

Rhodium and Iridium Aminoborane Complexes: Coordination Chemistry of BN Alkene Analogues**

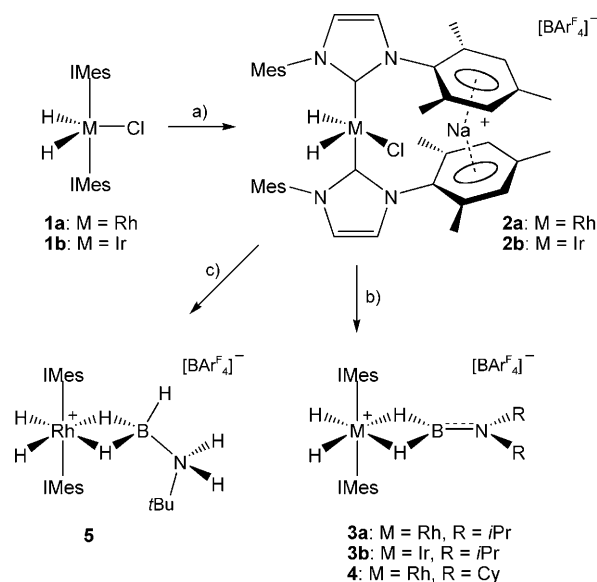
Christina Y. Tang, Amber L. Thompson, and Simon Aldridge*

The chemistry of boron donor ligands, isoelectronic with classical organometallic systems, has received considerable recent attention, not only from a structure/bonding perspective, but also from a desire to develop inherently useful patterns of reactivity (e.g. boryl complexes in hydro- and diboration, and in C–H activation).^[1–5] Such studies have also allowed comparative assays of ligand properties and reactivity (e.g. relative *trans* influences, comparative reactivity towards electrophiles/nucleophiles)^[6] for isoelectronic carbon/boron-containing ligand families, e.g. N-heterocyclic carbene/boryl,^[7,8] vinylidene/aminoborylene,^[1] CO/BF,^[9] and cyclopentadienyl/azaborolyl pairs.^[10,11] Such comparisons can also be exploited in a predictive capacity, as in the case of the ligating properties of alkanes/amineboranes, with structural data being widely available only for the latter class of donor.^[12,13] By contrast, while transition-metal complexes are well known for alkene ligands,^[14] the coordination chemistry of the isoelectronic aminoborane family ($R_2N=BX_2$) has yet to be elucidated,^[15] despite the potential relevance of such species to boron/nitrogen based hydrogen storage materials (for $X = H$).^[16]

The metal-catalyzed dehydrogenation of ammonia borane and related amine derivatives has been the subject of intense recent study, both with a view to unlocking the potential of such systems as hydrogen storage media, and with the aim of developing new Group 13/Group 15 materials by dehydrocoupling methodologies.^[17] Typically, in the absence of significant steric bulk, the dehydrogenation of an alkyl- or dialkylamineborane catalyzed by Group 9 metal systems leads to the formation of oligo- or polymeric products.^[18,19] The monomeric nature of R_2NBH_2 ($R = iPr, Cy$),^[18a,20] on the other hand, led us to consider the in situ rhodium- or iridium-catalyzed dehydrogenation of $iPr_2HN\cdot BH_3$ and $Cy_2HN\cdot BH_3$ as a potential route to complexes of the type $[L_nM(H_2BNR_2)]$. Related systems have been proposed as a potential resting state in the catalytic dehydrocoupling of amineboranes,^[16,19b] but as yet no structural data have been forthcoming. As part of a recently initiated study into the reactivity of unsaturated

group 9 N-heterocyclic carbene (NHC) systems,^[21] we hereby report the synthesis of cationic rhodium and iridium aminoborane complexes, together with that of a closely related 1,1-disubstituted alkene complex. Structural characterization of these species allows for the first time direct experimental comparison of the modes of binding of these topical ligand systems.

Halide abstraction is well established as a synthetic methodology for the generation of highly reactive cationic species stabilized, for example, by weak agostic or solvent molecule derived interactions.^[22] We have therefore investigated the reactivity of $[M(IMes)_2(H)_2Cl]$ ($M = Rh$ (**1a**), Ir (**1b**); $IMes = N,N$ -bis(2,4,6-trimethylphenyl)imidazol-2-ylidene)^[23] towards the potent halide abstraction agent $Na[Bar^F_4]$ ($Ar^F = 3,5-C_6H_3(CF_3)_2$) with a view to generating reactive cationic bis(NHC) systems capable of coordinating aminoborane molecules. Surprisingly, the reaction of either **1a** or **1b** with $Na[Bar^F_4]$ in fluorobenzene at 20 °C over 4 h does not proceed through salt metathesis, but rather to the formation of the sodium-containing cations $[M(IMes)_2(H)_2Cl(Na)]^+$ ($M = Rh$ (**2a**), Ir (**2b**)) as the $[Bar^F_4]^-$ salts (Scheme 1). **2a** and **2b** represent extremely rare examples of isolated NaCl metathesis intermediates and can



