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Efficient Homogeneous Hydridoirida-β-diketone-Catalyzed Methanolysis of Ammonia-Borane for Hydrogen Release in Air. Mechanistic Insights.

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ABSTRACT

The dihydridoirida-β-diketone $[(IrH\{(PPh_2(o\text{-}C_6H_4CO))_2H\})_2(\mu\text{-}Cl)][BF_4]$ (**2**) has been used as a homogeneous catalyst for the methanolysis of ammonia-borane to release up to 3 equivalents of hydrogen in the presence of air. With catalyst loadings as low as 0.2 mol%, ammonia-borane undergoes methanolysis within 6 min at 30 ºC, with $TOF_{50\%}$ of 320 $mol_{H_2}\cdot mol_{Ir}^{-1}\cdot min^{-1}$, or within 80 s at 60 ºC, with an excellent $TOF_{50\%}$ of 1991 $mol_{H_2}\cdot mol_{Ir}^{-1}\cdot min^{-1}$, and maintains its catalytic activity in consecutive runs. Triethylamine-borane fails to undergo methanolysis. Kinetic studies indicate first-order dependence on substrate and on catalyst concentration and suggest cleavage of the solvent O–H bond being involved in the rate determining step of the reaction. In methanol solution **2** forms cationic $[IrH(MeOH)\{(PPh_2(o\text{-}C_6H_4CO))_2H\}]^+$ (**3**) and reacts with $Et_3N{-}BH_3$ to afford a hydridoirida-β-diketone $[IrH(Me_3NBH_3)\{(PPh_2(o\text{-}C_6H_4CO))_2H\}]^+$ (**4**), with the borane adduct η^1-coordinated to iridium. Compound [**4**][$BAr^F{}_4$] shows dynamic behaviour in solution due to exchange of bridging and terminal B–H bonds. A multinuclear NMR study of the catalyzed reaction shows the formation of two ammonia-methoxyborane adduct

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intermediates, $H_3N–BH_2(OCH_3)$ and $H_3N–BH(OCH_3)_2$, and of iridium species proposed of the hydridodiacyl type $[IrH(H_3NBH_{3-x}(OCH_3)_x)(PPh_2(o\text{-}C_6H_4CO))_2]$ with a coordinated borane adduct. On account of experimental evidence, a simplified catalytic cycle is suggested for the methanolysis of AB to release hydrogen.

INTRODUCTION

Increasing energy requirements and environmental concerns are promoting an intensive reseach on renewable energy sources. Hydrogen, with high energy content, abundant and clean as fuel leading only to water as by-product, is considered a sustainable candidate. Nevertheless, its safe storage and release upon demand under mild reaction conditions is still a challenge.[1] The catalysed release of hydrogen from chemical materials appears suitable for this purpose and the ammonia-borane adduct (AB, $H_3N–BH_3$) is considered a promising candidate due to its high hydrogen content, air stability both in solid and solution at room temperature and portability.[2] Homogeneous transition metal-based catalyzed dehydrocoupling of AB, containing protons and hydrides, very often affords up to one equivalent of hydrogen requiring inert atmosphere and a variety of Ni, Pd, Mo or Ru complexes allow higher H_2 release, up to 2.8 hydrogen equivalents.[3] Depending on the type of catalyst, the activation of AB has been proposed to occur through activation of a B–H bond, activation of a N–H bond or of both sites simultaneously.[3-4] Dehydrocoupling has also been achieved using nanoparticles, obtaining more than 2 equivalents of H_2.[5]

Metal-assisted hydrolysis or methanolysis are also efficient for hydrogen release from AB. In this case, combining hydridic B–H and protons from the solvent can afford up to three equivalents of H_2 per mole of starting material.[3, 5-6] Mechanisms proposed for the heterogeneous transition-metal catalysed hydrolysis reactions to

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release H_2 include interaction of AB with the catalyst surface, followed by concerted cleavage of the B−N bond and hydrolysis of the resulting BH_3;[7] or formation of a $NH_4^+BH_3(OH)^-$ intermediate, which reacts with adjacent H_2O to release H_2.[8] Boron-to-metal hydrogen transfer and attack of H_2O on a transient M−H bond in analogy to BH_4^- hydrolysis has also been proposed.[9, 10] Cleavage of the O−H bond in water has been recently suggested to be involved in the rate-determining step of these reactions leading to hydrogen release and formation of $H_3NB(OH)_3$ that upon hydrolysis produces $[NH_4][B(OH)_4]$.[10, 11] Catalytic heterogeneous methanolysis reactions (see Equation 1) usually allow slower hydrogen evolution than hydrolysis reactions, whereas advantages of the former include higher stability of AB in methanol solution and possibility of hydrogen release below 0 ºC.[5] Also, the easy regeneration of AB from the methanolysis product, ammonium tetramethoxyborate $[NH_4][B(OCH_3)_4]$, by a room temperature reaction has been reported.[12] As in the hydrolysis reactions, noble metal nanoparticles are among the most active catalysts for the methanolysis of AB,[13] and recently homogenized heterogeneous metal nanoparticle catalysts have proved useful to achieve enhanced catalytic performance on the methanolysis of AB.[14]

$$H_3N{-}BH_3 + 4\ MeOH \rightarrow NH_4^+ + [B(OMe)_4]^- + 3\ H_2 \quad \text{(Eq. 1)}$$

