Amino-borane oligomers bound to a Rh(I) metal fragment†

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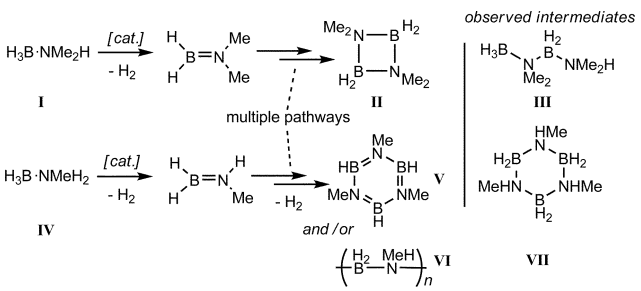
Coordination complexes of previously observed intermediates, $H_3B{\cdot}NMe_2BH_2{\cdot}NMe_2H$ and $[H_2BNMeH]_3$, in the transition metal catalysed dehydrocoupling of $H_3B{\cdot}NMe_2H$ and $H_3B{\cdot}NMeH_2$ have been isolated and structurally characterised using the $[Rh\{PR'_2(\eta^2\text{-}C_5H_7)\}]^+$ fragment. Their onward reactivity shows that further dehydrogenation is not a simple intramolecular process.

The transition metal catalysed dehydrocoupling of amine- and phosphine-boranes is attracting considerable current attention because of its central role in the generation of new group 13/15 materials and possible future energy transport vectors for the delivery of H_2.[1] Secondary and primary amine-borane adducts $H_3B{\cdot}NMe_2H$ (**I**) and $H_3B{\cdot}NMeH_2$ (**IV**) undergo dehydrocoupling to ultimately give $[H_2BNMe_2]_2$ (**II**), $[HBNMe]_3$ (**V**) or oligomeric/polymeric[2] materials alongside the release of H_2 (Scheme 1). Experimental and computational studies have established that the first step is dehydrogenation to form an amino-borane.[3–6] However, subsequent coupling/dehydrogenation steps are less well resolved. Oligomeric $H_3B{\cdot}NMe_2BH_2{\cdot}NMe_2H$ **III**[3,5,7,8] and $[H_2BNMeH]_3$ **VII**[5,9] have been observed as intermediates during the dehydrocoupling of **I** and **IV**, respectively, using a number of catalyst systems; although details of how these intermediates proceed to give the final products are still scarce,[10] and multiple pathways may be operating.[4,7,11] Such mechanistic information is important if fine control over these processes is to be achieved.

We have recently reported the synthesis, solution and solid-state structures of amine-boranes **I** and **IV** complexed



Scheme 1 Products and intermediates of the dehydrocoupling of **I** and **IV**.

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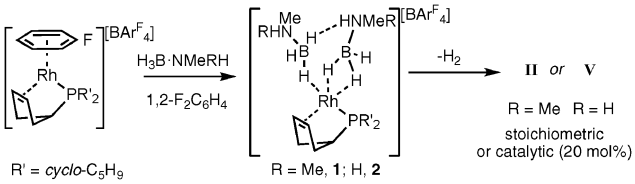
† Electronic supplementary information (ESI) available: Full experimental and analytical data. X-Ray structure of $[Rh\{P^iPr_2(\eta^2\text{-}C_5H_7)\}(\eta^6\text{-}C_6H_5F)][BAr^F{}_4]$. CCDC 767949–767951. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c003055d

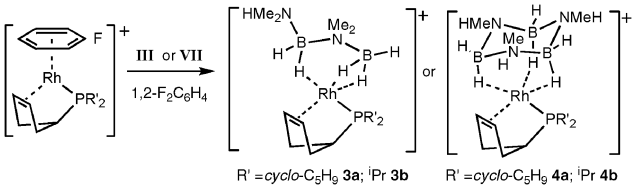


Scheme 2 Synthesis of bis-σ-amine-borane complexes.