Scheme 1. Syntheses of aminoborane adducts **3a**, **3b**, and **4** and amineborane complex **5**. Key reagents and conditions: a) $Na[Bar^F_4]$ (1.0 equiv), fluorobenzene, 3 h, 20 °C, ca. 70%; b) $R_2HN\cdot BH_3$ (typically 20 equiv for synthetic runs; 50 equiv for catalytic testing), fluorobenzene, 6 h, 20 °C 50–70%; c) $tBuH_2N\cdot BH_3$ (20 equiv), fluorobenzene, 6 h, 20 °C, ca. 50%.

[*] Dr. C. Y. Tang, Dr. A. L. Thompson, Dr. S. Aldridge
Inorganic Chemistry, University of Oxford
South Parks Road, Oxford, OX1 3QR (UK)
Fax: (+44) 1865-272-690
E-mail: simon.aldridge@chem.ox.ac.uk
Homepage: <http://users.ox.ac.uk/~quee1989/>

[**] We thank the EPSRC for funding and for access to the National Mass Spectrometry facility at Swansea University, the John Fell Fund for the provision of ESI-MS facilities, and Andrew Weller (Oxford) for stimulating discussions.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.200906171>.

be shown to eliminate the metal halide in the presence of a suitable donor ligand (see below).^[24] Both compounds have been characterized by standard spectroscopic techniques, by elemental microanalysis and, in the case of **2b**, by single-crystal X-ray diffraction. The cationic component of compound **2b** in the solid state (Figure 1) is formally derived from

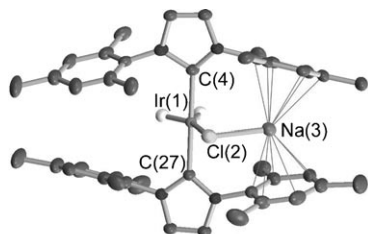


Figure 1. Structure of the cationic component of **2b**; counter-ion, hydrogen atoms (except those attached to the metal center) and second disorder component omitted for clarity. Thermal ellipsoids set at the 40% probability level. Key bond lengths [Å] and angles [°]: Ir(1)–Cl(2) 2.402(3), Cl(2)–Na(3) 2.612(7), C(4)–Ir(1)–C(27) 179.99(4).

1b by intercalation of the sodium cation between the mesityl rings of the two IMes ligands. The Na–arene centroid distances characterizing these interactions (2.455 and 2.463 Å for **2b**) are slightly longer than those associated with other reported NaCl inclusion compounds (for example, 2.145, 2.171 Å for [Zn₂–(ODipp)₄(Na)Cl(thf)₃] (Dipp = 2,6-*i*Pr₂C₆H₃)).^[25] However, the presence of the sodium cation is also signaled by the effects it has on the conformation of the M(IMes)₂ unit; thus the two carbene heterocycles in **2b** lie close to co-planar (angle between least squares planes 12.0°) in contrast to the more staggered geometry adopted, for example in **1a** (torsion 47.5°),^[23] presumably on steric grounds.

2a and **2b** catalyze the dehydrogenation of amineboranes R₂HN·BH₃ (R = *i*Pr, Cy) in fluorobenzene at room temperature (100% conversion over 6 h at 2 mol% loading), leading to the generation of monomeric R₂NBH₂; the metal-containing products isolated on completion of these reactions (after recrystallization from fluorobenzene/hexanes) are shown to be the aminoborane adducts [M(IMes)₂(H)₂(H₂BNR₂)]⁺[BAR^F₄][–] (M = Rh, R = *i*Pr (**3a**), M = Ir, R = *i*Pr (**3b**); M = Rh, R = Cy (**4**)). The ¹¹B NMR resonances for all three cations (δ_B = 35.4, 37.9, and 35.8 ppm) are as expected for a species containing a three-coordinate boron center formed by dehydrogenation of R₂HN·BH₃, and indeed are very close to those of the free aminoboranes themselves (cf. δ_B = 35.0 ppm for *i*Pr₂NBH₂).^[18a,20] Moreover, the pattern of ¹H NMR resonances in the hydride region in each case (for example, δ_H = –1.40 (2H), –16.02 ppm (2H) for the BH and RhH protons in **3a**; cf. δ_H = 4.32 ppm for *i*Pr₂NBH₂ and δ = –23.0 ppm for [Rh(IMes)₂(H)₂Cl]),^[18a,23] provides evidence for coordination of the aminoborane to the [M(IMes)₂(H)₂]⁺ fragment in solution. Similar patterns in the high-field region of the spectrum have been observed for [Ru(PCy₃)₂(H)₂–(η²-H₂BMes)] (δ_H = –5.90, –11.05 ppm) and [Rh–

