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COMMUNICATION

Intermediates in the Rh-catalysed dehydrocoupling of phosphine–borane†‡

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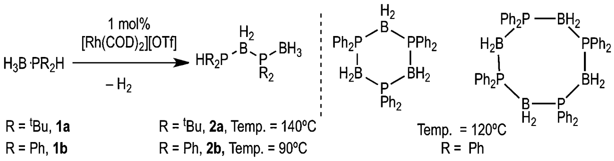
Active species, product distributions and a suggested catalytic cycle are reported for the dehydrocoupling of the phosphine–borane $H_3B{\cdot}P^tBu_2H$ to give $HP^tBu_2BH_2P^tBu_2BH_3$ using the $[Rh(COD)_2][BAr^F{}_4]$ pre-catalyst.

The transition-metal mediated catalytic dehydrocoupling[1] of primary and secondary phosphine–boranes is potentially a very useful process for delivering oligomeric and polymeric materials with P–B bonds, for example polyphosphinoboranes that find application as electron beam resists and as pre-ceramic precursors to semi-conducting boron-phosphide.[2] Such polymeric materials are also exciting in that they are valence isoelectronic with technologically ubiquitous polyolefins. Metal-catalysed routes to their synthesis offer the potential for control over molecular weight, stereochemistry and functional-group tolerance. The current best catalyst, originally reported in 1999, uses the $[Rh(COD)_2][OTf]$ precursor in neat phosphine–borane under melt conditions (90–140 °C),[3,4] although other catalyst systems have been reported.[4–6] For secondary phosphines, depending on the substituent on phosphorus and the reaction temperature, dimeric $HPR_2BH_2PR_2BH_3$ (R = ^{t}Bu, **2a**; Ph, **2b**) or cyclic (R = Ph) oligomers are formed, Scheme 1.[4,7]

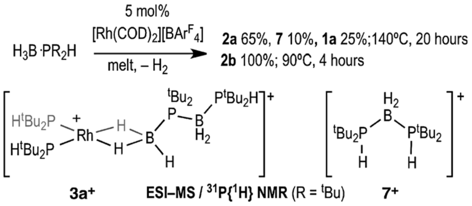
Although experimental evidence points strongly to a homogeneous, rather than heterogeneous, catalyst;[8] due to the high temperature melt conditions required, details regarding the active species and mechanism are scarce.[5,6,9] This is in contrast to amine–borane dehydrocoupling where reactions occurring at room temperature in common solvents have allowed for mechanistic details to be resolved.[10] For example we have recently reported complex pathways for dehydrocoupling that revolve around Rh(I) and Rh(III) sigma complexes of amine–boranes,[11,12] and such insight leads to the rationalisation of the relative efficiency of certain catalysts.[13] As the direct study of the species present in phosphine–borane dehydrocoupling under the melt conditions required for catalysis is problematic, we instead report complementary studies that interrogate *indirectly* the melt. These studies demonstrate that species closely related to those observed in analogous amine–borane chemistry are likely to be present during catalysis.



Scheme 1 Dehydrocoupling of $H_3B{\cdot}PR_2H$ using $[Rh(COD)_2][OTf]$ as a catalyst (R = ^{t}Bu, Ph) under melt conditions.

