ORGANOMETALLICS

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

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Supporting Information

ABSTRACT: A series of coordinatively unsaturated NHC– Ir(III) complexes are examined in terms of their catalytic activity toward the solvolysis of ammonia–borane (AB). Utilization of $[Ir(I'Bu')_2Cl]$ (2) and $[Ir(I'Bu')_2][PF_6]$ (3) at 50 ppm catalyst loading led to reactions evolving approximately 3 equiv of H₂ within 10 min at 40 °C. The activation parameters of the



reaction were measured to be $\Delta H^{\ddagger} = 11.1 \text{ kcal/mol and } \Delta S^{\ddagger} = 30.9 \text{ eu.}$ Mechanistic investigations revealed an equilibrium between $[\text{Ir}(\text{H})(\text{NH}_3)(\text{I}^t\text{Bu})(\text{I}^t\text{Bu}')][\text{PF}_6](4) + \text{H}_2 \text{ and } [\text{Ir}(\text{H})_2(\text{I}^t\text{Bu})_2][\text{PF}_6](6) + \text{NH}_3$. Spectroscopic data suggest that complexes 4 and 6 are the resting state of the active catalyst. X-ray structures of complex 4 and $[\text{Ir}(\text{NH}_3)(\text{I}^t\text{Bu}')_2][\text{PF}_6](5)$ are given.

INTRODUCTION

The ongoing search for alternative fuel supplies has, within the past decade, focused attention on the hydrogen-dense ammoniaborane (AB). Containing more hydrogen per weight then even liquid hydrogen, ammonia-borane provides a stable source of transportable hydrogen for subsequent consumption to produce energy. Catalytic solvolysis as shown in eq 1 is one method to liberate the hydrogen stored in the hydrogen-rich ammonia—borane. Several recent reviews highlight advances in the catalytic solvolysis of AB. $^{1-6}$ Acid-catalyzed solvolysis is the oldest known method to produce hydrogen from AB.⁷ Heterogeneous catalysts have shown high activity in the solvolysis. Platinum (20% on graphite)⁸ and rhodium colloids⁹ have both been shown to be highly active in the solvolysis of AB. Amoroso and Abdur-Rashid have recently disclosed a highly active Ir(III) pincer-type complex which is capable of rapidly releasing nearquantitative amounts of hydrogen at within 10 min at 40 °C with loadings of 90 ppm.¹⁰

$$NH_{3}BH_{3} \xrightarrow{[cat.]]{}} nH_{2} \uparrow + products \qquad (1)$$

In 2005 our group disclosed a series of ortho-metalated Ir and Rh complexes.¹¹ The complexes are prepared (Figure 1) by a simple substitution reaction of $[MCl(coe)_2]_2$ (M = Ir, Rh; coe = cyclooctene) with 4 equiv of I^tBu (I^tBu = 1,3-bis(*tert*-butyl)-2*H*-imidazol-2-ylidene). Complex 1 ([IrHCl(I^tBu')(I^tBu)]) is formed within 20 h and exhibits an ortho metalation of one I^tBu ligand. Ortho metalation of the second I^tBu is much slower and occurs over a period of 5 days; it is aided by repeated removal of liberated hydrogen using vacuum. The cationic complex is formed quickly when reacted with AgPF₆. Complexes 2 and 3 are remarkable, as the ortho metalation of the two NHCs occurs in a mutually cis arrangement. Also, the I^tBu ligand intramolecular C–H activation is reversible.^{12,13} Under pressures of H₂, 2 can be converted back to 1. Additionally, complex 3 has been reported to be

transformed into $[Ir(I^tBu)_2(H)_2][PF_6]$ when placed under an atmosphere of hydrogen. Only recently have we turned our attention to catalytic applications of these unusual complexes.¹⁴

Development of the bis-ortho-metalated NHC—Ir complexes shown in Figure 1 seemed a promising candidate for catalytic solvolysis of AB. Herein, we report details of these catalytic studies that showed the cationic iridium species **3** to be extremely active in the catalytic solvolysis of AB. Additionally, mechanistic aspects of the reaction have been investigated.

