ (R = ^{i}Bu, ^{i}Pr; n = 3-5).[3] We decided start this project expanding this well known reactivity to phosphino-boranes. The substrates $H_3B{\cdot}PR_3$ (R = Cy, Et, ^{t}Bu, Ph) does not contain PH group and cannot undergo a dehydrocoupling process in the metal center. These should be relatively stable after σ-coordination to Rh(I) and Rh(III) fragments. Reaction of $H_3B{\cdot}PR_3$ (R = Et, Cy, ^{t}Bu, Ph) with $[Rh(P^iBu_3)(C_6H_5F_2)][BAr^F{}_4]$ in 1,2-$F_2C_6H_4$ solution led to the

immediate change of colour from deep orange to dark blue. NMR data, ESI-MS, and solid state structure (when R = Cy) identify these new products as $[Rh(P^iBu_3)_2(\eta^2\text{-}H_3B{\cdot}PR_3)][BAr^F{}_4]$ (**1a**-**4a**) (Scheme 2). Air stable crystals of **1a** were grown from 1,2-$F_2C_6H_4$/pentane and the molecular structure is shown in Figure 1.



Scheme2. Synthesis of compounds **1**-**4**.

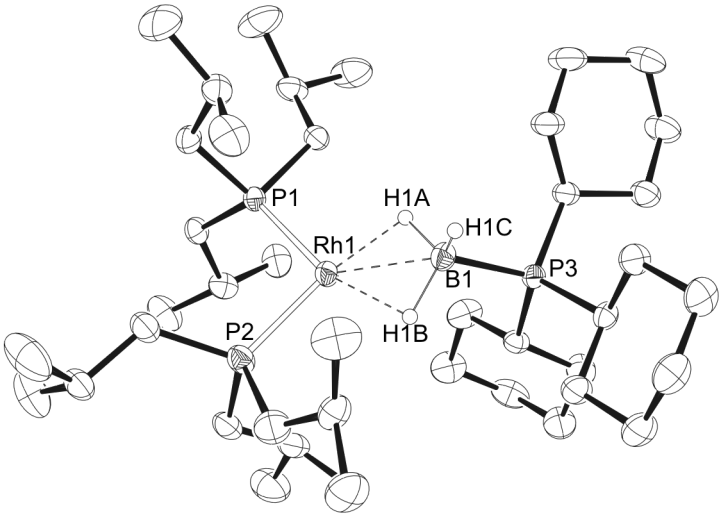
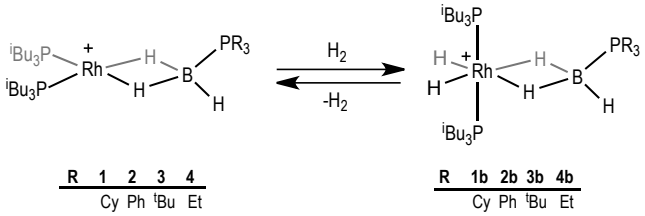


Figure 1. Molecular structure of the cationic portion of **1a**: Ellipsoids depicted at 40% probably level. Minor disordered components and most H atoms omitted for clarity.

The cation in salt **1a** has a pseudo-square-planar Rh(I) center (sum of angles around Rh1 = 360.16º) with cis-phosphines and an η^2-coordinated phosphine-borane bonding through two three-center, two-electron bonds. The Rh···B distance [2.194(3) Å] is significantly sorter than that observed in the Rh(I) chelated complex $[Rh(COD)(\eta^2\text{-}H_3B{\cdot}PR_2CH_2PPh_2)][BPh_4]$ [2.313(3) Å][4] but very similar to that observed in the amine-borane σ-complex of Rh(I) $[Rh(P^iBu_3)(\eta^2\text{-}H_3B{\cdot}NMe_3)][BAr^F{}_4]$ [2.180(4) Å].[3b] The two distances Rh1-H1A and Rh1-H1B are longer than found for the terminal hydride H1C, as expected.

In solution, the η^2-BH_3 binding observed in the solid state, is not observed. The ^1H NMR for compound **1** shows a signal at -1.7 ppm with relative integral 3H. This fact indicates rapid site exchange between bond and terminal B-H. Cooling at 190 K did no affect the observed spectrum at room temperature, the same experiment on $[Rh(P^iBu_3)(\eta^2\text{-}H_3B{\cdot}NMe_3)][BAr^F{}_4]$ shows an arrest of the fluxional process.[3b] While $^{31}P\{^1H\}$ NMR spectrum, one environment is observing coupling constant of 180 Hz (for two $^iBu_3P$ groups) is consistent with a Rh(I) centre. The ^{11}B NMR spectrum displays a broad signal at -4.1 ppm, shifted 38.3 ppm downfield from phosphine-borane free consistent with a significant Rh···B interaction. We can assume that the interaction Rh···B in phosphine-boranes is stronger than in amine-boranes. The ^1H, $^{31}P\{^1H\}$ and ^{11}B NMR spectra for **2a**, **3a**, and **4a** are similar to **1a**, and are consistent with the similar structure in solution.

The addition of H_2 to complexes **1a**-**4a** results in a immediate colour change to pale yellow in all cases. In comparison experiments previously reported with amine-boranes,[3] we assume that this change of colour is consistent with the formation of the Rh(III) species $[Rh(H)_2(P^iBu_3)_2(\eta^2\text{-}H_3B{\cdot}PR_3)][BAr^F{}_4]$ **1b-4b**. Scheme 3.



