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COMMUNICATION

Dimethylamine borane dehydrogenation chemistry: syntheses, X-ray and neutron diffraction studies of 18-electron aminoborane and 14-electron aminoboryl complexes†‡

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The reactions of Me₂NH·BH₃ with cationic Rh(III) and Ir(III) complexes have been shown to generate the 18-electron aminoborane adduct [Ir(IMes)₂(H)₂{κ²-H₂BNMe₂}]⁺ and the remarkable 14-electron aminoboryl complex [Rh(IMes)₂(H)-{B(H)NMe₂}]⁺. Neutron diffraction studies have been used for the first time to define H-atom locations in metal complexes of this type formed under catalytic conditions.
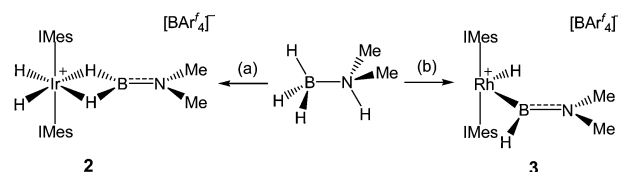
The metal-catalysed dehydrogenation of saturated element-element bonds represents a powerful approach both to synthetically valuable functional groups (*e.g.* alkenes from alkanes) and to novel polymeric materials.[1,2] In the case of saturated C–C bonds, such processes can be carried out either with or without a sacrificial hydrogen acceptor,[3] while formally isoelectronic B–N containing systems have been investigated explicitly as *in situ* sources of free H₂.[2] From the perspective of catalyst design, Group 9 metal complexes have been extensively studied,[3] and in the case of BN dehydrogenation chemistry, a number of potential intermediates have been isolated featuring small metal-bound borane fragments.[4–6] Thus, for example, several groups have reported the formation of κ²-aminoborane complexes [ML₂(H)₂(κ²-H₂B-NR₂)]ⁿ⁺ [L = N-heterocyclic carbene (NHC), tertiary phosphine; M = Rh, Ir: n = 1; M = Ru, n = 0] *via* the catalytic dehydrogenation of the corresponding amine borane, R₂NH·BH₃.[5–7]

Within this sphere we have recently focussed on the generation of catalytically active rhodium and iridium cations stabilized by a strongly electron donating *bis*(NHC) ligand set.[6] Thus, the reaction of M(IMes)₂(H)₂Cl (M = Rh, **1a**; M = Ir, **1b**; IMes = *N,N'-bis*(2,4,6-trimethylphenyl)imidazol-2-ylidene) with Na[BAr$^f_4$] in fluorobenzene has been shown to generate the

respective NaCl inclusion complexes [M(IMes)₂(H)₂Cl(Na)] [BAr$^f_4$], featuring a Na⁺ cation intercalated between two mesityl π systems. These isolated complexes (or an *in situ* mixture of **1a**/**1b** and Na[BAr$^f_4$]) act as viable sources of the 14-electron cations [M(IMes)₂(H)₂]⁺ in solution, and such systems have been shown to catalyze the dehydrogenation of bulky secondary amine boranes, to the corresponding (monomeric) aminoboranes, R₂NBH₂ (R = ^{i}Pr, Cy), at 20 °C with catalyst loadings of *ca.* 2%.[6]

Given recent interest in the dehydrogenative coupling of less bulky amine boranes to poly/oligomeric products,[4] we were keen to examine the ability of *bis*(NHC) rhodium and iridium systems to bring about similar transformations. Accordingly, the dehydrogenation of dimethylamine borane, Me₂NH·BH₃, by **1a**/**1b** in the presence of Na[BAr$^f_4$] leads to the isolation of the 18-electron aminoborane adduct [Ir(IMes)₂(H)₂{κ²-H₂BNMe₂}]⁺ (**2**, as the [BAr$^f_4$]⁻ salt) and the remarkable 14-electron rhodium aminoboryl complex [Rh(IMes)₂(H){B(H)NMe₂}]⁺ (**3**, also as the [BAr$^f_4$]⁻ salt). Crucially, for both complexes, key structural data have been obtained by single crystal neutron diffraction studies, thereby providing for the first time, evidence using this technique of key hydrogen atom positions in amino functionalized M-H-B and M-B-H species formed under catalytic conditions.[8]

