DOI: 10.1002/ejic.200900465

Selective B–H versus N–H Bond Activation in Ammonia Borane by $[Ir(dppm)_2]OTf$

Andrea Rossin,[a] Maria Caporali,[a] Luca Gonsalvi,[a] Annalisa Guerri,[b] Agustí Lledós,[c] Maurizio Peruzzini,*[a] and Fabrizio Zanobini[a]

Dedicated to The Italian Chemical Society (SCI) on the occasion of its 100th Anniversary

Keywords: Boranes / NMR spectroscopy / Iridium / Hydrogen storage / P ligands

Ammonia borane (AB, $NH_3{\cdot}BH_3$) was activated selectively *on the boron hydrogen atoms* by $[Ir(dppm)_2]OTf$, as shown by variable-temperature ^{31}P, ^{11}B and ^{1}H NMR studies, to yield *cis*- and *trans*-$[Ir(H)_2(dppm)_2]OTf$ dihydrides. X-ray crystal structures of these complexes were obtained. DFT calculations suggest the key reaction intermediate to be a Lewis base (L) stabilised adduct, *cis*-$[Ir(H)(BH_2{\cdot}L)(dppm)_2]^+$

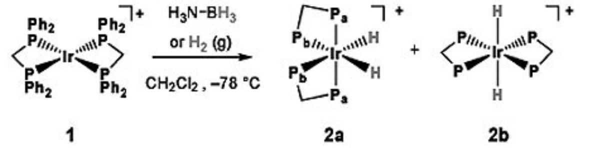
Introduction

Ammonia borane (AB, $NH_3{\cdot}BH_3$) represents a promising material for chemical hydrogen storage technology,[1,2] mainly because of its high hydrogen content (19.4 wt.-%) and its relative stability towards moisture and oxygen. In recent years, a growing number of publications on large-scale AB synthesis[3] and its thermal decomposition with H_2 release[4–7] have appeared. More recently, attention has been focussed on the interaction of AB with transition-metal complexes, in particular, those also used as catalysts for alkane dehydrogenation.[8–10] Transition-metal complexes of Rh,[11,12] Ni,[13] Ti,[14] Re,[15] Ru[16] and Ir[17–19] have been shown to catalyse H_2 release from AB under mild conditions. Very little attention has so far been devoted to the understanding of whether B–H versus N–H activation is preferred. We have recently started studying the chemistry of the highly reactive species $[Ir(dppm)_2]OTf$ (**1**), in particular, for P_4 activation.[20] As iridium complexes are able to catalytically dehydrogenate AB,[17–19] we thought to test **1** as a potential catalyst for AB activation.

Results and Discussion

Herein we report that **1** reacts with AB, which leads to the selective cleavage of the B–H bond to produce Ir^{III} hydrides as stable products in solution.

When a solution of **1** in CH_2Cl_2 was mixed with a thf solution of AB (1:1) at –78 °C, an immediate colour change from dark red to orange occurred, along with the formation of a dark brown precipitate. After slowly warming to room temperature, the supernatant turned from orange to yellow and finally to almost colourless. NMR analysis of the off-white solid obtained from the supernatant after workup showed that it consists of a mixture of *cis*- and *trans*-$[Ir(H)_2(dppm)_2]OTf$ (**2a**, **2b**), as confirmed by NMR and FTIR spectroscopy and X-ray crystal structure determination (Scheme 1). No boron-containing species was present, as shown by the absence of ^{11}B NMR signals.



Scheme 1. Synthesis of **2a**,**b** by reaction of **1** either with AB or H_2 (g).

The classical dihydrides **2** (T_{1min} = 490.4 ms, 257 K; 566.2 ms, 308 K for **2a** and **2b**, respectively)[21–24] were also obtained independently by gently bubbling H_2 (1 atm) into a CH_2Cl_2 solution of **1** at –78 °C. Variable-temperature NMR experiments (293–363 K) in CD_3NO_2 gave a $\Delta H°_r$ value of 0.72 kcal mol^{-1} for the **2a**/**2b** isomerisation from the van't Hoff plot of $\ln(K_{eq})$ vs. $1/T$. Anion exchange on **2** led

