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A *tert*-butyl-substituted amino-borane bound to an iridium fragment: A latent source of free $H_2B{=}N^tBuH$

Heather C. Johnson, Andrew S. Weller*

Department of Chemistry, Chemical Research Laboratories, Mansfield Road, Oxford OX1 3TA, United Kingdom

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ABSTRACT

Release of the primary amino-borane $H_2B{=}N^tBuH$ from $[Ir(PCy_3)_2(H)_2(\eta^2\text{-}H_2B{=}N^tBuH)][BAr^F_4]$, formed from dehydrogenation of $[Ir(PCy_3)_2(H)_2(\eta^2\text{-}H_3B{\cdot}N^tBuH_2)][BAr^F_4]$, results in the eventual formation of the corresponding cyclic borazine $[HBN^tBu]_3$. Observations point to the fact that off-metal hydrogen redistribution reactions play a major role in the final product formation, with $H_3B{\cdot}N^tBuH_2$ being formed alongside $[HBN^tBu]_3$.

1. Introduction

The metal-mediated dehydrocoupling of amine-boranes potentially provides kinetic control over both H_2 loss and B–N bond forming processes that allows for the development of catalysts for chemical hydrogen storage applications [1–6] and the formation of B–N polymeric materials that are isoelectronic with ubiquitous, and technologically important, polyolefins [7,8]. The mechanism of dehydrocoupling has attracted significant interest [6,9–12], as manipulation of the various steps on the cycle potentially allows for control of rates of hydrogen evolution or the B–N products formed [1]. Much of this work has centered around the dehydrocoupling reactions of $H_3B{\cdot}NH_3$ and $H_3B{\cdot}NMe_2H$ which either give generally ill-defined oligomeric/polymeric materials or dimeric $[H_2BNMe_2]_2$ respectively. The primary amine-borane $H_3B{\cdot}NMeH_2$ can also undergo dehydrocoupling forming oligomeric and polymeric materials [13–15], although trimethylborazine is the eventual thermodynamic product of such reactions (Scheme 1) [7].

Central to the understanding of the mechanism of dehydrocoupling is the formation by initial dehydrogenation, and subsequent reactivity, of amino-borane intermediates $H_2B{=}NRR'$ (R = e.g. H, Me; R′ = H, Me). As such species are highly reactive, their study often relies on their transient observation in reactions by ^{11}B NMR spectroscopy, or indirect observation by trapping of stable products (such as those arising from the hydroboration of cyclohexene [12,16]), polymer growth kinetics [7], or catalytic redistribution reactions [16]. We have recently reported a related methodology for their study, in which the amino-borane $H_2B{=}NMe_2$ is bound to a metal fragment, $[Ir(PCy_3)_2(H)_2(\eta^2{-}H_2B{=}NMe_2)][BAr^F_4]$, which then acts as a latent source of free $H_2B{=}NMe_2$ when released by addition of MeCN to the metal centre (Scheme 2) [17].

Central to the control of the dehydrocoupling of primary amine-boranes such as $H_3B{\cdot}NMeH_2$, with the goal of the delivery of tailored polyaminoboranes, is the understanding of the underlying chemistry of free $H_2B{=}NRH$. In particular, questions still remain over the subsequent reactivity of the amino-borane, once formed. One scenario is the initial trimerisation to form a trimeric borazane, as has been suggested [14], which then undergoes further dehydrogenation to form a borazine (Scheme 1). The study of such processes would rely on a reliable latent source of $H_2B{=}NRH$. Sabo-Etienne and Alcaraz have reported $H_2B{=}NMeH$ bound to a neutral Ru-fragment, accessed via dehydrogenation of the precursor amine-borane [18], but no further chemistry was reported. For our $[Ir(PCy_3)_2(H)_2]^+$ systems we have been unable access the equivalent complex and dehydrogenation reactions result instead in metal-mediated coupling to form a linear dimer, $H_3B{\cdot}NMeHBH_2{\cdot}NMeH_2$, although $H_2B{=}NMeH$ is implicated in the reaction. [19].

We thus chose instead to study the primary amino-borane $H_2B{=}N^tBuH$ bound to the $[Ir(PCy_3)_2(H)_2]^+$ fragment. Free $H_2B{=}N^tBuH$ has not, to our knowledge, been isolated, and its spectroscopic data has only been briefly mentioned as an intermediate in

* Corresponding author. Tel.: +44 1865 285151.
E-mail address: andrew.weller@chem.ox.ac.uk (A.S. Weller).