Scheme 3. Synthesis of compounds **1b**-**4b**.

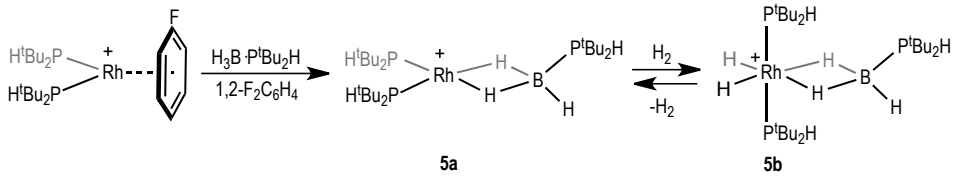
Complexes **1b-4b** loss H_2 to re-form **1-4** only degassing the solutions. ^{1}H, $^{31}P\{^{1}H\}$ and ^{11}B NMR spectrum for compound **1b** are consistent with the structure shown in the Scheme 3. ^{1}H NMR spectrum shows the coordinated borane group as a broad 3H signal δ -0.27 ppm, this suggests rapid exchange of terminal and coordinated hydrides. The two hydrido ligands are observed as a 2H dt, δ -19.8 [*J*(RhH) 28 Hz, *J*(PH) 17 Hz]. The presence of a Rh(III) center is indicated by a reduced ^{103}Rh-^{31}P coupling constant compared with **1**, δ 20.5 ppm [dt, *J*(RhP) 108 Hz, *J*(HP) 14 Hz]. The ^{11}B NMR spectrum shows the signal for the phosphine-borane group at -17.1 ppm, shifted 25.3 ppm downfield from phosphine-borane free consistent with a weaker Rh···B interaction in comparison with compound **1b.** The ^{1}H, $^{31}P\{^{1}H\}$ and ^{11}B NMR spectra for **2b**, **3b**, and **4b** are similar to **1b** ones, and are consistent with the same structure in solution.

Reaction of $H_3B{\cdot}PR_2H$ with Rh(I) compounds.

Showing after that phosphino-boranes are able to be η^2-coordinated, bonding through two three-centre, two-electron bonds to Rh(I) centres, we decided expand this reactivity to secondary phosphino-boranes. These PB compounds would be useful for dehydrocoupling reactions. In the introduction we reported as the conditions and final results of the dehydrocoupling of $H_3B{\cdot}P^tBu_2H$ and $H_3B{\cdot}PPh_2H$ are different.

Study of $H_3B{\cdot}P^tBu_2H$ reactions.

The addition of $H_3B{\cdot}P^tBu_2H$ to $[Rh(P^iBu_3)(C_6H_5F_2)][BAr^F_4]$ in 1,2-$F_2C_6H_4$ solution led to a mixture of complexes identifies as $[Rh(P^iBu_3)_n(P^tBu_2H)_{2-n}(H_3B{\cdot}PR_3)][BAr^F_4]$ (PR_3 = P^iBu_3, P^tBu_2H; n = 2-0). The observation of P^tBu_2H coordinated to Rh centre suggests P-B bond cleavage in the phosphine-borane has ocured, thus to synthesis the analogous compound to $[Rh(P^iBu_3)(C_6H_5F_2)][BAr^F_4]$ with two P^tBu_2H coordinated inside of the P^iBu_3. Reaction of $H_3B{\cdot}P^tBu_2H$ with $[Rh(P^tBu_2H)_2(C_6H_5F_2)][BAr^F_4]$ led to the formation of, in good yield, the compound $[Rh(P^tBu_2H)(\eta^2\text{-}H_3B{\cdot}P^tBu_2H)][BAr^F_4]$ (**5a**) (Scheme 4). NMR and ESI-MS data are in full accord in the description of this compound as σ-phosphine-borane adduct of the $\{Rh(P^tBu_2H)\}^+$ fragment, by comparison by the analogous $H_3B{\cdot}PR_3$ compounds, reported previously. As for $H_3B{\cdot}PR_3$ analogues, the compound **5a** react with H_2 at 4 atm. to form the compound $[Rh(H)_2(P^tBu_2H)_2(\eta^2\text{-}H_3B{\cdot}P^tBu_2H)][BAr^F_4]$ (**5b**). (Scheme 4)



Scheme 4. Synthesis of compounds **5a** and **5b**.

The compound **5a** could be crystallized as blue and square crystals. The solid state structure of **5a** is showed in the Figure 2.

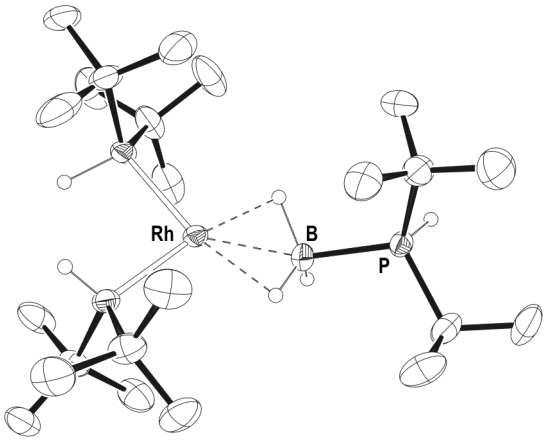
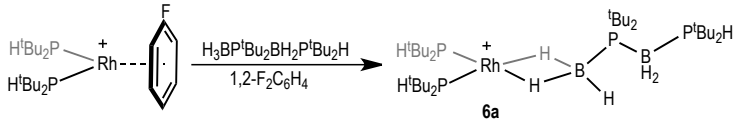


Figure 2. Molecular structure of the cationic portion of **5a**: Ellipsoids depicted at 40% probably level. Minor disordered components and most H atoms omitted for clarity.