We initially chose to study the dehydrocoupling of $H_3B{\cdot}PPh_2H$, **1b**, as this gives a single product, **2b**, in high conversion at 90 °C.[3] However, indirect monitoring of this melt reaction of $[Rh(COD)_2][BAr^F]$ by dissolving in 1,2-$F_2C_6H_4$ solvent, using electrospray ionisation mass spectrometry (ESI-MS) and $^{31}P\{^1H\}$ NMR spectroscopy, showed multiple organometallic species; while attempts to synthesise possible intermediate species also led to multiple products (*vide infra*). By contrast, the ^{t}Bu-substituted starting material, $H_3B{\cdot}P^tBu_2H$, **1a**, afforded generally well-defined species that allowed for the identification of likely intermediates. Thus after 20 hours under melt conditions (140 °C) catalysis using $[Rh(COD)_2][BAr^F]$ formed **2a** in moderate yield (~65%), as reported.[7] Interestingly the bis-phosphine-boronium $[(^tBu_2HP)_2BH_2][BH_4]$, **7[BH₄]**,[14] was also formed as a co-product (~10%, Scheme 2). Interrogation of a catalyst-mixture after 5 hours by $^{31}P\{^1H\}$ NMR spectroscopy and ESI-MS (1,2-$F_2C_6H_4$ solution) showed that the cations $[Rh(P^tBu_2H)_2(\eta^2\text{-}H_3B{\cdot}P^tBu_2BH_2P^tBu_2H)]^+$, **3a**$^+$, and $[Rh(P^tBu_2H)_2(\eta\text{-}F_2C_6H_4)]^+$, **8**$^+$, were present in a ~1 : 1 ratio.[15] We presume that **8**$^+$ is formed by reaction of a $[Rh(P^tBu_2H)_2]^+$ fragment with the excess of solvent.[11]

The observation of P^tBu_2H ligation in **3a**$^+$ suggests that P–B bond cleavage in **1a**, as commented on previously,[6,8] had occurred. To further explore this, addition of **1a** to $[Rh(P^iBu_3)_2(C_6H_5F)][BAr^F{}_4]$ in 1,2-$F_2C_6H_4$ solution, a catalyst we have successfully used in amine–borane dehydrocoupling,[11]



Scheme 2 Monitoring dehydrocoupling under melt conditions upon dissolving in 1,2-$F_2C_6H_4$.

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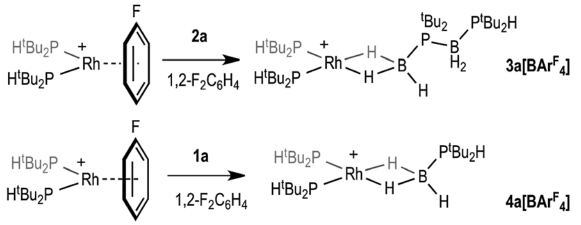
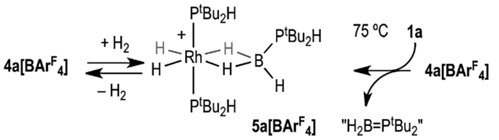
‡ Electronic supplementary information (ESI) available: Synthesis and characterisation of new complexes and catalysis monitoring. CCDC 865050. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc32696e



Scheme 3 Synthesis of **3a[BAr$^F_4$]** and **4a[BAr$^F_4$]**. [BAr$^F_4$] anions not shown.

resulted in a mixture of complexes identified as $[\mathrm{Rh}(\mathrm{P}^i\mathrm{Bu}_3)_n(\mathrm{P}^t\mathrm{Bu}_2\mathrm{H})_{2-n}(\mathrm{H}_3\mathrm{B}{\cdot}\mathrm{PR}_3)][\mathrm{BAr^F}_4]$ ($\mathrm{PR}_3 = \mathrm{P}^i\mathrm{Bu}_3$, $\mathrm{P}^t\mathrm{Bu}_2\mathrm{H}$; n = 2–0; ESI). Complex **3a[BAr$^F_4$]** could be synthesised in good yield by addition of **2a**[7] to $[\mathrm{Rh}(\mathrm{P}^t\mathrm{Bu}_2\mathrm{H})_2(\eta\text{-}\mathrm{C}_6\mathrm{H}_5\mathrm{F})][\mathrm{BAr^F}_4]$ **9[BAr$^F_4$]**, Scheme 3. The equivalent complex of **1a** can be synthesised: $[\mathrm{Rh}(\mathrm{P}^t\mathrm{Bu}_2\mathrm{H})_2(\eta^2\text{-}\mathrm{H}_3\mathrm{B}{\cdot}\mathrm{P}^t\mathrm{Bu}_2\mathrm{H})][\mathrm{BAr^F}_4]$ **4a[BAr$^F_4$]**.§ NMR and ESI-MS data are in full accord with the description of these complexes as σ-phosphine–borane adducts of the $\{\mathrm{Rh}(\mathrm{P}^t\mathrm{Bu}_2\mathrm{H})_2\}^+$ fragment, by comparison with the analogous amine–borane complexes[11,12] as well as other metal-complexes of phosphine–boranes.[16] In particular, a diagnostic upfield shifted signal in the ^{1}H NMR spectrum for the $\mathrm{Rh}\cdots H_3\mathrm{B}$ interaction (*e.g.* **4a[BAr$^F_4$]**, δ −1.89, 3 H), and down-field shifted signal in the ^{11}B NMR spectrum (*e.g.* **4a[BAr$^F_4$]**, δ 0.5), are observed. The solid-state structure of **4a[BAr$^F_4$]** is shown in Fig. 1. These complexes add to the small number of transition metal complexes reported to be sigma-bound with secondary phosphine–boranes.[17] Those with tertiary phosphine–boranes are better represented.[16,18,19] Attempts to prepare the analogous complexes using $\mathrm{PPh}_2\mathrm{H}$ were not successful, leading to mixtures of intractable products. Starting from isolated **3a[BAr$^F_4$]** or **4a[BAr$^F_4$]** as catalysts under melt conditions (5 mol%, 140 °C) gives productive turnover and the same mixture of products as with $[\mathrm{Rh}(\mathrm{COD}_2][\mathrm{BAr^F}_4]$ (**2a**, **7[BH$_4$]**) consistent with their role in catalysis.