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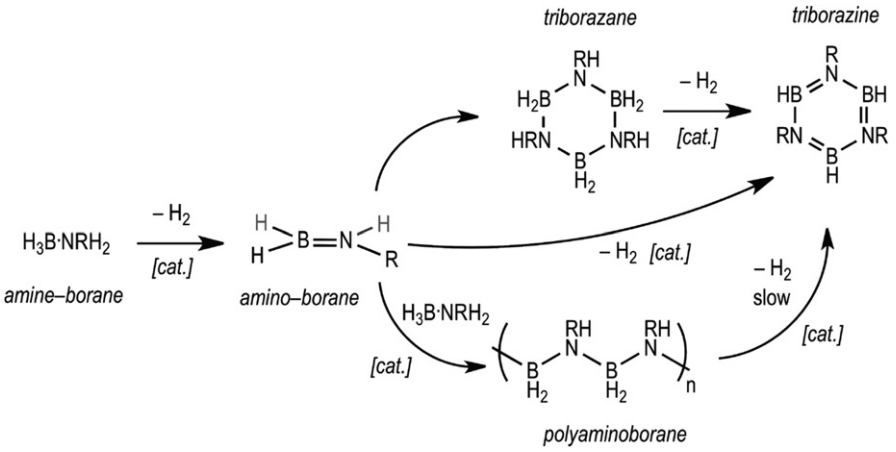
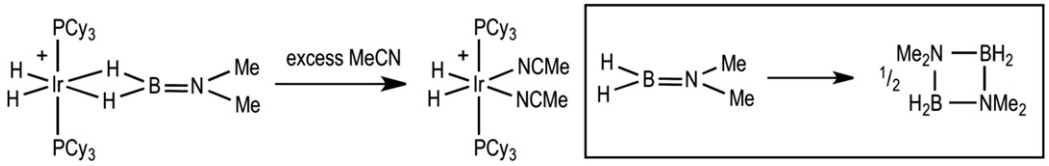


Scheme 1. General overview for the dehydrocoupling of primary amine-boranes.



Scheme 2. $[BAr^F_4]^-$ anions not shown.

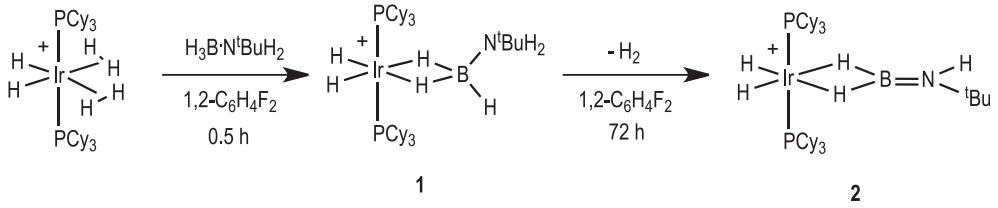
the dehydrogenation of $H_3B{\cdot}N^tBuH_2$ [12,20]. The cyclic dimer $[H_2BNH^tBu]_2$ [21] can be heated to generate reactive $H_2B{=}N^tBuH$ *in situ* [22]; while the metal-mediated dehydrocoupling of $H_3B{\cdot}N^tBuH_2$ has been described [23–25], and in some cases the solid-state structures of the resulting amino-borane coordination complexes have been reported: $[Rh(IMes)_2(H)_2(\eta^2\text{-}H_2B{=}NH^tBu)][BAr^F_4]$ (IMes = N,N′-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) and (Cy-PSiP)RuH(η^2-$H_2B{=}N^tBuH$) (Cy-PSiP = $(Cy_2PC_6H_4)_2SiMe$) [26,27].

In this contribution, we report the synthesis of a latent source of $H_2B{=}N^tBuH$ bound to a metal centre, and its subsequent reaction chemistry on release. In this we find that, when released by addition of excess MeCN, simple trimerisation of $H_2B{=}N^tBuH$ to form $[H_2BN^tBuH]_3$ [25] is not occurring, and the ultimate product of the reactions, the borazine $[HBN^tBu]_3$, potentially forms via a different route that involves a hydrogen redistribution reaction [16].