---

[a] Consiglio Nazionale delle Ricerche (CNR),
Istituto di Chimica dei Composti Organometallici (ICCOM)
Via Madonna del Piano 10, 50019 Sesto Fiorentino (Firenze), Italy
E-mail: maurizio.peruzzini@iccom.cnr.it
Homepage: http://www.iccom.cnr.it
[b] Università di Firenze, Centro di Cristallografia Strutturale (CRIST)
Sesto Fiorentino (Firenze), Italy
[c] Universitat Autònoma de Barcelona (UAB),
Departamento de Química Física,
Edifici Cn, Bellaterra (Barcelona), Spain

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.200900465.

to single crystals of *cis*-$[Ir(H)_2(dppm)_2]BF_4$ (**3**) and *trans*-$[Ir(H)_2(dppm)_2]PF_6{\cdot}(CH_3)_2CO$ (**4**), suitable for X-ray diffraction data collection (Figure 1). Both **3** and **4** exhibit geometrical features and metrical parameters in line with known octahedral classical Ir^{III} dihydrides (see Supporting Information).[25]

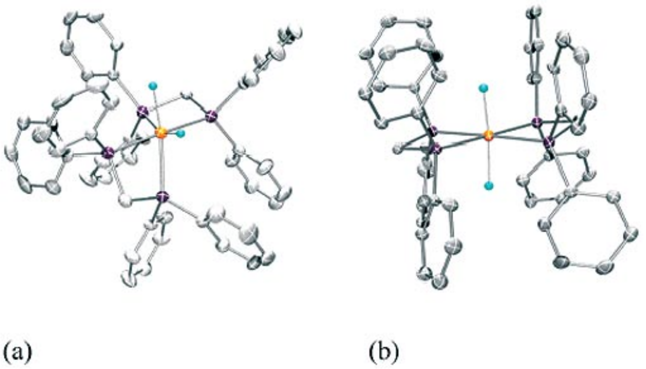

(a) (b)

Figure 1. ORTEP drawings of the cationic part of (a) *cis*-$[Ir(H)_2(dppm)_2]BF_4$ (**3**) and (b) *trans*-$[Ir(H)_2(dppm)_2]PF_6{\cdot}(CH_3)_2CO$ (**4**). H atoms on dppm omitted for clarity. Colour code: orange Ir, light grey C, violet P, turquoise hydrides. Ellipsoids drawn at 40% probability.

A small amount of dark precipitate was formed during the reaction and was found to be insoluble in most common organic solvents and poorly soluble in polar solvents such as dmso and MeCN. Preliminary ^{11}B NMR and IR analyses suggest the formation of (poly)borane derivatives.[26]

To shed some light on the reaction mechanism leading to **2**, we carried out a series of NMR-tube-scale reactions of **1** with AB, other Lewis base borane adducts $BH_3{\cdot}L$ [L = thf, SMe_2, NHC; NHC = $C\{N(2,6\text{-}Pr^i{}_2C_6H_3)CH\}_2$] and B_2H_6. No reaction of **1** with NH_3 was observed, even after prolonged bubbling at room temperature.[27] The same behaviour was observed by using the more basic diisopropylamine iPr_2NH. Reaction between **1** and borane adducts $BH_3{\cdot}L$ under the same conditions gave exactly the same products as those observed with AB, irrespective from the nature of L, thus strongly supporting the hypothesis that *only the borane part of AB reacts selectively* with **1**. Additional mechanistic information on the B–H activation process was obtained from variable-temperature (VT) NMR experiments (190–230 K range) and supported by DFT calculations.

^1H, ^{11}B and $^{31}P\{^1H\}$ VT-NMR spectra recorded on CD_2Cl_2 mixtures of **1** and different $BH_3{\cdot}L$ species reveal that the formation of **2** is preceded by the appearance of monohydride *cis*-$[Ir(H)(X)(dppm)_2]^+$ already at 190 K (X = donor ligand). This new species exhibits a broad doublet in the hydride region, whose chemical shift slightly depends on the nature of L [δ_H = –11.7 (L = NH_3), –11.1 (L = thf), –11.3 ppm (L = SMe_2)]. A strong $^2J_{H\text{-}Ptrans}$ with a value of ca. 110–120 Hz in all cases halves the intensity of the hydride signal, which suggests a *trans* disposition of this hydride with respect to one of the four dppm P atoms. Additional smaller H–P couplings broaden each doublet component into a broad multiplet (Figure S1, Supporting Information). In the $^{31}P\{^1H\}$ NMR spectra, a set of four different P atoms with the same multiplicity *but resonating at different chemical shifts* was detected for each L species; the observed δ_P differences, together with the aforementioned δ_H differences, may be considered as an indirect proof of the presence of L in the intermediate. For example, in the case L = NH_3 at 190 K, an ABCD spin system is observed; the four magnetically nonequivalent P atoms are clearly distinguishable (Figure 2). The signal labelled as P^4 is split into a doublet in the ^{31}P (proton-coupled) NMR spectrum, which confirms its *trans* disposition with respect to the hydride ligand in *cis*-$[Ir(H)(X)(dppm)_2]^+$. In the $^{11}B\{^1H\}$ NMR spectrum, only a broadening of the peak associated with the starting $BH_3{\cdot}L$ reagent was noticed, but no new peaks were observed.

