Coordination Chemistry

The Synthesis, Characterization and Dehydrogenation of Sigma-Complexes of BN-Cyclohexanes

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Dedicated to Professor Larry Sneddon in recognition of his outstanding contributions to the transition metal chemistry of boron

Abstract: The coordination chemistry of the 1,2-BN-cyclohexanes 2,2-R₂-1,2-B,N-C₄H₁₀ (R₂ = HH, MeH, Me₂) with Ir and Rh metal fragments has been studied. This led to the solution (NMR spectroscopy) and solid-state (X-ray diffraction) characterization of [Ir(PCy₃)₂(H)₂(H₂BNR₂C₄H₈)][BAr₄] (NR₂ = NH₂, NMeH) and [Rh(iPr₂PCH₂CH₂PCh₂P)iPr₂]₂(H₂BNR₂C₄H₈)][BAr₄] (NR₂ = NH₂, NMeH, NMe₂). For NR₂ = NH₂ subsequent metal-promoted, dehydrocoupling shows the eventual formation of the cyclic tricyclic borazine [BNC₄H₈]₃, via amino-boraneail and, tentatively characterized using DFT/GIAO chemical shift calculations, cycloborazane intermediates. For NR₂ = NMeH the final product is the cyclic amino-borane HBNMeC₄H₈. The mechanism of dehydrogenation of 2,2-H,Me-1,2-B,N-C₄H₁₀ using the (Rh(iPr₂PCH₂CH₂PCh₂P)iPr₂)₂ catalyst has been probed. Catalytic experiments indicate the rapid formation of a dimeric species, [Rh₂(iPr₂PCH₂CH₂PCh₂P)iPr₂]₂[BAr₄]. Using the initial rate method starting from this dimer, a first-order relationship to [amine-borane], but half-order to [Rh] is established, which is suggested to be due to a rapid dimer–monomer equilibrium operating.

Introduction

The metal-catalysed dehydrocoupling of amine-boranes is an important methodology for the production of polyaminoboranes that are isoelectronic analogues of polyolefins. The parent compound H₂B-NH₂ is also of significant interest with regard to its ability to act as a chemical hydrogen store, due to its high weight % H (19.6 %) and the ability to release H₂ for subsequent utilization in a fuel cell.[1–4] Such catalytic methodologies offer control of kinetics, product distributions and the temperatures of H₂ loss when compared to simple thermal activation.

Cyclic amine-boranes[5] such as 1,2-BN cyclohexanes (e.g., 1–3, Scheme 1A)[8,10] BN-methylcyclopentane (I, Scheme 1C)[10,11]

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and bis-BN cyclohexane (II, Scheme 1 C) are attractive candidates for H₂ storage applications as they release H₂ on heating to form well-defined molecular species (Scheme 1 B and C) for which viable regeneration routes can be developed. H₂ loss that is promoted by a transition-metal-based catalyst offers a significant reduction in the temperature of release (Scheme 1 C), and heterogeneous (e.g., FeCl₃, precatalyst) and homogeneous (Ru-based) systems have been developed for use with cyclic amine-boranes. Related B-substituted acyclic systems also undergo dehydrogenation using CoCl₂ as a precatalyst to form B-substituted borazines. However, the nature of likely intermediates in these dehydrogenating processes have not been determined, either because of the thermal conditions required in the absence of catalyst (e.g., 150 °C), the generally heterogeneous nature of the catalyst system, or lack of observable intermediates in homogeneous systems (Ru catalysts).

Sigma-amine-borane complexes are key intermediates in inner-sphere transition-metal-catalysed amine-borane dehydrocoupling, and they are now well-established in terms of both fundamental coordination chemistry, B–H/N–H activation processes and, increasingly, B–N coupling events. Of particular relevance to this work are those complexes that arise from interaction of either an [Ir(PCy₃)₃] (16–18) or a [Rh(chelating-diphosphine)] (19,20) fragment with amine-boranes. The former promotes dehydrogenation of the coordinated amine-boranes rather slowly, but leads to the isolation of metal bound intermediates (Scheme 2 A), while the latter promotes dehydrogenation much more rapidly, leading to the use of low catalyst loadings (e.g., Scheme 2 B).

As far as we are aware, the coordination chemistry of cyclic amine-boranes has not been explored, although rhodium sigma-complexes of the cyclic amino-borane oligomers [H₂BNMe₂] and [H₂BNMeH] have been described. The dehydrogenative cyclization of diaminomonoboranes has been reported to form cyclic diboranes using a [Ru(PCy₃)₃] (H₂)₂ catalyst; the metal-catalysed dehydrocoupling of base-stabilised diborane(6) [H₂B(hpp)], to give [HB(hpp)], [hpp , 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-al]pyrimidinate] has been reported, alongside subsequent coordination chemistry and there is an early report of sigma complexes formed from cyclic diboranes. Shore and co-workers have developed the coordination chemistry and reactivity of related cyclic anionic organohydroboranes of the early transition metals.

In this contribution we report the coordination chemistry of various N-substituted cyclic 1,2-BN-cyclohexanes, using [Ir(PCy₃)₃](H₂) or [Rh(chelating-diphosphine)] fragments, to afford the resulting sigma-complexes. We also comment on their subsequent dehydrogenation/dehydrocoupling that leads to insight into both: 1) the active species involved, and 2) the metal-free cyclic amino-borane intermediates formed during these transition-metal-catalysed routes, which operate at a significantly lower temperature than non-catalysed or heterogeneously catalysed alternatives.