with $[Rh\{PR'_2(\eta^2\text{-}C_5H_7)\}]^+$ (R′ = *cyclo*-C_5H_9), **1[BAr$^F_4$]** and **2[BAr$^F_4$]**, respectively (Scheme 2), which show an unique bis-amine-borane bonding mode.[12] These complexes proceed to afford the products of dehydrocoupling, **II** and **V**, respectively, both stoichiometrically and catalytically, although intermediate species were not observed under the conditions used. In the solid-state both show an intramolecular BH···HN hydrogen bond. One possible mechanism for the formation of **II** could be simple intramolecular H_2 elimination to form **III** directly on the metal centre, which then proceeds in a further intramolecular dehydrocoupling to give **II**. Trimer **V** could form in a similar fashion *via* involvement of **VII**. In order to probe these events we have targeted the synthesis of **III** and **VII** with the $[Rh\{PR'_2(\eta^2\text{-}C_5H_7)\}]^+$ fragments (R′ = *cyclo*-C_5H_9, ^{i}Pr).

Addition of **III**[5,13] or the *eee*-isomer of **VII**[14] to the complexes $[Rh\{PR'_2(\eta^2\text{-}C_5H_7)\}(\eta^6\text{-}C_6H_5F)][BAr^F{}_4]$ (Ar^F = $C_6H_3(CF_3)_2$; R′ = *cyclo*-C_5H_9,[15] ^{i}Pr see ESI†) in 1,2-$F_2C_6H_4$ solution resulted in the clean and quantitative (by NMR spectroscopy) formation of the new complexes $[Rh\{PR'_2(\eta^2\text{-}C_5H_7)\}(\eta^2\text{:}\eta^1\text{-}\mathbf{III})][BAr^F{}_4]$, **3[BAr$^F_4$]**, and $[Rh\{PR'_2(\eta^2\text{-}C_5H_7)\}(\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}\mathbf{VII})][BAr^F{}_4]$ **4[BAr$^F_4$]** (R′ = *cyclo*-C_5H_9 **a**; ^{i}Pr **b**), Scheme 3.‡ These new complexes have been characterised by NMR spectroscopy, ESI-MS and X-ray crystallography (Fig. 1), which show them to be sigma amine-borane adducts that bond with the metal centre *via* three 3 centre–2 electron bonds.§ We discuss in detail the analytical data for the R′ = ^{i}Pr complexes—those for the R′ = *cyclo*-C_5H_9 ligand are essentially the same (see ESI†).

The solid-state structure of **3b[BAr$^F_4$]** shows that the diborazane ligand binds to the metal centre in a $\eta^2\text{:}\eta^1$ Rh···HB coordination mode. The Rh···B distances, *viz.* 2.242(5) and 2.626(4) Å, respectively, are consistent with this



Scheme 3 Synthesis of the new complexes. Anions not shown.