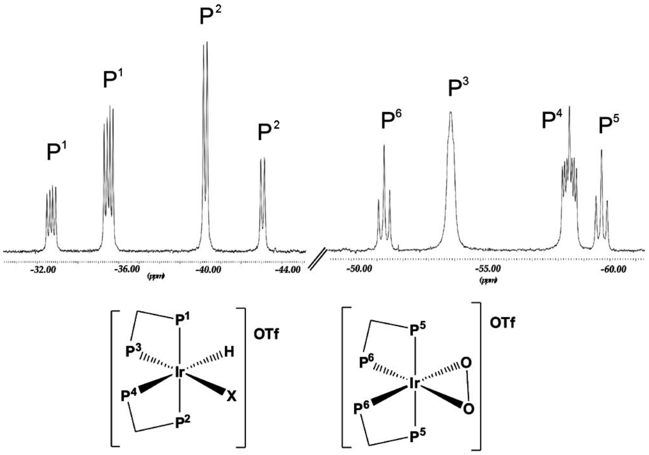


Figure 2. $^{31}P\{^1H\}$ NMR spectra of the 1:1 mixture of AB and **1** at 190 K (CD_2Cl_2/$[D_8]$thf). P^5 and P^6 belong to the *cis*-$[Ir(O_2)(dppm)_2]$-OTf (**5**) by-product.

Reaction of **1** with B_2H_6 does not show any intermediate, and **2a** is directly formed even at 190 K. Thus, the basicity of the Lewis base in $BH_3{\cdot}L$ can be used to tune the reactivity of borane with **1**. In the case of the NHC adduct, no reaction takes place, likely because of the steric hindrance around BH_3, which may limit access to the metal centre. On warming, *cis*-$[Ir(H)(X)(dppm)_2]^+$ slowly converts into **2a**, and completely disappears at 230 K. Above 273 K, **2b** starts to form, to reach a final 1:1 ratio to **2a** after 30 min. As boron is not detected by NMR methods after the formation of **2**, it is likely that all the boron introduced in solution as $BH_3{\cdot}L$ is lost in the dark precipitate that separated out.

At no time could the nature of ligand X in *cis*-$[Ir(H)(X)(dppm)_2]^+$ be unequivocally established by either ^{11}B or ^1H NMR spectroscopy, because of very dilute solutions with respect to $BH_3{\cdot}L$ (in order to have a 1:1 stoichiometric ratio with the metal complex) and rapid relaxation caused by the quadrupolar nature of both the ^{11}B and ^{15}N nuclei. Therefore, in order to gain additional insight, DFT calculations at the MPW1K//6-31+G(d,p) level were carried out to model possible intermediates along the reaction trajectory leading to **2**.

In order to have feasible computational times, the reaction key steps were studied by modelling **1** with the simpler cation [Ir(PH$_2$CH$_2$PH$_2$)$_2$]$^+$ (**1a**), by replacing the dppm phenyl groups with H atoms. Calculations confirmed the preferential interaction of **1a** with BH$_3$, as the interaction with NH$_3$ was found to be repulsive. Conversely, an energy barrier of only 7.8 kcal mol^{-1} for the B–H oxidative addition yielding *cis*-[Ir(H)(BH$_2$)(PH$_2$CH$_2$PH$_2$)$_2$]$^+$ (**7**) was found. DFT calculations show that **7** derives from an initial five-coordinate adduct [Ir(κ-B–BH$_3$)(PH$_2$CH$_2$PH$_2$)$_2$]$^+$ (**6**). The process is also thermodynamically favoured, as **7** lies at an energy level that is 11.9 kcal mol^{-1} below that of **6**. The same pathway was then modelled by considering AB instead of BH$_3$. An energy barrier of only 4.3 kcal mol^{-1} was found for the B–H oxidative addition (TS$_{\mathbf{8–9}}$, Figure 3), while the ΔE value for the formation of *cis*-[Ir(H)(BH$_2$·NH$_3$)(PH$_2$CH$_2$PH$_2$)$_2$]$^+$ (**9**, Figure 3) from an initial (κ^1-H)AB complex (**8**, Figure 3) was calculated to be –14.1 kcal mol^{-1}.