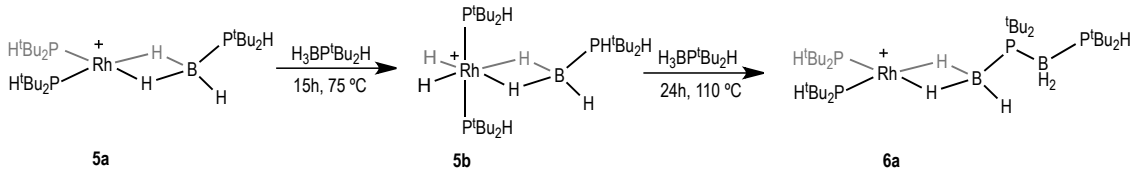
The solid estate structure of compound **5a** is consistent with the structure proposed in solution, but, as happened in the $H_3B{\cdot}PR_3$ analogues, in solution the η^2-BH_3 binding is not observed. The ^1H NMR for compound **5a** shows a signal at -1.7 ppm with one relative integral 3H. This fact indicates rapid site exchange between bond and terminal B-H.

The product in the dehydrogenated of $H_3B{\cdot}P^tBu_2H$ is mainly the dimer $H_3B{\cdot}P^tBu_2{\cdot}BH_2{\cdot}P^tBu_2H$. The reaction of this independently prepared dimer with the compound $[Rh(P^tBu_2H)_2(C_6H_5F_2)][BAr^F{}_4]$ led to the formation of the Rh(I) σ-complex with the dimer η^2-coordinated $[Rh(P^tBu_2H)(\eta^2\text{-}H_3B{\cdot}P^tBu_2{\cdot}BH_2{\cdot}P^tBu_2H)][BAr^F{}_4]$ (**6a**). NMR and ESI-MS data confirm this structure. (Scheme 5)



Scheme 5. Synthesis of compound **6a**.

The addition of other equivalent of $H_3B{\cdot}P^tBu_2H$ to **5a** results in the full conversion to **5b** (15 hours, 75 ºC) (scheme 6). Using higher temperatures (110 ºC) results in the formation of **6a** (Scheme 6). This fact manifest the possible deshydrogenation and oligomeration into the metallic centre.

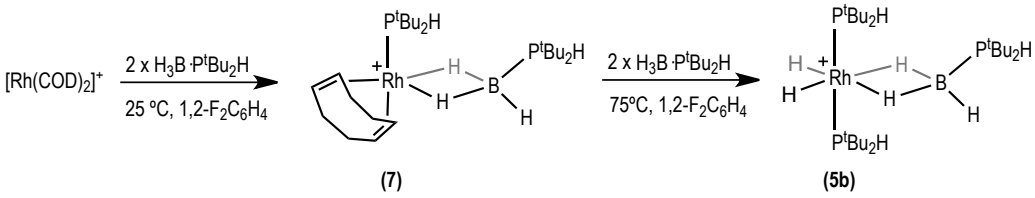


Scheme 6. Reactivity of compound **5a**.

The catalytic deshydrogenation reaction of $H_3B{\cdot}P^tBu_2H$ to form the dimer product $H_3B{\cdot}P^tBu_2{\cdot}BH_2{\cdot}P^tBu_2H$ was made under melt condition at 140 ºC in 20 hours using 10 mol % of $[Rh(P^tBu_2H)_2(C_6H_5F_2)][BAr^F{}_4]$. Interrogating of this catalyst-mixture after 5 hours by $^{31}P\{^1H\}$ and ESI-MS showed that the compounds **5a** and **6a** were present.

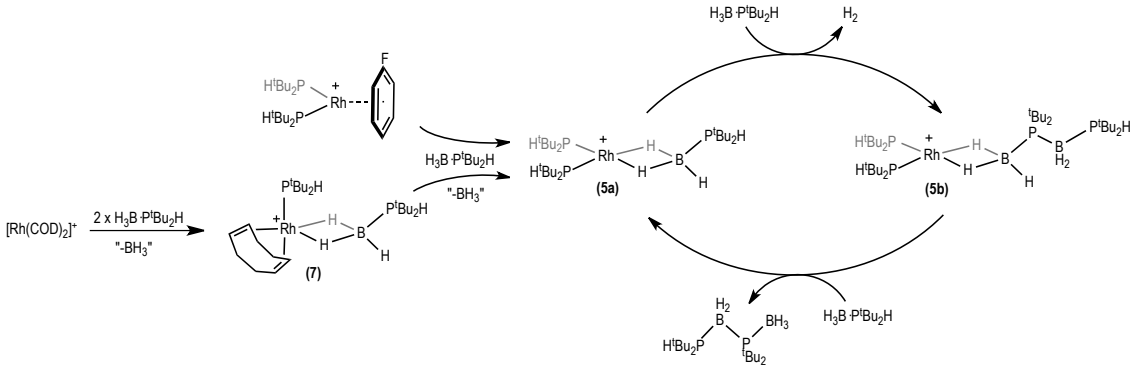
One of the most effective catalyse for this reaction is $[Rh(COD)_2][BAr^F_4]$. Monitoring this reactions in the same conditions (140 ºC under melt conditions) after 5 hours showed that the same **5a** and **6a** compounds are present in the catalyst mixture. We can thus assume that thess two compound are possible intermediates in the hydrogenation catalyst reaction from $H_3B{\cdot}P^tBu_2H$ to $H_3B{\cdot}P^tBu_2{\cdot}BH_2{\cdot}P^tBu_2H$.

