Dalton Transactions

PAPER

View Article Online
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Cite this: *Dalton Trans.*, 2024, **53**, 14212

Selective dehydrogenation of ammonia borane to borazine and derivatives by rhodium olefin complexes†

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Received 24th May 2024,
Accepted 24th July 2024

DOI: 10.1039/d4dt01520g

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This report presents a selective synthetic approach towards borazine from ammonia borane using a dinuclear rhodium olefin homogeneous catalyst. The synthesis and spectroscopic characterization of a dirhodium ammonia borane complex as an intermediate provides insight into a possible mode of activation.

Introduction

Borazine ($B_3N_3H_6$), isoelectronic to benzene, is referred to as 'inorganic benzene' due to its structural resemblance and represents an important precursor to develop BN-ceramics.[1,2] Both the electronic structure and reactivity patterns of $B_3N_3H_6$ differ largely from those of benzene. Borazine undergoes addition reactions and is sensitive to ambient humidity, unstable over time and decomposes upon heating in the presence of oxygen, which complicates the development of efficient synthetic protocols.[3] Recent research efforts have focused on materials derived from organoborazines, which in turn allow for the design of new gas storage and separation systems,[4] materials with specific (opto)electronic properties (especially hybrid BCN materials) and new applications in supramolecular chemistry.[5] However, practical applications of borazine and substituted borazines continue to be held back by the absence of convenient and selective synthetic routes. Principal constraints in current procedures include the utilization of harsh reaction conditions and excess organometallic hazardous reagents, boron halides or harmful solvents.[6] Since the first synthesis of borazine by thermolysis of an ammonia diborane adduct, nearly one century ago by Stock and Pohland,[7] several other procedures have been reported. Sneddon *et al.* reported a convenient synthesis of borazine by treating ammonia borane (**AB**) or a mixture of ammonium sulphate and sodium borohydride in tetraglyme at 120–140 °C.[8] To avoid the rather harsh conditions, the reaction can be carried out at $T < 50$ °C in the presence of aluminium chloride as a catalyst, obtaining borazine in yields of about 67%, which to date represents the best protocol to obtain $B_3N_3H_6$ on a gram scale.[9] There are limited examples of transition metal catalysts that are able to convert ammonia borane **AB** selectively to borazine.[10–13] The binuclear Ru complex known as Shvo's catalyst (**1**) and a nitrosyl Re(I) complex (**2**) (Fig. 1) allow the formation of borazine in good to excellent NMR yields (75%[10] and 99%,[11] respectively). However, relatively high catalyst loadings (5 mol%) were employed and the product was not isolated.

Manners *et al.* explored the photocatalytic dehydrogenation of **AB** with $[CpFe(CO)_2]_2$ as a catalyst (5 mol%), observing the formation of the oligomer *B*-(cyclodiborazanyl)amine-borane (BCDB) as an intermediate and its further dehydrogenation to borazine in 35% yield.[12] Only once the isolation of borazine was reported from a transition metal-catalysed reaction, using $[Rh_2(\mu\text{-Cl})_2(cod)_2]$ (cod = 1,5-cyclooctadiene) (1 mol%) as a catalyst. The reaction proceeded with high selectivity, but the isolated yield was merely 10% and the reaction was found to be catalysed by rhodium nanoparticles or clusters.[13] In our recent study, a ruthenium complex (**3**) with a Ru–Ru bond and a multidentate non-innocent ligand containing a diazadiene (dad) and olefins as bindings sites was able to catalyse the formation of soluble polycondensed borazine from ammonia

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† Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d4dt01520g

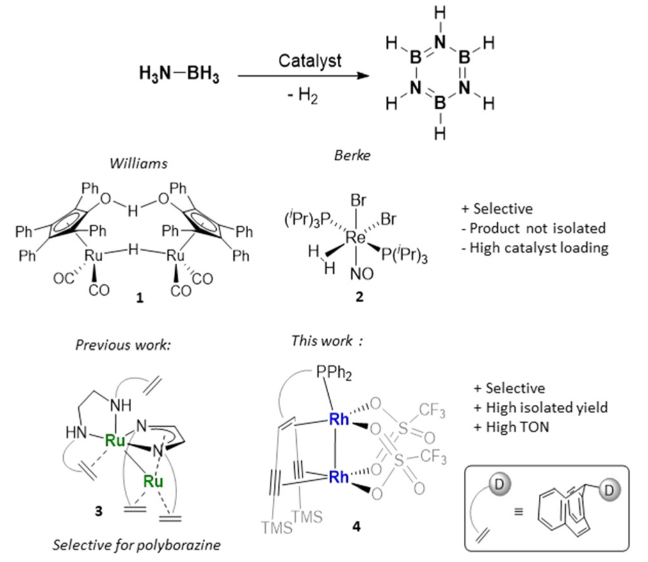


Fig. 1 Previously reported catalysts for the dehydrogenation of $H_3N–BH_3$ to borazine or polyborazine and the new catalyst (D = amine or phosphine group).