Results and Discussion

Synthesis of cyclic amine-boranes

To provide a comparison of the effect of increasing substitution at nitrogen with regard to both coordination chemistry and subsequent dehydrogenation, three 1,2-BN-cyclohexanes were prepared (Scheme 1 A): 2,2-H₂B,N-C₆H₁₄ (1), 2,2-H₂B,N-C₆H₁₂ (2) and 2,2-Me₂-1,2-B,N-C₆H₁₂ (3). The synthesis of compound 1 has recently been reported by hydroboration of a bistrimethylsilyl-substituted homoallylamine by one of us. Compound 2 is, to our knowledge, unreported in the open literature as an isolated compound while compound 3 was originally reported by Wille and Goubeau in 1972. We have isolated compounds 2 and 3 (see Experimental Section) as an analytically pure powder or liquid, respectively (Scheme 3). The ¹¹B and ¹H B-H NMR chemical shifts for these three compounds are also given for later comparison with their coordination complexes.

Reactivity with [Ir(PCy₃)₃](H₂)₂[BAr₄]⁺

Addition of one equivalent of cyclic amine-borane 1 to a C₆H₆ solution of in situ generated [Ir(PCy₃)₃](H₂)₂[BAr₄]⁺, III (a source of the [Ir(PCy₃)₃](H₂)₂] fragment), resulted in the formation of the complex [Ir(PCy₃)₃](H₂)[(η⁵-hexamethyl-2,3,5-(CF₃)₃C₆H₄]BAr₄]⁺ (4) in quantitative yield as measured by ¹H, ¹¹B and ¹³P NMR spectroscopies (Ar₄⁺ = 3,5-(CF₃)₃C₆H₄ in Scheme 4). Complex 4 can be characterised as a Shimo type sigma-amino-borane complex. Analytically pure, crystalline, material was isolated.
The solid-state structure of complex 4 is shown in Figure 1, and confirms the formulation. The Ir–H were located in the final difference map, while the bridging B–H–Ir were not located with any reliability and placed in calculated positions. The Ir–B [2.217(4) Å], B1–C1 [1.588(6) Å] and B1–N1 [1.605(6) Å] distances are all consistent with an amine-borane taking part in two Ir–H–B 3 center-2 electron interactions, comparing closely with sigma complexes of H2B·NMe3 [Ir–B, 2.207(7) Å],[17] H2B·NMeH [2.210(7) Å],[31] and H2B·NMeH [2.209(5) Å],[16] with the same metal fragment. Amine-boranes acting in a monodentate bonding mode through a single B–H bond, or as B–H activated boryls, show significantly shorter (ca. 2.6 Å or longer)[16,14] and shorter M–B distances (less than 2.1 Å), respectively.[36,37]

The cyclic amine-borate adopts a chair conformation (Figure 1B), meaning there is no plane of symmetry in the molecule in the solid state.

In solution (CD3Cl2), the 1H NMR spectrum of 4 shows a diagnostic [34,39] and significant, downfield shift on coordination with the metal, δ = 19.8 ppm, when compared to free ligand, δ = −11.3 ppm. This signal is broad (fwhm = 350 Hz) masking the expected reduction in J(BH)[15]. The 1H NMR spectrum displays a single Ir–H environment at δ = −20.53 ppm [t, J(PH) = 16 Hz] and a single Ir–B–H environment at δ = −6.23 ppm (br) that sharpens on decoupling of 1B and is shifted 8.04 ppm upfield from δ = 19.8 ppm. Finally, the 31P(1H) NMR spectrum shows a single N–H environment at δ = 4.07 ppm (confirmed by 1H/1H COSY and HSQC experiments). The 31P(1H) NMR spectrum displays two environments that show mutual 31P–1P coupling, consistent with a trans orientation: J(PP) = 268 Hz. These solution data are consistent with a sigma-amine-borate complex, interacting through two B–H–Ir interactions, in which the cyclic amine-borane is undergoing a fluxional process that gives a time-averaged mirror plane that makes the two sets of hydride ligands equivalent. A simple ring-flip is suggested, rather than a rotation around the B1–Ir1 vector that would also make the phosphine ligands equivalent,[17] and for the free amine-borane this ring-flip has been shown to proceed through a low barrier (8.8(±0.2) kcal mol−1).[19]

The corresponding sigma complex of 2, [Ir(PCy3)(H)(η2-η2-2,3-BH2NMeC2H3)][BARF4] (5), can be prepared in a manner similar to 4. The synthesis of 5 by displacement of the dihydrogen ligand in III takes longer than for 4: 90 min compared to on time of mixing, respectively. The solid-state structure of complex 5 is shown in Figure 2, which shows it to be very similar to that of 4, with the amine-borane also adopting a chair conformation. Unlike 4, the BN-cyclohexane ligand is disordered, occupying four chemically identical, but crystallographically different sites (see the Supporting Information). The Ir–B distance measured using this model, 2.230(4) Å, is within error the same as for 4, as is the P1-Ir-P2 angle of 155.13(3)°.

Despite repeated attempts, only a few crystals of complex 5 were produced, with the complex forming as an oil on attempts to re-crystallise, meaning that analytically pure material...
for microanalysis was not available. Nevertheless, NMR spectroscopy demonstrates the formulation of 5 in the bulk. In the 1H NMR spectrum the Ir–H groups are now observed as two relative 1-H signals, at $\delta = -20.58$ and $-20.82$ ppm, due to the asymmetry now imposed by the NMe group on the cyclic amine-borane that would not be removed by a low energy ring-flip. Likewise, two Ir–H–B signals are observed ($\delta = -6.24$, $-6.35$ ppm), and a more complicated aliphatic region compared with 4 is noted, as all the methylene C–H groups are now inequivalent. The 13B NMR spectrum shows a signal at $\delta = 22.24$ ppm, similar to that measured for complex 4 and shifted downfield from free ligand ($\delta = -6.5$ ppm). As with 4, there are two environments observed in the 31P(1H) NMR spectrum that show trans J(PP)-coupling ($J(PP) = -276$ Hz).