RESULTS AND DISCUSSION

Optimization of reaction conditions found the reaction to be most efficient in a 1:1 mixture of THF and H_2O . A mixture of isopropyl alcohol and H_2O (1:1) resulted in similar reaction times (see Figure 2). Of the two iridium complexes tested, the cationic complex 3 was found to display higher activity. While 2 was found to give an admirable TOF of 111 500 h⁻¹, 3 was considerabley more active with a TOF of 173 000 h⁻¹ at 24 °C and 500 ppm catalyst loadings (see Figure 3).¹⁵ Further reduction of catalyst loading of 3 to 50 ppm was possible and operated best at the slightly elevated temperature of 40 °C, as shown in eq 2. Figure 4 shows a plot of the pressure change as a result of hydrogen evolution from the isothermal reaction.

$$NH_{3}BH_{3} \xrightarrow{[Ir] 50 \text{ ppm}} 3H_{2} \uparrow + \text{ products}$$
(2)
$$\xrightarrow{H_{2}O/THF(1:1)} 3H_{2} \uparrow + \text{ products}$$

Although the byproduct of the reaction could not be unambiguously identified using analytical methods, single crystals suitable for diffraction revealed the production of the ammonium—borate salt $[NH_4][B_5O_{10}H_4] \cdot 2H_2O$ as shown in Figure 5. The ammonia borate salt is most likely in equilibrium with other

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Figure 1. Synthesis of [IrHCl(I'Bu')(I'Bu)] (1), $[IrCl(I'Bu')_2]$ (2), and $[Ir(I'Bu')_2][PF_6]$ (3).



Figure 2. Comparison of the use of ^{*i*}PrOH/H₂O (green \blacktriangle) vs THF/ H₂O (blue \blacklozenge) for the solvolysis of NH₃·BH₃ using [Ir(I^fBu')₂][PF₆]. Reaction conditions: 0.450 mmol of NH₃·BH₃; 50 ppm of [Ir]; 2 mL of solvent; 40 °C.

polyborate salts, as aqueous solutions of alkali borates are known to readily take part in these equilibria.^{17 11}B{¹H} NMR of the borate displayed a chemical shift of 19.9 ppm, consistent with a trigonal BO₃, and a shift at 1.3 ppm is in line with a tetrahedral BO₄⁻ boron.¹⁷ Formation of the polyborate salt in conjunction with the pungent smell of ammonia of the completed reaction mixture strongly suggests that the reaction may proceed as shown in eq 3.¹⁸ Interestingly, recent industrial interest has been noted for $[B_5O_{10}][NH_4] \cdot 2H_2O$ as a material for nonlinear fiber optics.¹⁹

$$NH_{3}BH_{3} + 2H_{2}O \xrightarrow[THF/H_{2}O(1:1)]{3500 \text{ ppm}}{}_{THF/H_{2}O(1:1)} 3H_{2} + \frac{1}{5}[NH_{4}][B_{5}O_{10}H_{4}] + \frac{4}{5}NH_{3}$$
(3)

If the reaction proceeds as shown in eq 3, this would denote that half of the hydrogen produced is derived from the water in the reaction media. To test this theory we chose to use Me_2HNBH_3 as a source of hydrogen. As shown in Figure 6, the reaction proceeded much slower, presumably due to the increased



Figure 3. Comparison of cationic $[Ir(I'Bu')_2][PF_6]$ (blue ◆) and the neutral $[IrCl(I'Bu')_2]$ (green ▲) in the solvolysis of NH₃·BH₃. Reaction conditions: 0.450 mmol of NH₃·BH₃; 500 ppm of [Ir]; 2 mL of THF/ H₂O (1/1); 24 °C.



Figure 4. Catalytic solvolysis of AB in THF/H₂O (1/1) with 50 ppm of $[Ir(I^{1}Bu')_{2}][PF_{6}]$ at 40 °C. The pressure change equates to approximately 3 mol of H₂ released/mol of AB.

steric bulk of the substrate, but approximately 3 mols of H_2 were evolved per mole of Me_2HNBH_3 . Solvolysis of Me_2NHBH_3 required 40 min to release 3 mol H_2 per mol of substrate.

Kinetic studies of the catalytic solvolysis were carried out between the temperatures of 24 and 60 °C. The reaction was found to be first order overall in ammonia-borane (see the Supporting Information, Figures S1 and S2). An Eyring plot (Figure 7) of the rate constants for the reaction revealed similar enthalpies and entropies of activation for the catalytic solvolysis of 2 (ΔH^{\ddagger} = +11.1 kcal/mol, ΔS^{\ddagger} = +44.6 cal/ (mol K)) and 3 (ΔH^{\ddagger} = +10.0 kcal/mol ΔS^{\ddagger} = +41.7 cal/(mol K)). These activation parameters suggest a similar rate-limiting transition state for both complexes. The $-\Delta S^{\dagger}$ term implies a more highly ordered transition state. Most likely this is derived from the initial Ir-AB interaction. The hydrolysis of the liberated borane should be relatively barrierless, and as such the activation enthalpies determined here are suspected to mainly result from the cleavage of the B-N bond of the ammonia-borane.