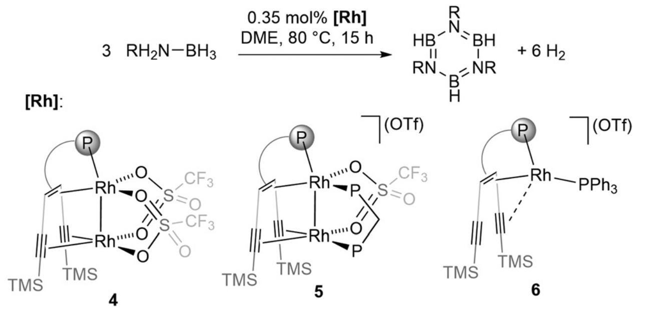
borane.[14] As a continuation of this investigation, we report here a dinuclear olefin Rh metal complex as an active and selective catalyst for the dehydrogenation of ammonia borane to borazine (Fig. 1). The catalyst was also employed in the dehydropolymerization of primary amine boranes to polymeric *N*-substituted borazines or BCN materials containing six-membered unsaturated B_3N_3 rings.

Results and discussion

Intrigued by the activity and selectivity of our previously reported catalyst (**3**) with two low-valent Ru centres, we investigated the reactivity of the dinuclear rhodium complexes **4** and **5** with two d^8-Rh(I) centres (Scheme 1). In both complexes, the ligand {(TMS)C≡C}$_2$tropPPh$_2$ containing a phosphane, an alkene, and two alkyne sites anchors two late transition metals in close proximity leading to complexes with dative intermetallic bonds.[15] The resulting species are able to either undergo hydrogen transfer to the unsaturated ligand (**4**) or add hydrogen reversibly (**5**).[15a] The reaction of **AB** in 1,2-dimethoxyethane (DME) solution at 80 °C with either **4** or **5** as a catalyst did not lead to noteworthy formation of condensed borazine or polyaminoborane, but selectively produced borazine, $B_3N_3H_6$. Catalyst **4** is superior to **5** concerning both activity and selectivity (entries 1 and 4, Table 1), affording almost exclusively borazine. A low catalyst loading of **4** (0.35 mol%) in a 1.1 M solution of ammonia borane in DME led to the formation of borazine in 95% yield (TOF = 18 h^{-1}), with polyborazine as a side product. Although the isolated yield (72%) is somewhat lower than the NMR yield, this is to the best of our knowledge the highest reported for any borazine synthesis.[9] By lowering the reaction temperature to 50 °C, dehydrogenation of ammonia borane with complex **4** formed borazine with low selectivity. Complete conversion of **AB** was achieved after 48 hours leading to a mixture of products. The related monometallic Rh(I) complex **6** [15a] leads to a mixture of BN products, suggesting that the bimetallic Rh_2 unit in **4** is essential for the activity and selectivity (entry 5, Table 1).

Thermal decomposition of **AB** in the absence of a catalyst leads to poor selectivity and low yield of borazine (entry 6, Table 1). The conversion rate of the reaction catalysed by **4** is not influenced by the addition of mercury while the addition of triphenylphosphine poisons the catalyst, indicating that the dehydrogenation is catalysed by a molecular species in homogeneous solution. This is in contrast to an earlier report in which the precatalyst [Rh_2(μ-Cl_2)(COD)$_2$] was converted under the reaction conditions to colloidal Rh particles as catalytically active species.[13b] The solvent has a significant impact on the selectivity of the reaction. Changing from DME to diglyme lowers the yield from 95% to 75%, while more polyborazylene is observed (see Fig. S4†). In acetonitrile, only traces of borazine are observed and polyaminoborane is formed as the main product. *N*-Monosubstituted amine boranes can also be dehydrogenated to the corresponding *N*-substituted borazine analogues in high yields (entries 2 and 3, Table 1). *N*-Dimethylamine borane reacts rapidly and selectively forms the four-membered ring [$Me_2N–BH_2$]$_2$ (quantitative yield after 4 h at 0.8% catalyst loading, TON = 125).

Cross-linked BCN materials are highly sought-after materials due to their remarkable properties such as wider



Scheme 1 Dehydrogenation of ammonia borane with rhodium olefin complexes **4**, **5** and **6** (P = PPh$_2$).

Table 1 Rh(I)-catalysed dehydrogenation of ammonia borane to borazine

Entry	Catalyst	R	Conv. [%]	Yield[a] [%]	TOF [h^{-1}]	TON
1	**4**	H	>99	95(72)[b]	18	271 (938)[c]
2	**4**	Me	>99	65[d]	6	81
3	**4**	^{t}Bu	>99	85[e]	3	107
4	**5**	H	>99	83	16	237
5	**6**	H	>99	63	12	188
6	—	H	>99	43	—	—

[a] Yield of borazine determined by ^{11}B NMR with $NaBPh_4$ as an internal standard. [b] Isolated yield. [c] Catalyst loading 0.08 mol%. [d] Catalyst loading 0.8 mol%. [e] Catalyst loading 0.8 mol%, 35 h.