Addition of 3 to a C4H6F solution of [Ir(PCy2)2(H2)]2[BAr4]2 resulted in no reaction to the detection limit of 31P(1H) NMR spectroscopy (ca. 5%) in a sealed NMR tube. However, the 1H NMR spectrum showed a very small peak at $\delta = -4.06$ ppm (less than 5%) that might be assigned to a sigma complex by comparison with the well-characterized examples 4 and 5. This might suggest an initial equilibrium is established between the starting bis-dihydrogen complex and a corresponding BN-cyclohexane sigma-complex that favours the starting material (presumably due to the steric clash between the PCy and the NMe groups). With the same metal fragment we have previously commented upon similar relative differences in the strength of the Ir–H–B sigma interaction when comparing H2BNr (R = H or Me)17,18 Over time (8 h), decomposition to [Ir(PCy2)2H3]43 and [Ir2(PCy2)3H3][BAr4]17 is observed.

**Catalytic dehydrocoupling using the Ir–BN complexes**

When prepared pure, complexes 4 and 5 are stable for at least 24 h in 1,2-F2C6H4 solution with no significant change observed by NMR spectroscopy. However, addition of five additional equivalents of the cyclic amine-borane 1 to complex 4 (i.e., 20 mol%) results in the slow (72 h, TOF $\approx 0.07$ h$^{-1}$, sealed NMR tube) dehydrocoupling to form the final amino-borane derived tricyclic borazine product [BNC6H4]6 [$\delta = 34.5$ ppm, s; lit. 34.8, C6D6]4,10 (Scheme 5). Inspection of the 11B NMR spectrum after 2 h shows compound 1 and a significant proportion of a new signal assigned to the new monomeric amino-borane HBNHC6H4. 7 [$\delta = 41.1$ ppm, d, $J$(BH) 124 Hz]. This chemical shift and coupling pattern is similar to other, transient, amino-boranes12,42,43 as well as stable HBNMeC6H4 8 (vide infra). After 24 h the signal due to 7 had essentially disappeared, with 6 now observed as a significant product. Also apparent after 24 h is a set of broad peaks centred around $\delta = -5$ ppm that also show $J$(BH) coupling. Over a further 48 h (72 h in total) these signals reduce in intensity at the overall gain of 6, and the temporal behaviour of the system suggests they are due to intermediates that follow 7 and precede 6. The final organometallic product observed is the pentahydride [Ir(PCy2)2H5]43. Reformation of compound 1 was not observed during these later processes; the observation of which would point to H-redistribution processes.42,44

Due to their transient nature, overlapping signals, and lack of charge, we have not been able to use detailed NMR spectroscopic or ESI-MS techniques to determine the identity of these intermediate species. The chemical shift/coupling constant data suggest four-coordinate BH groups that are not metal-bound, possibly due to a cycloborazene species (dimers and/or trimers, e.g., $n = 0$ or 1, Scheme 5) and isomers thereof.

In order to put the structures of these intermediates on a firmer footing we have used DFT geometry optimization coupled with GIAO 11B chemical shift calculations to help in their identification. Table 1 shows selected examples, with full details given in the Supporting Information. The chemical shifts of compounds 7 [exptl $\delta = 41.1$ ppm, calcd $\delta = 38.4$ ppm] and 6 [exptl $\delta = 34.5$ ppm, calcd $\delta = 31.9$ ppm] are reproduced well,
with a consistent small, approximately 2.5 ppm, difference between experiment and calculation (Table 1). Based on these calculations diborazane and triborazane species would be expected to show signals between $\delta = 0$ to $-7$ ppm and $\delta = -2$ to $-9$ ppm, respectively, in the experimentally determined spectrum as is observed (Scheme 5). Partially dehydrogenated trimers would be expected to show an additional signal about $\delta = +37$ ppm, very similar to 6, and thus might be obscured. The oligomerisation of amino-boranes to form cyclic borazane products is well-known, and these can, in certain cases, be further dehydrogenated by a transition metal-catalyst to form cyclic borazanes.$^{[22,45,46]}$

Addition of 5 equivalents of 2 to a 1,2-F$_2$C$_6$H$_4$ solution of III (as a precursor to 5) in a sealed NMR tube results in dehydrogenation and the formation of the monomeric cyclic amino-borane HBNMeC$_6$H$_4$ 8 (Scheme 6) after 24 h (TOF $\approx 0.2$ h$^{-1}$). Compound 8 was initially reported by Wille and Goubeau,$^{[30]}$ and has been independently prepared by intramolecular hydroborination of the N-methylhomoallylamine-borane adduct and subsequent one-pot thermal dehydrogenation (see Experimental Section). Compound 8 does not cyclotrimerise or cyclo-dimerise and remains monomeric in solution, as evidenced by a characteristic down-field chemical shift in the $^{11}$B NMR spectrum $\delta = 40.8$ ppm [J(BH) 125 Hz], very similar to 7. No other significant boron-containing products were observed during this process. The final organometallic species observed were 5 and Ir(PC$_5$)$_3$H$_2$ as identified by $^1$H and $^{31}$P($^1$H) NMR spectroscopy, in a 0.6:1 ratio, respectively.