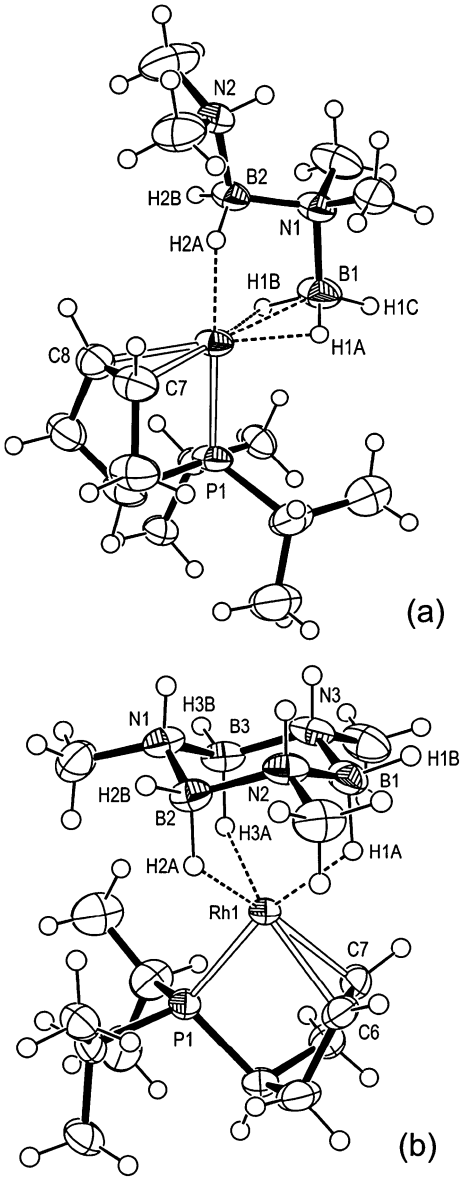


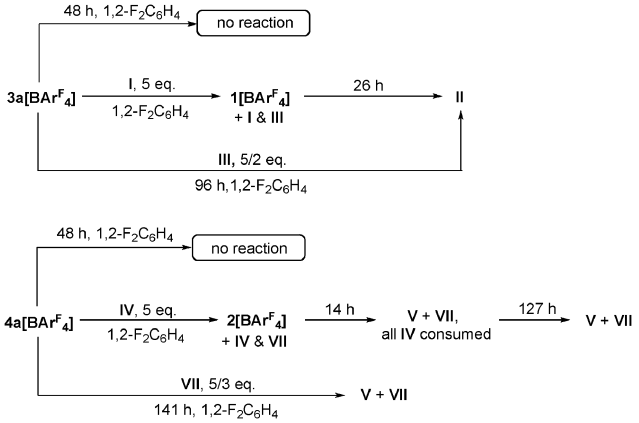
Fig. 1 Solid-state structure of **3b[BAr$^F_4$]** (a), and **4b[BAr$^F_4$]** (b); ellipsoids are depicted at the 50% probability level. Anions and minor disordered components omitted for clarity. Selected bond lengths (Å) and angles (°). **3b[BAr$^F_4$]**: Rh1–P1, 2.2058(9); Rh1–B1, 2.242(5); Rh1–B2, 2.626(4); Rh1–H1A, 1.85(5); Rh1–H1B, 1.84(5); Rh1–H2A, 1.96(4); Rh1–C7, 2.107(4); Rh1–C8, 2.121(4); B1–N1–B2, 103.3(3); N1–B2–N2, 112.7(3); Rh1–H2A–B2, 113(3). **4b[BAr$^F_4$]**: Rh1–P1, 2.2354(8); Rh1–B1, 2.693(4); Rh1–B2, 2.808(4); Rh1–B3, 2.761(4); Rh1–H1A, 1.84(4); Rh1–H2A, 1.94(4); Rh1–H3A, 1.86(4); Rh1–C6, 2.096(3); Rh1–C7, 2.094(3); B1–N2–B2, 112.9(3); B2–N1–B3, 111.7(3); B3–N3–B1, 112.6(3); Rh1–H1A–B1, 123(3); Rh1–H2A–B2, 128(3); Rh1–H3A–B3, 128(3).

description.[16] By contrast, **III** interacts with [Rh(P^{i}Bu$_3$)$_2$]$^+$ through only the BH$_3$ group.[3] For **4b[BAr$^F_4$]** cycloborazane **VII** binds to the metal through three long η^1 Rh···HB interactions [2.693(4), 2.761(4), 2.808(4) Å]. This tridentate coordination mode for **VII** is reminiscent of that observed for complexes of the [B$_3$H$_8$]$^-$ anion.[17] For both complexes the interaction of three BH bonds with the [Rh{PR′$_2$(η^2-C$_5$H$_7$)}]$^+$ fragment is similar to that observed for **1[BAr$^F_4$]** and **2[BAr$^F_4$]**.[12]