HOMO–LUMO gaps than those of carbon analogues and the possibility of achieving coatings on metal surfaces.[16] We investigated the dehydrogenation of *N*-propargylamine-borane **7**[17] which contains a cross-linkable functional group using **4** as a catalyst (Fig. 2a). MAS NMR spectroscopic analysis of the resulting insoluble polymeric material formed after 15 h at 80 °C indicated that partial dehydrogenation occurred, and we denote the material as **BCNH$_r^{cat}$** (where H$_r$ stands for residual hydrogen). ^{11}B MAS NMR spectroscopy showed that the catalytic dehydrogenation led to the formation of B_3N_3 rings as cross-linking points, while also indicating the presence of residual BH_3 (δ ^{11}B = −21 ppm) and BH_2 groups (δ ^{11}B = 0 ppm) (Fig. S8†). When the parent *N*-propargylamine-borane is thermally dehydrogenated at 80 °C without a catalyst, significantly fewer B_3N_3 rings are formed. Further loss of hydrogen from **BCNH$_r^{cat}$** is achieved by heating at 200 °C affording a hydrogen-poor BCN material (**BCNH$_p^{cat}$**). This transformation to a hydrogen-poor BCN material at a rather low temperature only occurs from the previously partially dehydrogenated BCN polymer **BCNH$_r^{cat}$**, but not from heating *N*-propargylamine borane alone, as was shown by TGA (Fig. S10–S14†). It cannot be excluded that the transformation from **BCN$_r^{cat}$** to **BCN$_p^{cat}$** is catalyzed by residual Rh in the material (1.943 ± 0.023 mg Rh per g **BCN$_r^{cat}$**, determined by ICPMS). During the annealing process, all signals from $\nu_{C\equiv C}$ and ν_{B-H} vanished in the IR spectrum while two absorption peaks at 1256 and 846 cm^{-1} (associated with the B–N bonds) characteristic for BCN materials increased in intensity (Fig. S15†). Furthermore, the ^{11}B-MAS-NMR spectrum showed a significant increase in the intensity of the signals corresponding to borazine units (Fig. S16†). Scanning electron microscopy (SEM) was used in order to investigate the change in morphology when the hydrogen-rich **BCNH$_r^{cat}$** was thermally dehydrogenated on a silicon support (Fig. 2b).

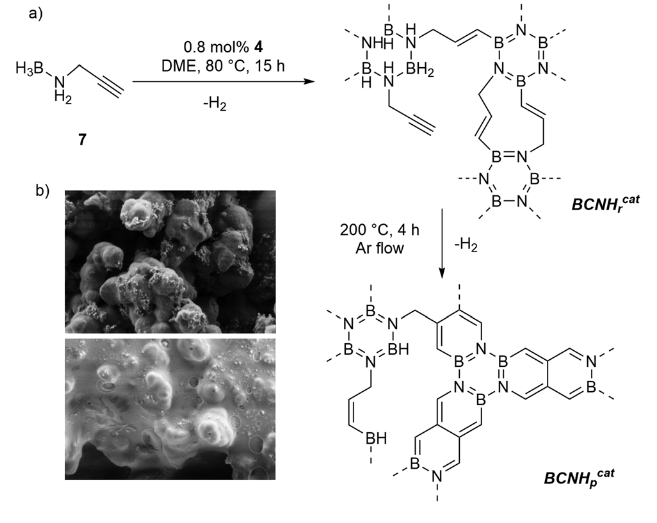
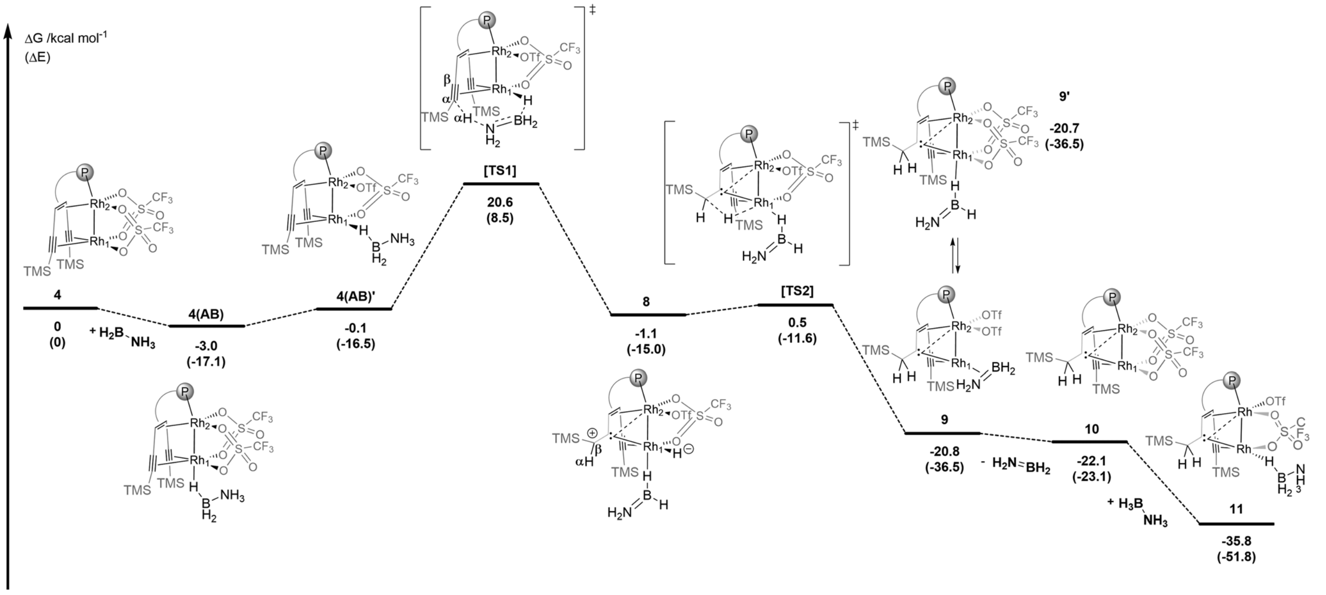


Fig. 2 (a) Dehydrogenation of *N*-propargylamine-borane catalyzed by **4** forming a highly crosslinked polymeric material **BCNH$_r^{cat}$** and conversion to an amorphous BCN material by thermal treatment (**BCNH$_p^{cat}$**). (b) SEM image of **BCNH$_r^{cat}$** (top) and **BCNH$_p^{cat}$** (bottom).