(P^{*t*}Bu₃)₂(H)₂(η²-H₃B·NMe₃)]⁺ (δ_H = –3.15, –17.4 ppm).^[19a,b,26] While such data are consistent with interaction of the aminoborane molecule with the Group 9 metal center through bridging B–H–M interactions, definitive characterization of the mode of ligation was reliant on single-crystal X-ray diffraction studies for **3a**, **3b**, and **4** (see Figure 2 and Supporting Information).

The structures of all three cations feature the expected *trans* arrangement of the NHC donors, *cis* hydride ligands (which were visible in the difference maps for **3a** and **3b**), and an aminoborane ligand featuring a planar C₂NBH₂ skeleton coordinated to the metal center through two B–H–Rh interactions that is, acting as a bis(σ-borane) ligand.^[26] The B–N distances (1.370(4), 1.379(8), and 1.380 (mean) Å, respectively) are consistent with appreciable π bond character (cf. 1.58 Å for the sum of the respective covalent radii)^[27] and the Rh···B separations for **3a** and **4** (2.204(4) and 2.176 (mean) Å) are notably shorter than those measured for related rhodium complexes containing an *amineborane* ligand (i.e. featuring a four-coordinate boron center). Thus, the

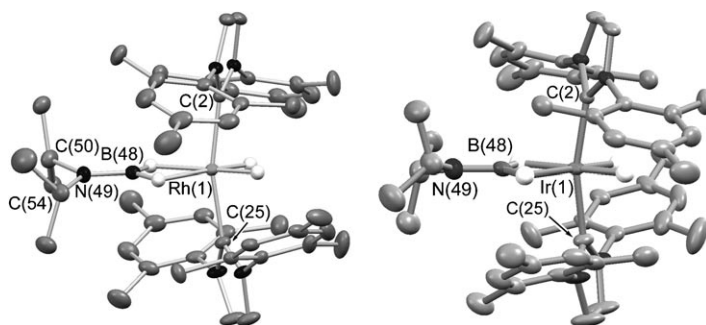


Figure 2. Structures of the cationic components of **3a** (left) and **3b** (right); counter-ions and hydrogen atoms (except those attached to the metal centers) omitted for clarity. Thermal ellipsoids set at the 40% probability level. Key bond lengths [Å] and angles [°]: for (**3a**) Rh(1)···B(48) 2.204(4), B(48)–N(49) 1.370(4), Rh(1)–B(48)–N(49) 179.6(3), C(2)–Rh(1)–C(25) 165.5(1); for (**3b**) Ir(1)···B(48) 2.088(5), B(48)–N(49) 1.379(8), Ir(1)–B(48)–N(49) 178.4(3), C(2)–Ir(1)–C(25) 165.6(2).

corresponding distance measured for [Rh–(IMes)₂(H)₂(H₃B·NH₂*t*Bu)]⁺[BAR^F₄][–] (**5**) is 2.305(4) Å (see below). The M···B distances for **3a** and **4** are, however, markedly longer than those associated with similarly bound (but much more electrophilic) H₂BR ligands in [Ru–(PCy₃)₂(H)₂(H₂BR)] (R = Mes, *t*Bu).^[26,28,29] In the case of these ruthenium complexes, the presence of a direct Ru–B interaction has been suggested, reflecting ruthenium–boron separations (1.938(4), 1.934(2) Å), which are approximately 0.15 Å (7.2%) shorter than the the sum of the respective covalent radii (2.09 Å).^[26–28] In the cases of **3a**, **3b**, and **4**, however, the extent of any analogous M–B interaction is likely to be significantly smaller, as indicated 1) by M···B separations which are comparable to, or (for Rh complexes **3a** and **4**) actually *longer* than the sum of the corresponding covalent radii (2.13 Å (Rh/B); 2.14 Å (Ir/B)),^[27] and 2) by the relatively small shifts in the aminoborane ¹¹B NMR resonance on coordination in each case (Δδ_B < 3 ppm cf. Δδ_B = 10 ppm for H₂B*t*Bu on coordination at ruthenium).^[28,30]