2. Results and discussion

Addition of $H_3B{\cdot}N^tBuH_2$ to $[Ir(PCy_3)_2(H)_2(H_2)_2][BAr^F_4]$ [17] generates the sigma amine-borane complex $[Ir(PCy_3)_2(H)_2(\eta^2\text{-}H_3B{\cdot}N^tBuH_2)][BAr^F_4]$ **1** (Scheme 3). Complex **1** has been characterized by NMR spectroscopy and electrospray ionization mass spectrometry (ESI-MS). The $[BAr^F_4]^-$ salt is formed as an intractable oily solid, but solid material can be isolated from the $[BAr^{Cl}_4]^-$ salt (Ar^{Cl} = 3,5-$C_6H_3Cl_2$) [28]. The NMR data for **1** are similar to that reported for $[Ir(PCy_3)_2(H)_2(\eta^2\text{-}H_3B{\cdot}NMe_2H)][BAr^F_4]$ [17] and show that the amine-borane is relatively tightly bound to the Ir centre through two 3 centre–2 electron bonds. The 298 K $^{31}P\{^1H\}$ NMR spectrum shows two broad environments at δ 39.7 and δ 32.8. Cooling to 250 K resolves these into a mutually coupled pair of sharp doublets, J(PP) 298 Hz. This large coupling constant is consistent with a *trans* geometry, and thus chemical inequivalence forced by a static amine-borane ligand that is not undergoing site exchange between terminal and bridging B–H groups [29]. In the ^1H NMR spectrum a diagnostic quadrupolar broadened integral 2H signal is observed at δ −5.83 assigned to Ir–*H*–B, while a doublet of doublets [2H, J(PH) 16, 17 Hz] is observed at δ −20.25 for the Ir–H. The remaining unbound B–H group is too broad to be observed at 298 K, but at 250 K is clearly seen at δ 6.15. The NH_2 group is observed at δ 4.21 as a broad integral 2H signal. The ^{11}B NMR spectrum shows a broad peak assigned to the borane at δ 11.2. Restricted rotation of amine-boranes bound to Ir-centres has been reported previously [17], and contrasts those of rhodium that, due to a weaker Rh–H–B interaction, undergo site exchange between bound and free B–H more readily [15,30].

Dehydrogenation of the amine-borane in **1** takes place slowly at room temperature (72 h at 298 K) to give the amino-borane bound complex $[Ir(PCy_3)_2(H)_2(\eta^2\text{-}H_2B{=}N^tBuH)][BAr^F_4]$, **2** (Scheme 3). This process occurs with quantitative yield (by NMR spectroscopy). The



Scheme 3. $[BAr^F_4]^-$ anions not shown.

small amount of H_2 (dissolved) that would be formed was not observed, but as the reaction is slow and its solubility in 1,2-$C_6H_4F_2$ would be expected to be low, [31], this is not unreasonable. We speculate this process operates via a constant oxidation-state sigma-CAM type mechanism [32], as calculated for the dehydrogenation of closely related $H_3B{\cdot}NMe_2H$ to give $H_2B{=}NMe_2$ when bound to the same {Ir} fragment [17]. This process can be accelerated by addition of the hydrogen acceptor tert-butylethene (tbe) which acts as a sacrificial hydrogen acceptor. The corresponding alkane, tert-butylethane, is formed. The NMR data for **2** are consistent with its formulation and are similar to those reported for other amino-borane complexes [17,18,26,30,33–35]. In particular the $^{31}P\{^1H\}$ NMR spectrum now shows a single resonance at δ 33.1, while the ^1H NMR spectrum shows the NH group at δ 4.44 as a relative integral 1H signal. A broad signal at δ −6.31 sharpens and splits on ^{11}B decoupling to reveal two integral 1H signals for the now inequivalent δ Ir–*H*–B groups, while two broadened integral 1H hydride resonances are observed at δ −13.94 and −14.97. The ^{11}B NMR spectrum shows a very broad signal at δ 46.6, which is similar to that reported for related amino-borane complexes of Ir [17,26,33].

