Amine–Boranes

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# Bis(σ-amine–borane) Complexes: An Unusual Binding Mode at a Transition-Metal Center**

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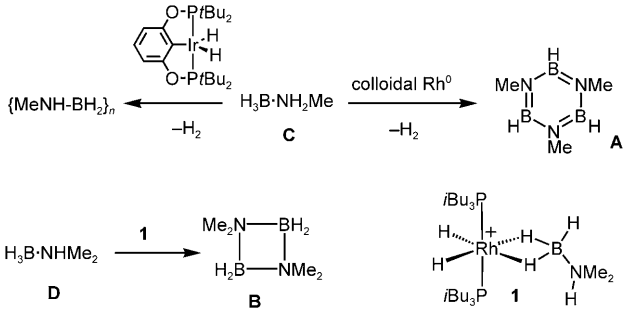
*Dedicated to Professor Jennifer Green*

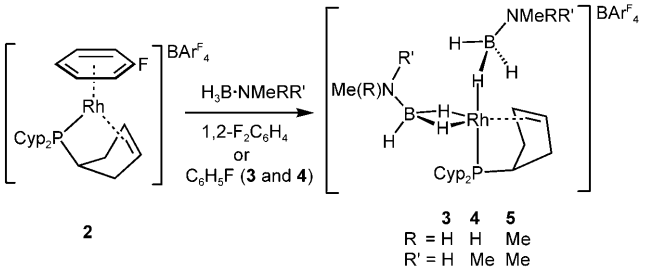
The coordination chemistry of amine–boranes and in particular the prototypical ammonia–borane $H_3B{\cdot}NH_3$, and the subsequent reactivity of their complexes, is an area of significant contemporary interest. This interest arises from the role the metal center plays in controlling kinetics and product distributions for dehydrocoupling reactions that form linear or cyclic oligomers and polymers alongside the concomitant release of $H_2$. Control of these processes has relevance to chemical hydrogen storage[1] and the synthesis of new main-group polymeric materials.[2] Although many dehydrocoupling/dehydrogenation systems have been reported,[2–9] experimental identification of intermediates in the catalytic cycle remain scarce, although computational studies[10,11] indicate that σ-borane complexes[12] play a key role in many systems. Recent studies[7] have shown that dehydrocoupling is a rather complex process, and the metal center and the identity of the amine–borane are both important in determining the outcome of the final Group 13/15 products. For example, Manners and co-workers have reported that dehydrocoupling of the primary amine–borane $H_3B{\cdot}NH_2Me$ (**C**) leads to polymeric $\{BH_2NHMe\}_n$[4] if




the Brookhart iridium pincer catalyst, which was initially used by Goldberg, Heinekey and co-workers in the dehydrogenation of $H_3B{\cdot}NH_3$,[8,9] is used. By contrast, cyclic $[BHNMe]_3$ (**A**) is formed when colloidal rhodium(0) is employed as a catalyst.[5] Insight into how amine–boranes approach, bind, and dehydrocouple on metal centers is thus of significant interest regarding the twin goals of controlling the kinetics of $H_2$ release and the pathways that lead to oligomeric or polymeric materials.

We have recently described the isolation of such intermediates using the latent twelve-electron complex $[Rh(P\mathit{i}Bu_3)_2]BAr^F_4$ ($Ar^F = (CF_3)_2C_6H_3$).[13] Using this precursor, σ-amine–borane complexes, such as $[Rh(H)_2(P\mathit{i}Bu_3)_2(\eta^2\text{-}H_3B{\cdot}NHMe_2)]BAr^F_4$ (**1**), which are competent in the catalytic dehydrocoupling of $H_3B{\cdot}NHMe_2$ (**D**) to form dimeric product **B**, could be isolated. Herein, we report further examples of intermediate σ-amine–borane complexes, but now using a significantly more open transition-metal fragment, which contain a bis(σ-amine–borane) binding motif.[14] These complexes provide new insight into bonding modes of mono-(amine–borane) ligands[15] at transition-metal centers, an area that has until this point been limited to complexes in which one amine–borane binds to the metal center.[16–18] These complexes also proceed to dehydrocouple to form cyclic products, and they may therefore help to elucidate further mechanistic details of the catalytic dehydrocoupling of amine–boranes.

