# Electronic Supplementary Information for

# Highly Active Ir(III)-NHC System for the Catalytic B-N Bond Activation and Subsequent Solvolysis of Ammonia Borane

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### **Experimental Section**

**General considerations.** Unless stated otherwise all reactions were carried out inside an MBraun Glovebox under inert conditions. Solvents were distilled and dried as required. Silanes were purchased from Sigma-Aldrich and used as received. [MCl(I<sup>t</sup>Bu')<sub>2</sub>] and [IrHCl(ItBu)(ItBu')] (2), [Ir(I<sup>t</sup>Bu')<sub>2</sub>][PF<sub>6</sub>] (3) and [Ir(H)<sub>2</sub>(I<sup>t</sup>Bu)<sub>2</sub>][PF<sub>6</sub>] (3) were prepared according to literature procedures.<sup>1,2</sup> <sup>1</sup>H, <sup>19</sup>F, <sup>31</sup>P and <sup>13</sup>C NMR spectra were recorded on either a Burker 400 MHz or a Bruker 300 MHz NMR spectrometer. Elemental Analyses were performed at the London Metropolitan University.

**Preparation of [Ir(NH<sub>3</sub>)(I'Bu')<sub>2</sub>][PF<sub>6</sub>].** A round bottom flask was charged with 100 mg (0.144 mmol) [Ir(I'Bu')<sub>2</sub>][PF<sub>6</sub>] and 7.0 mL CH<sub>2</sub>Cl<sub>2</sub>. NH<sub>3</sub> (30µL of 7.0 N in MeOH, 0.21 mmol) was added to the Ir solution and stirred for 10 minutes. The solvent was reduced to approximately 2.0 mL and the product was precipitated with 10 mL pentane. The product was collected in a glass frit and washed with 3 x 3.0 mL pentane to afford 97 mg (95% yield) of a brown powder. Crystals suitable for XRD were grown from a concentrated solution of CH<sub>2</sub>Cl<sub>2</sub> layered with pentane. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz)  $\delta$  (ppm): 7.35 (d, 2H, *J* = 1.7 Hz, imid-C*H*), 7.11 (d, 2H, *J* = 1.7 Hz imid-C*H*), 3.68 (br s, 2H, Ir-CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>), 3.60 (br s, 2H, Ir-CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>), 1.58 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.46 (s, 6H, Ir-CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>), NH<sub>3</sub> protons not observed. <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75.5 MHz)  $\delta$  (ppm): 119.37 (s, CH-imidazole), 116.41 (s, CH-imidazole), 67.40 (s, C'Bu), 58.25 (s, C'Bu),

<sup>&</sup>lt;sup>1</sup> Scott, N. M.; Dorta, R.; Stevens, E. D.; Correa, A.; Cavallo, L.; Nolan, S. P. J. Am. Chem. Soc. **2005**, *127*, 3516-3526.

<sup>&</sup>lt;sup>2</sup> Scott, N. M.; Pons, V.; Stevens, E. D.; Heinekey, D. M.; Nolan, S. P. Angew. Chem., Int. Ed. **2005**, 44, 2512-2515.

32.42 (s), 29.74 (s, C(CH<sub>3</sub>)<sub>3</sub>), 29.74 (s), 7.37 (s, C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>), carbenic C not observed. <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ (ppm) -73.4 ppm (d, <sup>1</sup>*J*<sub>FP</sub> = 711 Hz, PF<sub>6</sub>). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  (ppm): -150.2 ppm (sept, <sup>1</sup>*J*<sub>PF</sub> = 711 Hz, PF<sub>6</sub>). Anal. Calcd. for C<sub>22</sub>H<sub>41</sub>F<sub>6</sub>IrN<sub>5</sub>P (MW 712.78): C, 37.07; H, 5.80; N, 9.83. Found: C, 37.12; H, 5.88; N, 9.97.