With complex **2** in hand we next investigated the release of $H_2B{=}N^tBuH$ from the metal by addition of excess MeCN to form $[Ir(PCy_3)_2(H)_2(NCMe)_2][BAr^F{}_4]$, **3**, Scheme 4. Immediately after addition, liberated $H_2B{=}N^tBuH$ is observed in the ^{11}B NMR spectrum as a triplet at δ 35.0 [*J*(HB) 126 Hz] [12,20]. NMR data for complex **3** are as reported previously [17]. This solution changes in composition over time, as is shown in Fig. 1. Only three ^{11}B-containing species are observed: $H_2B{=}N^tBuH$, *borazine* $[HBN^tBu]_3$ and the *amine-borane* $H_3B{\cdot}N^tBuH_2$. Fig. 2 shows how these evolve with time. To our surprise $H_2B{=}N^tBuH$ did not simply trimerise to give the cyclotriborazane $[H_2BN^tBuH]_3$ [21] [δ −5.1 *J*(HB) 106 Hz, [25],] as has been suggested to occur for $H_2B{=}NMeH$ [14], but instead the corresponding *borazine* $[HBN^tBu]_3$ was formed [δ 25.7, *J*(HB) 127 Hz; lit. δ 27.2 *J*(HB) 125 Hz, d_6-benzene [25]], alongside the formation of an approximately equal proportion of $H_3B{\cdot}N^tBuH_2$ [δ −21.9, *J*(HB) 95 Hz, identical to a pure sample in the same solvent] as measured by ^{11}B concentration, at a similar rate to that of $[HBN^tBu]_3$ (Fig. 2) [36]. After *ca.* 14 h the concentration of $H_3B{\cdot}N^tBuH_2$ starts to drop while that of $[HBN^tBu]_3$ increases. The overall mass balance remains the same throughout. The cyclotriborazane $[H_2BN^tBuH]_3$ was not observed to the detection limit of ^{11}B NMR spectroscopy (~ 1%). We also do not observe the formation of the diaminoborane, $HB(N^tBuH)_2$, or the aminodiborane, $B_2H_5(NH^tBu)$ [20] which have been shown to arise from metal-mediated B–N bond cleavage in $H_3B{\cdot}N^tBuH_2$ [12,23,24]. After 36 h $[HBN^tBu]_3$ is the only boron-containing product in solution (Fig. 2).

In the control experiment complex **3** slowly dehydrogenates $H_3B{\cdot}N^tBuH_2$ to give $H_2B{=}N^tBuH$ and $[HBN^tBu]_3$ as observed by ^{11}B NMR spectroscopy (25% conversion to the borazine at 14 h), consistent with the overall time/concentration profile described above. This underlying process thus consumes the formed $H_3B{\cdot}N^tBuH_2$ to produce background levels of $H_2B{=}N^tBuH$ and increase the overall concentration of $[HBN^tBu]_3$. Due to this parallel process we cannot definitively rule out the possibility of an equilibrium being established between $H_3B{\cdot}N^tBuH_2$ and $[HBN^tBu]_3$ to form $H_2B{=}N^tBuH$. However, given the thermodynamic stability of

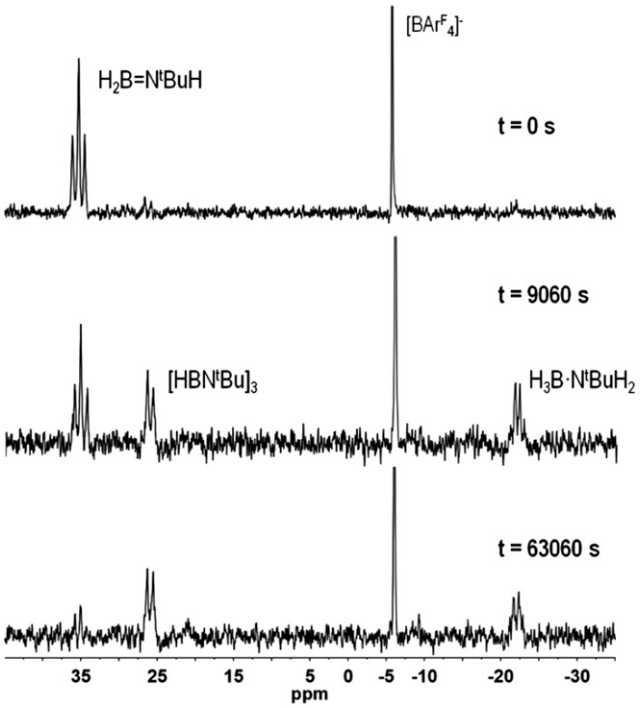


Fig. 1. ^{11}B NMR spectra (1,2-$C_6H_4F_2$) showing the temporal evolution of species on addition of excess MeCN to **2**.