The reaction of Me₂NH·BH₃ with **1b**/Na[BAr$^f_4$] (5 mol % of each; Scheme 1) in fluorobenzene leads to the complete disappearance of the borane starting material over 24 h and the formation of the well known [Me₂NBH₂]₂ dimer (δ$_B$ = 38 ppm). Spectroscopically, the ultimate iridium-containing product,

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‡ Electronic supplementary information (ESI) available: Synthetic and characterizing data for **2** and **3**; CIFs for all structures; DFT details. CCDC 880791–880794. See DOI: 10.1039/c2cc33361a

Scheme 1 Syntheses of iridium dimethylamino borane complex **2** and rhodium dimethylamino boryl system **3**. Key reagents and conditions: (i) **1b** (0.05 equiv.), Na[BAr$^f_4$] (0.05 equiv), fluorobenzene, –[Me₂NBH₂]₂, –H₂, 20 °C, 24 h, 76% (based on iridium); (ii) **1a** (0.05 equiv.), Na[BAr$^f_4$] (0.05 equiv), fluorobenzene, –[Me₂NBH₂]₂, –2H₂, 20 °C, 24 h, 71%.

isolated in *ca.* 75% yield, is characterized by ^{1}H resonances at $\delta_H = -15.24$ and -6.31 ppm. These chemical shifts can be compared to $\delta_H = -15.50/-15.44$ and $-5.83/-5.83$ ppm for $[Ir(IMes)_2(H)_2\{\kappa^2-H_2BNR_2\}]^+$ (R = ^iPr, Cy, respectively)[6] and -14.89, -6.68 ppm for $[Ir(PCy_3)_2(H)_2\{\kappa^2-H_2BNMe_2\}]^+$,[5c] and therefore provide persuasive evidence for the formation of $[Ir(IMes)_2(H)_2\{\kappa^2-H_2BNMe_2\}][BAr^f_4]$ (**2**). The identity of **2** was subsequently confirmed by multinuclear NMR, microanalysis and single crystal X-ray diffraction (see ESI),§ with the latter confirming a heavy atom skeleton similar to related phosphine containing systems.[5c]

In contrast to the well precedented chemistry leading to the formation of **2**, the reaction of $Me_2NH \cdot BH_3$ with *rhodium* precursor **1a** in the presence of $Na[BAr^f_4]$ under analogous conditions leads to the formation of a metal complex characterized by markedly different ^{1}H NMR signals. Thus, in toluene-d_8 solution a sharp (and essentially temperature invariant) upfield-shifted hydride resonance is observed at $\delta_H = -23.59$ ppm (integrating to 1H), together with two signals at $\delta_H = 1.41$ and 1.59 ppm (each 3H) corresponding to distinct *N*-bound methyl substituents and a broad somewhat shielded BH signal at $\delta_H = 0.51$ ppm. In addition, a downfield shifted ^{11}B resonance is observed ($\delta_B = 53$ ppm), in the region of the spectrum typically associated with aminoboryl complexes, $L_nM\{B(X)NR_2\}$ (*e.g.* $\delta_B = 57$ and 43 ppm for $CpFe(CO)_2\{B(Cl)NMe_2\}$ and *mer*-$[Ir(PMe_3)_3(H)Cl\{B(H)NCy_2\}]$, respectively).[9,10]

Single crystals of the metal-containing product could subsequently be obtained from fluorobenzene/pentane in *ca.* 70% yield, and the heavy atom skeleton thereby defined by X-ray diffraction (see ESI). The skeletal geometry is characterized by *trans* IMes ligands and a boron-containing ligand (orientated *cis* to the NHCs) which features a bent Rh-B–N framework [132.6(10)°] and Rh-B/B-N distances [1.960(9)/1.393(15) Å] which are consistent with the presence of a primary aminoboryl ligand, –B(H)NMe$_2$ (*cf.* 1.965(2) for Rh(P $^iPr_3)_2$H(Cl)Bcat and 1.401(5) Å for *mer*-$[Ir(PMe_3)_3(H)Cl\{B(H)NCy_2\}]$).[8b,10] However, in view of the location of the aminoboryl ligand close to the two-fold axis, together with the similarity of the X-ray scattering factors for boron, carbon and nitrogen, and the need to define hydrogen atom positions in **3** less ambiguously, block-like single crystals suitable for neutron diffraction were grown (5 × 3 × 2 mm) and a data set collected at 150 K using the time-of-flight Laue diffractometer SXD at the ISIS spallation neutron source.