The efficient homogeneous version of the hydrolysis reaction, was first reported in 2010, using a hydridoirida-β-diketone, hydrido-PNP-iridium complexes or dicarbonylruthenacyclic compounds as catalysts.[15] Other iridium unsaturated carbene,[16] or saturated proton responsive hydroxy-bipyridine complexes,[17] acylhydrido-rhodium or –iridium derivatives[18] or ruthenium-bipyridine-*p*-cymene complexes[19, 20] have also proved efficient for this hydrolysis reaction. Proposed

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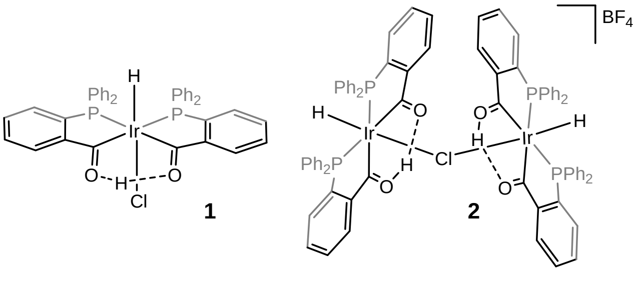
mechanisms of the homogeneous hydrolysis reactions catalysed by Ru[20, 21] or Ir[17] complexes include an initial interaction of the hydridic H–B in AB with the metal centre and hydrolysis through formation of $H_3N–BH_x(OH)_{3-x}$ intermediates. Efficient homogeneous hydrogen release from AB catalysed by Ir[15c] or Ru[19a] complexes using $^{i}PrOH/H_2O$ mixtures have also been reported. Our group has recently reported on the first alcoholysis homogeneous version, using a half sandwich ruthenium complex containing a proton responsive 6,6'-dihydroxy-2,2′-bipyridine ligand and with an excelent activity represented by an initial $TOF_{10\%}$ of 448 $mol_{H_2}\cdot mol_{Ir}^{-1}\cdot min^{-1}$ or $TOF_{50\%}$ of 120 $mol_{H_2}\cdot mol_{Ir}^{-1}\cdot min^{-1}$ at 60 ºC, showing an initial activity that surpases that of any other system known for the alcoholysis of AB, though the system suffered from deactivation at extended conversions.[22]

We report now on extraordinary efficiency of hydridoirida-β-diketones $[IrHCl\{(PPh_2(o\text{-}C_6H_4CO))_2H\}]$ (**1**) and $[(IrH\{(PPh_2(o\text{-}C_6H_4CO))_2H\})_2(\mu\text{-}Cl)][BF_4]$ (**2**), shown in Scheme 1, to catalyze the ammonia- or amine-borane methanolysis to release hydrogen, the unprecedented detection of intermediates in the catalyzed reaction and studies related to mechanistic aspects of the reaction.



Scheme 1

RESULTS AND DISCUSSION

The hydridoirida-β-diketone **1** is an efficient catalyst for the release of hydrogen by methanolysis of ammonia-borane in the presence of air. When using initial AB concentration of 0.46 M and a 0.4 mol% catalyst loading, at 30 ºC, release of up to 2.7 equivalents of hydrogen per mol of borane adduct within 14 min is obtained. As shown in Figure 1, the appearance of an induction period prior to fast turnover is observed, most likely related to the low solubility of complex **1** in methanol. When performing the reaction at a higher temperature, namely 60 ºC, the induction period almost disappears (10 s), allowing the release of up to three equivalents of hydrogen per mole of borane adduct, which according to equation 1 represents 100% of the maximum hydrogen content that can be produced, within only 2 min, with $\mathrm{TOF}_{50\%}$ of 865 $\mathrm{mol}_{\mathrm{H}_2}\cdot\mathrm{mol}_{\mathrm{Ir}}^{-1}\cdot\mathrm{min}^{-1}$, computing time as that elapsed post-induction. Addition of excess Hg during productive turnover leads to similar results suggesting the homogeneity of the catalytic reaction[23] (SI, Figure S1). No darkening of the clear yellow solution was observed. It is also remarkable that the present iridium catalyst remains active for at least six successive runs as shown in SI, Figure S2.