With a view to further investigating the scope of dehydrogenation chemistry in the synthesis of aminoborane complexes, we have also analyzed the reaction of **2a** with $i\text{BuH}_2\text{N}\cdot\text{BH}_3$ under analogous conditions to those employed for $i\text{PrH}_2\text{N}\cdot\text{BH}_3$ and $\text{CyH}_2\text{N}\cdot\text{BH}_3$. In this case, however, the organometallic product so formed is not an aminoborane adduct, but rather the product of simple coordination of the parent amineborane to the $[\text{Rh}(\text{IMes})_2(\text{H})_2]^+$ fragment. Thus, $[\text{Rh}(\text{IMes})_2(\text{H})_2(\text{H}_3\text{B}\cdot\text{NH}_2i\text{Bu})]^+[\text{BAr}^{\text{F}}_4]^-$ (**5**) has been isolated by recrystallization from fluorobenzene/hexanes and characterized by standard spectroscopic, analytical, and crystallographic methods (see Figure 3). The underlying

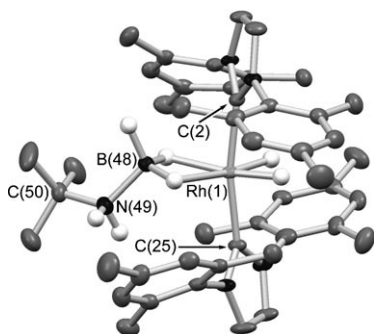


Figure 3. Structure of the cationic component of **5**; counter-ion and hydrogen atoms (except those attached to the metal center) omitted for clarity. Thermal ellipsoids set at the 40% probability level. Key bond lengths [Å] and angles [°]: $\text{Rh}(1)\cdots\text{B}(48)$ 2.305(4), $\text{B}(48)\cdots\text{N}(49)$ 1.604(5), $\text{Rh}(1)\cdots\text{B}(48)\cdots\text{N}(49)$ 127.0(3), $\text{C}(2)\cdots\text{Rh}(1)\cdots\text{C}(25)$ 168.7(1).

reasons for the different products obtained appear to reflect the relative rates of **2a**-catalyzed dehydrogenation of $i\text{BuH}_2\text{N}\cdot\text{BH}_3$ and $\text{R}_2\text{HN}\cdot\text{BH}_3$ ($\text{R} = i\text{Pr}, \text{Cy}$) in fluorobenzene, and consequently the identities of the predominant B/N containing species in solution (at the end of the 6 h reaction period) available to coordinate to the $[\text{M}(\text{IMes})_2(\text{H})_2]^+$ fragment. Thus, while the latter two boranes are efficiently dehydrogenated by **2a** over the time period of the synthetic experiment (6 h), effectively leaving R_2NBH_2 ($\text{R} = i\text{Pr}, \text{Cy}$) as the only borane remaining in solution, $i\text{BuH}_2\text{N}\cdot\text{BH}_3$ loses hydrogen much more slowly, such that over the same time frame, it remains overwhelmingly the major B/N constituent of the reaction mixture.^[31]

The bis(σ -borane) mode of coordination observed for aminoborane molecules bound to the $[\text{M}(\text{IMes})_2(\text{H})_2]^+$ fragment in **3a**, **3b**, and **4** clearly contrasts with the classical side-on mode of binding typically observed for alkenes with transition metals.^[14]

Moreover, it has been established unequivocally by crystallographic studies that the $[\text{M}(\text{NHC})_2(\text{H})_2]^+$ fragment does support a conventional mode of alkene coordination (that is, compound **7**; see Supporting Information), and it therefore seems likely that the alternative binding motif revealed for aminoborane ligands reflects the more hydridic nature of the B–H bonds (cf. C–H), and the significantly lower energy of the B=N π system (cf. C=C).^[32]

In summary, we report group 9 complexes featuring aminoboranes ($\text{R}_2\text{N}=\text{BH}_2$) as ligands, showing for the first

time that these systems (in contrast to related alkene donors) bind in an end-on fashion utilizing two M–H–B bridges to give a bis(σ -borane) binding motif. Further studies of the putative 14-electron rhodium and iridium cations **2a** and **2b** towards amineboranes will be reported in due course; preliminary studies of reactivity towards $\text{Me}_2\text{HN}\cdot\text{BH}_3$ are consistent with the formation of a reversible bis(σ -borane)/metal boryl equilibrium.

Experimental Section

Synthetic, spectroscopic, and crystallographic data for **2b** and **3b** are included here; the corresponding data for **2a**, **3a**, **4**, **5**, and alkene complex **7** are included in the Supporting Information.

2b: To a suspension of $\text{Na}[\text{BAr}^{\text{F}}_4]$ (1.06 g, 1.19 mmol) in fluorobenzene (20 cm³) at -30°C was added a solution of **1b** (1.00 g, 1.19 mmol) also in fluorobenzene (20 cm³) and the reaction mixture warmed to 20°C over a period of 1 h. After stirring for a further 3 h at 20°C , the resulting deep brown solution was filtered and concentrated in vacuo, and orange crystals suitable for X-ray diffraction were obtained by layering with pentane and storage at 20°C . Isolated yield 1.35 g, 72%.