Addition of two equivalents of $H_3B{\cdot}P^tBu_2H$ to a $[Rh(COD)_2][BAr^F_4]$ at 25 ºC formed the Rh(I) complex $[Rh(COD)(P^tBu_2H)(\eta^2\text{-}H_3B{\cdot}P^tBu_2H)][BAr^F_4]$ (**7**) (Scheme 7). Heating **7** with two further equivalents of $H_3B{\cdot}P^tBu_2H$ at 75 ºC resulted in the formation of **5b** in a good yield. We suggest that this compound is formed *via* **5a**.



Scheme 7. Reactivity of compound $[Rh(COD)_2][BAr^F_4]$ with $H_3B{\cdot}P^tBu_2H$.

Taken together our observations lead to an outline catalytic cycle as shown in the Scheme 8, with **5a** assigned as resting state in the cycle, although the precise details of the mechanism remain to be resolved.[5]



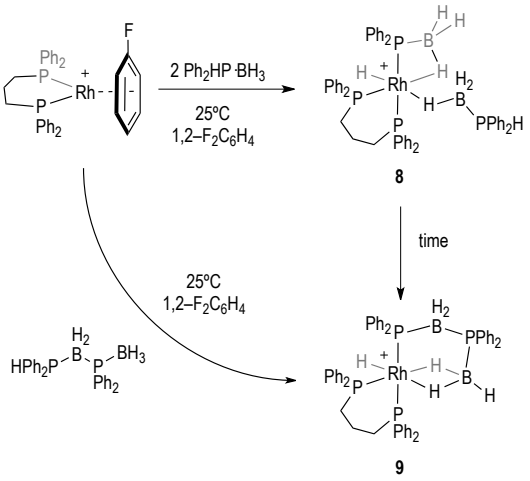
Scheme 8. Proposed catalytic cyclic for the dehydrocoupling of $H_3B{\cdot}P^tBu_2H$.

Study of $H_3B{\cdot}PPh_2H$ reactions.[6]

As we commented in the introduction, catalytic conditions and final products in the dehydrogenation of secondary phosphino-boranes depends of the substituent in the phosphorous atom. For this we have decided to study separately $H_3B{\cdot}P^tBu_2H$ and $H_3B{\cdot}PPh_2H$.

The reaction of one equivalent of $H_3B{\cdot}PPh_2H$ with $[Rh(P^iBu_3)(C_6H_5F_2)][BAr^F_4]$ led to the formation of a unresolved mixture of products, and analytical data suggest that P-B bond cleavage in the phosphine-borane had occured. We decided use Rh(I) compound $[Rh(Ph_2PCH_2CH_2CH_2PPh_2)(C_6H_5F_2)][BAr^F_4]$ to stop this and make the system simples. We thought that the chelate compound could be robust to interchanges in the phosphine ligand. The addition of $H_3B{\cdot}PPh_2H$ to $[Rh(Ph_2PCH_2CH_2CH_2PPh_2)(C_6H_5F_2)][BAr^F_4]$ in 1,2-$F_2C_6H_4$ solution led to 1:1 mixture of starting material and a new product $[Rh(Ph_2PCH_2CH_2CH_2PPh_2)H(PPh_2{\cdot}BH_3)(H_3B{\cdot}PPh_2H][BAr^F_4]$ (**8**). As shows the Scheme 9, compound **8** has coordinated two phosphine-boranes, for this we decided do the reaction in a

ratio 2:1 (phosphino-borane:Rh(I) compound). The reaction of two equivalents of $H_3B{\cdot}PPh_2H$ with one of $[Rh(Ph_2PCH_2CH_2CH_2PPh_2)(C_6H_5F_2)][BAr^F{}_4]$ results in the full conversion to **8** (Scheme 9). Compound **8** undergoes, with the time, a dimerization process and forms the compound **9** (Scheme 9). Compound **9** can be made by addition of the final dimeric product of dehydrocoupling of $H_3B{\cdot}PPh_2H$, $H_3B{\cdot}PPh_2BH_2{\cdot}PPh_2H$, to $[Rh(Ph_2PCH_2CH_2CH_2PPh_2)(C_6H_5F_2)][BAr^F{}_4]$ cleanly generates a new complex in which this oligomeric phosphine–borane is now bound.



Scheme 9. Synthesis of compounds **8** and **9**.

Complex **9** can also be prepared (~95% by $^{31}P\{^1H\}$ NMR spectroscopy) by simply leaving **8** at 25 ºC ($1,2–F_2C_6H_4$ solution) for 16 hours, Scheme 5. Dissolved H_2 (δ 4.40) is also observed, consistent with dehydrocoupling. At 40 ºC this process takes 4 hours and is essentially quantitative. With the generation of **9** from **8** established we then turned to studying this process in more detail. Complex **8** undergoes transformation to **9** by a first order process (25 ºC , k = (4.36 ± 0.07) x 10^{-5} s^{-1}, $t_{1/2}$ = 4.4 hr), Figure 3, as measured by the absolute integrals of the Rh–H signals in both **8** and **9.** This is consistent with a simple intramolecular process for the dehydrocoupling. Measurement of this process over the temperature range 20 ºC to 35 ºC allowed for an Eyring analysis, from which the following activation barriers were determined: $\Delta H^‡$ = 114.5 ± 1.5 kJmol^{-1}, $\Delta S^‡$ = +55.0 ± 5.3 Jmol^{-1}K^{-1} and $\Delta G(298)^‡$ = 98.0 ± 3.1 kJmol^{-1}.