Displacement of the labile fluoroarene ligand in the phosphine/alkene complex $[Rh(\eta^6\text{-}C_6H_5F)\{P(C_5H_9)_2(\eta^2\text{-}C_5H_7)\}]BAr^F_4$ **2**[19,20] by the amine–boranes $H_3B{\cdot}NH_2Me$ (**C**), $H_3B{\cdot}NHMe_2$ (**D**), or $H_3B{\cdot}NMe_3$ (**E**) in 1,2-difluorobenzene solvent results in the isolation of the corresponding bis(σ-amine–borane) complexes $[Rh\{P(C_5H_9)_2(\eta^2\text{-}C_5H_7)\}(\eta^2\text{-}H_3B{\cdot}NRR'Me)(\eta^1\text{-}H_3B{\cdot}NRR'Me)]BAr^F_4$ (**3–5**, where R = R′ = H: **3**; R = H, R′ = Me: **4**; R = R′ = Me: **5**). Salts **3** and **4**




can also be prepared in fluorobenzene, but for $H_3B{\cdot}NMe_3$, the arene solvent competes in metal binding, and only a small amount of **5** (20%) is observed alongside **2** (80%). In 1,2-

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difluorobenzene, these reactions are quantitative as determined by NMR spectroscopy, and the complexes are isolated in good yields (ca. 60% as crystalline material). All three complexes have been characterized in solution and the solid state; the structures of **3** and **4** are shown in Figure 1 (for **5**, see the Supporting Information).

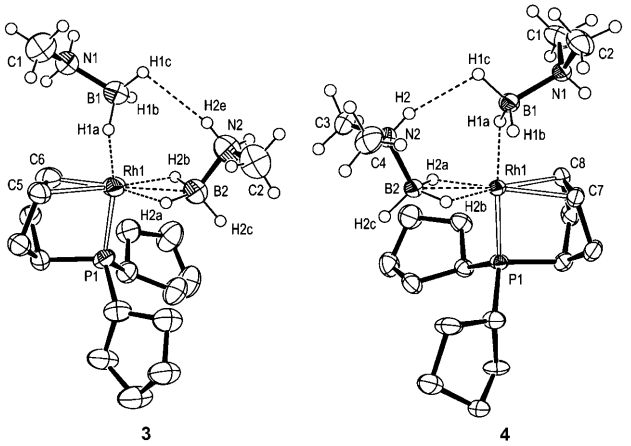
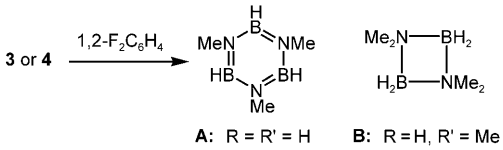



***Figure 1.*** Molecular structure of the cationic portions of **3** (left) and **4** (right); ellipsoids set at 50% probability. Minor disordered components and phosphine hydrogen atoms omitted for clarity. Selected bond lengths [Å]: **3**: Rh1–B1 2.642(11), Rh1–B2 2.289(6), Rh1–P1 2.2377(12), Rh1–C5 2.111(3), Rh1–C6 2.112(3), C5–C6 1.411(10), H2e–H1c 2.22 (calcd). **4**: Rh1–B1 2.661(3), Rh1–B2 2.282(3), Rh1–P1 2.2197(6), Rh1–C7 2.106(2), Rh1–C8 2.121(2), C7–C8 1.417(3), H2–H1c 2.12(4).