The (Ir(PC$_5$)$_3$)(H)$_2$ fragment thus acts as a slow catalyst (or precatalyst) for the dehydrogenation of these cyclic amine-boranes, as found for their acrylic counterparts.$^{[17,18,42]}$ That the onward dehydrogenation does not occur in 4 or 5 in the absence of additional amine-borane is a further demonstration of the promotional role that amine-borane plays in dehydrogenation chemistry. This is likely through the formation of B–H–H–N dihydrogen bonds,$^{[45,46]}$ which are commonplace in amine-borane chemistry, and have been shown by computational techniques to play an important role in lowering the barrier to B–H and N–H activation steps.$^{[18,49–51]}$ We have not explored the mechanism for the dehydrogenation process in 4 and 5 in detail, but other studies using this iridium fragment have shown that N–H activation of amine-boranes is rate-determining and preceded by B–H activation.$^{[18,49–51]}$

Interestingly, in this context, addition of D$_2$ to complex 4 in C$_6$H$_5$F solution results in the loss of the Ir–H, Ir–H–B and N–H resonances in the $^1$H NMR spectrum, and the appearance of corresponding signals in the $^2$H NMR spectrum while the $^{31}$P($^1$H) NMR spectrum remains unchanged (Scheme 7). Dissolved HD and H$_2$ were also observed ($\delta = 4.47$ ppm, t, J(HD) = 43 Hz; $\delta = 4.50$ ppm, respectively). This points to both rapid Ir–H/D$_2$ exchange,$^{[40]}$ and that sequential N–H or B–H activation (in either order) are of approximately similar energies and reversible. An alternative mechanism would be a concerted and reversible Nh and BH activation that leads to amino-borane, 7, that then re-adds D$_2$. That no free amino-borane 7, or the final cyclic trimer 6, were observed argues against a mechanism involving such reversible dehydrogenation.$^{[52]}$

Addition of D$_2$ followed by H$_2$ re-establishes the N–H ($\delta = 4.07$ ppm), Ir–H–B ($\delta = -6.23$ ppm) and Ir–H ($\delta = -20.53$ ppm) signals, showing that this process is reversible. N–H activation

**Table 1.** Calculated $^{11}$B NMR chemical shifts of representative dimers and trimers ($\sigma =$ standard (BF$_3$)OEt$_2$) - molecule.

| Molecule | $\sigma$ (ppm) | Molecule | $\sigma$ (ppm) |
|----------|---------------|----------|---------------|
| ![Diagram](image1.png) | +38.4 [exptl +41.1] | ![Diagram](image2.png) | +31.9 [exptl 34.5] |
| ![Diagram](image3.png) | -9.3 | ![Diagram](image4.png) | -2.2 |
| ![Diagram](image5.png) | -10.7 (B1) +34.3 (B2) -9.1 (B3) | ![Diagram](image6.png) | -11.0 (B1) -9.3 (B2) -5.6 (B3) |
is generally considered to have a larger barrier than B–H activation in cationic systems.\[^{[1,17,53,54]}\] For example, addition of D$_2$ to [Ir(Ph$_2$P)$_2$(C$_5$H$_5$)][BAr$_4$] results in H/D exchange only at Ir–H and B–H.\[^{[33]}\] However, products that arise from formal N–H activation over B–H activation have been isolated\[^{[55,56]}\] or postulated\[^{[57,58]}\] for neutral systems and are also proposed as intermediates in amine-borane dehydration.\[^{[28,59]}\] It thus appears likely that the cyclic nature of the amine-borane in 5 results in more levelled B–H/N–H activation energies. N–H activation may be additionally assisted by intramolecular hydrogen bonding.\[^{[22,60]}\] Related acyclic phosphido-borane complexes have been isolated and shown to undergo rapid and reversible P–H/B–H bond activation as probed by H/D scrambling experiments.\[^{[8,1]}\] As significant D incorporation into the P$_3$ ligand is also observed, we cannot discount more complicated mechanisms for H/D exchange that involve cyclometallated phosphine ligands.

Reactivity of cyclic amine–boranes with [Rh(P$_5$P$_2$CH$_2$CH$_2$P)$_2$(η$^2$-C$_5$H$_5$)][BAr$_4$]

Addition of 2 equivalents of the cyclic amine-borane 2 to [Rh(P$_5$P$_2$CH$_2$CH$_2$P)$_2$(η$^2$-C$_5$H$_5$)][BAr$_4$] results in 1,2-F$_2$C$_6$H$_4$ solution and monitoring in situ using $^{13}$P($^1$H) and $^{18}$B NMR spectroscopy showed that after 5 min a new complex was formed (C$_6$F$_2$H$_4$) in 1,2-F$_2$C$_6$H$_4$ solution. The amine-borane is equally disordered in the final difference map they were ultimately placed in calculated positions. The amine-borane is generally considered to have a larger barrier than B–H activation in cationic systems.\[^{[1,17,53,54]}\] For example, addition of D$_2$ to [Ir(Ph$_2$P)$_2$(C$_5$H$_5$)][BAr$_4$] results in H/D exchange only at Ir–H and B–H.\[^{[33]}\] However, products that arise from formal N–H activation over B–H activation have been isolated\[^{[55,56]}\] or postulated\[^{[57,58]}\] for neutral systems and are also proposed as intermediates in amine-borane dehydration.\[^{[28,59]}\] It thus appears likely that the cyclic nature of the amine-borane in 5 results in more levelled B–H/N–H activation energies. N–H activation may be additionally assisted by intramolecular hydrogen bonding.\[^{[22,60]}\] Related acyclic phosphido-borane complexes have been isolated and shown to undergo rapid and reversible P–H/B–H bond activation as probed by H/D scrambling experiments.\[^{[8,1]}\] As significant D incorporation into the P$_3$ ligand is also observed, we cannot discount more complicated mechanisms for H/D exchange that involve cyclometallated phosphine ligands.