Figure 5. ORTEP representation of the major product $[B_5O_{10}H_4]$ - $[NH_4]$ from AB solvolysis promoted by $[Ir(I'Bu')_2][PF_6]$. Two molecules of H_2O within the unit cell have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. X-ray data are consistent with those originally reported by Loboda et al.¹⁶

Mechanistic studies were conducted by examining a series of stoichiometric reactions (Figure 8). The reaction of 1 equiv of AB with complex 3 in a D_2O/d_8 -THF mixture (1/1) (eq 4) resulted in the formation of a mixture of $[Ir(H)(NH_3)-(I^tBu')][PF_6]$ (4) and $[Ir(H)_2(I^tBu)_2][PF_6]$ (6) as shown in eq 4. Product identification was performed by ¹H NMR (see the Supporting Information, Figure S3). Addition of an extra 2 equiv of AB led to a slight decrease in intensity of the shifts assigned to complex 4. These findings prompted us to investigate the reaction of NH₃ and H₂ with complex 3.



Reactions involving equimolar amounts of **3** and methanol solutions of ammonia resulted in the nearly quantitative production of $[Ir(NH_3)(I^tBu')_2][PF_6]$ (**5**), as shown in eq 5. In this complex both ^tBu groups remain ortho metalated. To confirm that the ortho demetalation observed in **4** was the result of the presence of H₂ in the reaction mixture, complex **5** was placed under 1.0 atm of H₂, as shown in eq 6. Somewhat surprisingly, this reaction produced the dihydride $[Ir(H)_2-(I^tBu)_2][PF_6]$ with loss of the bound NH₃ (see the Supporting Information, Figure S4). It appears as though ortho demetalation may help facilitate the loss of the weakly bound ammonia ligand.



Figure 6. Pressure change as the result of the solvolysis of Me_2NHBH_3 using $[Ir(1'Bu')_2][PF_6]$. Reaction conditions: 0.450 mmol of Me_2NHBH_3 ; 50 ppm of [Ir]; 2 mL of THF/H₂O (1/1); 40 °C. Even though Me_2 -NHBH₃ only possess 2 mol of H₂, the reaction still produces 3 mol of H₂. This confirms that H₂O is also a source of hydrogen in the reaction.



Figure 7. Eyring plot of the catalytic solvolysis of ammonia—borane in THF/H₂O (1:1) with $[IrCl(I^tBu')_2]$ (black squares) and $[Ir(I^tBu')_2][PF_6]$ (red triangles) releasing approximately 3 equiv of H₂.



Additionally a reversible equilibrium between complexes 4 and 6 was found to exist, as shown in eq 7. Results from ¹H NMR experiments are shown in Figure 9 and in Figure S5 in the Supporting Information. Spectrum A of Figure 9 shows complex 6 (formed in situ from 3 and 0.5 bar of H₂). In spectrum B, the addition of 2.65 equiv of NH₃ led to a mixture of complexes 4 (88%) and 6 (12%). Subsequent addition of 0.5 atm of H₂ to the



Figure 8. Reaction of $[Ir(I^tBu')_2][PF_6]$ (3; spectrum A) with 1.0 equiv of $NH_3 \cdot BH_3$ (spectrum B) and an additional 2.0 equiv (3 equiv total) of $NH_3 \cdot BH_3$ (spectrum C). Reaction of 3 with 1.0 equiv of $NH_3 \cdot BH_3$ shows the formation of $[Ir(H)(NH_3)(I^tBu')][PF_6]$ (4) and $[Ir(H)_2(I^tBu)_2][PF_6]$ (6). In spectrum C, a total of 3.0 equiv of $NH_3 \cdot BH_3$ has been added to the reaction mixture. Upon mixing, further gas evolution was observed. The NMR spectra show a decrease in intensity of the shifts assigned to 6 on going from spectrum B to spectrum C. This is attributed to the increase in the concentration of free NH_3 being greater than the concentration of dissolved H_2 in solution. This shifts the equilibrium formed between species 4 and 6 toward a greater concentration of 4.