In the solid state, two amine–borane units come together at a pseudo-octahedral rhodium(I) center. In the apical position, there is an $\eta^1$-coordinated amine–borane, whereas that in the equatorial position is $\eta^2$. Complex **3** has two disordered components in the solid state in which the orientation of the $\eta^1$-$H_3B{\cdot}NH_2Me$ group is slightly different; however, the $\eta^1/\eta^2$ binding motif is retained in both. For **4**, all the hydrogen atoms associated with the Rh···H–B interactions were located in the final difference maps. For all three complexes, the $\eta^1$ and $\eta^2$ binding motifs also differ from one another by the much shorter Rh···B distance in the $\eta^2$ motif (for example, 2.661(3) versus 2.282(3) Å in **4**). These distances are similar to those reported in other examples of $\eta^1$ [18] and $\eta^2$ [13] amine–borane complexes. In both **3** and **4**, there appears to be non-classical B–H···H–N hydrogen bonding between the amine–borane ligands (for example, H2–H1C 2.12(4) Å in **4**). These interactions are slightly longer than observed for the recently reported structures of the parent amine–borane ligands.[21] However, they are not necessary for the formation of the bis motif, as complex **5** also has a very similar structure (see Supporting Information) to **3** and **4**, although the $H_3B{\cdot}NMe_3$ ligand is unable to partake in such B–H···H–N bonding. To our knowledge, these three complexes are the first observations of the bis(σ-amine–borane) coordination mode, although related motifs have been investigated (and discounted) using computational methods on $\{Cp_2Ti\}$ dehydrocoupling systems.[11] It is likely that the rather open rhodium phosphine/alkene coordination environment allows the approach of two amine–borane ligands rather than just one as observed in, for example, **1**. Complex **3** also appears to be the first reported metal complex of $H_3B{\cdot}NH_2Me$.

In solution at room temperature the amine–borane ligands of complexes **3**, **4**, and **5** are in rapid site-exchange, both between themselves and with free amine–borane if present. The intramolecular exchange probably occurs by an opening and closing of the $\eta^1/\eta^2$ binding modes that couples with a low-energy axial–equatorial site exchange in a five-coordinate intermediate. This exchange is demonstrated by single broadened signals observed for NH (**3** and **4**), NMe, and BH groups (the latter having significant quadrupolar broadening). In the $^{11}$B NMR spectrum, one very broad signal is observed at room temperature. Cooling to 200 K arrests this intramolecular fluxional process. In particular, separate signals are observed for the NH groups in **3** and **4**, whilst in the high-field region of the $^1H\{^{11}B\}$ NMR spectrum, two similar environments in the ratio 3:2 are observed for **4** and **5**; the former is assigned to the $\eta^1$-$H_3B$ unit that is still ungoing site exchange between terminal and bridging hydrides,[16] and the latter to the $\eta^2$ unit. These separate environments are not resolved in **3**, and a broad five-proton signal is still observed at low temperature. The signals in the $^{11}$B NMR spectra undergo a small upfield shift on cooling, but the separate environments are still not resolved for the still very broad signals. Across all temperature ranges that were investigated, these complexes show a single $^{31}$P environment as a doublet ($\delta \approx 106$ ppm, $J(\mathrm{RhP}) \approx 170$ Hz), which is a chemical shift consistent with a phosphine/alkene ligand,[19] and a single signal for two equivalent alkene protons. All these data suggest that the solid-state structures are retained in solution.

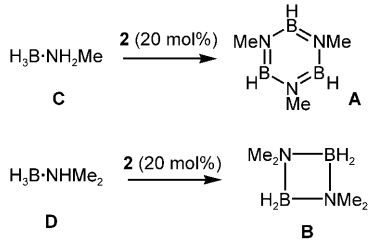
In 1,2-difluorobenzene solution, complex **5** is stable and remains unchanged over 48 h under an argon atmosphere; this lack of dehydrocoupling is consistent with the lack of NH protons. In contrast, **3** and **4** react relatively rapidly in either mono- or difluorobenzene (6 h), leading to the products of stoichiometric dehydrocoupling; release of $H_2$ is also




observed. For complex **3**, the main product is the cyclic trimer **A** ($\delta = 33.4$ ppm, $J$(HB) 134 Hz) by $^{11}$B NMR spectroscopy, whilst ill-defined signals at about $\delta = -8$ ppm might also indicate the formation of oligomeric species.[4,8] For **4**, the cyclic dimer **B** ($\delta = 5.5$ ppm, $J$(HB) 112 Hz) is the final product. No significant organometallic or main-group intermediate species were observed under these conditions. For **4** in fluorobenzene, the final organometallic product is **2** ($^{31}$P and ESI-MS), suggesting a "catch and release" mechanism at the end of the reaction in this arene solvent. In contrast, for **3**, decomposition occurs to give as yet unidentified products. Addition of a further two equivalents of **D** to **2** results in the reformation of **4**.