For comparative purposes, crystals of the aminoborane complex **2** were also studied by neutron diffraction and the results of the two crystallographic studies shown in Fig. 1. The structure of **2** is consistent with the heavy atom skeleton determined by X-ray diffraction measurements; in addition, the four hydrogen atoms within the coordination sphere of Ir(1) are found to lie in the plane of the IrBNC$_2$ unit (largest deviation from least squares plane = 0.20 Å) with terminal Ir–H distances of 1.591(17), 1.599(15) Å and Ir–H(B) contacts of 1.822(19), 1.886(16) Å. The B–H(Ir) distances [1.30(2), 1.41(2) Å] conform to expectations for borane σ-complexes [*e.g.* 1.22(4), 1.28(4) Å for $[Ir(PCy_3)_2(H)_2\{\kappa^2-H_2BNMe_2\}]^+$; 1.29(2) Å for $(\eta^5-C_5H_4Me)Mn(CO)_2(\kappa^1-HBcat)$; 1.45(5) Å for $Ir\{C_6H_3(OP^tBu_2)_2\}(H)_2(BH_3)$],[5c,8a,11] and, at a more
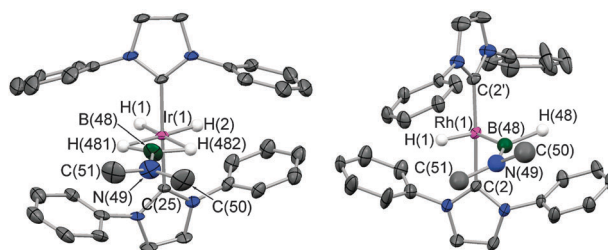

Fig. 1 Structures of the cationic components of **2** (left) and **3** (right) as determined by neutron diffraction. Counter-ion, mesityl Me groups, second disorder component and H atoms (except Rh- and B-bound Hs) omitted for clarity. Key bond lengths (Å) and angles (°) for **2** (neutron refinement): Ir(1)···B(48) 2.044(11), B(48)-N(49) 1.381(12), Ir(1)-H(1) 1.591(17), Ir(1)-H(2) 1.599(15), Ir(1)-H(481) 1.886(16), Ir(1)-H(482) 1.822(19), B(48)-H(481) 1.30(2), B(48)-H(482) 1.41(2).

Table 1 Key structural parameters determined for **3** by DFT and by diffraction techniques

Parameter	X-ray	Neutron	DFT
d(Rh-C)/Å	2.042(4)	2.034(5)	2.088
d(Rh-H)/Å	—	1.40(2)	1.548
d(Rh-B)/Å	1.960(9)	1.960(15)	2.005
d(B-N)/Å	1.390(15)	1.395(17)	1.398
d(B-H)/Å	—	^{a}	1.214
∠ C-Rh-C	176.7(2)	176.0(5)	169.9
∠ B-Rh-H	—	95.7(15)	95.7
∠ Rh-B-N	132.7(9)	132.6(10)	134.4

^{a} Precise determination problematic due to disorder (see text).

general level, this study provides the first verification by neutron diffraction of the 'end-on' doubly hydride-bridged *bis*(σ-borane) coordination motif for aminoboranes (*cf.* the 'side-on' mode of coordination typical of isoelectronic alkene donors).