The crosslinked polymer, derived from **BCNH$_r^{cat}$**, is obtained as beige powder and forms small lumps on silicon as a support material. A much smoother and more extended layered structure of a BCN material is observed from the precursor material **BCNH$_p^{cat}$** (the material produced when **BCNH$_r^{cat}$** was further dehydrogenated at 200 °C for 12 h). The difference between both BCN@Si materials is shown by the SEM images in Fig. 2b.

To gain some insight into a possible reaction mechanism for the catalysed dehydrogenation of **AB**, the progress of the reaction was monitored by ^{11}B NMR spectroscopy in the presence of complex **4**. Previously reported compounds cyclotriborazane (**CTB**), *B*-(cyclodiborazanyl)amine-borane (**BCDB**), and the tetramer *B*-(cyclotriborazanyl)amine-borane (**BCTB**) were detected as intermediates (Fig. S21†).[18] To demonstrate that these oligomers stem from the tri- or tetramerization of the highly reactive monomeric aminoborane $H_2N{=}BH_2$, an excess of cyclohexene as a trapping reagent was added. Under these conditions, the disubstituted aminoborane $H_2N{=}BCy_2$ was observed as the only boron-containing compound in quantitative yield. This result suggests indeed that $H_2N{=}BH_2$ is formed and released from the catalyst in solution and serves as a source for the formation of **CTB**, **BCDB**, and **BCTB**. Likely, **CTB** with its saturated six-membered ring is simply dehydrogenated to give borazine and three equivalents of H_2. Autrey *et al.* have shown that the constitutional isomer **BCDB** with a four-membered B_2N_2 ring can be converted to **CTB** at 80 °C. Consequently, we assume that **BCDB** is likewise converted to $B_3N_3H_6$.[19] The tetramer **BCTB** can thermally decompose to tetrahydroborazine, $B_3N_3H_{10}$, and $H_3N–BH_3$[20] and this is likely the route by which this intermediate is converted to borazine. But it may also be responsible for the minor formation of polyborazines as side products. To probe this hypothesis, a catalytic reaction was carried out with **BCTB** as a starting material. In this reaction, the selectivity for borazine formation dropped to 63% yield (Fig. S22†). The salt $[H_2B(NH_3)_2]^+[BH_4]^-$ (**DADB**) when used as a substrate led to even lower yields of $B_3N_3H_6$ and considerable amounts of polyaminoborane are observed instead. Note that heating borazine for 15 h at 80 °C in the presence of **4** does not lead to any condensation reaction which explains the notable selectivity of this bimetallic complex in comparison with other catalysts.

DFT calculations were performed on the reaction between **4** and **AB** (Scheme 2). In the first slightly exothermic step, a simple adduct **4(AB)** is obtained in which a B–H binds terminally to Rh1 – the external rhodium centre of the Rh2 core – such that a Rh1–H–B bridge is formed in the *trans*-position to Rh2 – the internal rhodium centre. Adduct **4(AB)** is almost isoenergetic with its isomer **4(AB)′** in which the Rh1–H–B bridge is in the *cis*-position to Rh2. *Via* the activated complex [**TS1**] one of the protons from the NH_3 group is transferred to the α-carbon centre of the coordinated alkyne unit while one hydride is simultaneously transferred from the BH_3 group to Rh1. This unusual intramolecular hydrogen transfer reaction gives complex **8** with an $H_2N{=}BH_2$ molecule bound *via* a B–H–Rh bridge formed in the *trans*-position to Rh2 and is the



Scheme 2 Proposed mechanism for the dehydrogenation of AB by complex **4** leading to **11** as the resting state calculated by DFT (Gaussian09, SMD/PBE0-D3/def2-SVP). Structures **4(AB)′** and **11** are stabilized by hydrogen bridges between the NH_3 and the OTf^- groups (not shown for clarity, see the optimized structures in the ESI†).

rate-determining step. In a β-hydride insertion, **8** rearranges *via* a small barrier to **9**, which contains a bridging carbene ligand between the rhodium centres Rh1 and Rh2 and a π-side-on coordinated $H_2N{=}BH_2$ ligand bound to Rh1.