Figure 9. NMR spectra displaying the equilibrium formed between $[Ir(H)_2(I^tBu)_2][PF_6]$ (6) and $[Ir(H)(NH_3)(I^tBu)_2][PF_6]$ (4). The shifts of the complexes shown are the carbene backbone and hydride peaks. The asterisk denotes the residual protio impurities in the solvent. See text for details.

reaction mixture resulted in a decrease of NMR shifts attributed to species 4 (74%) and an increase in intensity of shifts of complex 6 (26%) (Figure 9, spectrum C). Removal of H_2 from the NMR tube converts the remaining 6 into 4, as shown in spectrum D of Figure 9.



Complexes 4 and 6 were both tested in the catalytic solvolysis of ammonia—borane. Both exhibited equal activity to 3 (see the Supporting Information, Figure S6). Most likely, these complexes act as the resting state of the active catalyst, as stoichometric reactions between 3 and AB in D_2O/d_8 -THF resulted in a mixture of both complexes, as determined by ¹H NMR (see Figure 8).

Single crystals of complexes 4 and 5 suitable for X-ray analysis were grown from slow vapor diffusion of pentane into a saturated solution of THF. ORTEP representations of these complexes are shown in Figure 10.²⁰ Relatively few crystal structures of monomeric Ir^{III} —NH₃ complexes are known.²¹ The Ir—N(1) bond lengths confirmed the ligation of NH₃ (as opposed to NH₂ through N—H bond activation by the metal center). The Ir—N bond lengths were determined to be 2.260(7) and 2.233(7) Å for complexes 4 and 5, respectively. The formation of an ammonia adduct is not surprising, as complex 3 was shown to readily bind CO.¹¹

A mechanism consistent with the aforementioned experimental results is depicted in Scheme 1. The coordinatively unsaturated cationic complex is suspected of forming a loosely bonded complex with AB. Aldridge et al. have recently reported the similar complex [Ir(IMes)₂(H)₂(μ -H)₂B(H)NMe₃][BAr⁷₄] (IMes = $N_{,}N'$ bis(2,4,6-trimethylphenyl)imidazol-2-ylidene).²² The next step involves cleavage of the B–N bond of AB and subsequent hydrolysis of borane. In the presence of an aqueous medium, the borane should readily hydrolyze to form a number of different borate salts with the concomitant release of H₂. Reaction of the Ir–NH₃ complex with H₂ serves to promote the reverse ortho metalation process, forming complex **5**.



Figure 10. ORTEP representations of $[Ir(H)(NH_3)(I^tBu)']^{-}$ [PF₆] (4) and $[Ir(NH_3)(I^tBu')_2][PF_6]$ (5). All hydrogens except hydride and the counterion PF₆⁻ are omitted for clarity. Ir(1)-N(1) = 2.260(7) Å (4) and 2.233(7) Å (5).

Scheme 1. Plausible Mechanism for the Catalytic Solvolysis of Ammonia–Borane Promoted by $[Ir(I^tBu')_2][PF_6]$ (3)



If a significant amount of hydrogen is present, complex 5 would be converted to the dihydride complex 6. These complexes would serve as the resting state of the active catalyst. Dissociation of the weak ammonia ligand from complex 5 followed by ligation of AB completes the catalytic cycle. Likewise, complexation of AB to 6 could result in a species similar to those disclosed by the Aldridge group.²²

An interesting aspect of the reaction is that 3 mol of H_2 is produced from 1 mol of AB. Half of the evolved hydrogen is obtained from H_2O . If the ultimate fate of the released H_2 is combustion, then the H_2O used in the overall reaction of hydrolysis and combustion would then, formally be used in a catalytic fashion. The resulting energy would therefore be produced from the recycling of water.

In conclusion, we have demonstrated the use of unusual, formally 14e, bis-ortho-metalated Ir–NHC complexes as highly active catalysts in the solvolysis of ammonia–borane. The reaction is proposed to proceed through Ir-mediated cleavage of the B–N bond followed by hydrolysis of the liberated borane by the reaction solvent. Two cationic Ir–NH₃ complexes have been isolated and are proposed to be resting states of the active catalyst. Further development of the ortho-metalated complexes $[Ir(I^tBu')_2][PF_6]$ as catalysts is currently underway in our laboratories.

ASSOCIATED CONTENT

Supporting Information. Text giving the experimental section and figures, tables, and CIF files giving NMR spectra for high-pressure experiments, data for kinetic experiments, and crystallographic data for $[B_5O_{10}H_4][NH_4]$, 4, and 5. This material is available free of charge via the Internet at http://pubs.acs.org.

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