**Preparation of [Ir(H)(NH<sub>3</sub>)(I'Bu)(I'Bu')][PF<sub>6</sub>].** A Schlenk tube was charged with 100 mg (0.144 mmol)  $[Ir(I'Bu')_2][PF_6]$  and 4 mL CH<sub>2</sub>Cl<sub>2</sub>. The solution was placed under 1 bar H<sub>2</sub> and stirred for 20 minutes. The hydrogen was removed and replaced with an Ar atmosphere. NH<sub>3</sub> (60µL of 7.0 N in MeOH, 0.42 mmol) was added to the Ir solution and stirred for 20 minutes. The solvent was reduced to approximately 2 mL and the product was precipitated with 10 mL pentane. The product was collected in a glass frit and washed with 3 x 3 mL pentane to afford 57 mg (55 % yield) of a brown powder. Crystals suitable for XRD were grown from a concentrated solution of CH<sub>2</sub>Cl<sub>2</sub> layered with pentane. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz) δ (ppm): 7.22 (br s, 1H, imid-CH), 7.15 (d, 1H, J = 2.2 Hz imid-CH), 7.05 (br s, 1H, imid-CH), 6.92 (d, 2H, J = 2.2 Hz imid-CH), 2.59 (br s, 3H, NH<sub>3</sub>) 2.37 (d, 1H, J = 12.5 Hz, Ir-CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>), 2.01 (d, 1H, J = 11.5 Hz, Ir- $CH_2C(CH_3)_2$ , 1.82 (br s, 9H,  $C(CH_3)$ ), 1.67 (s, 9H,  $C(CH_3)_3$ ), 1.48 (s, 3H, Ir- $CH_2C(CH_3)_2$ , 1.24 (s, 3H, Ir- $CH_2C(CH_3)_2$ ), 1.16 (br s, 9H,  $C(CH_3)_3$ ), -32.89 (s, 1H, Ir-H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75.5 MHz) δ (ppm): 171.45 (s, carbene C), 162.137 (s, carbene C) 119.48 (br s, CH-imidazole), 118.24 (s, CH-imidazole), 117.23 (br s, CH-imidazole), 115.27 (s, CH-imidazole), 65.10 (s, C'Bu), 59.44 (br s, C'Bu), 58.00 (br s, C'Bu), 56.94 (s, C<sup>t</sup>Bu), 30.40 (s), 30.738 (br s), 30.39 (s), 30.14 (s), 29.76 (s), 28.87 (br s), (s,  $C(CH_3)_3$ , 8.09 (s,  $C(CH_3)_2CH_2$ ).<sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ (ppm): -73.2 ppm (d, <sup>1</sup>J<sub>FP</sub> = 711 Hz, PF<sub>6</sub>). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  (ppm): -144.4 ppm (sept, <sup>1</sup>J<sub>PF</sub> = 711 Hz, PF<sub>6</sub>). Anal. Calcd. for C<sub>22</sub>H<sub>43</sub>F<sub>6</sub>IrN<sub>5</sub>P (MW 715.28): C, 36.97; H, 6.06; N, 9.80. Found: C, 36.89; H, 6.10; N, 9.73.

**Preparation** [NH<sub>4</sub>][B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>]. In the glovebox, a Schlenk tube was charged with 100 mg (3.24 mmol) NH<sub>3</sub>BH<sub>3</sub> and 5 mL THF. Separately, a 4 mL vial with a septum cap was filled with 3 mg (4.3 x 10-3 mmol) [Ir(I'Bu')<sub>2</sub>][PF<sub>6</sub>] and 0.5 mL THF. Both were brought from the glovebox. The Schlenk tube was attached to a bubbler. Using Schlenk techniques, 5.0 mL of degassed H<sub>2</sub>O was added to the AB solution and 0.5 mL of degassed H<sub>2</sub>O was added to the Ir solution. The catalyst solution was added to the ammonia borane solution. The reaction was stirred for 20 minutes. The THF was removed from the reaction mixture by vacuum distillation. The aqueous solution was washed 3 times with 4 mL of EtOAc. The aqueous layer was collected and evacuated to dryness to yield 220 mg (28 % yield) of a white powder. <sup>11</sup>B NMR (DMSO)  $\delta$  (ppm): 19.93 (br s, BO<sub>3</sub>), 1.30 (s, BO<sub>4</sub>). FTIR (KBr) v (cm-1): 3423 (sh), 3222 (s), 1457 (s) 1195(m), 1104 (w), 1024 (w), 924 (w) 884 (w) 781 (m), 740 (m) 645 (w), 546 (w).

**Catalytic Solvolysis of NH<sub>3</sub>BH<sub>3</sub>:** A solution of consisting of 13.9 mg (0.450 mmol) NH<sub>3</sub>BH<sub>3</sub> in 2.0 mL THF/H<sub>2</sub>O (1:1) was introduced to a sealed vessel under an N<sub>2</sub> atmosphere. The vessel possesses an injection port and stir bar and is adapted with a pressure gauge. The solution was warmed to the required temperature and allowed to equilibrate for at least 10 minutes at which point the catalyst was added to the reaction. Pressure change was recorded as a function of time. The ideal gas law equation PV = nRT was used to calculate the number of moles H<sub>2</sub> which evolved during catalysis. TOFs were calculated using the time required to reach  $[AB] = \frac{1}{2} [AB]_{int}$ .