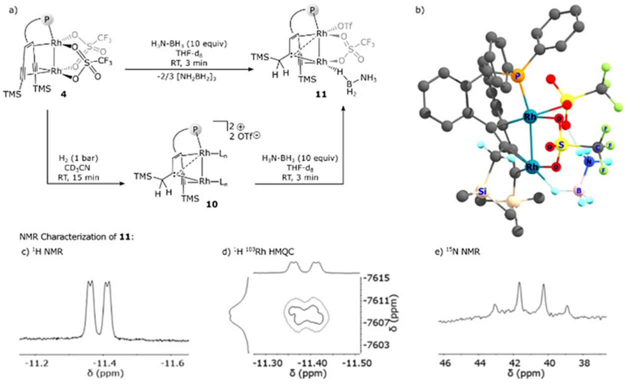
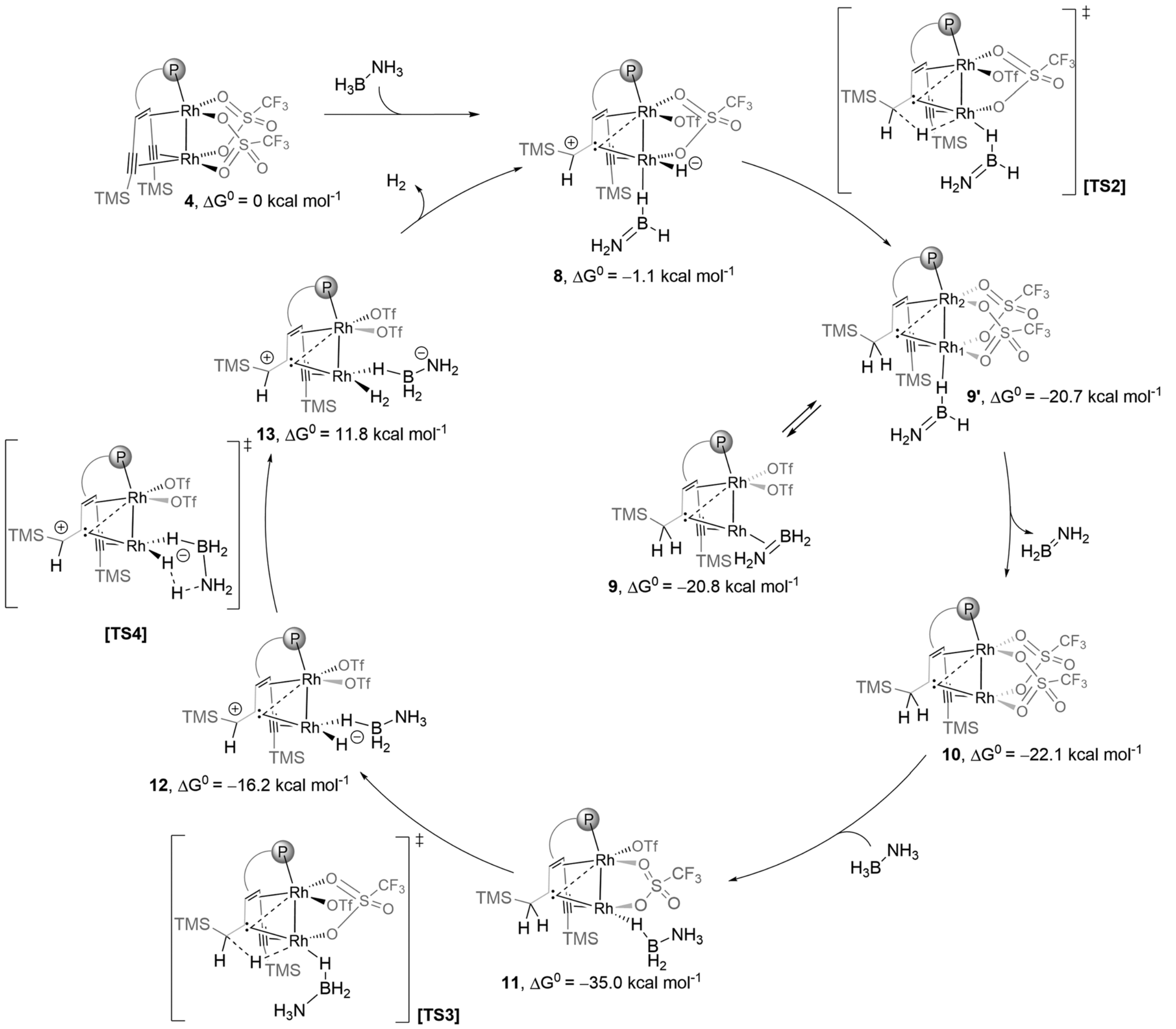


Fig. 3 (a) Synthesis and proposed structure of **11** (L_n = CD_3CN). (b) DFT calculated and geometry optimized structure of **11** (see the ESI†). (c) Hydride region of the ^1H NMR spectrum of **11**. (d) ^1H ^{103}Rh HMQC spectrum of **11**; section showing the signal from the coupling of the hydridic proton with the rhodium center. (e) ^{15}N NMR spectrum of **11** showing the presence of NH_3.