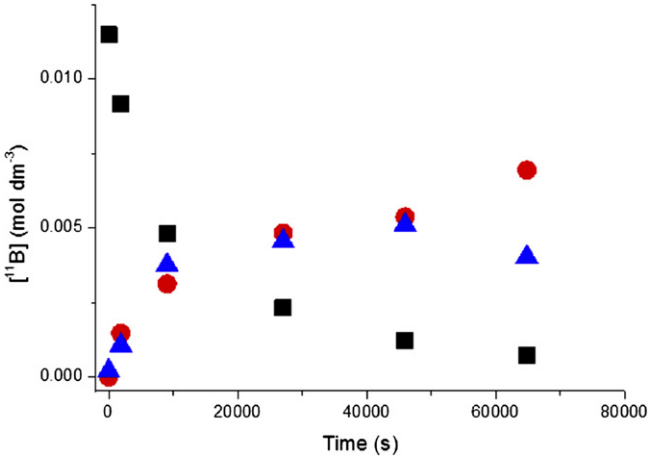
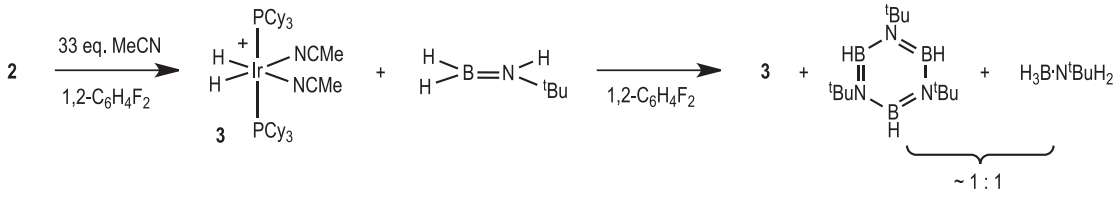


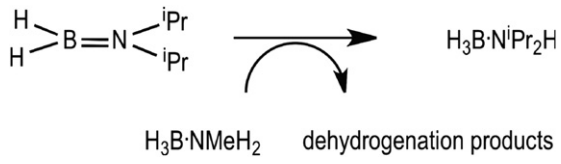
Fig. 2. Time-concentration graph for the evolution of $H_2B{=}N^tBuH$, generated by addition of excess MeCN to **2**. ■, $H_2B{=}N^tBuH$; ▲, $H_3B{\cdot}N^tBuH_2$; ●, $[HBN^tBu]_3$. After 36 h $[HBN^tBu]_3$ is the only boron-containing product in solution.



Scheme 4. $[BAr^F{}_4]^-$ anions not shown.

borazines [7] such a process is unlikely, in contrast to the hydrogen redistribution reactions observed between amine-boranes and amino-boranes (vide infra) [16].

The formation of significant amounts of $H_3B{\cdot}N^tBuH_2$ suggests that a hydrogen redistribution reaction has occurred. Similar chemistry has recently been reported by Manners et al. in as much that amino-boranes such as $H_2B{=}N^iPr_2$ can act as hydrogen acceptors with amine-boranes $H_3B{\cdot}NRR'H$ (R = Me, R′ = Me, H) [16], resulting in hydrogen redistribution products (Scheme 5). Intrigued that similar chemistry was happening in our system, as evidenced by the formation of $H_3B{\cdot}N^tBuH_2$, we investigated the likely route of formation of $H_3B{\cdot}N^tBuH_2$. At a first approximation it might be expected that $H_2B{=}N^tBuH$ would trimerise to give the cyclic cyclotriborazane $[H_2BN^tBuH]_3$ [25]. This could then potentially react with more $H_2B{=}N^tBuH$ by a hydrogen redistribution reaction (exemplified in Scheme 5) to form $[HBN^tBu]_3$ and $H_3B{\cdot}N^tBuH_2$. If initial trimerisation was slow compared with hydrogen redistribution this might account for the observed behaviour. To probe this, ideally the cyclotriborazane $[H_2BN^tBuH]_3$ would be reacted with $H_2B{=}N^tBuH$. Although the crystal structure of this material has recently been reported [25], it is only produced in low yields from the $Al(NMe_2)_3$ catalyzed dehydrogenation of $H_3B{\cdot}N^tBuH_2$ or by pyrolysis of $H_3B{\cdot}N^tBuH_2$ [21]. As an alternative [37] we instead used the sterically less encumbered methyl-substituted cyclotriborazane $[H_2BNMeH]_3$, which is readily prepared [38]. Addition of MeCN to **2** to release $H_2B{=}N^tBuH$ in the presence of one equivalent (per boron) of $[H_2BNMeH]_3$ resulted in the formation of **3**, $[HBN^tBu]_3$ and $H_3B{\cdot}N^tBuH_2$, as before. However the $[H_2BNMeH]_3$ remains untouched (Scheme 6, Eq. (1)). Experiments using $[Ir(PCy_3)_2(H)_2(\eta^2\text{-}H_2B{=}NMe_2)][BAr^F_4]$ as a latent source of $H_2B{=}NMe_2$ also resulted in no consumption of $[H_2BNMeH]_3$ and the formation only of the cyclic dimer $[H_2BNMe_2]_2$ (via free $H_2B{=}NMe_2$) as reported previously (Scheme 6, Eq. (2)) [17]. The control reaction of **3** with $[H_2BNMeH]_3$ resulted in no reaction, and this lack of dehydrogenation is similar to that reported for other systems [39] but contrasts observations for colloidal Rh-catalysts [14] or $[Ir(PCy_3)(H_2)_2(H)_2][BAr^F_4]$ [19] that do dehydrogenate $[H_2BNMeH]_3$ to give $[HBNMe]_3$.