Spectroscopic data for **2b**: ^1H NMR ($\text{C}_6\text{D}_5\text{CD}_3$, 300 MHz, 20°C): $\delta_{\text{H}} = -34.21$ (br, 2 H, IrH), 1.85 (s, 24 H, *ortho*-CH₃ of IMes), 2.13 (s, 12 H, *para*-CH₃ of IMes), 5.95 (s, 4 H, NCHCHN of IMes), 6.53 (s, 8 H, aromatic CH of IMes), 7.64 (s, 4 H, *para*-CH of $[\text{BAr}^{\text{F}}_4]^-$), 8.32 ppm (s, 8 H, *ortho*-CH of $[\text{BAr}^{\text{F}}_4]^-$). ^{13}C NMR ($\text{C}_6\text{D}_5\text{CD}_3$, 126 MHz, 20°C): 1) signals due to cation: $\delta_{\text{C}} = 19.8$ (br, *ortho*-CH₃ of IMes), 21.3 (*para*-CH₃ of IMes), 121.5 (NCH of IMes), 124.8 (*ortho*-quaternary C of IMes), 127.7 (*meta*-CH of IMes), 136.8 (*para*-quaternary C of IMes), 12.3 ppm (br, carbene quaternary C of IMes), N-bound aryl quaternary signal not observed; 2) signals due to $[\text{BAr}^{\text{F}}_4]^-$ ion: $\delta = 118.0$ (*para*-CH), 125.2 (q, $J = 273.0$ Hz, CF₃), 129.9 (q, $J = 30.2$ Hz, *meta*-quaternary C), 135.5 (*ortho*-CH), 162.6 (q, $J = 50.3$ Hz, *ipso*-quaternary C). ^{11}B NMR ($\text{C}_6\text{D}_5\text{CD}_3$, 96 MHz, 20°C): $\delta_{\text{B}} = -6.1$ ppm ($[\text{BAr}^{\text{F}}_4]^-$). ^{19}F NMR ($\text{C}_6\text{D}_5\text{CD}_3$, 282 MHz, 20°C): $\delta_{\text{F}} = -62.1$ ppm. Elemental microanalysis calcd. for $\text{C}_{74}\text{H}_{62}\text{N}_4\text{IrCnNaBF}_{24}$: C 51.53, H 3.62, N 3.25; found: C 51.52, H 3.53, N 3.21.

Crystallographic data for **2b**: $M_r = 1724.76$, monoclinic, $C2/c$, $a = 22.7234(3)$, $b = 18.7031(3)$, $c = 19.6595(2)$ Å, $\beta = 116.0509(7)^\circ$, $V = 7506.39(18)$ Å³, $Z = 4$, $\rho_{\text{c}} = 1.526$ Mg m⁻³, $T = 150(2)$ K, $\lambda = 0.71073$ Å. 60375 reflections collected, 8541 independent $R(\text{int}) = 0.0380$, which were used in all calculations. $R_1 = 0.0629$, $wR_2 = 0.1461$ for observed unique reflections [$F^2 > 2\sigma(F^2)$] and $R_1 = 0.0773$, $wR_2 = 0.1554$ for all unique reflections. Max. and min. residual electron densities 2.99 and -1.45 e Å⁻³.

3b: To a suspension of **2b** (0.431 g, 0.25 mmol) in fluorobenzene (50 cm³) at -30°C was added excess $i\text{Pr}_2\text{HN}\cdot\text{BH}_3$ (0.57 g, 5 mmol) and the reaction mixture warmed to 20°C over a period of 1 h. After stirring for a further 6 h at 20°C , the resulting deep brown solution was filtered and concentrated in vacuo, and yellow crystals suitable for X-ray diffraction were obtained by layering with pentane and storage at 20°C . Isolated yield: 0.249 g, 56%.