Complex **9** is in equilibrium with isomer **9′**, which contains a $H_2N{=}BH_2$ moiety bound *via* a B–H–Rh unit to the external rhodium centre Rh1. The dissociation of $H_2N{=}BH_2$ from this complex is a weakly exothermic reaction ($\Delta G = -1.2$ kcal mol^{-1}) to give the carbene bridged Rh_2 complex **10** (*vide infra*). Finally, **10** reacts with **AB** in an exothermic reaction ($\Delta G = -11.6$ kcal mol^{-1}) to give complex **11** which is an adduct between **10** and an ammonia borane molecule that binds end-on *via* a B–H bond to Rh1 in the *cis*-position to Rh2 and is further stabilized by a hydrogen bond between the NH_3 group and a coordinated triflate (OTf^-). According to the DFT calculations, adduct **11** is the resting state of the catalytic system and might be an observable species. Therefore, **4** was reacted with 10 equivalents of ammonia borane in THF-d_8 at room temperature (Fig. 3a). After a few minutes a new complex **11** is formed, and the proposed structure of which is based on multi-nuclear two-dimensional NMR spectroscopic analysis (Fig. 3b–d) combined with DFT calculations. The NMR resonance of the bridging carbene ^{13}C nucleus is observed at $\delta\ ^{13}C = 184.0$ ppm. The ^{13}C chemical shifts of the coordinated alkyne unit are observed at $\delta\ ^{13}C = 80.7$ and 107.6 ppm. A characteristic signal in the ^1H NMR spectrum at $\delta\ ^1H = -11.37$ ppm (Fig. 3b) with a large $^1J_{HRh}$ coupling constant of 25.3 Hz (determined by ^1H–^{103}Rh HMQC; Fig. 3c) indicates a direct Rh–H bond. A triplet at $\delta\ ^{11}B = -0.24$ ppm with a $^1J_{BH}$ coupling constant of $^1J_{BH} = 118$ Hz is observed in the ^{11}B NMR spectrum (Fig. S29†). Furthermore, when ^{15}N labeled ammonia borane, H_3N^{15}–BH_3, is used as a substrate, a quartet at $\delta\ ^{15}N = 28.4$ ppm ($^1J_{NH} = 69.8$ Hz) is observed, which proves the presence of an NH_3 group in the molecule (Fig. 3d). In principle, these data would be consistent with a dinuclear rhodium complex in which the BH_3 group has been oxidatively added to one Rh center. However, DFT calculations indicate that the formation of a boryl hydride $Rh^{+3}(H)(BH_2$–$NH_3)$ is rather endothermic ($\Delta E = 36.8$ kcal mol^{-1}) and therefore highly unlikely. Neither the formation of an anionic hydride complex with the formula $[(THF)BH_2(NH_3)][Rh_2(H)(OTf)_2(^{\{(TMS)C\equiv C(TMS)CH2C\}}tropPPh_2)]$ seems possible (20.0 kcal mol^{-1}) (see the ESI† for details). Another possibility instead is that structure **11** (Fig. 3e) is a more plausible alternative, which contains a bridging Rh–H–B unit in the *trans*-position to the bridging carbene unit. Related coordination modes have been observed in aminoborane complexes with a dinuclear Rh_2 core where either a BH_2 group bridges both Rh centres to give a Rh–H–B–H–Rh unit[21] or coordinates *via* both B–H bonds to one Rh centre.[22] The coordination mode *via* only one B–H bond is rare and has so far only been observed for a Ru complex.[23] Note that the $^1J_{BH}$ coupling in M–H–B bridges may be too small to observe.[24,25]

Complex **11** is closely related to compound **10** ($\delta\ ^{13}C_{carbene}$ = 171.0 ppm; $\delta\ ^{13}C_{alkyne}$ = 76.9, 101.7 ppm), which contains likewise a central Rh_2 core bridged by a carbene. The alkyne group acts as a hydride reservoir. Similar hydrogen transfer to a single alkyne C atom and metal carbene formation was reported by Fürstner *et al.*[26] Complex **10** was previously isolated from the reaction of complex **4** with hydrogen.[15a] In fact, complex **10** reacts cleanly with **AB** to give complex **11** as the sole product (Fig. 3a), which strongly supports our assignment of the structure of **11**. In addition, complex **11** is likewise catalytically active (Fig. S35†) and was also detected in the reaction catalyzed by complex **4**. Complex **11** is only observed in ethereal solvents, while deactivation occurs in acetonitrile or dichloromethane, in line with the observation that efficient catalysis fails in these solvents. Based on these experimental results, we propose a possible full catalytic cycle for the conversion of $H_3B–NH_3$ to $H_2B{=}NH_2$ and H_2, which is presented in Scheme 3. This is still a very simplified model and some ΔG^0 values are too high, yet, to explain the comparatively high activity. It is likely that the reactions are even more complicated, and in some steps, more than one molecule of ammonia borane may be involved.

Although the results of the DFT calculations can merely be regarded as preliminary in view of the complexity of the reaction, they indicate that the bis(alkynyl)trop platform – as an



Scheme 3 Proposed catalytic cycle according to DFT (Gaussian09, SMD/PBE0-D3/def2-SVP). Structures **11**, **12**, **[TS3]** and **[TS4]** are stabilized by hydrogen bonding between the NH_3 and the OTf groups (not shown for clarity, see the optimized structures in the ESI†).

unsaturated molecular hydrocarbon support for the Rh_2 unit – can act as an unusual cooperating ligand.[15a,27] Specifically, protonation of one of the coordinated alkynyl units converts this into a bridging carbene ligand to which a carbenium unit is attached in the β-position to the metal centres. This electrophilic carbenium unit serves as an acceptor for a hydride ligand from a metal centre, such that in the simplified form the process $M–M \leftarrow (RC{\equiv}CR') + H_2 \rightleftarrows M–M(H^-) \leftarrow :CR\text{-}C^+HR' \rightleftarrows M \leftarrow :CR\text{-}CH_2R'$ is rather easily feasible (in the present example, the highest activation barrier is about 20 kcal mol^{-1}; see the sequence **4(AB)′** ⇄ **TS1** ⇄ **8** ⇄ **TS2** ⇄ **9** in Scheme 3).