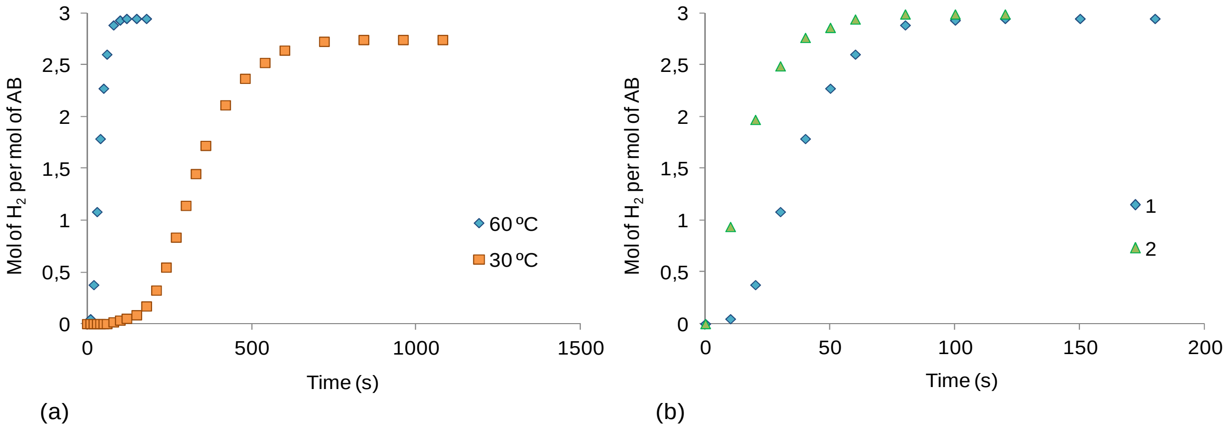


Figure 1.- Hydrogen release from 0.46 M MeOH solution of AB.with complexes **1** and **2**. (a) Using 0.4 mol% of **1** as catalyst, at 30 ºC (□, orange) or 60 ºC (◊, blue) (b) Using 0.4 mol% of **1** (◊, blue) or 0.2 mol% of **2** (Δ, green) as catalyst, at 60 ºC.

The kinetic profile obtained in the methanolysis of AB catalysed by complex **1** at 60 ºC can be considered to follow a pseudo-first-order reaction rate model with respect to the substrate, as shown by the linear plots in SI, Figure S3, which was applied to determine the overall rate constants, k_{obs}. The rate of the hydrogen release depends also on the catalyst loading (SI, Figure S3). Assuming a first order dependence with respect to the catalyst the rate law agrees with: $v_{exp} = k_{cat}[catalyst]_0[substrate]$, where $k_{cat}[catalyst]_0 = k_{obs}$. A plot of the pseudo-first-order rate constant (k_{obs}) versus $[catalyst]_0$ in the 1.86×10^{-3} to 0.46×10^{-3} M range (SI, Table S1 and Figure S4) allows the proposal of a first-order dependence on catalyst and $k_{cat} = 16.0 \pm 0.6$ M^{-1} s^{-1}.

Our search for a methanol more soluble hydridoirida-β-diketone than **1** led us to study the catalytic activity of the ionic dimer $[(IrH\{(PPh_2(o\text{-}C_6H_4CO))_2H\})_2(\mu\text{-}Cl)][BF_4]$ (**2**) (see Scheme 1). Complex **2**, with two hydridoirida-β-diketone fragments bonded by a chloride bridge, shows higher solubility in MeOH than **1** and certainly allows faster hydrogen release from methanolysis of AB (see Figure 1). When using initial AB concentration of 0.46 M and a 0.2 mol% loading of **2**, which represents a 0.4 mol% loading of iridium, at 30 ºC, the appearance of a now short induction period (40 s) is observed, and the release of up to 2.8 equivalents of hydrogen per mol of borane adduct within 6 min is obtained, with $TOF_{50\%}$ of 320 $mol_{H_2}\cdot mol_{Ir}^{-1}\cdot min^{-1}$ (SI, Figure S5). When carrying the reaction at 60 ºC, the induction period is no longer observed and the release of up to three equivalents of hydrogen per mole of borane adduct, according to equation 1, occurs within 80 s, with an excellent $TOF_{50\%}$ of 1991 $mol_{H_2}\cdot mol_{Ir}^{-1}\cdot min^{-1}$. It thus appears that the induction period, most likely arising out of an active species formation, becomes markedly shorter upon higher solubility of the precatalyst. No darkening of the clear yellow solution, neither appearance of any insoluble material was observed during

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the course of the reaction. The Hg test (SI, Figure S6) supports the homogeneity of the reaction.[23] We were pleased to observe that catalyst **2** remains active for at least six successive runs, as shown in SI, Figure S7.

The linear plots shown in SI, Figure S8 allow a pseudo-first-order reaction rate model with respect to [AB] to calculate the overall rate constants, k_{obs}. The rate of the hydrogen release depends also on the catalyst loading (SI, Table S2). A plot of the pseudo-first-order rate constants (k_{obs}) versus $[Ir]_0$, in the 1.86×10^{-3} to 0.46×10^{-3} M range (0.4 to 0.1 mol%), agrees with a first order dependence on iridium. From this plot, a value of $k_{cat} = 42.0 \pm 3.5\ M^{-1}\ s^{-1}$ was obtained for compound **2**.

Complex **2** is also able to release hydrogen by methanolysis of amine-borane adducts such as dimethylamine-borane (DMAB) or *tert*-butylamine-borane (TBAB), while it is unable to promote the methanolysis of triethylamine-borane (TEAB) as shown in SI, Figure S10. This observation suggests that, as in the hydrolysis reactions, the presence of a NH functionality in the amine-borane substrate is a requirement for an efficient catalyzed methanolysis. At 60 ºC, with initial 0.46 M substrate and using a 0.2 mol% loading of **2** (0.4 mol% of Ir), DMAB requires a short, 10 s, activation period and releases up to 2.9 equivalents of hydrogen per mole of borane adduct within 100 s, with $TOF_{50\%}$ of 848 $mol_{H_2} \cdot mol_{Ir}^{-1} \cdot min^{-1}$. The more encumbered TBAB requires also this short activation period and releases up to 2.6 equivalents of hydrogen per mole of borane adduct within 4 min, with $TOF_{50\%}$ of 271 $mol_{H_2} \cdot mol_{Ir}^{-1} \cdot min^{-1}$.