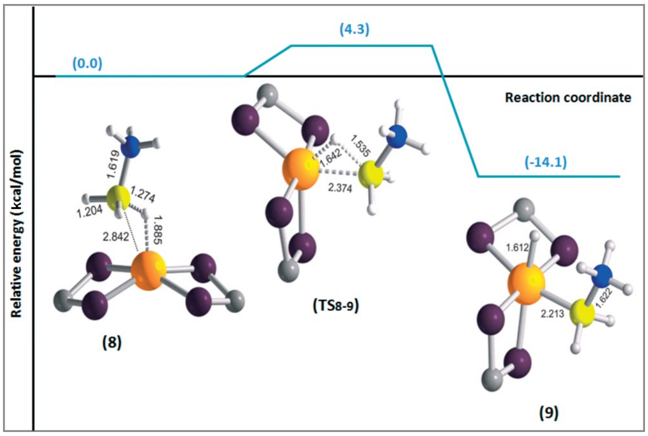
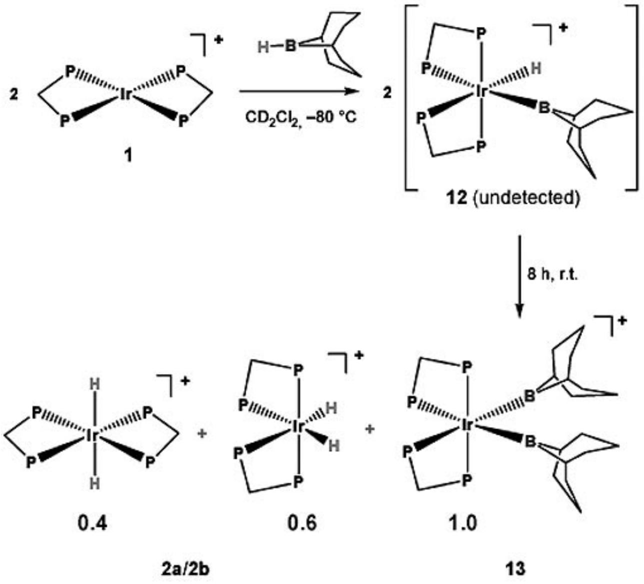


Figure 3. Reagent **8**, transition state TS$_{\mathbf{8–9}}$ and product **9** for the oxidative addition of AB to the model complex cation **1a**. H atoms on the dppm ligands omitted for clarity. Colour code: orange Ir, grey C, white H, violet P, yellow B, blue N. Selected calculated bond lengths reported in Å.

Formation of **8** strongly lowers the total energy content with respect to the isolated reagents AB and **1a** (ΔE = –13.5 kcal mol^{-1}). Optimisations and relative energy comparisons of the intermediate *cis*-[Ir(H)(X)(dppm)$_2$]$^+$ were performed on the real systems, with the inclusion of the dppm phenyl groups, through a QM:MM approach. The presence of the phenyl rings in the model system is fundamental in obtaining a properly small ΔE(**2a**–**2b**) value, calculated to be 0.64 kcal mol^{-1}, as already observed in analogous systems.[28]

Among the structures compatible with the NMR spectroscopic data, the only minima found were related to the oxidative addition product *cis*-[Ir(H)(BH$_2$·NH$_3$)(dppm)$_2$]$^+$ (**11**) and the η^1-(BH)-bound AB (**10**, see Supporting Information). Neither η^2-(BH)- nor σ(B–H)-bound borane complexes were found to be stable at the computational level used; in both cases, the QM:MM optimisation led to the separate reagents. A PES scan for the transformation **10** → **11** was attempted, which led to an approximate value of ca. 6.2 kcal mol^{-1} for the (overestimated) energy barrier of the oxidative addition reaction in the real system. The full-QM ΔE(**10**–**11**) value is –10.8 kcal mol^{-1}; the transformation is strongly favoured also in the real molecule. Thus, on the basis of the combined theoretical and experimental results, we suggest the ligand X in *cis*-[Ir(H)(X)(dppm)$_2$]$^+$ to be the BH$_2$·L fragment,[29] which forms by selective B–H cleavage from the η^1-(BH)-bound AB in **10**.

