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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Table of Contents

Experimental section	S2-6
Kinetic experiments and stoichiometric experiments	S6-11
XRD data	S12
Spectroscopic data	S13-S26

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^tBu')₂] and [IrHCl(ItBu)(ItBu')] (2), [Ir(I^tBu')₂][PF₆] (3) and [Ir(H)₂(I^tBu)₂][PF₆] (3) were prepared according to literature procedures.^{1,2} ¹H, ¹⁹F, ³¹P and ¹³C 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(NH₃)(I'Bu')₂][PF₆]. A round bottom flask was charged with 100 mg (0.144 mmol) [Ir(I'Bu')₂][PF₆] and 7.0 mL CH₂Cl₂. NH₃ (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 CH₂Cl₂ layered with pentane. ¹H NMR (CD₂Cl₂, 400 MHz) δ (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-CH₂C(CH₃)₂), 3.60 (br s, 2H, Ir-CH₂C(CH₃)₂), 1.58 (s, 18H, C(CH₃)₃), 1.46 (s, 6H, Ir-CH₂C(CH₃)₂), NH₃ protons not observed. ¹³C NMR (CD₂Cl₂, 75.5 MHz) δ (ppm): 119.37 (s, CH-imidazole), 116.41 (s, CH-imidazole), 67.40 (s, C'Bu), 58.25 (s, C'Bu),

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

² 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(CH₃)₃), 29.74 (s), 7.37 (s, C(CH₃)₂CH₂), carbenic C not observed. ¹⁹F NMR (CD₂Cl₂) δ (ppm) -73.4 ppm (d, ¹*J*_{FP} = 711 Hz, PF₆). ³¹P NMR (CD₂Cl₂) δ (ppm): -150.2 ppm (sept, ¹*J*_{PF} = 711 Hz, PF₆). Anal. Calcd. for C₂₂H₄₁F₆IrN₅P (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)(NH₃)(I'Bu)(I'Bu')][PF₆]. A Schlenk tube was charged with 100 mg (0.144 mmol) $[Ir(I'Bu')_2][PF_6]$ and 4 mL CH₂Cl₂. The solution was placed under 1 bar H₂ and stirred for 20 minutes. The hydrogen was removed and replaced with an Ar atmosphere. NH₃ (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 CH₂Cl₂ layered with pentane. ¹H NMR (CD₂Cl₂, 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, NH₃) 2.37 (d, 1H, J = 12.5 Hz, Ir-CH₂C(CH₃)₂), 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). ¹³C NMR (CD₂Cl₂, 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^tBu), 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, $C(CH_3)_2CH_2$).¹⁹F NMR (CD₂Cl₂) δ (ppm): -73.2 ppm (d, ¹J_{FP} = 711 Hz, PF₆). ³¹P NMR (CD₂Cl₂) δ (ppm): -144.4 ppm (sept, ¹J_{PF} = 711 Hz, PF₆). Anal. Calcd. for C₂₂H₄₃F₆IrN₅P (MW 715.28): C, 36.97; H, 6.06; N, 9.80. Found: C, 36.89; H, 6.10; N, 9.73.

Preparation [NH₄][B₅O₆(OH)₄]. In the glovebox, a Schlenk tube was charged with 100 mg (3.24 mmol) NH₃BH₃ 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')₂][PF₆] 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 H₂O was added to the AB solution and 0.5 mL of degassed H₂O 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. ¹¹B NMR (DMSO) δ (ppm): 19.93 (br s, BO₃), 1.30 (s, BO₄). 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 NH₃BH₃: A solution of consisting of 13.9 mg (0.450 mmol) NH₃BH₃ in 2.0 mL THF/H₂O (1:1) was introduced to a sealed vessel under an N₂ 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 H₂ 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')₂][**PF**₆] with NH₃BH₃. In the glovebox, a J-Young NMR tube was charged with 10.0 mg (0.0143 mmol) [Ir(I'Bu')₂][PF₆] and dissolved in 0.4 mL of d₈-THF. The tube was brought out of the glovebox and an additional 0.4 mL of D₂O was added to the solution using Schlenk techniques. The sample was analyzed by ¹H NMR spectroscopy. Under an atmosphere of Ar, 50 mL of a solution consisting of 4.4 mg (0.143 mmol) NH₃BH₃ in 0.5 mL d₈-THF was added to the tube. The content of the tube was analyzed by ¹H NMR spectroscopy. The sample was again placed under inert atmosphere and an additional 100 μ L (2 equiv.) of the AB solution was added. Gas evolution was observed. A ¹H NMR spectrum was subsequently recorded.

Reaction of [Ir(I'Bu')₂][**PF**₆] with NH₃ and H₂. In the glovebox, a J-Young NMR tube was charged with 10.0 mg (0.0143 mmol) [Ir(I'Bu')₂][PF₆] and dissolved in 0.7 mL CD₂Cl₂. The tube was brought outside of the glovebox and a ¹H NMR spectrum recorded. The tube was brought back in the glovebox and 3.0 μ L (0.021 mmol) of a 7.0N NH₃ in MeOH solution was added. The tube was brought out and a ¹H 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 H₂. A ¹H NMR spectrum was subsequently recorded.

Reaction of [Ir(I'Bu')_2][PF_6] with NH₃ and H₂. 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 CD₂Cl₂. The tube was brought out of the box and a ¹H 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 H₂. A ¹H 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 NH₃ in MeOH solution was added. The tube was brought out and a ¹H 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 H₂. A ¹H 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 H₂ from the sample and a final ¹H NMR was recorded.



Figure S1. First order plot of the solvolysis of NH_3BH_3 mediated by [IrCl(I^{*t*}Bu²)]. Reactions run at 24, 38, 50 and 60°C. Reaction conditions: 0.450 mmol NH_3BH_3 ; 0.05 mol% [Ir]; 2 mL THF/H₂O (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/H₂O (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 NH₃ (spectrum B; 1.5 eqiuv NH₃ 7.0 N in MeOH) and subsequently H₂ (1.0 atm) (spectrum C). * CD₂Cl₂ denotes protio impurities and + denotes MeOH from NH₃ solution. Spectrum B shows quantitative formation of complex **5** from the reaction of **3** with NH₃. Spectrum C shows that the reaction of Ir-NH₃ with 1.0 atm of H₂ 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 H₂ (spectrum A) in CD₂Cl₂, addition of 2.65 equiv NH₃ 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 H₂ results in some of the Ir reverting to complex **6** (spectrum C). Removal of all the H₂ 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 NH₃BH₃. Reaction conditions: 0.450 mmol NH₃BH₃; 50 ppm [Ir]; 2 mL THF/H₂O (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 ₄ •2(H ₂ O)	$C_{22}H_{43}IrN_5 \cdot PF_6$	C ₂₂ H ₄₁ IrN ₅ PF ₆
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 ³	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 _{int}	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









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





