Deuteration and NMR studies on the catalytic reaction. In order to obtain further insights on the course of the catalytic methanolysis of AB we have undertaken deuteration and multinuclear "in situ" NMR studies in CD_3OD. Performing the methanolysis of H_3NBH_3 catalysed by **2** at 60 ºC in CH_3OH results in k_{obs} = (73.2 ± 1.6)x10^{-3} s^{-1} for the hydrogen release, while the methanolysis of H_3NBH_3 with CD_3OD (k_{obs} = (28.2 ± 0.2)x10^{-3} s^{-1}) or with CH_3OD (k_{obs} = (30.0 ± 0.5)x10^{-3} s^{-1}), following similar rates, were slower than that observed when using CH_3OH, as shown in SI, Figure S11. Calculated KIE of 2.60 ± 0.08 (k_{CH_3OH/CD_3OD}) or 2.44 ± 0.09 (k_{CH_3OH/CH_3OD}), suggest that cleavage of the solvent O−H bond is involved in the rate determining step of the catalysed reaction. On the other hand, the methanolysis of H_3NBD_3 catalysed by **2** at 60 ºC in CH_3OH results in k_{obs} = (80.4 ± 2.1)x10^{-3} s^{-1} for the hydrogen release, leading to an inverse KIE of 0.91 ± 0.03 ($k_{H_3NBH_3/H_3NBD_3}$). This inverse KIE would be consistent with a rate determining step involving protonation of a Ir−H (or Ir−D) species to form H−H, when H_3NBH_3 is used, or the more strongly bound H−D for H_3NBD_3..[24]

The multinuclear NMR study of the methanolysis of AB catalysed by **2** was carried out in CD_3OD (SI, Figure S12). Due to the reaction being extremely fast, the ^{11}B NMR spectrum shows the presence of only a singlet at 9.3 ppm, corresponding to the methoxyborate species in $[NH_4][B(OCH_3)_4]$,[12] which indicates the quantitative transformation of AB (–23.5 {q, $J_{H,B}$ = 93 Hz} ppm). Consequently, the ^1H NMR spectrum shows no signal due to AB at 1.45 ppm and the release of HD (4.55 ppm {t, $J_{D,H}$ = 42.6 Hz}) is observed. The appearance of a multiplet at high field (–21.4 ppm) in the ^1H NMR spectrum and of a signal at 19.3 ppm in the $^{31}P\{^1H\}$ NMR spectrum suggest the formation of new iridium species (**F**, *vide infra*) containing a hydride *cis* to Ir-coordinated phosphorus atoms.

The AB methanolysis reaction using complex **1** as catalyst is markedly slower than that catalysed by **2**, therefore we carried out the corresponding multinuclear NMR study using **1** as catalyst and were able to observe some intermediates formed in the catalysed reaction. The ^{11}B NMR spectrum of a freshly prepared solution in CD_3OD shows the presence of the $H_3N–BH_3$ substrate and of the anionic reaction product $[B(OCH_3)_4]^-$. More interestingly minor amounts of two ammonia-methoxyborane adduct intermediates, up to our knowledge previously undetected, were now observed in the coupled spectrum shown in Figure 2: a triplet at –13.9 {t, $J_{H,B}$ = 100 Hz} ppm and a doublet at 5.9 {d, $J_{H,B}$ = 120 Hz} ppm, which can be attributed to the $H_3N–BH_2(OCH_3)$ and $H_3N–BH(OCH_3)_2$ adducts, respectively, considering the reported sequence for the different anions in $Na[BH_x(OCH_3)_{4-x}]$[25] and the recently reported adduct formed by pinacolborane and a NNNN macrocycle.[26]

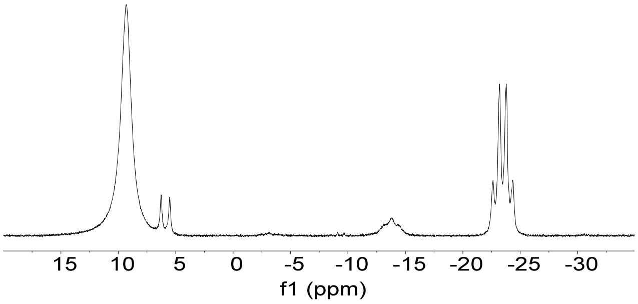

Figure 2.- ^{11}B NMR spectrum of the freshly prepared AB (0.65 mmol) / **1** (0.006 mmol) solution in 0.5 mL CD_3OD.