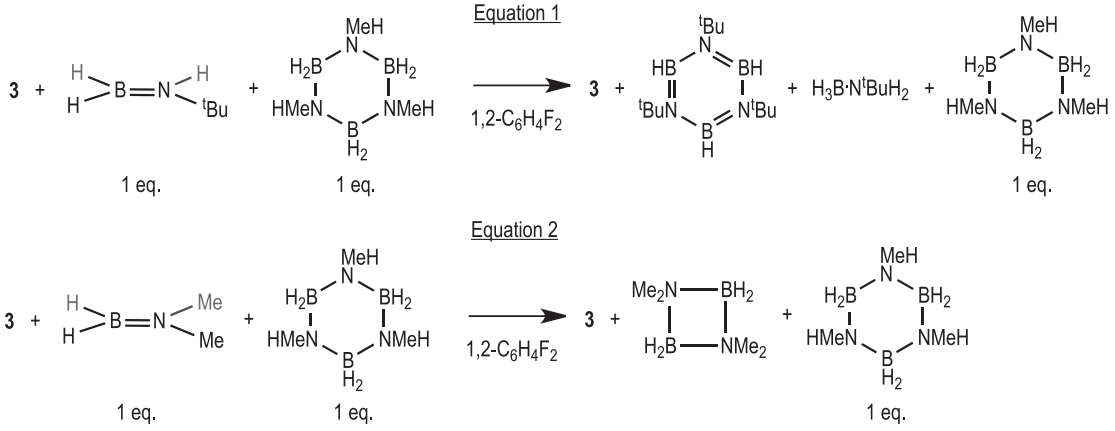


Scheme 5. Manners' hydrogen redistribution reaction.

Extrapolation of these results might suggest that in our system the bulkier cyclotriborazane $[H_2BN^tBuH]_3$ is unlikely to be an intermediate in the formation of $[HBN^tBu]_3$, albeit this inference obtained using the proxy system of $[H_2BNMeH]_3$. Alternatively if $[H_2BN^tBuH]_3$ *is* formed then it must undergo rapid hydrogen redistribution (with the concomitant formation of $H_3B{\cdot}N^tBuH_2$) to form borazine. We also do not observe linear dimer species such as (unreported) $H_3B{\cdot}NBuHBH_2{\cdot}NBuH_2$. Such oligomeric species have been suggested to form in the dehydrocoupling chemistry of the parent amine-borane $H_3B{\cdot}NH_3$, to ultimately give borazine [12,40–42], where autocatalysis by $H_2B{=}NH_2$ is also suggested to occur [43]. They have also been shown to undergo redistribution reactions with amino-boranes [16]. In our system, if they are being formed then they must also have a short lifetime. A detailed study of the possible involvement of $[H_2BN^tBuH]_3$ and $H_3BN^tBuHBH_2N^t$-BuH_2 will have to wait until practicable synthetic routes are reported for these materials. Notwithstanding this the formation of significant amounts of amine-borane indicates hydrogen redistribution reactions (from whatever intermediate) are occurring, further demonstrating this pathway has a role in the overall mechanism of dehydrocoupling [16,43].

3. Conclusions

We have demonstrated for the first time that release of a primary amino-borane from a metal centre results in the eventual formation of the corresponding cyclic borazine. Intriguingly for the $H_2B{=}N^tBuH$ systems described here observations indicate that off-metal hydrogen redistribution reactions play a major role in the final product formation. We can observe this behaviour in our particular system as the generation of $H_3B{\cdot}N^tBuH_2$ from such a process is not masked by the fact that it is not also a starting substrate and that the metal centre (as the MeCN adduct) only dehydrogenates it slowly once formed. However it is likely that such processes are not system specific, and could occur whatever the metal fragment and starting amine- or amino-boranes. The dehydrocoupling of amine-boranes sits in a remarkably complex and nuanced landscape. Initial dehydrogenation to form amino-boranes is just the first step in a complex set of interconnecting reactions that involve both on-metal and off-metal processes. Off-metal hydrogen redistribution reactions add yet further complexity. These results further support previous observations [12,16,17,41] that whether the amino-borane is bound or unbound to the metal can dictate the course of the reaction, and that the observation of borazine suggests free amino-borane is generated. Such insight will be important in delivering systems that can



Scheme 6. Complex **3** is generated by addition of MeCN to the appropriate amino-borane precursor.

dehydrocouple amine-boranes to give desirable products (e.g. polyaminoboranes) while avoiding the production of unwanted borazines.