Conclusions

The dinuclear rhodium compound **4**, which contains a direct metal–metal bond, is a highly selective catalyst for the dehydrogenation of ammonia borane, $H_3N–BH_3$, to borazine, $B_3N_3H_6$. This leads to a synthetic protocol for the synthesis of borazine in high yield and purity from a homogeneously transition metal-catalysed reaction. The method could be extended to the preparation of organic borazines from primary amine boranes and highly cross-linked BNC amorphous polymers with a high content of six-membered B_3N_3 rings as cross-linkers. We assume that the dinuclear low-valent Rh(I) metal complexes investigated in this study lead to the formation of $H_2N{=}BH_2$ as the first product of **AB** dehydrogenation. This assumption is bolstered by trapping experiments. Subsequently amino borane $H_2N{=}BH_2$ as a highly reactive monomer forms cyclic oligomers, detected by NMR spectroscopy as intermediates, which finally converge selectively into borazine as a main product. Experiments combined with DFT calculations indicate that the bis(alkynyl)trop ligand in **4** and **5** is (i) converted into a bridging carbene ligand and (ii) the latter may play a cooperative role in the catalytic dehydrogenation of **AB** in the sense that the carbon centre adjacent to the μ_2-carbene unit serves as a reservoir for a hydrogen centre. In combination with our previous observation that a low-valent dinuclear Ru complex allows for the selective production of polyborazine, the results reported in this paper show that dinuclear metal complexes may hold high potential for the syntheses of related BN and BNC materials and therefore should be further explored.

Data availability

The authors confirm that the data supporting the findings of this study are available within the article and its ESI.†

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

Financial support by SNF (grants 192106, 181966) and ETH-Zürich is gratefully acknowledged. D. H. acknowledges the Austria Science Fund (FWF) (J-4571-N).

References

1 (*a*) E. Wiberg and A. Bolz, *Ber. Dtsch. Chem. Ges. A/B*, 1940, **73**, 209; (*b*) R. T. Paine and C. K. Narula, *Chem. Rev.*, 1990, **90**, 73.

2 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley-Interscience, New York, 5th edn, 1988, pp. 204.

3 (*a*) H. I. Schlesinger, L. Horvitz and A. B. Burg, *J. Am. Chem. Soc.*, 1936, **58**, 409; (*b*) H. I. Schlesinger, D. M. Ritter and A. B. Burg, *J. Am. Chem. Soc.*, 1938, **60**, 1296; (*c*) P. v. R. Schleyer, H. Jiao, N. J. R. van Eikema Hommes, V. G. Malkin and O. L. Malkina, *J. Am. Chem. Soc.*, 1997, **119**, 12669.

4 (*a*) T. Wilberforce, A. G. Olabi, E. T. Sayed, K. Elsaid and M. A. Abdelkareem, *Sci. Total Environ.*, 2021, **761**, 143203; (*b*) J. K. Stolaroff, S. Bhattacharyya, C. A. Smith, W. L. Bourcier, P. J. Cameron-Smith and R. D. Aines, *Environ. Sci. Technol.*, 2012, **46**, 6455; (*c*) J. O. Abe, A. P. I. Popoola, E. Ajenifuja and O. M. Popoola, *Int. J. Hydrogen Energy*, 2019, **44**, 15072.

5 (*a*) A. Wakamiya, T. Ide and S. Yamaguchi, *J. Am. Chem. Soc.*, 2005, **127**, 14859; (*b*) M. Lorenzo-García and D. Bonifazi, *Chimia*, 2017, **71**, 550; (*c*) J. Dosso, T. Battisti, B. D. Ward, N. Demitri, C. E. Hughes, P. A. Williams, K. D. M. Harris and D. Bonifazi, *Chemistry*, 2020, **26**, 6608.

6 For recent reviews of the synthesis of borazines, see: (*a*) I. Neogi and A. M. Szpilman, *Synthesis*, 2022, **54**, 1877; (*b*) D. Marchionni, S. Basak, A. N. Khodadadi, A. Marrocchi and L. Vaccaro, *Adv. Funct. Mater.*, 2023, **33**, 2303635.

7 A. Stock and E. Pohland, *Chem. Ber.*, 1926, **59**, 221.

8 T. Wideman and L. G. Sneddon, *Inorg. Chem.*, 1995, **34**, 1002.

9 J. S. Li, C. R. Zhang, B. Li, F. Cao and S. Q. Wang, *Eur. J. Inorg. Chem.*, 2010, 1763.

10 Ru: (*a*) Z. Lu, B. L. Conley and T. J. Williams, *Organometallics*, 2012, **31**, 6705–6714; (*b*) X. Zhang, Z. Lu, L. K. Foellmer and T. J. Williams, *Organometallics*, 2015, **34**, 3732.

11 Re: Y. Jiang and H. Berke, *Chem. Commun.*, 2007, 3571.

12 Fe: J. R. Vance, A. P. M. Robertson, K. Lee and I. Manners, *Chem. – Eur. J.*, 2011, **17**, 4099.

13 Rh: (*a*) C. A. Jaska, K. Temple, A. J. Lough and I. Manners, *J. Am. Chem. Soc.*, 2003, **125**, 9424; (*b*) C. A. Jaska, K. Temple, A. J. Lough and I. Manners, *Chem. Commun.*, 2001, 962; (*c*) J. L. Fulton, J. C. Linehan, T. Autrey, M. Balasubramanian, Y. Chen and N. K. Szymczak, *J. Am. Chem. Soc.*, 2007, **129**, 11936; (*d*) R. Rousseau,

G. K. Schenter, J. L. Fulton, J. C. Linehan, M. H. Engelhard and T. Autrey, *J. Am. Chem. Soc.*, 2009, **131**, 10516.

14 D. Himmelbauer, F. Müller, C. Schweinzer, F. Casas, B. Pribanic, G. Le Corre, D. Thöny, M. Trincado and H. Grützmacher, *Chem. Commun.*, 2024, **60**, 885.