NMR spectrum at room temperature (δ = 57.9 ppm, J(RhP) = 162 Hz). Cooling to 190 K reveals two signals (δ = 57.8 ppm, dd, J(PP) = 56 Hz, J(RhP) = 160 Hz; δ = 56.9 ppm, dd, J(PP) = 56 Hz, J(RhP) = 160 Hz). This suggests a fluxional process that makes equivalent the two phosphine groups. A mechanism that invokes a bidentate to monodentate change in amine-borane binding and then a rotation around the remaining Rh–H bond is suggested.\[^{[40]}\] The $^{18}$B NMR spectrum shows a broad signal at δ = 32.1 ppm, downfield shifted from free 2 by 38.6 ppm, consistent with a bidentate binding mode of the amine-borane at a Rh centre.\[^{[21]}\]

Figure 3 shows the solid-state structure of the cationic portion of complex 10, demonstrating that the cyclic amine-borane, 2, interacts with the Rh centre in a bidentate manner through two Rh–H–B interactions at a pseudo-square planar Rh centre. Although the bridging hydrogen atoms were located in the final difference map they were ultimately placed in calculated positions. The amine-borane is equally disordered over two positions, which can be modelled as either the NMe pointing axial or equatorial with respect to the Rh$_2$P$_2$ plane. The Rh–B distance measured from this model at 2.150(6) Å is slightly shorter, but still similar, to that in closely related [Rh(P$_5$P$_2$CH$_2$CH$_2$P)$_2$(η$^2$-H$_2$BNMe$_2$)](BAr$_4$) (9) and the complete consumption of the amine-borane to form the amino-borane 7 (Scheme S2, Supporting Information). Over 8 h, this mixture evolves by further dehydrocoupling to give cyclotritaborazine 6 and complex 9 as the organometallic product. At the early
stages of the reaction, NMR signals due to amine-borane and the sigma-complex 9 are too broad to be observed in the $^1\text{H}$ and $^{13}\text{B}$ NMR spectra, but the $^{31}\text{P}[^1\text{H}]$ NMR spectrum is sharper, thus suggesting a rapid exchange between bound and free amine-borane. In support of this rapid exchange hypothesis, when all of 1 is consumed, and the opportunity for exchange is reduced, sigma-complex 9 is observed as a characteristic broad signal at $\delta = 29.3$ ppm in the $^1\text{H}$ NMR spectrum while the Rh–H–B groups are observed at $\delta = -4.83$ ppm in the $^1\text{H}$ NMR spectrum as a broad signal (relative integral of 2H). The $^{31}\text{P}[^1\text{H}]$ NMR spectrum shows a single environment that couples to $^{103}\text{Rh}$ ($\delta = 57.1$ ppm, $J(\text{RhP}) = 160$ Hz). As this rapid exchange is not observed in 10 or 11, we suggest that the increasing levels of substitution on nitrogen slow down this process, which might indicate an associative mechanism for ligand substitution. Recrystallisation of the reaction mixture from 1,2-F$_2$C$_6$H$_4$/pentane resulted in a small number of red crystals of complex 9 that required mechanical separation from co-crystallised orange V. The solid-state structure of complex 9 is shown in Figure 4, and is closely related to 10. In particular, the Rh–B and B–N distances are the same within error or very similar, respectively: 2.155(5) and 1.588(6) Å. As complex 9 cannot be isolated pure in bulk, we have not pursued the H/D exchange experiments.

Addition of cyclic-amine-borane 3 to V in 1,2-F$_2$C$_6$H$_4$ solution results in the slow (24 h) substitution of the arene and the formation of $[\text{Rh}((\text{Pr}_{3}P)(\text{CH}_2\text{CH}_2\text{CH}_2\text{Pr})_2)\text{H}_2\text{BNNMe}_2\text{C}_6\text{H}_4][\text{BAF}_4]$ (11) which can be recrystallised by addition of pentane. Complex 11 has been characterized by NMR spectroscopy and single-crystal X-ray diffraction, and shows very similar data to that of 9 and 10. The $^1\text{H}$ NMR spectrum shows a single NMe$_2$ environment at $\delta = 2.85$ ppm (6H) and a single Rh–H–B environment at $\delta = -5.17$ ppm, while the $^{13}\text{B}$ NMR spectrum shows a down-field shifted signal at $\delta = 34.4$ ppm. The solid-state structure (Figure 4) also reflects these similarities with the pseudo-square planar Rh$^1$ centre coordinated with the cyclic amine-borane in a bidentate manner. Comparing 9, 10, and 11, there is no change in the Rh–B bond distances [2.155(5), 2.150(6), 2.172(3) Å, respectively] within the experimental error. There is a slight change in chemical shift of the boron atom when compared with free ligand [A$\delta$ = +40.6, +38.6, +37.4 ppm], which suggests a trend in that increasing N-substitution leads to a decreasing M–B interaction that is not captured by an associated change in bond lengths.$^{[38,63]}$

**Catalytic dehydrogenation using the Rh–BN complexes**

We have explored the catalytic dehydrogenation/dehydrocoupling of the cyclic amine-boranes 1 and 2 using the $[\text{Rh}((\text{Pr}_3\text{P})(\text{CH}_2\text{CH}_2\text{CH}_2\text{Pr})_2)_2\text{H}_2\text{BNNMe}_2\text{C}_6\text{H}_4][\text{BAF}_4]$ fragment. Using 10 mol% V slow
The likely involvement of potential dimer/monomer forms from which V(o) was also independently synthesized by the addition of dimers and dimerization to form intermediate species (Scheme 1). A single crystal X-ray diffraction study demonstrated the gross structure, but the hydrides were not located (see Supporting Information). Complex 12 is similar to previously reported [Rh(bis-phosphine),H$_2$]$^+$ cations that are formed by hydrogenation of [Rh(bis-phosphine)]$^+$ precursors, through dimerization/deprotonation.$^{46-48}$ It is stable to H$_2$ loss under vacuum (10$^{-3}$ Torr) in the solid-state and in solution. We did not observe any evidence for the formation of boronium cations (e.g., [LBHNMMe(CH$_2$)$_2$]$_2^+$) which might indicate a hydride abstraction route to form intermediate monocatic systems with odd numbers of hydrides.$^{49}$