4. Experimental

All manipulations, unless otherwise stated, 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, toluene and MeCN were dried using a Grubbs type solvent purification system (MBraun SPS-800) and degassed by successive freeze-pump-thaw cycles [44]. 1,2-$C_6H_4F_2$ and C_6H_5F were dried over CaH_2, vacuum distilled and stored over 3 Å molecular sieves. 3,3-dimethylbut-1-ene was dried over Na, vacuum distilled and stored over 3 Å molecular sieves. $H_3B{\cdot}N^tBuH_2$ was purchased from Aldrich and sublimed prior to use (5×10^{-2} mbar, 298 K). $[Ir(H)PCy_2(\eta^2\text{-}C_6H_9)PCy_2(\eta^3\text{-}C_6H_8)][BAr^F_4]$ [17], $[Ir(H)PCy_2(\eta^2\text{-}C_6H_9)PCy_2(\eta^3\text{-}C_6H_8)][BAr^{Cl}_4]$ [19], $H_3B{\cdot}NMeHBH_2{\cdot}NMeH_2$ [19], $[H_2BNMeH]_3$ [38] and $[Ir(H)_2(PCy_3)_2(H_2B{=}NMe_2)][BAr^F_4]$ [17] were prepared by literature methods. NMR spectra were recorded on a Unity Plus 500 MHz spectrometer at room temperature, unless otherwise stated. In 1,2-$C_6H_4F_2$, ^1H NMR spectra were referenced to the centre of the downfield solvent multiplet, $\delta = 7.07$. ^{31}P and ^{11}B NMR spectra were referenced against 85% H_3PO_4 (external) and $BF_3{\cdot}OEt_2$ (external) respectively. The spectrometer was pre-locked to CD_2Cl_2. Chemical shifts (δ) are quoted in ppm and coupling constants (J) in Hz. ESI-MS were recorded on a Bruker MicrOTOF instrument interfaced with a glove-box [45]. Microanalyses were performed at London Metropolitan University.

4.1. $[Ir(H)_2(PCy_3)_2(\eta^2\text{-}H_3B{\cdot}N^tBuH_2)][BAr^{Cl}_4]$ (**1**)

$[Ir(H)_2(H_2)_2(PCy_3)_2][BAr^{Cl}_4]$ was formed *in situ* by the hydrogenation of $[Ir(H)PCy_2(\eta^2\text{-}C_6H_9)PCy_2(\eta^3\text{-}C_6H_8)][BAr^{Cl}_4]$ (40 mg, 0.03 mmol) at 4 atm in 1,2-$C_6H_4F_2$. After 30 min, the colourless solution was opened under argon and rapidly transferred to a Schlenk containing solid $H_3B{\cdot}N^tBuH_2$ (2.6 mg, 0.03 mmol) and stirred for 15 min. Pentane (30 mL) was added, and the mixture turned cloudy and was cooled to −18 °C for 6 days, after which a cream-coloured solid had formed. The solid was washed with pentane (2 × 5 mL) and dried *in vacuo*. Yield: 13 mg (30%). The preparation of **1** with the $[BAr^F_4]^-$ anion was conducted *in situ* and gave similar NMR spectra to the $[BAr^{Cl}_4]^-$ salt, although solid material could not be isolated. Despite repeated attempts, material suitable for single crystal X-ray diffraction could not be isolated.

^1H NMR (500 MHz, 1,2-$C_6H_4F_2$): δ 7.57 (br, 8H, $[BAr^{Cl}_4]^-$), 4.17 (br, 2H, NH_2), 1.60 (s, 9H, N^tBu), 2.24–1.19 (m, 66H, Cy), −5.83 (br, 2H, σ-bound BH_2), −20.25 (overlapping dd, $^2J_{HP} \sim 16$, $^2J_{HP} \sim 17$, 2H, IrH_2). The remaining BH signal is not observed, presumably as too broad. Other $[BAr^{Cl}_4]^-$ peak is obscured by the solvent.

^1H NMR (500 MHz, 1,2-$C_6H_4F_2$, 250 K): δ 7.61 (br, 8H, $[BAr^{Cl}_4]^-$), 6.15 (br, 1H, BH not σ-bound), 4.22 (br, 2H, NH_2), 1.59 (s, 9H, N^tBu), 2.24–1.19 (m, 66H, Cy), −5.94 (br, 2H, σ-bound BH_2), −20.07 (m, 2H, IrH_2). Other $[BAr^{Cl}_4]^-$ peak is obscured by the solvent.