#### NMR Reactions

**Reaction of [Ir(I'Bu')**<sub>2</sub>][**PF**<sub>6</sub>] with NH<sub>3</sub>BH<sub>3</sub>. In the glovebox, a J-Young NMR tube was charged with 10.0 mg (0.0143 mmol) [Ir(I'Bu')<sub>2</sub>][PF<sub>6</sub>] and dissolved in 0.4 mL of d<sub>8</sub>-THF. The tube was brought out of the glovebox and an additional 0.4 mL of D<sub>2</sub>O was added to the solution using Schlenk techniques. The sample was analyzed by <sup>1</sup>H NMR spectroscopy. Under an atmosphere of Ar, 50 mL of a solution consisting of 4.4 mg (0.143 mmol) NH<sub>3</sub>BH<sub>3</sub> in 0.5 mL d<sub>8</sub>-THF was added to the tube. The content of the tube was analyzed by <sup>1</sup>H NMR spectroscopy. The sample was again placed under inert atmosphere and an additional 100  $\mu$ L (2 equiv.) of the AB solution was added. Gas evolution was observed. A <sup>1</sup>H NMR spectrum was subsequently recorded.

**Reaction of [Ir(I'Bu')**<sub>2</sub>][**PF**<sub>6</sub>] with NH<sub>3</sub> and H<sub>2</sub>. In the glovebox, a J-Young NMR tube was charged with 10.0 mg (0.0143 mmol) [Ir(I'Bu')<sub>2</sub>][PF<sub>6</sub>] and dissolved in 0.7 mL CD<sub>2</sub>Cl<sub>2</sub>. The tube was brought outside of the glovebox and a <sup>1</sup>H NMR spectrum recorded. The tube was brought back in the glovebox and 3.0  $\mu$ L (0.021 mmol) of a 7.0N NH<sub>3</sub> in MeOH solution was added. The tube was brought out and a <sup>1</sup>H NMR spectrum was recorded. The sample was then connected to a Schlenk line and frozen in a dryice/acetone slurry. The atmosphere in the tube was evacuated and replaced with 1.0 atm H<sub>2</sub>. A <sup>1</sup>H NMR spectrum was subsequently recorded.

**Reaction of [Ir(I'Bu')\_2][PF\_6] with NH<sub>3</sub> and H<sub>2</sub>.** In the glovebox, a J-Young NMR tube was charged with 5.5 mg (0.0079 mmol)  $[Ir(I'Bu')_2][PF_6]$  and dissolved in 0.7 mL CD<sub>2</sub>Cl<sub>2</sub>. The tube was brought out of the box and a <sup>1</sup>H NMR spectrum was recorded. The sample was then connected to a Schlenk line and frozen in a dryice/acetone slurry. The atmosphere in the tube was evacuated and replaced with 0.5 atn H<sub>2</sub>. A <sup>1</sup>H NMR spectrum

was recorded of the sample. The tube was then taken in the glovebox and  $3.0 \ \mu\text{L}$  (0.021 mmol) of a 7.0N NH<sub>3</sub> in MeOH solution was added. The tube was brought out and a <sup>1</sup>H NMR spectrum recorded. The sample was then reconnected to a Schlenk line and cooled with a dry ice/acetone slurry. The atmosphere in the tube was evacuated and replaced with 1.0 atm H<sub>2</sub>. A <sup>1</sup>H NMR spectrum was subsequently recorded. Finally, the tube was connected to a Schlenk line, subjected to three free-pump-thaw cycles to remove any residual H<sub>2</sub> from the sample and a final <sup>1</sup>H NMR was recorded.



**Figure S1.** First order plot of the solvolysis of  $NH_3BH_3$  mediated by [IrCl(I<sup>*t*</sup>Bu<sup>2</sup>)]. Reactions run at 24, 38, 50 and 60°C. Reaction conditions: 0.450 mmol  $NH_3BH_3$ ; 0.05 mol% [Ir]; 2 mL THF/H<sub>2</sub>O (1:1). Additionally, first order dependence in catalyst concentration was observed when reaction was run at 0.025 mol% [Ir]. Reactions were monitored through at least 3 half-lives.



**Figure S2.** First order plot of the solvolysis of  $NH_3BH_3$  mediated by  $[Ir(I'Bu')][PF_6]$ . Reactions run at 24, 40, 50 and 60°C. Reaction conditions: 0.450 mmol  $NH_3BH_3$ ; 0.05 mol% [Ir]; 2 mL THF/H<sub>2</sub>O (1:1). Reactions were monitored through at least 3 half-lives.