The neutron structure determined for **3** (Fig. 1 and Table 1) has also been used to verify the presence of rhodium- and boron-bound hydrogen atoms implied by spectroscopic data and DFT calculations (ESI). Thus, the terminal Rh-H linkage is characterized by a separation of 1.40(2) Å, which is slightly shorter than the values of 1.53(1) and 1.57(1) Å measured for Rh(P$^iPr_3)_2$H(Cl)Bcat and Rh(P$^iPr_3)_2$H(Cl)Bpin - albeit with the latter two compounds known to possess additional 'modest' B···H interactions.[8b] The existence of the boron-bound hydrogen atom, implied by X-ray measurements on the basis of the bent Rh-B-N unit [132.6(10)°], is also confirmed, although precise determination of the B-H separation is made difficult by the proximity of the N-bound methyl group of the second disorder component. In addition, the mutually *cis* orientation of the hydride and boryl ligands within the rhodium coordination sphere is reflected by a B-Rh-H angle of 95.7(15)° (DFT: 95.7°). No evidence could be obtained crystallographically for any significant ligation of the rhodium centre in the coordination sites *trans* to either the boryl or hydride ligands. Additionally, the possibility, for example, for the coordination of dihydrogen is thought unlikely on the basis of solution phase spectroscopic data, *i.e.* the absence of either a distinct resonance characteristic of coordinated H$_2$, or of any significant temperature dependence of the strongly upfield Rh-H signal ($\delta_H = -23.59$ ppm). Moreover, further evidence

that **3** is indeed coordinatively unsaturated, comes from the fact that at −90 °C and under 4 atm pressure of H_2, new ^1H NMR signals become apparent, consistent with the coordination of dihydrogen. These signals disappear and those due to **3** are regenerated on warming to room temperature.

In the solid state at least, it also seems unlikely that there is any significant agostic stabilization of the metal centre, with the closest Rh···C contacts being > 3.8 Å.[12] The cationic component of **3**, *viz.* [Rh(IMes)$_2$(H){B(H)NMe$_2$}]$^+$, thus appears to feature a four-coordinate *cis* di-vacant 14-electron Rh(III) cation, of a sort finding precedent in the work of Nolan and co-workers.[13] In Nolan's system the metal coordination sphere comprises *trans* NHC and mutually *cis* (tethered) alkyl ligands, and has in common with the cationic component of **3**, vacant coordination sites that are located opposite ligands (alkyl, hydride or boryl) which are known to possess a very strong *trans* influence.[14] Other examples of Rh(III) and Ru(II) cations possessing related coordination geometries have been reported, albeit typically stabilized by secondary agostic interactions.[15,16] Moreover, this type of bent ML$_4$ geometry (*i.e.* a *cis*-di-vacant system derived from an octahedron) has been shown by Eisenstein and Caulton to be the lowest energy structure for d^6 Ir(III) systems,[15a,b] while a planar geometry is feasible for a triplet Ru(II) species.[17]

An 18-electron iridium aminoborane complex and a formally 14-electron *cis*-di-vacant rhodium aminoboryl compound are formed under closely related reaction conditions, designed to bring about the dehydrogenation of Me$_2$NH·BH$_3$. The difference in reactivity between the two systems conceivably relates to the differing propensity for M(III) dihydride species of the type [M(IMes)$_2$(H)$_2$(κ^2-H$_2$BNMe$_2$)]$^+$ (M = Rh, Ir) to reductively eliminate dihydrogen.[18] Although the highly unsaturated Rh(III) species [Rh(IMes)$_2$(H){B(H)NMe$_2$}]$^+$ appears to coordinate dihydrogen at low temperatures and under pressure, it shows no tendency to rehydrogenate the coordinated aminoboryl fragment.

Notes and references

§ X-ray diffraction data were collected at 150 K on a Nonius Kappa CCD diffractometer; neutron diffraction data were collected at 150 K on the time-of-flight Laue diffractometer SXD at the ISIS spallation neutron source.[19] The X-ray structure solutions were refined in each case, using SHELXL.[20]

1 See, for example (*a*) G. E. Dobereiner and R. H. Crabtree, *Chem. Rev.*, 2010, **110**, 681; (*b*) S. D. Jackson, P. C. Stair, L. F. Gladden and J. McGregor, in *Metal Oxide Catalysis*, ed. S. D. Jackson and J. S. J. Hargreaves, Wiley-VCH, Weinheim, 2008, pp. 595–612.