Spectroscopic data for **3b**: ^1H NMR ($\text{C}_6\text{D}_5\text{CD}_3$, 300 MHz, 20°C): $\delta_{\text{H}} = -15.50$ (br, 2 H, IrH), -5.83 (br, 2 H, BH₂), 0.75 (d, $J = 7.2$ Hz, 12 H, CH₃ of $i\text{Pr}$), 1.51 (s, 24 H, *ortho*-CH₃ of IMes), 2.24 (s, 12 H, *para*-CH₃ of IMes), 2.79 (sept, $J = 7.2$ Hz, 2 H, CH of $i\text{Pr}$), 6.95 (s, 4 H, NCHCHN of IMes), 6.65 (s, 8 H, aromatic CH of IMes), 7.71 (s, 4 H, *para*-CH of $[\text{BAr}^{\text{F}}_4]^-$), 8.33 ppm (s, 8 H, *ortho*-CH of $[\text{BAr}^{\text{F}}_4]^-$). ^{13}C NMR ($\text{C}_6\text{D}_5\text{CD}_3$, 75 MHz, 20°C): 1) signals due to cation: $\delta = 14.3$ (CH₃ of $i\text{Pr}$), 17.8 (*ortho*-CH₃ of IMes), 23.4 (*para*-CH₃ of IMes), 49.0 (CH of $i\text{Pr}$), 122.1 (NCHCHN of IMes), 127.0 (*ortho*-quaternary C of IMes), 135.2 (*meta*-CH of IMes), 138.7 (*para*-quaternary C of IMes), 172.9 ppm (br, carbene quaternary C of IMes), N-bound aryl quaternary signal not observed; 2) signals due to $[\text{BAr}^{\text{F}}_4]^-$ ion: $\delta = 117.6$ (s, *para*-CH), 123.1 (q, $J = 273.0$ Hz, CF₃), 129.6 (q, $J = 32.7$ Hz,

meta-quaternary C), 134.3 (*ortho*-CH), 162.6 ppm (q, $J = 50.3$ Hz, ipso-quaternary C). ^{11}B NMR ($\text{C}_6\text{D}_5\text{CD}_3$, 96 MHz, 20°C): $\delta_{\text{B}} = -6.0$ ($[\text{BAr}^{\text{F}}_4]^-$), 37.9 (br, H_2BNiPr_2). ^{19}F NMR ($\text{C}_6\text{D}_5\text{CD}_3$, 282 MHz, 20°C): $\delta_{\text{F}} = -62.1$. IR (cm^{-1}): $\nu = 2239$ br [$\nu(\text{B}-\text{H})$]. Elemental microanalysis calcd. for $\text{C}_{80}\text{H}_{78}\text{N}_5\text{IrB}_2\text{F}_{24}$: C 54.00, H 4.42, N 3.94; found: C 53.88, H 4.33, N 4.02.

Crystallographic data for **3b**: $M_r = 1779.3$, triclinic, $P\bar{1}$, $a = 12.2427(1)$, $b = 18.0382(2)$, $c = 18.8848(2)$ Å, $\alpha = 84.3098(5)$, $\beta = 89.8394(5)$, $\gamma = 74.7171(4)^\circ$, $V = 4001.96(7)$ Å³, $Z = 2$, $\rho_c = 1.447$ Mg m⁻³, $T = 150(2)$ K, $\lambda = 0.71073$ Å. 53 098 reflections collected, 18 123 independent [$R(\text{int}) = 0.0303$], which were used in all calculations. $R_1 = 0.0498$, $wR_2 = 0.0944$ for observed unique reflections [$F^2 > 2\sigma(F^2)$] and $R_1 = 0.0696$, $wR_2 = 0.1088$ for all unique reflections. Max. and min. residual electron densities 3.34 and -2.704 e Å⁻³. CCDC 758029 (**2b**) and 758031 (**3b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: November 3, 2009

