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Rhodium-catalyzed formation of boron–nitrogen bonds: a mild route to cyclic aminoboranes and borazines

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Secondary amine–borane adducts $R_2NH{\cdot}BH_3$, which are stable to H_2 elimination below 100 °C, undergo efficient catalytic dehydrocoupling at 25–45 °C in the presence of Rh^I or Rh^{III} complexes to quantitatively form cyclic aminoboranes $[NR_2–BH_2]_2$ (1: R = Me or 2: *cyclo*-C_4H_8); under similarly mild conditions, the analogous adducts $NH_3{\cdot}BH_3$ and $MeNH_2{\cdot}BH_3$ yield borazines $[RN–BH]_3$ (3: R = H or 4: R = Me) in yields limited by intermolecular coupling reactions.

The application of transition metal catalysis to organic synthesis is of enormous current importance. In contrast, the development of analogous methods for the formation of homonuclear or heteronuclear bonds between main group elements is relatively unexplored. Nevertheless, the discovery of new synthetic methods, which can complement the classical reactions used in main group chemistry such as salt eliminations, is likely to be of key future importance for the general development of molecular and macromolecular p-block chemistry. Recent work has focused on catalytic dehydrocoupling routes[1] and the well-established catalytic dehydropolymerization of silanes, germanes and stannanes represents a key advance.[2–6] More recently, homodehydrocoupling chemistry has been extended to include P–P bond formation[7] and catalytic heterodehydrocoupling reactions to form B–Si,[8] Si–P,[9] Si–N,[10] and Si–O bonds[11,12] have also been reported. Recently, we reported the first examples of the transition metal-catalyzed formation of P–B bonds.[13] Thus, dehydrocoupling of phosphine–borane adducts at 60–130 °C in the presence of a range of precatalysts (*e.g.* Rh^I complexes) was found to provide a new route to phosphinoborane rings, chains and macromolecules.[13,14] In this preliminary communication we report well-characterized examples of the use of catalytic dehydrocoupling to form new boron–nitrogen bonds under mild conditions.[15]

Amine–borane adducts undergo thermally-induced dehydrocoupling at elevated temperatures to afford mixtures of small rings such as cyclic aminoboranes and borazines. For example, dimethylamine–borane, $Me_2NH{\cdot}BH_3$, eliminates hydrogen at 130 °C to quantitatively yield the cyclic dimer $[Me_2N–BH_2]_2$ **1**.[16] However, when a solution of $Me_2NH{\cdot}BH_3$ in toluene was treated with *ca.* 0.5 mol% of $[Rh(1,5\text{-cod})(\mu\text{-Cl})]_2$ (1,5-cod = 1,5-cyclooctadiene) or $RhCl_3{\cdot}3H_2O$ at 25 °C for 48–60 h, the quantitative formation of the cyclic aminoborane **1** was detected by ^{11}B NMR spectroscopy. The reaction time was reduced to 24 h when the temperature was raised to *ca.* 45 °C or the amount of catalyst increased to 5 mol%. The iridium complex $[Ir(1,5\text{-cod})(\mu\text{-Cl})]_2$ also catalyzed the dehydrocoupling reaction but this precatalyst (*ca.* 0.5 mol%) proved less active with the reaction time for quantitative conversion to **1** increasing to 72 h at 45 °C. Significantly, prolonged heating of neat $Me_2NH{\cdot}BH_3$ in the absence of catalyst over a period of 7 days at 45 °C resulted in the quantitative recovery of unreacted adduct, which clearly demonstrated the catalytic effect of the Rh and Ir complexes.

Cyclic aminoborane **1** was isolated as a colorless, extremely volatile yet air-stable crystalline solid.† The ^1H-coupled ^{11}B NMR spectrum showed a triplet at δ 4.75 ($^1J_{BH}$ 110 Hz), which was consistent with the coupling of two hydrogens to the boron centre. While ^1H and ^{13}C NMR spectra were also consistent with the proposed product, single-crystal X-ray diffraction‡ provided definitive confirmation (Fig. 1).[17] Notably, the B–N bond lengths of **1** (1.595(4) Å) closely match those of the analogous cyclic trimer $[Me_2N–BH_2]_3$ (1.61(4) Å)[18] and moreover, are in the range observed for amine–boranes (*ca.* 1.58 Å). The four-membered ring appears to be strained with bond angles deviating significantly from the tetrahedral ideal with values of 93.7(2) and 86.3(2)° for the N(1)–B(1)–N(1A) and B(1)–N(1)–B(1A) angles, respectively.