2 For recent reviews relating to BN-containing materials, see, for example: (*a*) T. J. Clark, K. Lee and I. Manners, *Chem.-Eur. J.*, 2006, **12**, 8634; (*b*) T. B. Marder, *Angew. Chem., Int. Ed. Engl.*, 2007, **46**, 8116; (*c*) F. H. Stephens, V. Pons and R. T. Baker, *Dalton Trans.*, 2007, **2**, 2613; (*d*) C. W. Hamilton, R. T. Baker, A. Staubitz and I. Manners, *Chem. Soc. Rev.*, 2009, **38**, 279; (*e*) N. C. Smythe and J. C. Gordon, *Eur. J. Inorg. Chem.*, 2010, 509; (*f*) A. Staubitz, A. P. M. Robertson, M. E. Sloan and I. Manners, *Chem. Rev.*, 2010, **110**, 4023; (*g*) A. Staubitz, A. P. M. Robertson and I. Manners, *Chem. Rev.*, 2010, **110**, 4079; (*h*) G. Alcaraz and S. Sabo-Etienne, *Angew. Chem., Int. Ed. Engl.*, 2010, **49**, 7170.

3 See, for example: J. Choi, A. H. R. MacArthur, M. Brookhart and A. S. Goldman, *Chem. Rev.*, 2011, **111**, 1761.

4 For selected examples involving Group 9 metals, see: (*a*) C. A. Jaska, K. Temple, A. J. Lough and I. Manners, *J. Am. Chem. Soc.*, 2003, **125**, 9424; (*b*) C. A. Jaska and I. Manners,

J. Am. Chem. Soc., 2004, **126**, 9776; (*c*) A. Rossin, M. Caporali, L. Gonsalvi, A. Guerri, A. Lledós, M. Peruzzini and F. Zanobini, *Eur. J. Inorg. Chem.*, 2009, 3055; (*d*) T. M. Douglas, A. B. Chaplin, A. S. Weller, X. Yang and M. B. Hall, *J. Am. Chem. Soc.*, 2009, **131**, 15440; (*e*) A. B. Chaplin and A. S. Weller, *Angew. Chem., Int. Ed. Engl.*, 2010, **49**, 581; (*f*) A. B. Chaplin and A. S. Weller, *Inorg. Chem.*, 2010, **49**, 1111; (*g*) A. Staubitz, M. E. Sloan, A. P. M. Robertson, A. Friedrich, S. Schneider, P. J. Gates, J. S. A. D. Guenne and I. Manners, *J. Am. Chem. Soc.*, 2010, **132**, 13332; (*h*) H. C. Johnson, A. P. M. Robertson, A. B. Chaplin, L. J. Sewell, A. L. Thompson, M. F. Haddow, I. Manners and A. S. Weller, *J. Am. Chem. Soc.*, 2011, **133**, 11076; (*i*) R. Dallangegra, A. P. M. Robertson, A. B. Chaplin, I. Manners and A. S. Weller, *Chem. Commun.*, 2011, **47**, 3763; (*j*) L. J. Sewell, G. C. Lloyd-Jones and A. S. Weller, *J. Am. Chem. Soc.*, 2012, **134**, 3598.

5 (*a*) G. Alcaraz, L. Vendier, E. Clot and S. Sabo-Etienne, *Angew. Chem., Int. Ed.*, 2010, **49**, 918; (*b*) G. Alcaraz, A. B. Chaplin, C. J. Stevens, E. Clot, L. Vendier, A. S. Weller and S. Sabo-Etienne, *Organometallics*, 2010, **29**, 5591; (*c*) C. J. Stevens, R. Dallanegra, A. B. Chaplin, A. S. Weller, S. A. Macgregor, B. Ward, D. McKay, G. Alcaraz and S. Sabo-Etienne, *Chem.-Eur. J.*, 2011, **17**, 3011.

6 (*a*) S. Aldridge, A. J. Downs, C. Y. Tang, S. Parsons, M. C. Clarke, R. D. L. Johnstone, H. E. Robertson, D. W. H. Rankin and D. A. Wann, *J. Am. Chem. Soc.*, 2009, **131**, 2231; (*b*) C. Y. Tang, A. L. Thompson and S. Aldridge, *Angew. Chem., Int. Ed. Engl.*, 2010, **49**, 921; (*c*) C. Y. Tang, A. L. Thompson and S. Aldridge, *J. Am. Chem. Soc.*, 2010, **132**, 10578.