The consecutive ^{11}B NMR spectra (SI, Figure S13a) show the disappearance of the signal at higher field due to the $H_3N–BH_3$ substrate and an increasing amount of $[B(OCH_3)_4]^-$, while the small resonances due to the intermediates remain throughout the course of the reaction and finally disappear, to appear again upon addition of a new amount of AB to the NMR tube. The ^1H NMR spectra of the methanolysis of $H_3N–BH_3$ catalysed by **1** show the gradual disappearance of AB, the release of hydrogen and the formation of new hydridoiridium species also observed in the $^{31}P\{^1H\}$ NMR spectra (SI, Figure S13b-c). The initial appearance of broad resonances at δ = –9.15 ppm in the ^1H NMR and δ = 5.5 ppm in the $^{31}P\{^1H\}$ NMR spectra, similar to those reported in the hydrolysis of AB catalysed by **1**,[15b] suggests the formation of an iridium species (**B**) containing a hydride *trans* to the carbon atom of an acyl group and *cis* to phosphorus atoms, which disappears rapidly allowing the appearance of new species **F**, (δ^1H –21.40 ppm and δ^{31}P{^{1}H}, 19.3 ppm), already observed along with the ammonium tetramethoxyborate final product in the methanolysis reaction catalysed by **2**. The addition of a new amount of AB to the NMR tube, restarts the hydrogen evolution and the immediate appearance of **B**, which is observed in the ^{1}H NMR spectrum.

Reactivity of 2 towards amine-boranes in MeOH. We have also undertaken studies on the behaviour of complex **2** in methanol and towards amine-borane adducts. The NMR spectra of a freshly prepared solution of complex **2** in a $CD_3OD/CDCl_3$ mixture indicates that methanol is able to cleave the chlorine bridge in complex **2**. As shown in Scheme 2i, this unsymmetrical cleavage affords a cationic complex with coordinated methanol [IrH{(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$H}(MeOH)][BF$_4$] ([**3**]BF$_4$), along with complex **1.** Complex **3** was identified by NMR[27] (SI, Figure 14) showing spectroscopic features similar to those of related [IrH{(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$H}(acetone)]$^+$.[28] According to the ^{1}H NMR spectrum a mixture of all three complexes, in a **2**/**3**/**1** = 3.5:1:1 ratio is formed and the equimolar **3**/**1** ratio confirms the proposed cleavage. Attempts to isolate [**3**][BF$_4$] proved unsuccessful.

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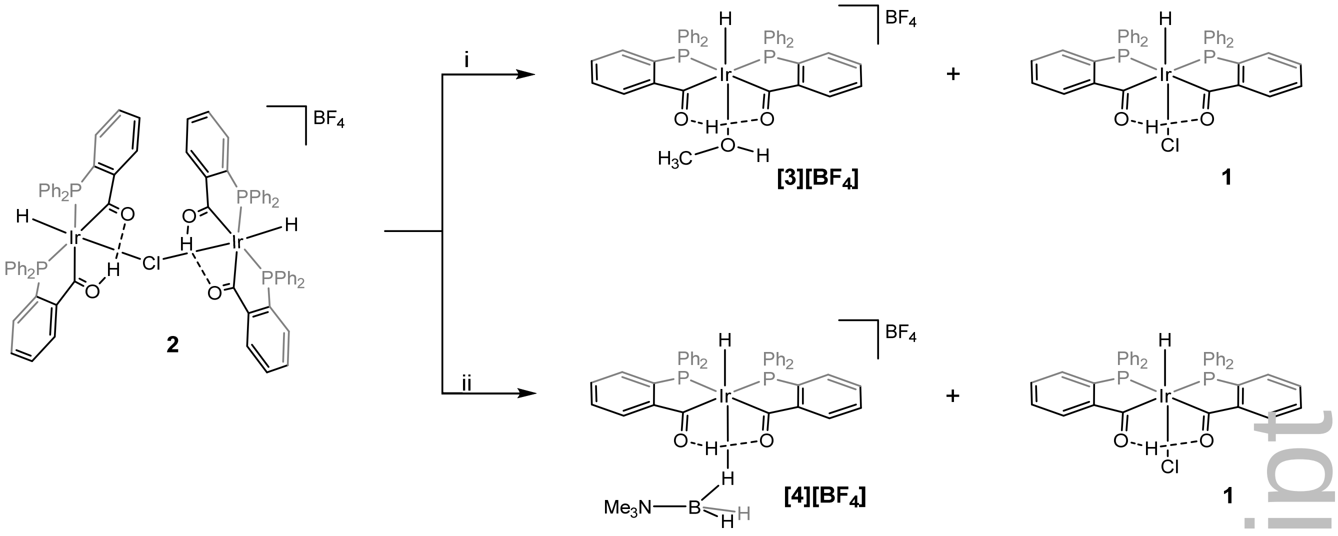
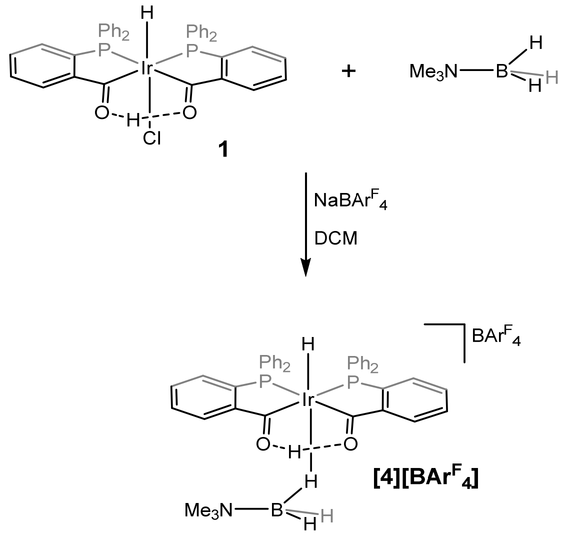


Scheme 2. Cleavage of the chloride bridge in **2**. (i) $CD_3OD/CDCl_3$. (ii) $Me_3N–BH_3$ in CD_3OD.