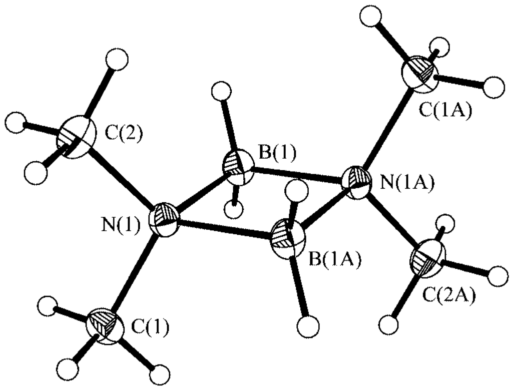
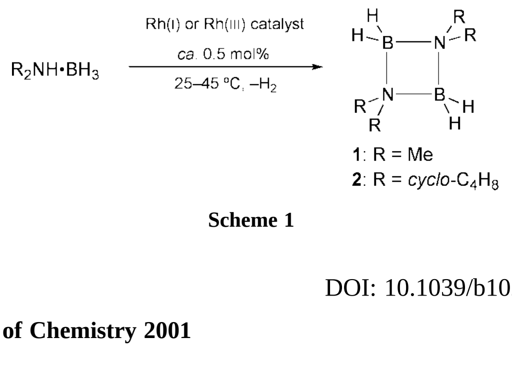


Fig. 1 Molecular structure of **1**. Selected bond lengths (Å) and angles (°): N(1)–B(1) 1.596(4), N(1A)–B(1) 1.595(4), N(1)–C(1) 1.478(4); N(1)–B(1)–N(1A) 93.7(2), B(1)–N(1)–B(1A) 86.3(2).

The formation of the cyclic dimer **1** *via* metal-catalyzed dehydrocoupling of a secondary amine–borane adduct represents a new, mild route to boron–nitrogen rings. We found that the strategy can be extended to other adducts such as pyrrolidine–borane, $(CH_2)_4NH{\cdot}BH_3$. Thus, the addition of catalytic (*ca.* 0.5 mol%) amounts of $[Rh(1,5\text{-cod})(\mu\text{-Cl})]_2$ or $RhCl_3{\cdot}3H_2O$ to a solution of the adduct (toluene, 25 °C, 24 h) similarly led to the quantitative formation of the cyclic aminoborane **2** (Scheme 1). Cyclic **2** was also characterized by multinuclear NMR spectroscopy† and by single-crystal X-ray diffraction.[19]

The catalytic dehydrocoupling methodology is not restricted to secondary amine–borane adducts. Thus, in the presence of $[Rh(1,5\text{-cod})(\mu\text{-Cl})]_2$ (1.5 mol%), the parent ammonia–borane adduct $NH_3{\cdot}BH_3$ was found to eliminate *two* equivalents of hydrogen to form borazine **3** (diglyme or tetraglyme, 45 °C, 72 h) by ^{11}B NMR (Scheme 2).[20] However, isolation from the reaction mixture by vacuum fractionation proved difficult; pure



Scheme 1

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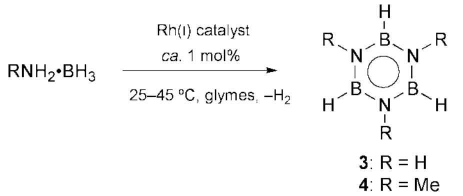

Scheme 2

3 was isolated in only *ca.* 10 % yield† with the major products being non-volatile, oligomeric species.[21,22]

Current preparations of borazine (*e.g.* from $NaBH_4$ and $(NH_4)_2SO_4$) require rather forcing conditions (elevated temperatures of 140–160 °C),[23] and, in our hands, are aggravated by similar difficulties in isolation. If optimized, the metal-catalyzed route may be advantageous, which is potentially significant as borazine and borazine oligomers have been shown to be useful precursors to cyclolinear polymers, boron nitride ceramics and nanotubes.[24–27]