In CD_2Cl_2 solution at room temperature **3b[BAr$^F_4$]** shows two BH···Rh signals at δ −0.02 (3H) and δ −2.26 (2H) that sharpen on decoupling ^{11}B, the former also resolves into a doublet, J(RhH) = 21 Hz. These are assigned to BH_3 and BH_2 groups, respectively, that undergo rapid site exchange between coordinated and terminal BH groups. These signals are also shifted upfield from the free ligand,[5] consistent with coordination to the metal. Cooling to 200 K results in the collapse of the 3H signal into a very broad 2H signal at δ −1.34, assigned to Rh–*H*–B, indicating that BH_3 site exchange has been slowed.[3,18] The corresponding terminal BH signal is not resolved. The BH_2 signal does not split or change significantly in chemical shift at 200 K, while the signal due to the alkene (C7/C8) remains sharp, indicating that the BH_2 group is still undergoing site exchange at 200 K. In the ^{11}B NMR spectrum a broad peak centred at δ −4.29 is observed. For **4b[BAr$^F_4$]** the room temperature NMR data show that the cyclic borane ligand is undergoing site exchange, with one Rh···HB (3H, δ −3.44) and one NMe_3 (9H, δ 2.62) signal observed. The ^{11}B NMR spectrum is a doublet of doublets at δ −5.45, J(HB) = 118, 87 Hz; the latter reduced coupling constant is consistent with a Rh···HB interaction.[19] Cooling to 200 K halts the fluxional process and two very broad signals are observed at δ −8.80 (1H) and δ −1.11 (2H) in the ^{1}H NMR spectrum. For both complexes the ^{31}P{^{1}H} NMR spectrum shows a single environment coupling to ^{103}Rh, and ESI-MS shows strong molecular ions. These data show that the solid-state structures are retained in solution.

When pure samples of **3a[BAr$^F_4$]** and **4a[BAr$^F_4$]** are dissolved in 1,2-$F_2C_6H_4$ there is no reaction over 48 hours, with unchanged material recovered. This is in contrast to **1[BAr$^F_4$]** and **2[BAr$^F_4$]** that proceed in six hours to give the products of dehydrocoupling (Scheme 2). These observations indicate that simple intramolecular dehydrogenation of **III** and **VII** is not operating. This is the same as found for [Rh(P^{i}Bu$_3$)$_2$(η^2-**III**)][BAr$^F_4$] that remains unchanged in solution in the absence of excess amine-borane.[3]

The stability of pure **3a[BAr$^F_4$]** and **4a[BAr$^F_4$]** towards intramolecular dehydrogenation prompted us to study their reactions under catalytic conditions (Scheme 4). Addition of **I** to a solution of **3a[BAr$^F_4$]** (20 mol%) immediately formed complex **1[BAr$^F_4$]**, with **III** displaced. After 26 hours all **I** and **III** were consumed to give **II** as the major B–N product by ^{11}B



Scheme 4 Reactivity of complexes **3a[BAr$^F_4$]** and **4a[BAr$^F_4$]**.

NMR spectroscopy. When only **III** was added to **3a[BAr$^F_4$]** (20 mol%), conversion to **II** was slower but still went to completion after 96 hours. For **4a[BAr$^F_4$]** (20 mol%) addition of **IV** results in the initial formation of **2[BAr$^F_4$]** with **VII** displaced, and the complete conversion of **IV** to **V** in 14 hours; but by contrast with the reaction of **3a[BAr$^F_4$]** with **III**, **VII** was still persistent in solution after a further 127 hours. Addition of **VII** to **4a[BAr$^F_4$]** (20 mol%) gave very slow formation of **V** although **VII** was still present after 141 hours (see ESI†), Scheme 4. When a 1 : 2 mixture of the *eee* and *eea* isomers of **VII** was used, there is no significant change in the ratio of isomers over this time period showing that an isomer effect was not operating in the dehydrocoupling process here.

These observations show that a *simple* metal-based intramolecular dehydrogenation involving the oligomeric intermediates **III** and **VII** is not occurring with these systems, and a more complex regime, possibly involving B–N bond cleavage[7] or a bi-molecular outersphere mechanism,[6a] is probably operating. Moreover the data also suggest that in these systems **VII** is not a viable intermediate in the overall dehydrocoupling, while **III** is. The former observation is in contrast to results previously reported by Manners and co-workers that show using colloidal Rh(0) catalysts **VII** is an observed intermediate,[5,9,20] demonstrating that even though the final products are the same, the pathways to reach them can be different.