In order to further support the proposed mechanism and to clarify the fate of the boron-containing by-products, **1** was also reacted with the (less reactive) R$_2$BH derivative 9-BBN (9-borabicyclononane, Scheme 2).



Scheme 2. Reaction of **1** and 9-BBN to give **2a/2b** and **13**.

In keeping with our expectations, after 8 h of standing at room temperature, a mixture of **2a**, **2b** and *cis*-[Ir(BBN)$_2$(dppm)$_2$]OTf (**13**) was obtained in a 0.6:0.4:1 ratio (see Supporting Information for details); the latter species likely derives from ligand scrambling in the putative intermediate hydrido-boryl *cis*-[Ir(H)(BBN)(dppm)$_2$]$^+$ (**12**) complex, analogue of **11**.[30] The pathway leading from **12** to **2** and **13** is currently being examined by DFT methods.

Conclusions

In summary, [Ir(dppm)$_2$]OTf (**1**) reacts with ammonia borane by selective B–H versus N–H activation to give Ir^{III} dihydrides as final stable products. Initial B–H oxidative addition at low temperatures gives the labile complex *cis*-[Ir(H)(BH$_2$·NH$_3$)(dppm)$_2$]$^+$, which is stable in solution only between 190 and 230 K and at higher temperatures it evolves to the dihydrides **2a**,**b**. To the best of our knowledge, this is the first report on the oxidative addition of a (Lewis) base stabilised borane (BH$_3$·L) to an Ir centre.[31–37] The process also represents an additional step towards the understanding of hydrogen abstraction from aminoboranes and may contribute to the development of novel transition-metal-based organometallic systems capable of transforming AB efficiently for hydrogen storage purposes.

Experimental Section

Here, only the reaction of **1** with AB will be described; the remaining experimental details are provided in the Supporting Information. At first, a dilute solution of AB in thf was prepared by dissolving solid AB (200 mg, 1.61 mmol) in thf (50 mL) to give an AB concentration of 0.032 M. In a typical experiment, **1** (200 mg, 1.8 mmol) was dissolved in CH_2Cl_2 (30 mL). The solution was cooled to –78 °C by using a dry ice/acetone bath. AB (5.5 mL, 0.032 M solution in thf, 1 equiv. to **1**) was then syringed into the solution, and the mixture stirred at –78 °C for 15 min. An immediate colour change from dark red to orange was observed. The cooling bath was then removed, and the solution brought back to room temperature slowly, while stirring. After 15 h of stirring at room temperature, a small amount of dark brown precipitate (ca. 5 mg) formed, whilst an almost colourless supernatant was left behind. The mixture was filtered, and the filtrate dried in vacuo. The resulting off-white solid containing **2a/2b** was then redissolved in CD_2Cl_2 for NMR characterisation. The conversion based on **1** is quantitative and gives a mixture of **2a** (56.5%) and **2b** (43.5%). The **2a/2b** ratio was obtained by NMR methods by careful integration of the ^1H NMR signals in the hydride region. **2a**: IR (CH_2Cl_2): ν(Ir–H) = 2064 (br., m) cm^{-1}. ^1H NMR (300.13 MHz, CD_2Cl_2): δ_H = –11.4 (br. dpsq, $^2J_{H\text{-}Ptrans}$ = 105.4, $^2J_{H\text{-}Pcis}$ = 10.3 Hz, Ir–H) ppm. $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2): δ_P = –46.0 (t, $^2J_{P\text{-}P}$ = 22.2 Hz, P *trans* to P); δ_P = –57.0 (t, P *trans* to H) ppm. **2b**: IR (CH_2Cl_2): ν(Ir–H) = 1786 (br., m) cm^{-1}. ^1H NMR (300.13 MHz, CD_2Cl_2): δ_H = –7.50 (quintet, $^2J_{H\text{-}P}$ = 14.6 Hz, Ir–H) ppm. $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2): δ_P = –50.5 (s) ppm. By repeating the reaction by using either different ratios of AB/**1** (e.g. 3:1) or different $BH_3\cdot L$ species, a change in the nature and in the distribution of the products is not observed.