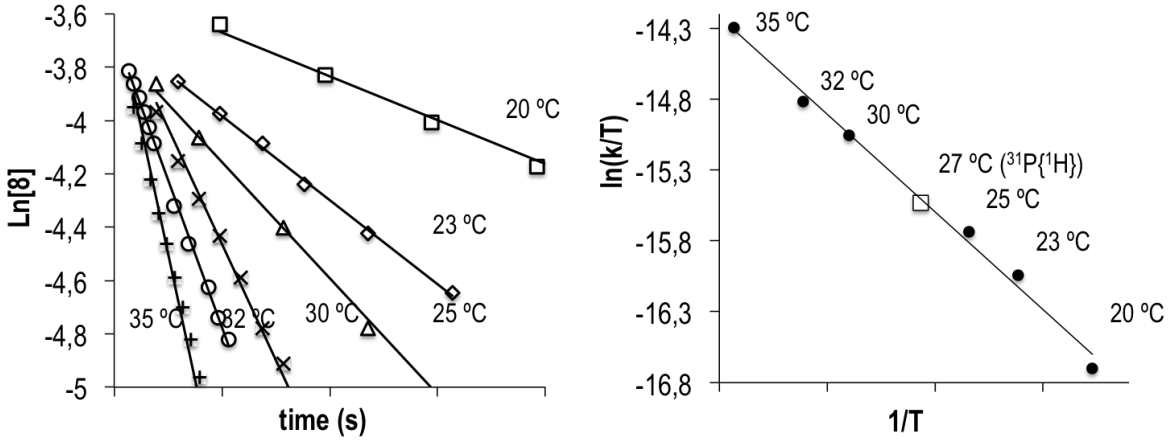
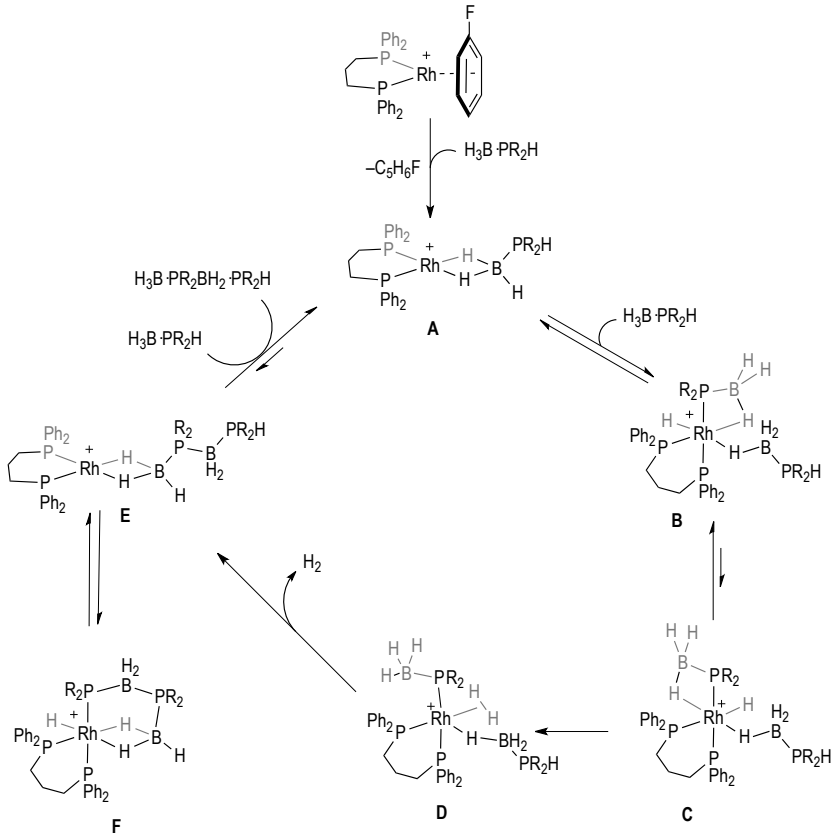


Figure 3. First order plots and Eyring analysis.