Complex 12 is a competent catalyst itself for the dehydrogenation of compound 2, taking approximately 2 h to effect complete conversion ([Rh] = 10 mol%, sealed NMR tube, TOF = 5 h$^{-1}$). When comparing 10 and 12 as catalysts (10 mol% [Rh]) both follow an overall first-order profile ($k$ = 1.18(3) × 10$^{-5}$ s$^{-1}$; 2.16(7) × 10$^{-4}$ s$^{-1}$, respectively) with dimeric 12 much faster than monomeric 10. No induction period was observed.$^{15,20}$ As these are sealed conditions, inhibition by H$_2$ may well be occurring, complicating a detailed kinetic analysis, as observed previously for Rh systems.$^{10,70}$ Unfortunately, we have been unable to reliably measure the rate in an open system (under Ar) due to partial decomposition of 8 upon sampling.$^{50}$

Addition of a hindered base (2,6-di-tertbutylpyridine, 5 equivalents relative to catalyst) to the mixture with 10/2 resulted in faster catalysis ($k$ = 1.4(1) × 10$^{-4}$ s$^{-1}$) and the observation of 12 as the only organometallic species at the end of catalysis. Addition of [H(OEt)$_2$]$_2$[BAr$_4$]$_2$/10 equivalents of 2 to dimer 12 resulted in the formation of 10 and catalysis at a slower rate, similar to starting from 10 ($k$ = 2.3(1) × 10$^{-5}$ s$^{-1}$). Addition of [H(OEt)$_2$]$_2$[BAr$_4$]$_2$/CH$_2$CN to dimer 12 resulted in the formation of [Rh(PR$_3$CH$_2$CH$_2$PR$_3$)(NMe$_2$)$_2$][BAr$_4$]$_2$ (13: Scheme 11). Complex 13 was also independently synthesized by the addition of CH$_2$CN to V. These, and our previous observations, suggest: 1) dimeric 12 is a more active (pre)catalyst than monomeric 10; 2) under catalytic conditions, 12 forms from 10 by slow dehydrogenation of 2, subsequent oxidative addition of H$_2$ and dimerization to form intermediate B, which adds further H$_2$ and is reversibly deprotonated to form [H(solvent)$_2$]$_2$[BAr$_4$]$_2$ and 12 (Scheme 12); 3) H$^+$ inhibits catalysis presumably by channelling the resting state away from 12; 4) addition of base promotes the formation of 12.

That dimeric 12 is an active catalyst or precatalyst for amine-borane dehydrogenation has resonance with previous reports of dimeric (Rh(L$_2$)$_2$) being implicated in dehydrocoupling of acyclic amine-boranes,$^{19,18,70,71}$ although in some systems dimers have been discounted on the basis of computational analysis.$^{49}$ The likely involvement of potential dimer/monomer equilibria during catalysis using 12 as a precursor was probed using the method of initial rates, monitoring over the first 5% of turnover in the pseudo-zero-order regime of catalysis (Figure 5).

These data show a first-order dependence on [2] and a half-order dependence on [12]. This is consistent with a rapid dimer/monomer equilibrium in which the dimer is dominant but sits off the cycle and is the active species. Such equilibria have been suggested before for arene complexes.
alkylations,[72] alkene hydrogenation[65] and hydroboration,[73]
amine-borane dehydrogenation,[58] C–S bond activations,[74]
and arylation of BCl-1,2-azaborines,[75] amongst others. Perhaps
most closely related to the system under discussion here are
dimer/monomer equilibria operating for Shvo’s catalyst in both
amine-borane dehydrogenation and hydrogen transfer reactions.[76,77] In these cases a dimer is suggested to be in
equilibrium with two, different, monomers (of equal relative
concentration); one of which is active in catalysis.

For the system here we speculate a rapid equilibrium is es-

tablished between 12 and cationic (C) and neutral (D) monomers,
for which one of the latter is the active catalyst (Scheme 13). We discount the alternative reason for half-order
dependence that involves dissociation of either chelating
phosphine or H₂ from 12[78] as this does not fit with other
experimental observations. Reversible monomer/dimer equilibria
for [Rh(L₂)H₅]⁺ species involving reversible protonation have
previously been noted,[66,67] but we suggest that this is not oc-
curring due to the positive effect that exogenous base has on
the observed rate when starting from 10, conditions that
favour the formation of 12. Consistent with the rapid equilibri-
um proposed, addition of MeCN (10 equivalents) to 12 result-
ed in the immediate formation of the monomeric MeCN-
adduct 13 plus gas evolution (H₂), which could arise from C.
Also formed are uncharacterised hydride products [¹H NMR:
δ = –11.79 and –17.45 ppm] that decompose after 1 h,
suggestive of a reactive neutral species such as D.

Scheme 11. Synthesis and reactivity of complex 12. [BAR₄⁺]⁻ anions are not shown.

Scheme 12. Suggested relationships between 12 and 10. (S) = solvent.
[BAR₄⁺]⁻ anions are not shown.

Figure 5. Initial rate versus concentration for the dehydrogenation of 2
mediated by 12 in a sealed NMR tube. A) [2]; B) [12]¹/₂; inset shows relation
to [12]².

Scheme 13. Suggested dimer/monomer equilibrium for 12. [BAR₄⁺]⁻ anions
are not shown. (S) = weakly bound solvent.
Conclusion

Presented here is the first study of the coordination chemistry, and subsequent dehydrogenation, of BN-cyclohexanes. Perhaps unsurprisingly the sigma-amine borane complexes formed with the [Ir(PCy3)2(H)2]+ and [Rh(P(Pr)3(CH2)3)2P(Pr)3]+ fragments are broadly similar to those that result from coordination of acyclic amine-boranes, such as H2B,NMe2, although there are interesting differences in reactivity (e.g., the more levelled B–H/N–H activation energies when probed with exogenous D2). The real insight that comes from these systems is their ability to mediate (albeit slowly) the dehydrogenation of the coordinated cyclic-amine boranes at room temperature that allows for intermediate species to be observed in the dehydrocoupling of the parent 2,2-H2,B,N-C6H6; as well as (for the Rh system) the kinetics of dehydrogenation to be probed, which show first-order behaviour for the catalyst, suggesting a rapid dimer–monomer equilibrium is operating. Such insight is valuable in both determining dehydrocoupling pathways of cyclic amine-boranes and determining the speciation of the active catalyst species.