In a sealed NMR tube, complex **2** is competent in the slow catalytic (20 mol%, 1,2-$F_2C_6H_4$, 12 h at 298 K) dehydrocoupling of amine boranes **C** and **D** to afford **A** and **B**, respectively, as the main soluble products. Inspection of




time/concentration plots that do not indicate a sigmodial kinetic profile ($^{11}$B NMR spectroscopy; see Supporting Information) coupled with the fact that addition of mercury to the reaction solution in a non-sealed system under argon did not result in suppression of catalytic activity, together suggest a homogeneous, rather than colloidal, mechanism.[22] With **4**/**D**, the aminoborane $H_2B{=}NMe_2$[6] is observed at a low, but steady, concentration throughout catalysis, along with other low concentrations of borane species (see Supporting Information). For both **3**/**C** and **4**/**D**, decomposition of the catalyst to a number of as yet unidentified products occurs during catalysis. This observation, together with the fact that cyclopentylphosphines are known to undergo ready reversible dehydrogenation,[19] hampers a more detailed analysis of the mechanism.

The NH···HB hydrogen bonds present in the solid state in **3** and **4** might point to a low-energy dehydrocoupling pathway that proceeds in an intramolecular fashion by simple $H_2$ loss to give an oligomeric amine–borane. Taking **D** as an example, this could lead to $H_3BNMe_2BH_2NHMe_2$[5] directly on the metal center, followed by further dehydrocoupling. Alternatively, B–H/N–H activation by oxidative addition/proton transfer pathways could be operating to afford $H_2B{=}NMe_2$, which then undergoes further reactivity on or off the metal to form **B**.[7,23] The observation of $H_2B{=}NMe_2$ in the dehydrocoupling of **D** suggests the latter in this system, although subsequent B–N bond cleavage of a linear oligomeric species could also give this fragment.[7,23]

Whatever the mechanism of dehydrocoupling, we present herein the first examples of two amine–borane ligands coordinated to a transition-metal fragment, and demonstrate that these complexes undergo stoichiometric and catalytic dehydrocoupling to form aminoboryl species **A** and **B**. Given that proximate coordination sites are likely to be present on colloidal[22] or related[6] systems, it is tempting to speculate that bonding modes as observed for **3**–**5** might be present on their surface. For iridium pincer systems, bis(σ-amine–borane) complexes seem less likely, although not impossible, given the steric constraints of the ligand set.[9,24] Whether such bonding motifs are actually important in determining the general course of the dehydrocoupling reactions thus remains to be determined.