Notes and references

‡ Selected NMR data: **3b[BAr$^F_4$]** ^{1}H NMR (500 MHz, CD_2Cl_2, 200 K): δ 7.74 (s, 8H, BAr$^F_4$), 7.56 (s, 4H, BAr$^F_4$), 4.25 (br s, 1H, NH), 3.70 (s, 2H, HC=CH), 2.58–2.53 (m, 12H, NH–CH_3, N–CH_3), 1.99 (m, 2H, P^{i}Pr–CH), 1.88 (br m, 1H, PCyp CH), 1.82 (dd, 2H, J(HH) 13, J(PH) 12, PCyp′–CH_2), 1.37 (br dd, 2H, J(PH) 46, J(HH) 13 PCyp′–CH_2), 1.14 (dd, 6H, J(PH) 14, J(HH) 7, P^{i}Pr–CH_3), 1.09 (dd, 6H, J(PH) 14, J(HH) 7, P^{i}Pr–CH_3), −1.34 (br, 2H, BH_3), −2.48 (br, 2H, BH_2). The remaining B–H signal was not observed, presumably it was broad and/or obscured by the aliphatic signals. ^{1}H{^{11}B} NMR (500 MHz, CD_2Cl_2, 200 K): −1.35 (v br, 2H, RhH_2BH), −2.49 (br, 2H, BH_2). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 200 K): δ 121.59 [d, J(RhP) 172]. ^{11}B NMR (160 MHz, CD_2Cl_2, 200 K): δ very broad, no clear signals observed. ESI-MS ($C_6H_4F_2$, 60 °C, 4.5 kV): positive ion: m/z 403.2066, [M]$^+$ (23% calcd 403.2092). **4b[BAr$^F_4$]**: ^{1}H NMR (500 MHz, CD_2Cl_2, 200 K): δ 7.73 (s, 8H, BAr$^F_4$), 7.55 (s, 4H, BAr$^F_4$), 3.73 (s, 2H, HC=CH), 3.20 (br s, 3H, NH), 2.56 (v br, 9H, N–CH_3), 2.00 (m, 2H, P^{i}Pr–CH), 1.90 (br m, 1H, PCyp′–CH), 1.70 (virtual triplet, 2H, J(HH) ≈ J(PH) 13, PCyp′–CH_2), 1.16 (dd, 12H, J(HH) 7, J(PH) 14, P^{i}Pr–CH_3) 1.23–0.97 (partially obscured multiplet, 2H, PCyp′–CH_2), −1.11 (br, 2H, RhHBH), −8.80 (v br, 1H, RhHBH). The remaining RhHBH signals were not unequivocally identified, presumably they are broad and/or obscured by the aliphatic signals. ^{1}H{^{11}B} NMR (500 MHz, CD_2Cl_2, 200 K): δ −1.11 (br, 2H, RhHBH), −8.85 (br, 1H, RhHBH). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 200 K): δ 119.33 [d, J(RhP) 162]. ^{11}B NMR (160 MHz, CD_2Cl_2, 200 K): δ very broad, no clear signal observed. ESI-MS ($C_6H_4F_2$, 60 °C, 4.5 kV): positive ion: m/z 416.2230, [M]$^+$ (calcd 416.2218).

§ Crystallographic data. **3b[BAr$^F_4$]**: $C_{47}H_{51}B_3F_{24}N_2PRh$, M = 1266.21, triclinic, $P\bar{1}$ (Z = 2), a = 13.11340(10) Å, b = 15.09320(10) Å, c = 15.6507(2) Å, α = 84.6142(4)°, β = 78.4318(4)°, γ = 86.9282(4)°. V = 3019.40(5) Å^3, T = 150(2) K, 12 244 unique reflections [R_{int} = 0.0154]. Final R_1 = 0.0466 [$I > 2\sigma(I)$]. **4b[BAr$^F_4$]**: $C_{46}H_{51}B_4F_{24}N_3PRh\cdot\frac{1}{2}(C_5H_{12})$, M = 1315.09, monoclinic, $P2_1/c$ (Z = 4), a = 13.22060(10) Å, b = 18.33470(10), c = 24.0722(2) Å, β = 98.7365(4)°. V = 5767.30(7) Å^3, T = 150(2) K, 11 699 unique reflections [R_{int} = 0.0231]. Final R_1 = 0.0415 [$I > 2\sigma(I)$].

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20 Shimoi and co-workers have recently suggested that **VII** may undergo metal promoted dehydrogenation to give **V** using Cr–carbonyl catalysts in the dehydrocoupling of $H_3B\cdot NH_2Me$. See ref. 6*a*.