Scheme 4 Routes to **5a[BAr$^F_4$]**. 1,2-F$_2$C$_6$H$_4$ solution [BAr$^F_4$] anions not shown.

Addition of H$_2$ to **4a[BAr$^F_4$]** results in oxidative addition and formation of the Rh(III) dihydride complex $[\mathrm{Rh}(\mathrm{P}^t\mathrm{Bu}_2\mathrm{H})_2(\mathrm{H})_2(\eta^2\text{-}\mathrm{H}_3\mathrm{B}{\cdot}\mathrm{P}^t\mathrm{Bu}_2\mathrm{H})][\mathrm{BAr^F}_4]$ **5a[BAr$^F_4$]** as characterised by NMR spectroscopy (Scheme 4), with diagnostic signals observed in the ^{1}H NMR spectrum at δ −17.67 (2 H, dt, Rh–H, *J*(RhH) 20, *J*(PH) 15 Hz) and δ −0.94 (3 H, br, Rh–H–B, *J*(BH) 104 Hz). Placing **4a[BAr$^F_4$]** under a D$_2$ atmosphere resulted in the formation of $[\mathrm{Rh}(\mathrm{P}^t\mathrm{Bu}_2\mathrm{H})_2(\mathrm{D})_2(\eta^2\text{-}\mathrm{H}_3\mathrm{B}{\cdot}\mathrm{P}^t\mathrm{Bu}_2\mathrm{H})][\mathrm{BAr^F}_4]$ **5a[BAr$^F_4$]-*d*$_2$**. Over time slow H–D exchange occurred at B–H and Rh–D but not at P–H, similar to that observed for analogous amine–borane complexes.[11] HD$_{\text{(dissolved)}}$ was also observed by ^{2}H NMR spectroscopy. Addition of H$_2$ to **4a[BAr$^F_4$]** is reversible, and passing Ar over **5a[BAr$^F_4$]** (less than 5 minutes), or exposure to a hydrogen acceptor or a vacuum regenerates **4a[BAr$^F_4$]**. Interestingly, addition of H$_2$ to **3a[BAr$^F_4$]** did not result in any reaction. These data suggest that cations **4a**$^+$/**5a**$^+$ and **3a**$^+$ are all likely to be present under catalytic conditions.