## Experimental Section

Details of the synthesis, characterization, and dehydrocoupling activity of **3**–**5** are given in the Supporting Information. CCDC 735077, CCDC 735078, and CCDC 735079 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Selected characterization data: **3**: $^1$H NMR ($CD_2Cl_2$, 200 K, 500 MHz): $\delta = 7.73$ (s, 8H, $BAr^F_4$), 7.56 (s, 4H, $BAr^F_4$), 4.00 (br, 2H, $NH_2$), 3.51 (br, 2H, $NH_2$), 3.43 (s, 2H, HC=CH), 2.54 (br m, 6H, 2 × N-$CH_3$), 2.25–1.05 (m, 23H, PCyp), −1.45 ppm (br, 5H, $BH_2$ + $BH_3$). The remaining 1H $BH_3$ signal was not observed, presumably as it was broad and/or obscured by the aliphatic signals.$^{31}$P{$^1$H} NMR ($CD_2Cl_2$, 200 K, 202 MHz): $\delta = 105.57$ ppm (d, $J$(RhP) = 164 Hz). $^{11}$B NMR ($CD_2Cl_2$, 200 K, 160 MHz): $\delta = -24.03$ ppm (br). ESI-MS ($C_6H_4F_2$, 60 °C, 4.5 kV): positive ion: $m/z$ 384.1757 $[M-H_3B{\cdot}NMeH_2]^+$ (27%, calcd 384.1496). **4**: $^1$H NMR ($CD_2Cl_2$, 200 K, 500 MHz): $\delta = 7.74$ (s, 8H, $BAr^F_4$), 7.56 (s, 4H, $BAr^F_4$), 4.33 (br, 1H, NH), 3.52 (br, 1H, NH), 3.45 (s, 2H, HC=CH), 2.52 (d, $J$(HH) 5, 12H, 2 × N-$CH_3$), 2.20–1.05 (m, 23H, PCyp), −1.57 ppm (br, 5H, $BH_2$ + $BH_3$). The remaining 1H $BH_3$ signal could not be unambiguously assigned. $^{31}$P{$^1$H} NMR ($CD_2Cl_2$, 200 K, 202 MHz): $\delta =$ 105.30 ppm (d, $J$(RhP) = 165 Hz). $^{11}$B{$^1$H} NMR ($CD_2Cl_2$, 200 K, 160 MHz): $\delta = -20.32$ ppm (br). ESI-MS ($C_6H_4F_2$, 60 °C, 4.5 kV): positive ion: $m/z$ 457.2647 $[M]^+$ (100%, calcd 457.2563). **5**: $^1$H NMR ($CD_2Cl_2$, 200 K, 500 MHz): $\delta = 7.74$ (s, 8H, $BAr^F_4$), 7.56 (s, 4H, $BAr^F_4$), 3.78 (s, 2H, HC=CH), 2.63 (s, 18H, 2 × N-$CH_3$), 2.22–1.01 (m, 23H, PCyp), −0.02 (v br, 2H, $BH_3$), −1.54 ppm (v br, 3H, $BH_3$). The remaining 1H $BH_3$ signal was not observed, presumably as it was broad and/or obscured by the aliphatic signals. $^{31}$P{$^1$H} NMR ($CD_2Cl_2$, 200 K, 202 MHz): $\delta = 107.45$ ppm (d, $J$(RhP) = 171 = Hz). $^{11}$B{$^1$H} NMR ($CD_2Cl_2$, 200 K, 160 MHz): $\delta = -8.90$ (br). ESI-MS ($C_6H_4F_2$, 60 °C, 4.5 kV): positive ion: $m/z$ 412.2041 $[M-H_3B{\cdot}NMe_3]^+$ (50%, calcd 412.1812).

Crystal data for **3**: $C_{55}H_{58}B_3F_{25}N_2PRh$, $M_r = 1388.34$, pale yellow blocks, $0.32 \times 0.22 \times 0.22$ mm$^3$, triclinic, $P\bar{1}$, $a = 14.7071(2)$, $b = 14.8581(2)$, $c = 16.3258(2)$ Å, $\alpha = 67.6439(7)$, $\beta = 66.3534(6)$, $\gamma = 82.1548(8)$°, $V = 3021.80(7)$ Å$^3$, $Z = 2$, $\rho_{calc} = 1.526$ g cm$^{-3}$, $\mu = 0.425$ mm$^{-1}$, KappaCCD, $Mo_{K\alpha}$ radiation $\lambda = 0.71073$ Å, $T = 150(2)$ K, $5.10 \le \theta \le 26.37$, 20676 reflections, 12248 unique ($R_{int} = 0.0187$), Final $GoF = 1.027$, $R1$ ($I > 2\sigma(I)$) = 0.0510, $wR2$ (all data) = 0.1415.

Crystal data for **4**: $C_{51}H_{57}B_3F_{24}N_2PRh$, $M_r = 1320.30$, pale yellow blocks, $0.38 \times 0.28 \times 0.25$ mm$^3$, triclinic, $P\bar{1}$, $a = 12.6080(2)$, $b = 13.6943(2)$, $c = 16.9699(3)$ Å, $\alpha = 104.7624(6)$, $\beta = 90.8926(6)$, $\gamma = 96.0267(6)$°, $V = 2814.88(8)$ Å$^3$, $Z = 2$, $\rho_{calc} = 1.558$ g cm$^{-3}$, $\mu = 0.449$ mm$^{-1}$, KappaCCD, $Mo_{K\alpha}$ radiation $\lambda = 0.71073$ Å, $T = 150(2)$ K, $5.09 \le \theta \le 26.37$, 20087 reflections, 11416 unique ($R_{int} = 0.0213$), Final $GoF = 1.049$, $R1$ ($I > 2\sigma(I)$) = 0.0328, $wR2$ (all data) = 0.0774.

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