7 For related κ^1 systems, see: D. Vidovic, D. A. Addy, T. Krämer, J. McGrady and S. Aldridge, *J. Am. Chem. Soc.*, 2011, **133**, 8494.

8 For a neutron diffraction study of an iridium BH$_3$ adduct, see: (*a*) T. J. Hebden, M. C. Denney, V. Pons, P. M. B. Piccoli, T. F. Koetzle, A. J. Schultz, W. Kaminsky, K. I. Goldberg and D. M. Heinekey, *J. Am. Chem. Soc.*, 2008, **130**, 10812; for a neutron diffraction study of Rh(^{i}Pr$_3$P)$_2$H(Cl)Bcat see: (*b*) W. H. Lam, S. Shimada, A. S. Batsanov, Z. Lin, T. B. Marder, J. A. Cowan, J. A. K. Howard, S. A. Mason and G. J. McIntyre, *Organometallics*, 2003, **22**, 4557.

9 H. Braunschweig, C. Kollann and U. Englert, *Eur. J. Inorg. Chem.*, 1998, 465.

10 M. O'Neill, D. A. Addy, I. Riddlestone, M. Kelly, N. Phillips and S. Aldridge, *J. Am. Chem. Soc.*, 2011, **133**, 11500.

11 S. Schlecht and J. F. Hartwig, *J. Am. Chem. Soc.*, 2000, **122**, 9435.

12 M. Brookhart, M. L. H. Green and G. Parkin, *Proc. Natl. Acad. Sci. U. S. A.*, 2007, **104**, 6908.

13 (*a*) N. M. Scott, V. Pons, E. D. Stevens, D. M. Heinekey and S. P. Nolan, *Angew. Chem., Int. Ed.*, 2005, **44**, 2512; (*b*) N. M. Scott, R. Dorta, E. D. Stevens, A. Correa, L. Cavallo and S. P. Nolan, *J. Am. Chem. Soc.*, 2005, **127**, 3516.

14 J. Zhu, Z. Lin and T. B. Marder, *Inorg. Chem.*, 2005, **44**, 9384.

15 (*a*) A. C. Cooper, W. E. Streib, O. Eisenstein and K. G. Caulton, *J. Am. Chem. Soc.*, 1997, **119**, 9069; (*b*) A. C. Cooper, E. Clot, J. C. Huffman, W. E. Streib, F. Maseras, O. Eisenstein and K. G. Caulton, *J. Am. Chem. Soc.*, 1999, **121**, 97; for a more recent, closely related, rhodium complex see: (*c*) T. M. Douglas, A. B. Chaplin and A. S. Weller, *Organometallics*, 2008, **27**, 2918.

16 (*a*) D. Huang, J. C. Huffman, J. C. Bollinger, O. Eisenstein and K. G. Caulton, *J. Am. Chem. Soc.*, 1997, **119**, 7398; (*b*) D. Huang, W. E. Streib, J. C. Bollinger, K. G. Caulton, R. F. Winter and T. Scheiring, *J. Am. Chem. Soc.*, 1999, **121**, 8087; (*c*) D. Huang, J. C. Bollinger, W. E. Streib, K. Folting, V. Young Jr., O. Eisenstein and K. G. Caulton, *Organometallics*, 2000, **19**, 2281.

17 L. A. Watson, O. V. Ozerov, M. Pink and K. G. Caulton, *J. Am. Chem. Soc.*, 2003, **125**, 8426.

18 For an illustration of the propensity of rhodium and iridium to favour the +1 and +3 oxidation states, respectively, in related boron-containing ligand systems see (*a*) R. T. Baker, D. W. Ovenall, J. C. Calabrese, S. A. Westcott, N. J. Taylor, I. D. Williams and T. B. Marder, *J. Am. Chem. Soc.*, 1990, **112**, 9399; (*b*) S. A. Westcott, T. B. Marder, R. T. Baker, R. L. Harlow, J. C. Calabrese, K. C. Lam and Z. Lin, *Polyhedron*, 2004, **23**, 2665.

19 D. A. Keen, M. J. Gutmann and C. C. Wilson, *J. Appl. Crystallogr.*, 2006, **39**, 714.

20 G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.