Deuteration experiments have been used to probe the mechanism of this coupling process. Addition of two equivalents of $D_3B{\cdot}PPh_2H$ to $[Rh(Ph_2PCH_2CH_2CH_2PPh_2)(C_6H_5F_2)][BAr^F{}_4]$ resulted in incorporation of D into *all* the B–H/P–H and Rh–H positions of **8** as measured by ^1H and ^2H NMR spectroscopy after only 10 minutes (25 ºC) to give ***h/d*–8**. The H/D incorporation into both the B and P sites was equitable, i.e. 1:3 H : D, as follows from the starting borane (Scheme 7). This suggests that relatively rapid reversible B–H and P–H activation occurs in **8** with similar barriers. This exchange operates at a rate slower than the NMR timescale, as in the presence of excess $H_3B{\cdot}PPh_2H$ signals are observed for free phosphine–borane and **8** which are essentially unchanged in line width [$^{31}P\{^1H\}$ NMR]. Heating isotopically enriched ***h/d*–8** for 8 hours at 40ºC results in incorporation of D into all the B–H/P–H and Rh–H positions of the thus formed ***h/d*–9**. The kinetics of this process were followed using $^{31}P\{^1H\}$ NMR spectroscopy as, due to isotopic scrambling, monitoring the hydride resonances added extra complexity to the analysis by ^1H NMR spectroscopy. To validate this approach the first order consumption of **8** to give **9** was followed by $^{31}P\{^1H\}$ NMR spectroscopy at 27 ºC, giving a rate constant fully consistent with those measured from ^1H NMR spectroscopy, k = (5.4 ± 0.2) x 10^{-5} s^{-1}; Figure 1c. Using ***h/d*–8** the rate was measured as (2.77 ± 0.05) x 10^{-5} s^{-1} giving a KIE of 1.9 ± 0.1 for this level of deuteration. Use of the fully deuterated $D_3B{\cdot}PPh_2D$ resulted in the formation of ***d*-9** [k = (2.26 ± 0.03) x 10^{-5} s^{-1}] and a KIE of 2.3 ± 0.2. These data indicate that either BH or PH activation are involved in the rate determining process

Bringing our observations together allows a catalytic cycle for the dehydrocoupling of $H_3B{\cdot}PPh_2H$ to give $H_3B{\cdot}PPh_2BH_2{\cdot}PPh_2H$, as catalysed by $[Rh(Ph_2PCH_2CH_2CH_2PPh_2)(C_6H_5F_2)][BAr^F{}_4]$, to be proposed, Scheme 10. The main features of this catalytic cycle (P–H activation followed by B–H activation) are related to those reported for Rh–catalysed homo– and heterodehydrocouplings of phosphines, although the precise details of the activation / bond forming steps differ.



Scheme 10. Proposed catalytic cycle for the dehydrocoupling of $H_3B{\cdot}PR_2H$ to give $H_3B{\cdot}R_2BH_2{\cdot}R_2H$. $[BAr^F{}_4]^-$ anions are not shown.

We have demonstrated that $[Rh(Ph_2PCH_2CH_2CH_2PPh_2)(h^6{-}FC_6H_5)][BAr^F{}_4]$ is a competent catalyst for the dehydrocoupling of $H_3B{\cdot}PPh_2H$ to give $H_3B{\cdot}PPh_2BH_2{\cdot}PPh_2H$. The isolation of intermediates, alongside kinetic and isotopic labelling experiments, point to a mechanism in which the rate-limiting process for dehydrocoupling involves B–H (or P–H) bond cleavage. The turnover limiting process for catalysis involves the substitution of the oligomeric product by $H_3B{\cdot}PPh_2H$, as the former forms a strong chelate complex with the Rh(III) centre, in which P–H activation has also occurred. In contrast, dehydrocoupling of $H_3B{\cdot}P^tBu_2H$ gives $H_3B{\cdot}P^tBu_2BH_2{\cdot}P^tBu_2H$ which does not form a chelate complex with the metal and does not undergo P–H activation. For this substrate we suggest that the turnover limiting step in catalysis is the dehydrocoupling processes. The inference from these observations is that the relatively harsh melt conditions used for dehydrocoupling are not necessarily related to the P–B bond forming step, but product–release from the metal; with the relative barriers to these two processes dependent on the identity phosphine–borane.

Extending this study to other secondary phosphine–boranes.[7]

The behaviour of the phosphine-boranes in the dehydrocoupling reaction is different depending if the phosphine is $^tBu_2HP{\cdot}BH_3$ or $Ph_2HP{\cdot}BH_3$, we attribute this performance to different steric and electronic profiles. We decided then, synthesize several phosphine-boranes (**a**, **b**, **c** and **d,** Figure 4). **a** and **b** have as substituents on the phosphine two 3,5-bis(trifluorometylphenyl) and *para*-trifluoromethylphenyl respectively. The presence of the fluorinated substituents (EWG) on phosphorous will make dehydrocoupling reaction more favourable. The problem of use these EWG is that thy make weaker the P–B bond. To compare different phosphines we decided synthetises the phosphine-borane with two *para*-methoxyphenyl groups as substituents on the phosphorous (**c**, Figure 4). We expected that methoxy groups (EDG, Electron donating groups) are making the dehydrocoupling reaction slower than when $Ph_2HP{\cdot}BH_3$ is used.<Huertos, 2013 #2> Steric factors could be important in the dehydrocoupling reaction, for this, we decided synthetized the phosphine–borane **d** (Figure 4), that have two adamantyl groups on the phosphorous atom.

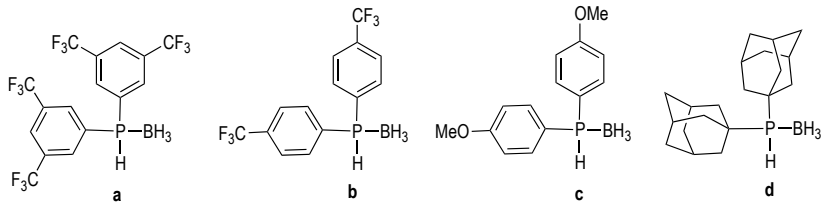
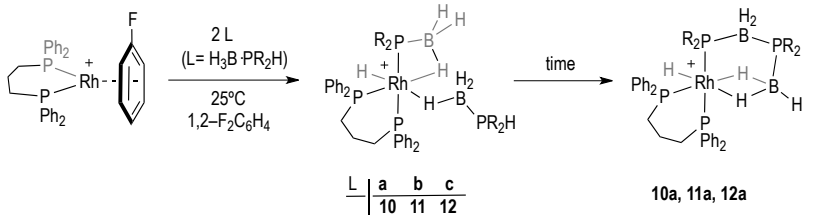


Figure 4. Phosphine-boranes used.