15 (*a*) P. Jurt, O. G. Salnikov, T. L. Gianetti, N. V. Chukanov, M. G. Baker, G. Le Corre, J. E. Borger, R. Verel, S. Gauthier, O. Fuhr, K. V. Kovtunov, A. Fedorov, D. Fenske, I. V. Koptyug and H. Grützmacher, *Chem. Sci.*, 2019, **10**, 7937; (*b*) C. Schweinzer, P. Coburger and H. Grützmacher, *Adv. Sci.*, 2024, 2400072.

16 (*a*) T. Lorenz, A. Lik, F. A. Plamper and H. Helten, *Angew. Chem., Int. Ed.*, 2016, **55**, 7236; (*b*) A. W. Baggett, F. Guo, B. Li, S.-Y. Liu and F. Jäkle, *Angew. Chem., Int. Ed.*, 2015, **54**, 11191; (*c*) L. Türker, *Polycyclic Aromat. Compd.*, 2012, **32**, 61; (*d*) N. Otero, K. E. El-kelany, C. Pouchan, M. Rérat and P. Karamanis, *Phys. Chem. Chem. Phys.*, 2016, **18**, 25315; (*e*) N. Otero, P. Karamanis, K. E. El-Kelany, M. Rérat, L. Maschio, B. Civalleri and B. Kirtman, *J. Phys. Chem. C*, 2017, **121**, 709; (*f*) T. Hatakeyama, S. Hashimoto, S. Seki and M. Nakamura, *J. Am. Chem. Soc.*, 2011, **133**, 18614; (*g*) A. Wakamiya, T. Ide and S. Yamaguchi, *J. Am. Chem. Soc.*, 2005, **127**, 14859; (*h*) N. Kalashnyk, P. Ganesh Nagaswaran, S. Kervyn, M. Riello, B. Moreton, T. S. Jones, A. De Vita, D. Bonifazi and G. Costantini, *Chem. – Eur. J.*, 2014, **20**, 11856.

17 For previous work on the synthesis of functionalized borazines as precursors of BCN polymers, see: (*a*) J. Haberecht, A. Krummland, F. Breher, B. Gebhardt, H. Rüegger, R. Nesper and H. Gruetzmacher, *Dalton Trans.*, 2003, 2126; (*b*) J. Haberecht, F. Krumeich, R. Nesper and H. Gruetzmacher, *Chem. Mater.*, 2004, **16**, 418; (*c*) J. Haberecht, R. Nesper and H. Gruetzmacher, *Chem. Mater.*, 2005, **17**, 2340.

18 (*a*) H. A. Kalviri, F. Gärtner, G. Ye, I. Korobkov and R. T. Baker, *Chem. Sci.*, 2015, **6**, 618; (*b*) S. Bhunya, P. M. Zimmerman and A. Paul, *ACS Catal.*, 2015, **5**, 3478.

19 W. J. Shaw, J. C. Linehan, N. K. Szymczak, D. J. Heldebrant, C. Yonker, D. M. Camaioni, R. T. Baker and T. Autrey, *Angew. Chem., Int. Ed.*, 2008, **47**, 7493.

20 V. Kumar, B. Roy and P. Sharma, *Int. J. Hydrogen Energy*, 2019, **44**, 22022.

21 A. Kumar, N. A. Beattie, S. D. Pike, S. A. Macgregor and A. S. Weller, *Angew. Chem., Int. Ed.*, 2016, **55**, 6651.

22 (*a*) D. Han, F. Anke, M. Trose and T. Beweries, *Coord. Chem. Rev.*, 2019, **380**, 260; (*b*) A. Rossin and M. Peruzzini, *Chem. Rev.*, 2016, **116**, 8848.

23 A. E. W. Ledger, C. E. Ellul, M. F. Mahon, J. M. J. Williams and M. K. Whittlesey, *Chem. – Eur. J.*, 2011, **17**, 8704.

24 (*a*) T. M. Douglas, A. B. Chaplin and S. A. Weller, *J. Am. Chem. Soc.*, 2008, **130**, 14432; (*b*) A. B. Chaplin and A. S. Weller, *Angew. Chem., Int. Ed.*, 2010, **49**, 581.

25 (*a*) R. D. Adams, *Chem. Rev.*, 1989, **89**, 1703; (*b*) D. J. Cardin, B. Cetinkaya and M. F. Lappert, *Chem. Rev.*, 1972, **72**, 545.

26 M. Leutzsch, L. M. Wolf, P. Gupta, M. Fuchs, W. Thiel, C. Farès and A. Fürstner, *Angew. Chem.*, 2015, **127**, 12608.

27 M. Trincado and H. Grützmacher, Cooperating Ligands in Catalysis, in *Cooperative Catalysis*, ed. R. Peters, Wiley-VCH, 2015.