**Figure S3.** NMR reaction of  $[Ir(I'Bu')_2][PF_6]$  (spectrum A) with NH<sub>3</sub> (spectrum B; 1.5 eqiuv NH<sub>3</sub> 7.0 N in MeOH) and subsequently H<sub>2</sub> (1.0 atm) (spectrum C). \* CD<sub>2</sub>Cl<sub>2</sub> denotes protio impurities and + denotes MeOH from NH<sub>3</sub> solution. Spectrum B shows quantitative formation of complex **5** from the reaction of **3** with NH<sub>3</sub>. Spectrum C shows that the reaction of Ir-NH<sub>3</sub> with 1.0 atm of H<sub>2</sub> results in loss of ammonia from the iridium along with bis-de-*ortho*-metalation of the 'Bu to for the dihydride species  $[Ir(H)_2(I'Bu')_2][PF_6]$  (**6**).



**Figure S4.** Starting from a solution of  $[Ir(H)_2(I^tBu)_2][PF_6]$  (6) generated in-situ from  $[Ir(I^tBu')_2][PF_6]$  and 0.5 atm H<sub>2</sub> (spectrum A) in CD<sub>2</sub>Cl<sub>2</sub>, addition of 2.65 equiv NH<sub>3</sub> led to a mixture of complex **6** and  $[Ir(H)(NH_3)(I^tBu)(I^tBu')][PF_6]$  (4) (spectrum B). Placing the reaction under one atmosphere of H<sub>2</sub> results in some of the Ir reverting to complex **6** (spectrum C). Removal of all the H<sub>2</sub> from the NMR tube resulted in a solution containing only **4** (spectrum D).  $K_{eq}$  at 298 K was calculated to be 0.85 for the reaction shown in eq. 7.



**Figure S5.** Comparison between  $[Ir(I'Bu')_2][PF_6]$  ( $\diamondsuit$ ),  $[Ir(NH_3)(I'Bu')_2][PF_6]$  ( $\blacktriangle$ ) and  $[Ir(H)_2(I'Bu)_2][PF_6]$  ( $\blacksquare$ ) in the solvolysis of NH<sub>3</sub>BH<sub>3</sub>. Reaction conditions: 0.450 mmol NH<sub>3</sub>BH<sub>3</sub>; 50 ppm [Ir]; 2 mL THF/H<sub>2</sub>O (1:1); 40°C.

Table S1	Crystallographic	data for com	plexes 4, 5	and [NH4][	$(B_5O_6)(OH)_4$
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Compound reference	borate	4	5
Complex	$[NH_4][(B_5O_6)(OH)_4]$	$[Ir(H)(NH_3)(I'Bu)(I'Bu')][PF_6]$	$[Ir(H)_2(I'Bu)_2][PF_6]$
Chemical formula	$B_5H_4O_{10}$ •NH <sub>4</sub> •2(H <sub>2</sub> O)	$C_{22}H_{43}IrN_5 \cdot PF_6$	C <sub>22</sub> H <sub>41</sub> IrN <sub>5</sub> PF <sub>6</sub>
Formula Mass	272.16	714.78	712.77
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
a/Å	11.304(6)	24.477(4)	11.312(4)
b/Å	11.020(6)	10.024(2)	23.910(7)
$c/\text{\AA}$	9.152(5)	22.326(5)	10.387(3)
$\alpha / ^{\circ}$	90.00	90.00	90.00
$\beta/^{\circ}$	90.00	90.00	100.755(4)
$\gamma/^{\circ}$	90.00	90.00	90.00
Unit cell volume/Å <sup>3</sup>	1140.0(10)	5478(2)	2760.1(14)
Temperature/K	93(2)	93(2)	93(2)
Space group	Aba2	Pbcn	P2(1)/c
No. of formula units per unit cell, $Z$	4	8	4
No. of reflections measured	3209	31789	27813
No. of independent reflections	1027	5024	5063
R <sub>int</sub>	0.0395	0.0659	0.0598
Final $R_l$ values $(l > 2\sigma(l))$	0.0241	0.0529	0.0493
Final $wR(F^2)$ values $(I > 2\sigma(I))$	0.0605	0.1208	0.1196
Final $R_1$ values (all data)	0.0242	0.0614	0.0544
Final $wR(F^2)$ values (all data)	0.0606	0.1256	0.1235
CCDC number			



S 13





![](_page_15_Figure_0.jpeg)

![](_page_16_Figure_0.jpeg)

 $[Ir(H)(NH_3)(I'Bu)(I'Bu')][PF_6] \mathbf{4}$  $^{31}P NMR CD_2Cl_2$ 

![](_page_17_Figure_1.jpeg)

![](_page_17_Figure_2.jpeg)

![](_page_18_Figure_0.jpeg)

![](_page_19_Figure_0.jpeg)

![](_page_20_Figure_0.jpeg)

![](_page_21_Figure_0.jpeg)

![](_page_21_Figure_1.jpeg)

![](_page_22_Figure_0.jpeg)

![](_page_23_Figure_0.jpeg)

![](_page_24_Figure_0.jpeg)

![](_page_25_Figure_0.jpeg)