This observation prompted us to perform the reaction of complex **2** with the $Me_3N–BH_3$ adduct, unable to undergo the methanolysis reaction, in CD_3OD to determine the ability of borane adducts to cleave the chlorine bridge and coordinate to the iridium atom. Late transition metals are known to bind Lewis base-borane adducts to afford borane-bonded complexes.[29] Indeed, according to the NMR spectra (SI, Figure S15) the reaction shown in Scheme 2ii afforded a mixture of two species, namely a new cationic complex **4** in compound [**4**][BF_4], containing a coordinated borane, and complex **1**, which precipitated readily from the methanol solution. Complex **4** was isolated as compound [**4**][$BAr^F{}_4$] by reacting **1** with $Me_3N–BH_3$ in dichloromethane in the presence of the halide scavenger Na[$BAr^F{}_4$], as shown in Scheme 3.



Scheme 3. Formation of compound [IrH(Me_3NBH_3){($PPh_2(o\text{-}C_6H_4CO))_2H$}]$BAr^F{}_4$.

Compound [**4**][$BAr^F{}_4$] is stable and was characterized in solution by NMR spectroscopy (SI, Figures S16-17) and ESI-MS (SI, Figure S19). The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 23.1 ppm, due to equivalent phosphorus atoms. The ^1H NMR spectrum shows a triplet in the high field region, at −18.39 ppm, which agrees with a hydride being *trans* to a B−H bond,[30] and *cis* to both phosphines ($J_{P,H}$ = 14.6 Hz) and a low field singlet at 22.61 ppm in agreement with a fairly strong O···H···O hydrogen bond and complex **4** being of the irida-β-diketone type containing a formally tetradentate ligand PCCP. At room temperature the BH_3 fragment is observed as a very broad resonance, almost indistinguishable from the base line, at ca. −2.4 ppm. As other complexes containing base-stabilized η^1-H_3B−L ligands,[23b-c, 29, 31] **4** shows dynamic behavior in solution so that by 213 K two broad resonances due to the bridging (−10.50 ppm, 1 H relative integral) and terminal (+1.40 ppm, 2 H relative integral) B−H protons of the coordinated adduct are observed, while the hydride and O···H···O resonances remain unaltered. This behaviour suggests coordination of borane in an end-on η^1-fashion, through a B−H−M three-center two

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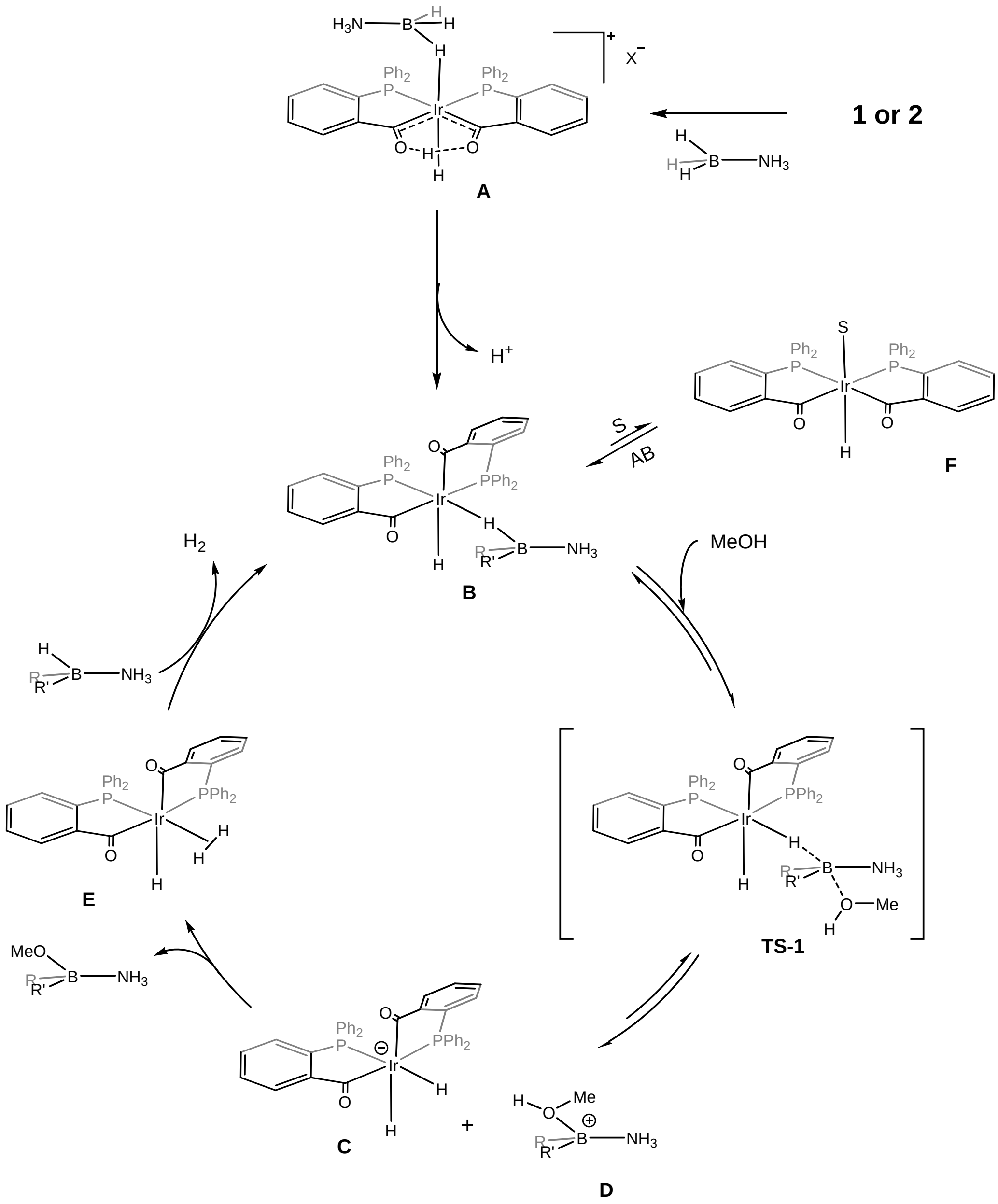
electron bond and fluxionality being due most likely to exchange between terminal and bridging B−H protons or to dissociation of the ligand. In the IR spectrum (SI, Figure S18) two bands at 2504 and 2444 cm^{-1}, in the range expected for terminal boron hydrides, are observed. The broad signal at 1792 cm^{-1}, attributed to ν(Ir-H), may include bridging BH stretching. These results show coordination of the borane adduct to iridium, provided the chloride is removed from the coordination sphere of the iridium atom.