Experimental Section

All manipulations were performed under an argon atmosphere using standard Schlenk and glove-box techniques. Glassware was oven dried at 130 °C overnight, and flamed under vacuum prior to use. Pentane and MeCN were dried using a G rubbs-type solvent dryer. Pentane and MeCN were dried using a G rubbs-type solvent dryer. Microanalysis Ltd. For hydrogenation reactions high pressure (100 mL) and N,N-dimethyloctylamine (3.00 g, 30.3 mmol, 1 equiv). Borane-tetrahydrofuran solution (36 mL, 1 m in THF, 36 mmol, 1.2 equiv) was added dropwise. The pressure vessel was sealed, and the reaction was heated to 100 °C for 18 h. The reaction was cooled to room temperature then opened in the air. The volatiles were removed in vacuo. The resulting residue, a viscous, colourless liquid, was subjected to silica gel chromatography in the air with 2:3 CH2Cl2/hexane as the eluent system to furnish a colourless, viscous liquid (102 mg, 32%). 1H NMR (300 MHz, CD2Cl2): δ = 2.96–2.13 (m, overlapping BCHF3, 5H), 2H), 1.36–1.29 (m, 33 H, PCy2CMe2); 13C NMR (126 MHz, CD2Cl2): δ = 55.1, 42.4, 28.8, 26.2, 16.6 ppm (t, J(13CH) = 6.5 Hz); HRMS (El-): m/z calcd for C21H25NB [M]+ 319.14105, found 319.14265.

N,N-Dimethyl-1,2-azaborinane 3: The preparation of this compound was adapted from that of Wille and Goubeau.34 In a glove-box, a 300 mL pressure vessel was charged with tetrahydrofuran (100 mL) and N,N-dimethyloctylamine (3.00 g, 30.3 mmol, 1 equiv). Borane-tetrahydrofuran solution (36 mL, 1 m in THF, 36 mmol, 1.2 equiv) was added dropwise. The pressure vessel was sealed, and the reaction was heated to 100 °C for 18 h. The reaction was cooled to room temperature then opened in the air. The volatiles were removed in vacuo. The resulting residue, a viscous, colourless liquid, was subjected to silica gel chromatography in the air with 2:3 CH2Cl2/hexane as the eluent system to furnish a colourless, viscous liquid (102 mg, 32%). 1H NMR (300 MHz, CD2Cl2): δ = 2.96–2.13 (m, overlapping B–H signals), 2.06 (app t, 2H), 1.95 (s, 6H), 1.76 (brs 2H), 1.34–1.16 (m, 2H, 2H), 0.92 (brs, 2H). 11C NMR (126 MHz, CD2Cl2): δ = 64.2, 50.3, 26.4, 25.0, 14.8 (br). 1B NMR (96 MHz, CD2Cl2): δ = −3.0 (t, J = 96.8 Hz). HRMS (El-): m/z calcd for C31H36NB [M]+ 449.27457, found 449.27479. 1H NMR (500 MHz, CD2Cl2): δ = 7.76 (s, 8H, [BAr6]+), 7.60 (s, 4H, [BAr6]+), 4.07 (br, 2H, NH3), 3.23 (br, 2H, CH2 next to NH3), 1.33 (m, CH2 and CH3 (2H), 1.36–1.29 (m, 33 H, PCy2CMe2), 0.92 (m, 4H, CH3), −2.63 (br, 2H, BH2). −20.53 ppm (t, J, = 16 Hz, IH3). The NH3/CH3 resonances were identified on the basis of the number of cross-peaks in the 1H/1H COSY spectrum. Furthermore the HSO4 spectrum shows no cross peak between the signal at δ = 4.07 ppm, while the signal at δ = 3.23 ppm is coupled to a 13C NMR signal at 48 ppm. 31P(1H) NMR (202 MHz, CD2Cl2): δ = 37.12 (d, J31P = 268 Hz, 1P), 35.26 ppm (d, J31P = 268 Hz, 1P); 13C NMR (160 MHz, CD2Cl2): δ = 19.8 (br, bound BH2). −6.63 ppm (s, [BAr6]+); ESI-MS (1,2-C6H6F3/60 °C) positive ion: m/z 840.5431 [M]+ (calc 840.5492); elemental microanalysis: calcd [C31H36BF3N3P]+