Published online: December 22, 2009

Keywords: alkenes · aminoboranes · dehydrogenation · iridium · rhodium

- [1] a) H. Braunschweig, C. Kollann, D. Rais, *Angew. Chem.* **2006**, *118*, 5380–5400; *Angew. Chem. Int. Ed.* **2006**, *45*, 5254–5274; b) S. Aldridge, D. L. Kays, *Main Group Chem.* **2006**, *5*, 223–249; c) H. Braunschweig, C. Kollann, F. Seeler, *Struct. Bonding (Berlin)* **2008**, *130*, 1–27; d) D. Vidovic, G. A. Pierce, S. Aldridge, *Chem. Commun.* **2009**, 1157–1171.
- [2] a) G. J. Irvine, M. J. G. Lesley, T. B. Marder, N. C. Norman, C. R. Rice, E. G. Robbins, W. R. Roper, G. R. Whittell, L. J. Wright, *Chem. Rev.* **1998**, *98*, 2685–2722; b) D. L. Kays, S. Aldridge, *Struct. Bonding (Berlin)* **2008**, *130*, 29–122.
- [3] a) T. B. Marder, N. C. Morman, *Top. Catal.* **1998**, *5*, 63–73; b) T. Ishiyama, N. Miyaoura, *Chem. Rec.* **2004**, *3*, 271–280; c) N. Miyaoura, *Bull. Chem. Soc. Jpn.* **2008**, *81*, 1535–1553.
- [4] For a recent review see, for example: C. M. Crudden, D. Edwards, *Eur. J. Org. Chem.* **2003**, 4695–4712.
- [5] For recent references see, for example: a) T. Ishiyama, N. Miyaoura in *Handbook of C-H Transformations, Vol. 1* (Ed.: G. Dyker), Wiley-VCH, Weinheim, **2005**, pp. 126–131; b) J. F. Hartwig, J. D. Lawrence in *Handbook of C-H Transformations, Vol. 2* (Ed.: G. Dyker), Wiley-VCH, Weinheim, **2005**, pp. 605–616; c) F. Shi, M. R. Smith, R. E. Maleczka, *Org. Lett.* **2006**, *8*, 1411–1414; d) T. A. Boebel, J. F. Hartwig, *J. Am. Chem. Soc.* **2008**, *130*, 7534–7535; e) P. Harrisson, J. Morris, T. B. Marder, P. G. Steel, *Org. Lett.* **2009**, *11*, 3586–3589.
- [6] a) J. Zhu, Z. Lin, T. B. Marder, *Inorg. Chem.* **2005**, *44*, 9384–9390; b) H. Braunschweig, P. Brenner, A. Miller, K. Radacki, D. Rais, K. Uttinger, *Chem. Eur. J.* **2007**, *13*, 7171–7176.
- [7] a) Y. Segawa, M. Yamashita, K. Nozaki, *Science* **2006**, *314*, 113–115; b) Y. Segawa, Y. Suzuki, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2008**, *130*, 16069–16079.
- [8] See, for example: a) D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–92; b) S. Diez-Gonzalez, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612–3676.
- [9] D. Vidovic, S. Aldridge, *Angew. Chem.* **2009**, *121*, 3723–3726; *Angew. Chem. Int. Ed.* **2009**, *48*, 3669–3672.
- [10] A. J. Ashe, *Organometallics* **2009**, *28*, 4236–4248.
- [11] For a recent article highlighting analogies between the isolobal BN and CC units in materials science, see: Z. Liu, T. B. Marder, *Angew. Chem.* **2008**, *120*, 248–250; *Angew. Chem. Int. Ed.* **2008**, *47*, 242–244.
- [12] a) G. Alcaraz, M. Grellier, S. Sabo-Etienne, *Acc. Chem. Res.* **2009**, *42*, 1640–1649; b) Y. Kawano, M. Uruichi, M. Shimoi, S. Taki, T. Kawaguchi, T. Kakizawa, H. Ogino, *J. Am. Chem. Soc.* **2009**, *131*, 14946–14957, and references therein.
- [13] For a recent reference, see: W. H. Bernskoetter, C. K. Schauer, K. I. Goldberg, M. Brookhart, *Science* **2009**, *326*, 553–556.
- [14] J. P. Collman, L. S. Hege, J. R. Norton, R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Sausalito, **1987**.
- [15] For an early spectroscopic report examining aminoborane interactions with transition metals see: a) G. Schmid, *Chem. Ber.* **1970**, *103*, 528–533. For recent reports revealing “side-on” modes of binding for anionic BN-containing ligands see, for example: b) J. Spielmann, S. Harder, *J. Am. Chem. Soc.* **2009**, *131*, 5064; c) T. D. Forster, H. M. Tuononen, M. Parvez, R. Roesler, *J. Am. Chem. Soc.* **2009**, *131*, 6689.
- [16] V. Pons, R. T. Baker, N. K. Szymczak, D. J. Heldebrant, J. C. Linehan, M. H. Matus, D. J. Grant, D. A. Dixon, *Chem. Commun.* **2008**, 6597–6599.
- [17] See, for example: a) T. J. Clark, K. Lee, I. Manners, *Chem. Eur. J.* **2006**, *12*, 8634–8648; b) T. B. Marder, *Angew. Chem.* **2007**, *119*, 8262–8264; *Angew. Chem. Int. Ed.* **2007**, *46*, 8116–8118; c) F. H. Stephens, V. Pons, R. T. Baker, *Dalton Trans.* **2007**, 2613–2626; d) C. W. Hamilton, R. T. Baker, A. Staubitz, I. Manners, *Chem. Soc. Rev.* **2009**, *38*, 279–293.
- [18] a) C. A. Jaska, K. Temple, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **2003**, *125*, 9424–9434; b) C. A. Jaska, I. Manners, *J. Am. Chem. Soc.* **2004**, *126*, 9776–9785; c) M. C. Denney, V. Pons, T. J. Hebden, D. M. Heinekey, K. I. Goldberg, *J. Am. Chem. Soc.* **2006**, *128*, 12048–12049; d) J. L. Fulton, J. C. Linehan, T. Autrey, M. Balasubramanian, Y. Chen, N. K. Szymczak, *J. Am. Chem. Soc.* **2007**, *129*, 11936–11949; e) T. J. Hebden, M. C. Penney, V. Pons, P. M. B. Piccoli, T. F. Koetzle, A. J. Schulz, W. Kaminsky, K. I. Goldberg, D. M. Heinekey, *J. Am. Chem. Soc.* **2008**, *130*, 10812–10820; f) B. L. Dietrich, K. I. Goldberg, D. M. Heinekey, T. Autry, J. C. Linehan, *Inorg. Chem.* **2008**, *47*, 8583–8585; g) R. Rousseau, G. K. Schenter, J. L. Fulton, J. C. Linehan, M. H. Engelhard, T. Autry, *J. Am. Chem. Soc.* **2009**, *131*, 10516–10524.
- [19] a) T. M. Douglas, A. B. Chaplin, A. S. Weller, *J. Am. Chem. Soc.* **2008**, *130*, 14432–14433; b) T. M. Douglas, A. B. Chaplin, A. S. Weller, X. Yang, M. B. Hall, *J. Am. Chem. Soc.* **2009**, *131*, 15440–15456; c) R. Dallanegra, A. B. Chaplin, A. S. Weller, *Angew. Chem.* **2009**, *121*, 7007–7010; *Angew. Chem. Int. Ed.* **2009**, *48*, 6875–6878.
- [20] a) L. Pasumansky, D. Haddenham, J. W. Clary, G. B. Fisher, C. T. Goralski, B. Singaram, *J. Org. Chem.* **2008**, *73*, 1898; b) L. Euzenat, D. Horhant, Y. Ribourdouille, C. Duriez, G. Alcaraz, M. Vaultier, *Chem. Commun.* **2003**, 2280–2281.
- [21] C. Y. Tang, W. Smith, D. Vidovic, A. L. Thompson, A. B. Chaplin, S. Aldridge, *Organometallics* **2009**, *28*, 3059–3066.
- [22] For a related example in Ir^{III} chemistry see: A. C. Cooper, E. Clot, J. C. Huffman, W. E. Streib, F. Maseras, O. Eisenstein, K. G. Caulton, *J. Am. Chem. Soc.* **1999**, *121*, 97–106.
- [23] J. Huang, E. D. Stevens, S. P. Nolan, *Organometallics* **2000**, *19*, 1194–1197.
- [24] For a previous example of an isolated metathesis intermediate see, for example: N. J. Patmore, M. L. Ingelson, M. F. Mahon, A. S. Weller, *Dalton Trans.* **2003**, 2894–2904.
- [25] D. J. Darensbourg, J. C. Yoder, G. E. Struck, M. W. Holtcamp, J. D. Draper, J. H. Reibenspies, *Inorg. Chim. Acta* **1998**, *274*, 115–121.
- [26] a) G. Alcaraz, E. Clot, U. Helmstedt, L. Vendier, S. Sabo-Etienne, *J. Am. Chem. Soc.* **2007**, *129*, 8704–8705; b) G. Alcaraz, U. Helmstedt, E. Clot, L. Vendier, S. Sabo-Etienne, *J. Am. Chem. Soc.* **2008**, *130*, 12878–12879.
- [27] J. Emsley, *The Elements*, 2nd ed., Oxford University Press, Oxford, **1991**.