Addition of two equivalents of **a** to $[Rh(Ph_2PCH_2CH_2CH_2PPh_2)(\eta^6{-}FC_6H_5)][BAr^F{}_4]$ in 1,2–$F_2C_6H_4$ at 25 ºC, rapidly results the formation of $[Rh(Ph_2PCH_2CH_2CH_2PPh_2)H(\sigma,\eta{-}PPh_2BH_3)(\eta^1{-}H_3B{\cdot}PPh_2H)][BAr^F{}_4]$, **10** (Scheme 11). One of the phosphine–boranes undergo a P–H activation, while the other equivalent is bounded to the metal *via* a *sigma* B–H–Rh interaction. The reaction of $[Rh(Ph_2PCH_2CH_2CH_2PPh_2)(\eta^6{-}FC_6H_5)][BAr^F{}_4]$ with two equivalents of **b** or **c** results in the formation of the compounds **11** and **12** respectively. These compounds are analogous to **10**

(Scheme 11). We reported that the analogous compound to **10** using $Ph_2HP{\cdot}BH_3$ (**8** in this report) react cleanly to form the stoichiometric dehydrocoupling product (**9** in this report), for this reaction was reported several rate constants at different temperatures. We decided study the effect of EWG (CF_3) or EDG (OMe) on the aromatic ring in the reaction rate. Compound **12** undergo stoichiometric dehydrocoupling to form **12a** (Scheme 3) in 8 hours at 35 ºC. We decided study this process by ^1H NMR and observed that this transformation undergoes by a first order process (35 ºC, k = (1.40 ± 0.05) x 10^{-4} s^{-1}), as measured by the absolute integrals of the Rh–H signals in both **12** and **12a**. This is consistent with that expected that methoxy groups (EDG) makes the dehydrocoupling reaction slower than when $Ph_2HP{\cdot}BH_3$ is used (35 ºC, k = (1.90 ± 0.04) x 10^{-4} s^{-1}). Compounds **10** and **11** do not undergo to **10a** and **11a** cleanly, but we can measure the first order process in the consume of **10** and **11**. These experiments results of a rate constant of (3.12 ± 0.05) x 10^{-4} s^{-1} for **9** and (2.93 ± 0.07) x 10^{-4} s^{-1} for **8** at 25 ºC. These processes are clearly quicker that when $Ph_2HP{\cdot}BH_3$ is used (25 ºC , k = (4.36 ± 0.07) x 10^{-5} s^{-1}) (Figure 6).



Scheme 11. Formation of **10**, **11**, **12** and **10a**, **11a**, **12a**

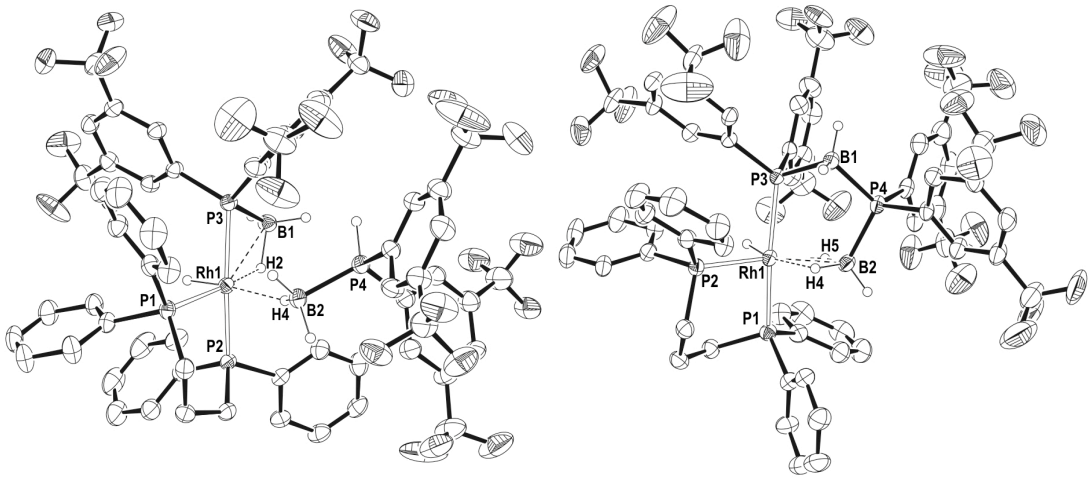


Figure 5. Molecular structure of the cationic portions of **10** (left) and **10a** (right): Ellipsoids depicted at 40% probably level. Minor disordered components and most H atoms omitted for clarity.