Synthesis and characterization

N-Methyl-1,2-azaborinane 2: B-Cl-N-Me-1,2-BN-cyclohexene was prepared as described by Chrostowska and Liu.35 In a glovebox, a Fischer–Porter tube was charged with the starting material (4.00 g, 30.5 mmol) and palladium on carbon (64 mg, 10 wt% Pd metal, 0.061 mmol, 0.2 mol% palladium). The vessel was sealed and flushed with hydrogen before pressurizing to 45 psi with hydrogen. The reaction was heated for 16 h with monitoring of the internal pressure and refluxing as often as required. The reaction was then cooled to room temperature, and the solids were filtered off giving 1.68 g crude product (41% crude yield, 12.8 mmol). This crude product was dissolved in THF, and lithium aluminium hydride (1.12 g, 29.5 mmol, 2.3 equiv) was added carefully at room temperature. The reaction was stirred for 24 h at room temperature, and the solids were filtered off in the glovebox. The filtrate was cooled to −78 °C, and methanol (10 mL) was added dropwise to quench excess LiAlH4, and to install the proton on the product. The reaction was warmed to room temperature over 30 min, and the volatiles were removed in vacuo. The residue was extracted with hexane (4 × 80 mL), and the hexane was removed using a rotary evaporator. This residue was rinsed with cold pentane to furnish 374 mg of desired product (12% yield overall). 1H NMR (500 MHz, CD2Cl2): δ = 2.93–2.07 (m, B–H signals), 1.93 (m, 3H), 1.72 (brs, 3H), 1.54 (brs, 2H), 1.35 (brs, 1H), 1.23 (brs, 1H), 0.87 (brs, 1H), 0.59 ppm (brs, 1H); 13C NMR (126 MHz, CD2Cl2): δ = −55.1, 42.4, 28.8, 26.2, 16.6 ppm (t, J(13CH) = 6.5 Hz); HRMS (El-): m/z calcd for C21H25NB [M]+ 319.14105, found 319.14265.
(1703.28 g mol⁻¹): C 50.77, H 5.44, N 0.82; found: C 50.32, H 5.33, N 1.03.

[\text{Ir(H)}_2(\text{PCy}_3)_2(\text{n}^2-\text{H})_2\text{BNMeH(CH}_2)_2\text{]}(\text{BAr}_4^-) (5): In a high pressure NMR tube equipped with a J. Young’s valve, [\text{IrHPCy}_3(\text{n}^2-\text{CH}_2)\text{PCy}_3(\text{n}^2-\text{H})_2\text{BNMeH(CH}_2)_2\text{]}(\text{BAr}_4^-) (16 mg, 1 × 10⁻³ mmol) in CH₂F₂ was hydrogenated at 4 atm as described in the general procedures. It was stirred for 20 min to produce a colourless solution of [\text{IrHPCy}_3(\text{n}^2-\text{CH}_2)\text{PCy}_3(\text{n}^2-\text{H})_2\text{BNMeH(CH}_2)_2\text{]}(\text{BAr}_4^-) which was rapidly transferred under argon to another high pressure NMR tube containing 2 (1 mg, 1 × 10⁻³ mmol). Gentle inversion of NMR tube for 1.5 h resulted in the colourless solution of 5 and [\text{IrHPCy}_3(\text{PCy}_3)_2(\text{n}^2-\text{H})_2\text{BNMeH(CH}_2)_2\text{]}(\text{BAr}_4^-) in 20:1 ratio. Compound 5 was characterized in situ by NMR spectroscopy and ESI-MS. A few single crystals suitable for X-ray diffraction studies was obtained by diffusion of pentane at –35 °C. 1H NMR (500 MHz, CD₂Cl₂): δ = 7.76 (s, 8H, [\text{BAr}_4^-], 7.60 (s, 4H, [\text{BAr}_4^-]), 3.94 (br, 1H, NH), 3.33 (br d, 1H, CH), 2.32 (9d, 1H, CH), 1.99–1.92 (br, 6H, 4H (CH₂)), 1.65 (s, 1H, CH), 1.5–1.0 (br m, 26H, CH₂) and 0.52 (br, 6H, CH₂), –5.38 ppm (br, 1H, BH), –6.60 ppm (s, [\text{BAr}_4^-]: ESI-MS (1,2-C₂H₆F, 60 °C) positive ion: m/z 478.2417 [M⁺] (calcld 478.2408; elemental microanalysis: calcd [C₄₂H₃₆F₆N₇P₂]⁺ 474.8149 g mol⁻¹; C 46.56, H 4.51, N 1.04; found: C 46.17, H 4.16, N 0.68).
–6.19 ppm (s, 1 [Ar^+]_2); elemental microanalysis: calcd (C_{24}H_{32}F_8P_2Rh)_2 (1626.34 g mol^-1): C 46.7, H 3.9; found: C 46.3, H 4.8.

[Rh(IPr)(P)Cl(C=C)]_2[Pr]_2[N(Me)]_2[Ar^+ ]_2 (13): V (20 mg, 1.4 × 10^-2 mmol) was dissolved in 1.2-F_2C=H (1 mL) in a Schlenk flask to which CH_2CN (16 μL, 0.28 mmol, 20 equivalents) was added. Addition of CH_2CN immediately changed the colour of solution from orange to pale yellow. Resulting solution was stirred for 10 min. 1.2-F_2C=H, and unreacted CH_2CN were removed in vacuo to obtain pale yellow solid of 13. 1H NMR (500 MHz, CDCl_3): δ: 7.76 (s, 8H, [Ar^+ ]_2), 7.61 (s, 4H, [Ar^+ ]_2), 2.25 (s, 6H, NCCl_2), 1.97 (br, 6H, CH_3), 1.33 (m, 16H, CH_2(12H) and CH(4H)), 1.19 ppm (m, 12H, CH_2); 13[C(H)] NMR (202 MHz, CDCl_3): δ = 42.51 ppm (d, J_NH = 167 Hz); ESI-MS (1,2-C_3H_4F_2, 60 °C) positive ion: m/z 461.1748 [M+H] (calcd 461.1722); elemental microanalysis: calcd (C_{13}H_{16}F_2N_2P_2Rh) (1324.62 g mol^-1): C 46.24, H 3.96, N 2.11; found: C 46.31, H 3.95, N 1.99.

Computational Methods

The geometries were optimized at the density functional theory (DFT)[32] level with the hybrid B3LYP[41] exchange-correlation functional and the DFT-optimized DZVP basis set for all atoms.[62] Vibrational frequencies were calculated to show that the structures were minima. The nuclear magnetic shielding tensors were calculated using the gauge-independent atomic orbital (GIAO) approach.[47,46] The NMR calculations were carried out with the TZVP basis set and B3LYP exchange-correlation functional.[86] All calculations were carried out with Gaussian 09.[90]

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