- [28] Y. Gloaguen, G. Alcaraz, L. Vendier, S. Sabo-Etienne, *J. Organomet. Chem.* **2009**, 694, 2839–2841.
- [29] A ruthenium half-sandwich complex containing an η^2 -H₂BMes ligand has also been reported, featuring a Ru–B separation of 1.921(2) Å: K. D. Hesp, M. A. Rankin, R. McDonald, M. Stradiotto, *Inorg. Chem.* **2008**, 47, 7471–7473.
- [30] For an analysis of the effects of metal–boron bonding on ¹¹B chemical shifts see, for example: A. S. Weller, T. P. Fehlner, *Organometallics* **1999**, 18, 447–450.
- [31] Preliminary structural results indicate that if the reaction with *t*BuH₂N·BH₃ is allowed to proceed for ca. 72 h, then the corresponding *aminoborane* adduct [M(IMes)₂(H)₂-(H₂BNH*t*Bu)]⁺[BAR^F₄][–] is obtained.
- [32] Results derived from photoelectron spectroscopy imply that the BN π bonding orbital in H₂N=BH₂ is stabilized by 0.85 eV (ca. 80 kJ mol^{–1}) with respect to the corresponding orbital in H₂C=CH₂: N. P. C. Westwood, N. H. Westiuk, *J. Am. Chem. Soc.* **1986**, 108, 891–894.
-