Our experimental results suggest that the present methanolysis of AB is a homogeneous metal-catalyzed intermolecular process with release of hydrogen occurring in succesive steps for a particular AB to afford $H_3N{-}BH_2(OMe)$, $H_3N{-}BH(OMe)_2$ and $H_3N{-}B(OMe)_3$, and in a parallel fashion for the whole substrate. MeOH assisted B−N bond cleavage in the trimethoxy substituted adduct $H_3N{-}B(OMe)_3$ leads to the observed $[NH_4][B(OMe)_4]$ final product as in the related AB hydrolysis.[11, 17] Taking into account i) that coordinated boranes are liable to undergo H_2O nucleophilic attack;[20, 22] ii) the ability of methanol solutions of transient dihydridobis(acyldiphenylphosphine)iridate(III) species to release hydrogen with formation of hydride derivatives by O-to-Ir hydrogen transfer from a hydroxyl fragment;[32] and iii) the present experimental evidences, we may propose a simplified mechanism for the methanolysis of AB catalysed by irida-β-diketones, shown in Scheme 4, which represents a general catalytic cycle that can be applied to all the three succesive steps leading to the hydrogen release.



Scheme 4.- Simplified mechanism for the methanolysis of ammonia-borane with hydridoirida-β-diketones. First step: R = R' = H; Second step: R = H, R' = OMe; Third step: R = R' = OMe. [S = Solvent and AB = ammonia-borane]

In methanol solution AB may react with **1** or **2** to afford a cationic irida-β-diketone (**A**) with coordinated AB. Irida-β-diketones are known to undergo deprotonation in the presence of bases and also in methanolic basic solution, which can result in loss of the planar Ir(PCCP) arrangement and isomerisation.[33] In the present case, the

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deprotonation of **A** most likely gives neutral species that may undergo isomerisation, leading to species **B**, with hydride *trans* to acyl. The early observation of **B** (by "in situ" NMR analysis) in such a fast process suggests it could be the resting state. Nucleophilic attack of MeOH to the boron atom in **B** may lead, via TS-1, to the formation of a dihydridoiridate(III) (**C**) and a methanol-stabilized boronium cation (**D**). The O-to-Ir hydrogen transfer, with O−H cleavage, results in the dihydrogen species **E** and release of the observed intermediate ammonia-methoxyborane adducts $H_3N{-}BH_2(OMe)$, $H_3N{-}BH(OMe)_2$ or $H_3N{-}B(OMe)_3$. On account of the OH/OD and H_3NBH_3/H_3NBD_3 KIEs we propose the **C** to **E** step as the rate determinig step. Finally, coordination of a borane adduct displaces hydrogen from **E** and affords species **B**, able to restart the hydrogen release. At high conversions, the solvent may presumably become competitive as ligand affording species **F**, with coordinated solvent. Species **F** would thus be the only observable species in solution upon consumption of the substrate. The reaction of the fully dehydrogenated adduct $H_3N{-}B(OMe)_3$, with MeOH affords the tetramethoxyborate final product. Our experimental findings have allowed for the proposal of a simplified mechanism. Nevertheless, alternative mechanisms for this complex process involving at least three successive methanolysis reactions and agreeing with our experimental data cannot be excluded.