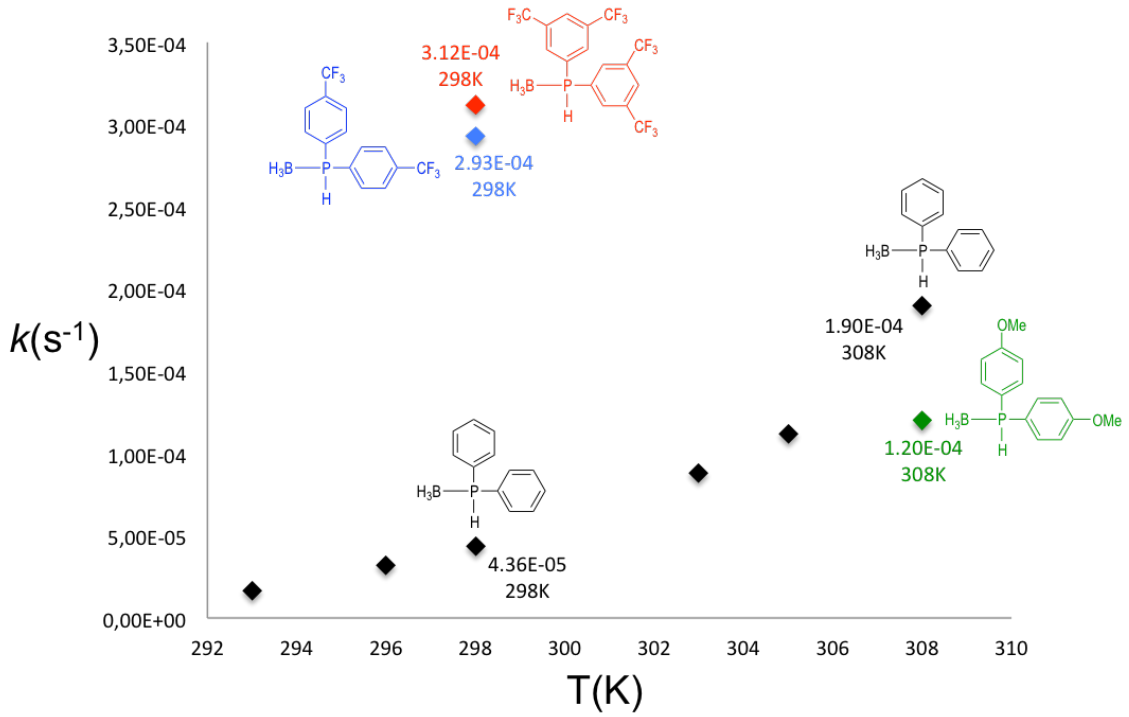
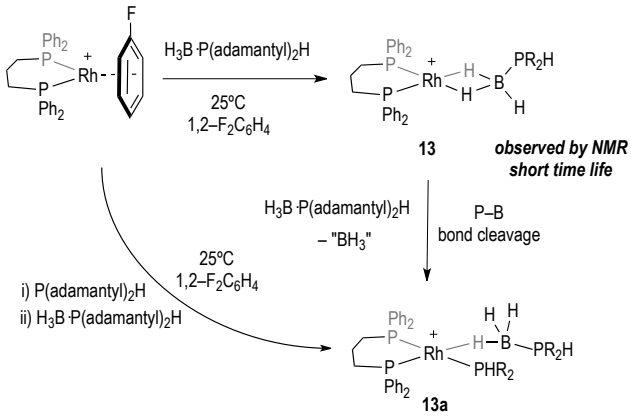


Figure 6. Graphic representation of rates at different temperatures using different phosphine-boranes.

To probe the steric effects that have the phosphine-boranes in the dehydrocoupling, we decided synthetize (adamantyl)$_2$HP·BH$_3$ (**d** in Figure 4). Addition of two equivalents of **d** to [Rh(Ph$_2$PCH$_2$CH$_2$CH$_2$PPh$_2$)(η^6-FC$_6$H$_5$)][BAr$^F{}_4$] in 1,2–F$_2$C$_6$H$_4$ solution at 25ºC rapidly results in a colour change from orange to purple, and the formation of the new sigma phosphine–borane complex [Rh(Ph$_2$PCH$_2$CH$_2$CH$_2$PPh$_2$)(η^2-H$_3$B·P(adamantyl)$_2$H)][BAr$^F{}_4$], **13**, which could not be isolated because of react quickly to form **13a** (Scheme 12). Compound **13a** can be synthetized in two steps, addition of one equivalent of PH(adamantyl)$_2$ and after 5 minutes stirring, addition of one equivalent of **d**.



Scheme 12. Formation of **13** and **13a**

REMARKS

At the final of the projec the following results have been achieved, according to the planning proposed:

- Synthesis of precursor complexes and isolation of model phosphine-borane *σ*-complexes.
- Evaluation in dehydrocoupling reaction of known phosphino-borane precursors.
- Elucidate intermediates and models in dehydrogenation reactions.
- Kinetic and Thermodynamic data for the dehydrocoupling process.

SUMARY OF THE PROGRESS OF THE RESEARCH TRAINING

Research skills and techniques

- Experience of developing new transition-metal catalysed synthetic methodology for the synthesis of new catalyst systems and intermediate complexes relevant to the catalytic cycle.
- Advanced level training in analytical techniques. ^{1}H, ^{31}P, ^{11}B NMR spectroscopy over a variable temperature range, associated analyses of kinetic data. ESI-MS interfaced with an inert atmosphere glove box. Run and solve my own X-ray crystal structures.

Communication skills

- Advising Ph.D. students with the day-to-day running of their projects, as well as identifying breakthrough results for further development.
- Supervising PartII student (Rosalin Faconer).
- Improving presentation and communication skill by regular presentation of research results at weekly research Weller-group meetings.
- Attendance to IME boron XIV (September 2011, Niagara Falls, Canada), presenting a poster.
- Attendance to XXV ICOMC (September 2012, Lisbon, Portugal) presenting a poster.

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