CCDC-723631 (**3**) and -723632 (**4**) 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.

Supporting Information (see footnote on the first page of this article): All the experimental procedures used to run VT-NMR studies of **1** with different $BH_3\cdot L$ species, crystallographic tables with selected bond lengths and angles for **3** and **4**, the computational methodology describing the DFT functional/basis set used and the optimised Cartesian coordinates of the calculated molecules (**8**, $TS_{\mathbf{8\text{–}9}}$, **9**, **10**, **11**), together with their gas phase absolute internal energies are presented.

Acknowledgments

The authors thank “FIRENZE HYDROLAB”, a project sponsored by Ente Cassa di Risparmio di Firenze (ECRF) and MIUR Rome (PRIN 2007), for supporting this project. A. R. would also like to thank the Centre de Supercomputació de Catalunya (CESCA) for providing additional computational resources.

---

[1] T. B. Marder, *Angew. Chem. Int. Ed.* **2007**, *46*, 8116.
[2] F. H. Stephens, V. Pons, R. T. Baker, *Dalton Trans.* **2007**, 2613.
[3] P. V. Ramachandran, P. D. Gagare, *Inorg. Chem.* **2007**, *46*, 7810.
[4] D. J. Heldebrandt, A. Karkamkar, N. J. Hess, M. Bowden, S. Rassat, F. Zheng, K. Rappe, T. Autrey, *Chem. Mater.* **2008**, *20*, 5332.
[5] A. C. Stowe, W. J. Shaw, J. C. Linehan, B. Schmid, T. Autrey, *Phys. Chem. Chem. Phys.* **2007**, *9*, 1831.
[6] M. E. Bluhm, M. G. Bradley, R. B. III, U. Kusari, L. G. Sneddon, *J. Am. Chem. Soc.* **2006**, *128*, 7748.
[7] F. H. Stephens, R. T. Baker, M. H. Mataus, D. J. Grant, D. A. Dixon, *Angew. Chem. Int. Ed.* **2007**, *46*, 746.
[8] I. Gottker-Schnetmann, P. White, M. Brookhart, *J. Am. Chem. Soc.* **2004**, *126*, 1804.
[9] C. M. Jensen, *Chem. Commun.* **1999**, 2443.
[10] K. Krogh-Jespersen, M. Czerw, N. Summa, K. B. Renkema, P. D. Achord, A. S. Goldman, *J. Am. Chem. Soc.* **2002**, *124*, 11404.
[11] Y. Chen, J. L. Fulton, J. C. Linehan, T. Autrey, *J. Am. Chem. Soc.* **2005**, *127*, 3254.
[12] J. L. Fulton, J. C. Linehan, T. Autrey, M. Balasubramanian, Y. Chen, N. K. Szymczac, *J. Am. Chem. Soc.* **2007**, *129*, 11936.
[13] R. J. Keaton, J. M. Blacquiere, R. T. Baker, *J. Am. Chem. Soc.* **2007**, *129*, 1844.
[14] T. J. Clark, C. A. Russell, I. Manners, *J. Am. Chem. Soc.* **2006**, *128*, 9582.
[15] Y. Jiang, H. Berke, *Chem. Commun.* **2007**, 3571.
[16] N. Blacquiere, S. Diallo-Garcia, S. I. Gorlesky, D. A. Black, K. Fagnou, *J. Am. Chem. Soc.* **2008**, *130*, 14034.
[17] X. Yang, M. B. Hall, *J. Am. Chem. Soc.* **2008**, *130*, 1798.
[18] A. Paul, C. B. Musgrave, *Angew. Chem. Int. Ed.* **2007**, *46*, 8153.
[19] M. C. Denney, V. Pons, T. J. Hebden, D. M. Heinekey, K. I. Goldberg, *J. Am. Chem. Soc.* **2006**, *128*, 12048.
[20] D. Yakhvarov, P. Barbaro, L. Gonsalvi, S. Manas-Carpio, S. Midollini, A. Orlandini, M. Peruzzini, O. Sinyashin, F. Zanobini, *Angew. Chem. Int. Ed.* **2006**, *45*, 4182.
[21] V. I. Bakhmutov, E. V. Bakhmutova, N. V. Belkova, C. Bianchini, L. M. Epstein, D. Masi, M. Peruzzini, E. S. Shubina, E. V. Vorontsov, F. Zanobini, *Can. J. Chem.* **2001**, *79*, 479.
[22] P. J. Desroisiers, L. Cai, Z. Lin, R. Richards, J. Halpern, *J. Am. Chem. Soc.* **1991**, *113*, 4173.
[23] V. L. Bakhmutov, E. V. Vorontsov, *Rev. Inorg. Chem.* **1998**, *18*, 183.
[24] V. I. Bakhmutov, *Practical Nuclear Magnetic Resonance for Chemists*, John Wiley & Sons Inc., NJ, **2005**.
[25] F. H. Allen, *Acta Crystallogr., Sect. B* **2002**, *58*, 380.
[26] All attempts at obtaining an unequivocal characterisation of the dark precipitate failed. The solid (typically 3–5 mg) was dried under vacuum for 5 h at room temperature prior to analysis. ^{11}B NMR (96.3 MHz, [D_6]dmso): δ_B = 1.39 (br. s); 20.13 (br. s, ca. 1:8 ratio) [cfr. $B(OH)_3$, δ_B = 18.0 ppm]. IR (CH_3CN): ν(B–O) = 1413 (as hydrolysed product) and ν(B–B) = 1276 cm^{-1}, frequencies calculated with the DFT/B3LYP method by using a 6-31G(d,p) basis set in the gas phase, model molecule was $B(OH)_2$–B(OH)–$B(OH)_2$. Examples of this behaviour are scarce in the literature; however the data do not match the formulation $[NH_2BH_3]_n$ proposed by Heinekey for the white precipitate obtained by Ir-catalysed AB dehydrogenation.[19] Neither DIP-MS analysis nor ATR-FTIR analyses carried out on the solid sample at the University of Parma (I) provided meaningful data (see Supporting Information).
[27] Only a small amount (<2%) of *cis*-[Ir(η^2-O_2)(dppm)$_2$]OTf (**5**) was observed, as detected from the appearance of two triplets at –52.3 and –61.0 ppm ($^2J_{PP}$ = 25.2 Hz) in the $^{31}P\{^1H\}$ NMR spectrum. A parallel experiment in which pure O_2 was bubbled into a solution of **1** confirmed our assignment. In the reaction with ammonia, **5** may be produced from traces of water and/or oxygen contained in the NH_3 used for the tests.
[28] M. Baya, O. Maresca, R. Poli, Y. Coppel, F. Maseras, A. Lledos, N. V. Belkova, P. A. Dub, L. M. Epstein, E. S. Shubina, *Inorg. Chem.* **2006**, *45*, 10248.
[29] The absence of a well-resolved ^{11}B-NMR signal may be due to both signal broadening at low temperature and extreme di-