In an attempt to minimize the intermolecular dehydrocoupling reactions, we also investigated the catalytic elimination of H_2 from *N*-methylamine–borane adduct. Indeed, we found that $MeNH_2{\cdot}BH_3$ undergoes dehydrocoupling in the presence of $[Rh(1,5\text{-cod})(\mu\text{-Cl})]_2$ (5 mol%), under similarly mild conditions (monoglyme or diglyme, 45 °C, 60 h) to afford *N*-trimethylborazine **4** by ^{11}B NMR. Pure **4** was isolated† in moderate yield (*ca.* 35–40%) by vacuum fractionation.[21,22] Previously developed routes to **4** typically involve high temperature dehydrogenation reactions such as the thermolysis of $MeNH_2{\cdot}BH_3$ at 100 °C to give the cyclic trimer $(MeNH–BH_2)_3$, followed by further pyrolysis at 200 °C.[28] Interestingly, through monitoring of the Rh catalyzed reaction by ^{11}B NMR, dehydrocoupling to form the cyclic aminoborane $(MeNH–BH_2)_3$ was found to occur first (δ −5.1, $^1J_{BH}$ 108 Hz; lit. δ −5.4, $^1J_{BH}$ 107 Hz),[29] followed by further loss of hydrogen to yield **4**. The isolation of a *ca.* 50% yield of non-volatile residue, indicates that intermolecular coupling also occurs in this case.[22] This process may involve catalytic dehydrocoupling of the intermediate $(MeNH–BH_2)_3$.

In summary, amine–borane adducts undergo B–N bond formation reactions under mild conditions in the presence of rhodium dehydrocoupling precatalysts (Schemes 1 and 2). Future work will involve an expansion of the scope of this new chemistry, which offers the prospect of improved routes to B–N compounds, and mechanistic investigations.

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Notes and references

† *Selected spectroscopic data*: for **1**: yield (isolated) (0.18 g, 62%). ^1H NMR (300 MHz, $CDCl_3$): δ 3.2–2.0 (q, br, BH_2), 2.42 (s, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 52.0 (s, CH_3). ^{11}B NMR (160 MHz, $CDCl_3$): δ 4.75 (t, $^1J_{BH}$ 110 Hz, BH_2). For **2**: yield (isolated) (1.22 g, 73%). ^1H NMR (300 MHz, $CDCl_3$): δ 3.2–2.0 (q, br, BH_2), 2.84 (t, br, NCH_2CH_2), 1.70 (m, NCH_2CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 60.1 (s, NCH_2CH_2), 23.7 (s, NCH_2CH_2). ^{11}B NMR (160 MHz, $CDCl_3$): δ 2.56 (t, $^1J_{BH}$ 110 Hz, BH_2). For **3**: yield (isolated) (0.57 g, *ca.* 10%). ^1H NMR (300 MHz, C_6D_6): δ 5.54 (t, br, NH), 4.45 (q, br, BH). ^{11}B NMR (160 MHz, C_6D_6): δ 30.2 (d, $^1J_{BH}$ 141 Hz, BH). For **4**: yield (isolated) (0.39 g, 40%). ^1H NMR (300 MHz, C_6D_6): δ 4.65 (q, br, BH), 2.96 (s, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 38.5 (s, CH_3). ^{11}B NMR (160 MHz, C_6D_6): δ 33.2 (d, $^1J_{BH}$ 132 Hz, BH). EI-MS (70 eV): 122 ($M^+ - H$, 100%).

‡ *Crystal data* for **1**: $C_4H_{16}B_2N_2$, M = 113.81, triclinic, space group $P\bar{1}$, a = 5.8330(7), b = 6.0290(10), c = 6.2400(10) Å, α = 80.372(8)°, β = 81.533(10)°, γ = 65.942(8)°, U = 196.80(5) Å^3, Z = 1, D_c = 0.960 Mg m^{-3}, μ = 0.055 mm^{-1}, $F(000)$ 64, T = 103(1) K, λ(Mo-Kα) = 0.71070 Å, crystal size 0.30 × 0.30 × 0.25 mm, 895 independent reflections, 3782 collected. Goodness-of-fit on F^2 = 1.162, final R indices $[I > 2\sigma(I)]$, R_1 = 0.0963, wR_2 = 0.2866. Refinement was by full-matrix least squares on F^2 using all data. All hydrogens were included in calculated positions and refined isotropically.

CCDC 160965. See http://www.rsc.org/suppdata/cc/b1/b102361f/ for crystallographic data in .cif or other electronic format.