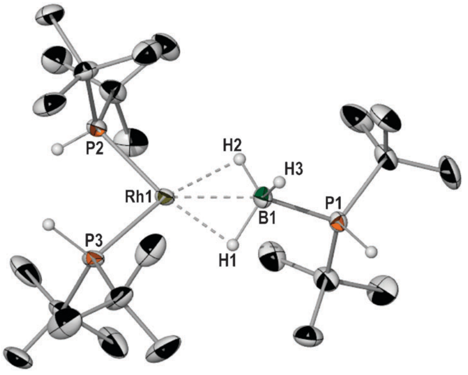
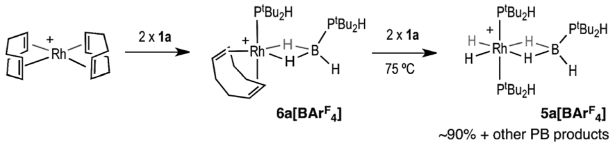


Fig. 1 Solid-state structure of **4a[BAr$^F_4$]**. Most hydrogen atoms and the anion are omitted for clarity, as is the minor disordered component. Displacement ellipsoids are shown at the 40% probability level. Selected bond lengths [Å] and angles [°]: Rh1–B1, 2.188(3); B1–P1, 1.946(3); Rh1–P2, 2.2155(7); Rh1–P3, 2.2035(7); Rh1–H1, 1.87(3); Rh1–H2, 1.90(3); P2–Rh1–P3, 91.12(3).

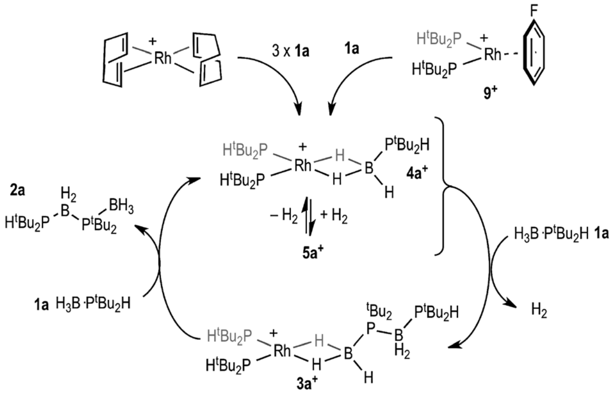
Addition of **1a** to **4a[BAr$^F_4$]** results in the ~10% formation of **5a[BAr$^F_4$]** (5 hours, 60 °C, 1,2-F$_2$C$_6$H$_4$) and unreacted starting material. Full conversion to **5a[BAr$^F_4$]** (~95%) is only achieved at 75 °C after 15 hours, Scheme 4, alongside unidentified phosphine–borane products. Under these non-melt conditions, use of higher temperatures (110 °C) results in the formation of **7**$^+$ and **2a** in an approximate 1 : 1 ratio, but also in the decomposition of the metal fragment. This shows that although melt conditions are not explicitly required for the formation of **2a**, they do influence the balance of final products. We speculate that this reaction proceeds *via* formation of a very reactive (and as yet unreported) $\mathrm{H}_2\mathrm{B}{=}\mathrm{P}^t\mathrm{Bu}_2$ species,[20] by analogy with amine–borane chemistry.[11,21] In the absence of **1a** at 75 °C complex **4a[BAr$^F_4$]** only slowly (5 days) changes into **5a[BAr$^F_4$]** and other as yet to be identified products, demonstrating the requirement for excess **1a** to cleanly form **5a[BAr$^F_4$]**.



Scheme 5 Reactivity of $[\mathrm{Rh}(\mathrm{COD})_2][\mathrm{BAr^F}_4]$ with **1a**. Conditions: sealed NMR tube; 1,2-F$_2$C$_6$H$_4$ solution. [BAr$^F_4$] anions not shown.