$^{31}P\{^1H\}$ NMR (202 MHz, 1,2-$C_6H_4F_2$): δ 39.7 (br d, 1P), 32.8 (br d, 1P).

$^{31}P\{^1H\}$ NMR (202 MHz, 1,2-$C_6H_4F_2$, 250 K): δ 39.4 (d, $^2J_{PP} = 283$, 1P), 32.7 (d, $^2J_{PP} = 283$, 1P).

^{11}B NMR (160 MHz, 1,2-$C_6H_4F_2$): δ 11.2 (br, BH_3), −6.5 (s, $[BAr^F_4]^-$).

ESI-MS (C_6H_5F, 60 °C, 4.5 kV): m/z 842.5512 $[M]^+$ (calc. 842.5648).

Elemental microanalysis: Calc. $C_{64}H_{94}B_2Cl_8IrNP_2$ (1436.85 $gmol^{-1}$): C, 53.50; H, 6.59; N, 0.97. Found: C, 53.28; H, 6.50; N, 1.02.

4.2. $[Ir(H)_2(PCy_3)_2(\eta^2\text{-}H_2B{=}N^tBuH)][BAr^F_4]$ (**2**)

$[Ir(H)_2(PCy_3)_2(H_3B{\cdot}N^tBuH_2)][BAr^F_4]$ (50 mg $[Ir(H)PCy_2(\eta^2\text{-}C_6H_9)PCy_2(\eta^3\text{-}C_6H_8)][BAr^F_4]$, 0.03 mmol) was formed *in situ* in 1,2-$C_6H_4F_2$ in a Young's flask. The solution was degassed by freeze-pump-thawing twice to remove any residual H_2. 3,3-dimethylbut-1-ene (15 μL, 0.115 mmol) was added to the solution using a gastight syringe. The solution was stirred for an hour, during which the colour changed from colourless to yellow. The solvent was removed *in vacuo* to yield a 'sticky' yellow solid. Pentane (5 mL) was added with sonication for 10 minutes and then decanted. The resulting solid was a cream powder. The solid was washed once with pentane (5 mL) and dried *in vacuo*. Yield: 35 mg (66%). Despite repeated attempts, material suitable for single crystal X-ray diffraction could not be isolated.

^1H NMR (500 MHz, 1,2-$C_6H_4F_2$): δ 8.33 (br, 8H, $[BAr^F_4]^-$), 7.69 (br, 4H, $[BAr^F_4]^-$), 4.44 (br, 1H, NH), 1.50 (s, 9H, ^tBu), 2.20–1.10 (m, 66H, Cy), −6.31 (br, 2H, BH_2), −13.94 (br, 1H, IrH), −14.97 (br, 1H, IrH).

$^1H\{^{11}B\}$ NMR (500 MHz, 1,2-$C_6H_4F_2$): δ 8.33 (br, 8H, $[BAr^F_4]^-$), 7.69 (br, 4H, $[BAr^F_4]^-$), 4.44 (br, 1H, NH), 1.50 (s, 9H, ^tBu), 2.20–1.10 (m, 66H, Cy), −6.26 (br, 1H, BH_2), −6.36 (br, 1H, BH_2), −13.94 (br, 1H, IrH), −14.97 (br, 1H, IrH).

$^{31}P\{^1H\}$ NMR (202 MHz, 1,2-$C_6H_4F_2$): δ 33.1 (s).

^{11}B NMR (160 MHz, 1,2-$C_6H_4F_2$): δ 46.6 (v. br), −6.1 (s, $[BAr^F_4]^-$).

ESI-MS (1,2-$C_6H_4F_2$, 60 °C, 4.5 kV): m/z 840.5401 $[M]^+$ (calc. 840.5492).

Elemental microanalysis: Calc. $C_{72}H_{92}B_2F_{24}IrNP_2$ (1703.26 $gmol^{-1}$): C, 50.77; H, 5.44; N, 0.82. Found: C, 50.72; H, 5.42; N, 0.76.

4.3. General procedure for $H_2B{=}N^tBuH$ release

2 (8 mg, 0.005 mmol) was added to a high pressure NMR tube and dissolved in 0.4 mL 1,2-$C_6H_4F_2$. MeCN (8 μL, 0.153 mmol) was added via a gastight syringe and the sample immediately frozen in liquid N_2 before monitoring with ^{11}B NMR spectroscopy. Immediately, liberated $H_2B{=}N^tBuH$ was observed with no **2** present. ^1H and $^{31}P\{^1H\}$ NMR spectroscopy indicated full conversion to **3**.

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