1 For a recent review, see: F. Gauvin, J. F. Harrod and H.-G. Woo, *Adv. Organomet. Chem.*, 1998, **42**, 363.
2 C. Aitken, J. F. Harrod and E. Samuel, *J. Am. Chem. Soc.*, 1986, **108**, 4059.
3 T. D. Tilley, *Acc. Chem. Res.*, 1993, **26**, 22.
4 J. A. Reichl and D. H. Berry, *Adv. Organomet. Chem.*, 1998, **43**, 197.
5 T. Imori, V. Lu, H. Cai and T. D. Tilley, *J. Am. Chem. Soc.*, 1995, **117**, 9931.
6 For a related example of demethanative coupling of germanes, see: S. M. Katz, J. A. Reichl and D. H. Berry, *J. Am. Chem. Soc.*, 1998, **120**, 9844.
7 N. Etkin, M. C. Fermin and D. W. Stephan, *J. Am. Chem. Soc.*, 1997, **119**, 2954.
8 Q. Jiang, P. J. Carroll and D. H. Berry, *Organometallics*, 1993, **12**, 177.
9 R. Shu, L. Hao, J. F. Harrod, H. G. Woo and E. Samuel, *J. Am. Chem. Soc.*, 1998, **120**, 12 988.
10 J. He, H. Q. Lui, J. F. Harrod and R. Hynes, *Organometallics*, 1994, **13**, 336.
11 Y. Li and Y. Kawakami, *Macromolecules*, 1999, **32**, 6871.
12 R. Zhang, J. E. Mark and A. R. Pinhas, *Macromolecules*, 2000, **33**, 3508.
13 H. Dorn, R. A. Singh, J. A. Massey, A. J. Lough and I. Manners, *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 3321.
14 H. Dorn, R. A. Singh, J. A. Massey, J. M. Nelson, C. A. Jaska, A. J. Lough and I. Manners, *J. Am. Chem. Soc.*, 2000, **122**, 6669.
15 To our knowledge, no examples of transition metal catalyzed dehydrocoupling routes to B–N bonds have appeared in the open literature. A patent (see Y. Blum and R. M. Laine, *US Pat.*, 4,801,439 1989) claims the catalytic formation of partially characterized mixtures of B–N compounds (including borazines) and insoluble polymeric products by the dehydrocoupling of mixtures of primary amines and $Me_3N–BH_3$ over extended periods of time at elevated temperatures. The conditions for the examples cited, typically 30–80 h, *ca.* 60 °C, in the presence of $Ru_3(CO)_{12}$, are also more forcing than with the Rh catalysts used in this communication.
16 A. B. Burg and C. L. Randolph Jr., *J. Am. Chem. Soc.*, 1949, **71**, 3451.
17 The crystal structure of **1** has been performed previously, but was only published as part of a dissertation by P. J. Schapiro from Cornell University (*Dissertation Abstr.*, 1962, **22**, 2607). This structure was found to have a different space group (*C*2/*m*) and unit cell dimensions than the one presented here.
18 L. M. Trefonas and W. N. Lipscomb, *J. Am. Chem. Soc.*, 1959, **79**, 4435.
19 C. A. Jaska, K. Temple, A. J. Lough and I. Manners, unpublished results.
20 Blank reactions performed in the absence of catalyst showed no dehydrocoupling products under the same conditions. Pure **3** and **4** were obtained through vacuum fractionation using traps at −45, −78 and −196 °C.
21 For an example of the trap-to-trap vacuum fractionation set-up for product purification, see: T. Wideman, P. J. Fazen, A. T. Lynch, K. Su, E. E. Remsen and L. G. Sneddon, *Inorg. Synth.*, 1998, **32**, 232.
22 The non-volatile residue was analyzed by ^{11}B NMR spectroscopy. Several distinct resonances were observed in the region δ = 26–36 suggesting further coupling. See, for comparison: P. J. Fazen, E. E. Remsen, P. J. Carroll, J. S. Beck, A. R. McGhie and L. G. Sneddon, *Chem. Mater.*, 1995, **7**, 1942.
23 T. Wideman and L. G. Sneddon, *Inorg. Chem.*, 1995, **34**, 1002.
24 R. T. Paine and L. G. Sneddon, *Chemtech*, 1994, **24**, 29.
25 P. J. Fazen, J. S. Beck, A. T. Lynch, E. E. Remsen and L. G. Sneddon, *Chem. Mater.*, 1990, **2**, 96.
26 T. Wideman and L. G. Sneddon, *Chem. Mater.*, 1996, **8**, 3.
27 O. R. Lourie, C. R. Jones, B. M. Bartlett, P. C. Gibbons, R. S. Ruoff and W. E. Buhro, *Chem. Mater.*, 2000, **12**, 1808.
28 T. C. Bissot and R. W. Parry, *J. Am. Chem. Soc.*, 1955, **77**, 3481.
29 C. K. Narula, J. F. Janik, E. N. Duesler, R. T. Paine and R. Schaeffer, *Inorg. Chem.*, 1986, **25**, 3346.