Having established the base-line synthesis and reactivity for complexes of **1a**, we next explored how they might be formed, albeit in solution rather than melt conditions. Addition of two equivalents of **1a** to $[\mathrm{Rh}(\mathrm{COD})_2][\mathrm{BAr^F}_4]$ at 25 °C (1,2-F$_2$C$_6$H$_4$ solution) formed the Rh(I) complex $[\mathrm{Rh}(\mathrm{COD})(\mathrm{P}^t\mathrm{Bu}_2\mathrm{H})(\eta^2\text{-}\mathrm{H}_3\mathrm{B}{\cdot}\mathrm{P}^t\mathrm{Bu}_2\mathrm{H})][\mathrm{BAr^F}_4]$ **6a[BAr$^F_4$]** in essentially quantitative yield (Scheme 5), which was characterised by NMR spectroscopy, by comparison with the chelating phosphine–borane complex $[\mathrm{Rh}(\mathrm{COD})(\kappa^1,\eta^2\text{-}\mathrm{H}_3\mathrm{BPh}_2\mathrm{CH}_2\mathrm{PPh}_2)][\mathrm{PF}_6]$.[18] Heating **6a[BAr$^F_4$]** with two further equivalents of **1a** at 75 °C in a sealed NMR tube resulted in the formation of **5a[BAr$^F_4$]** as the major (90%) organometallic product, alongside unidentified phosphine–borane materials. We suggest that this process likely proceeds *via* the intermediate **4a[BAr$^F_4$]** (*e.g.*, Scheme 4), and that the COD ligands are lost as the hydroboration products.

Taken together our observations lead to an outline catalytic cycle as shown in Scheme 6 with **3a**$^+$ assigned to a resting-state in the cycle, although the precise details of the mechanism remain to be resolved.



Scheme 6 Proposed and simplified catalytic cycle for the dehydrocoupling of **1a**.

As described (Scheme 2), alongside the starting material **1a** and final product **2a**, an additional phosphine–borane species is also formed. This compound is characterised by a quadrupolar broadened 1 : 1 : 1 : 1 quartet at δ 36 in the ^{31}P{^{1}H} NMR spectrum, and a very strong molecular ion in the ESI-MS at m/z = 305.27 with the correct isotope pattern for the bis-phosphine boronium $[(P^tBu_2H)_2BH_2]^+$, **7**$^+$.[22] Complex **7**$^+$ (as $[BAr^F{}_4]^-$ and $[BH_4]^-$ salts) has been independently synthesised (ESI) confirming this assignment. We discount the formation of **7**$^+$ as coming from P–B bond cleavage in **2a** as heating (melt, 140 °C, 20 hours) **2a** with $[Rh(P^tBu_2H)_2(\eta^6\text{-}C_6H_5F)][BAr^F{}_4]$ results in no further reaction. **7[BAr^F]** is not an intermediate and must be formed by a parallel route to **2a**, as using it as a substrate in catalysis results in no reaction. We speculate that **7**$^+$ might arise from reaction of $H_2B{=}P^tBu_2$ with P^tBu_2H,[2] and subsequent protonation in the melt conditions. Stephan *et al.* have reported a related compound by the addition of 4-^{t}Bu–C_6H_4N to $Cy_2P–B(C_6F_5)_2$.[20b] We cannot discount, however, alternative mechanisms similar to those discussed for the formation of $[(NH_3)_2BH_2][BH_4]$.[23]

Polymeric phosphine–boranes, formed from transition-metal-mediated dehydrocoupling, have significant potential to be technologically interesting materials. However, catalyst development for their production lags behind those used for amine–borane dehydrocoupling, mainly due to the melt conditions currently required. Our observations provide compelling clues as to the species that may be present during catalysis under melt conditions. With such information in hand, the next steps of catalyst development, which must be aimed at lowering dehydrocoupling temperatures, avoiding the requirement for melt conditions and elucidation of the initial dehydrogenation product, can now be realistically tackled.

Notes and references

§ *Crystallographic data for* **4a**: $C_{59}H_{74}B_2F_{25}P_3Rh$, M = 1475.62, triclinic, $P\bar{1}$ (Z = 2), a = 12.8587(1) Å, b = 13.3769(1) Å, c = 20.2366(2) Å, α = 87.9016(4)°, β = 80.6774(4)°, γ = 82.2782(5)°. V = 3403.373(50) Å^3, T = 150(2) K, 15 457 unique reflections [R(int) = 0.0174]. Final R_1 = 0.0427 [$I > 2\sigma(1)$]. CCDC 865050.

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