lution of the solution, as reported in the literature for similar cases. See, for example: K. D. Hesp, M. A. Rankin, R. McDonald, M. Stradiotto, *Inorg. Chem.* **2008**, *47*, 7471.

[30] A similar scrambling behaviour was observed for the reaction of B_2Cat_2 [bis(catecholato)diboron] and HBCat (catecholborane)in the presence of Pt^0 species: A. Rossin, PhD Thesis, Cardiff University, **2004**.

[31] A. Staubitz, M. Besora, J. N. Harvey, I. Manners, *Inorg. Chem.* **2008**, *47*, 5910.

[32] M. W. Campian, E. Clot, O. Eisenstein, U. Helmstedt, N. Jasim, R. N. Perutz, A. C. Whitwood, D. Williamson, *J. Am. Chem. Soc.* **2008**, *130*, 4375.

[33] M. V. Campian, J. L. Harris, N. Jasim, R. N. Perutz, T. B. Marder, A. C. Whitwood, *Organometallics* **2006**, *25*, 5093.

[34] H. W. Lam, S. Shimada, A. S. Batsanov, Z. Lin, T. B. Marder, J. A. Cowan, J. A. K. Howard, S. A. Mason, G. J. McIntyre, *Organometallics* **2003**, *22*, 4557.

[35] R. T. Baker, D. W. Ovenall, J. C. Calabrese, *J. Am. Chem. Soc.* **1990**, *112*, 9399.

[36] Y. Kawano, M. Shimoi, *Chem. Lett.* **1998**, 935.

[37] Y. Kawano, T. Yasue, M. Shimoi, *J. Am. Chem. Soc.* **1999**, *121*, 11744.

Received: May 21, 2009