CONCLUSIONS

The cationic hydridoirida-β-diketone $[(IrH\{(PPh_2(o\text{-}C_6H_4CO))_2H\})_2(\mu\text{-}Cl)][BF_4]$ is a very efficient homogeneous catalyst for the methanolysis of ammonia-borane in air to release hydrogen. The measured activities for methanolysis of ammonia-borane using compounds **1** and **2** ($TOF_{50\%}$ of 865 $mol_{H_2}\cdot mol_{Ir}^{-1}\cdot min^{-1}$ and 1991 $mol_{H_2}\cdot mol_{Ir}^{-1}\cdot min^{-1}$ at

60 ºC respectively) surpass those ever reported previously for this process. Namely, compound **2** is ten times faster than the only homogeneous system known to be active in this reaction up to date (TOF$_{50\%}$ of 120 $\mathrm{mol_{H_2}\cdot mol_{Ir}^{-1}\cdot min^{-1}}$ at 60ºC).[22] Amine-borane adducts may coordinate to iridium to afford fluxional borane-coordinated cationic hydridoirida-β-diketones [IrH(R_3NBH_3){(PPh_2(*o*-C_6H_4CO))$_2$H}]$^+$. A multinuclear NMR study allows a proposal for the catalyzed reaction to occur in successive and parallel steps for the whole substrate. Adduct $H_3N{-}BH_3$, $H_3N{-}BH_2(OCH_3)$ or $H_3N{-}BH(OCH_3)_2$ coordination to iridium *via* the borane fragment in hydridodiacyl [IrH($H_3NBH_{3-x}(OCH_3)_x$)(PPh_2(*o*-C_6H_4CO))$_2$] species, followed by nucleophilic attack of MeOH to boron and O-to-Ir hydrogen transfer results in the release of hydrogen. Cleavage of the O–H bond in MeOH appears involved in the rate determining step of the catalyzed reaction.

EXPERIMENTAL SECTION

General Procedures: Synthetic procedures were carried out at room temperature under nitrogen by standard Schlenk techniques. [IrHCl{(PPh_2(*o*-C_6H_4CO))$_2$H}] (**1**)[34] and [(IrH{(PPh_2(*o*-C_6H_4CO))$_2$H})$_2$(μ-Cl)]BF_4 (**2**)[28] were prepared as previously reported. All other reagents were purchased from commercial sources and used without further purification. Microanalysis was carried out with a Leco Truspec Micro microanalyzer. IR spectra were recorded with a Nicolet FTIR 510 spectrophotometer in the range 4000-400 cm^{-1} using KBr pellets. ^1H (TMS internal standard), $^{31}P\{^1H\}$ (H_3PO_4 external standard) and ^{11}B ($BF_3\cdot Et_2O$ external standard) NMR spectra were recorded with Bruker Avance DPX 300 or Bruker Avance 500 spectrometers. ESI-MS spectra were recorded on a Bruker MicrOTOF-Q Instrument. Good fit to both the principal molecular ion and the overall isotopic distribution were obtained.

Preparation of [IrH(Me_3NBH_3){(PPh_2(*o*-C_6H_4CO))$_2$H}][BAr$^F{}_4$] ([4]BAr$^F{}_4$). To a solution of complex [IrHCl{PPh_2(*o*-C_6H_4CO))$_2$H}] (0.037mmol, 30 mg) in dichloromethane trimethylamine borane (0.037 mmol, 2.7 mg) and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate salt (0.037 mmol, 32.8 mg) were added. The resultant yellow solution was stirred for 30 min and then washed three times with distilled water and dried over magnesium sulphate. Filtration and solvent removal under low pressure afforded an off-yellow solid that was collected. Yield 46 mg (72%). IR (KBr, cm^{-1}): 2504 (w), ν(B-H$_t$); 2444 (w), ν(B-H$_t$); 1792 (br), ν(Ir-H); 1609 (m), ν(C=O). Anal. Calcd. For $IrC_{74}H_{57}P_2O_2NB_2F_{24}\cdot(CH_2Cl_2)_{0.5}$ C 50.66, H 3.31, N 0.79; found C 50.59, H 3.22, N 0.58. ESI-MS (CH_3OH): calcd For $C_{41}H_{42}BNO_2P_2Ir$ 846.2; observed 846.2 {M}$^+$. ^{1}H NMR ($CDCl_3$, 298 K, 500 MHz): δ −18.39 (t, $^2J_{P,H}$= 14.6 Hz, 1H, *H*-Ir); −2.4 (br, 3H, *H*-B); 1.83 (s, 9H, *H*$_3$C); 7−8.5 (28H, Aromatics); 22.61 (br, 1H, O--*H*--O) ppm. ($CDCl_3$, 213 K, 500 MHz): δ −18.09 (t, $^2J_{P,H}$= 14.6 Hz, 1H, *H*-Ir); −10.50 (s, 1H, *H*-B); 1.40 (br, 2H, *H*-B); 1.83 (s, 9H, *H*$_3$C); 7−8.5 (28H, Aromatics); 22.75 (s, 1H, O--*H*--O) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K, 162 MHz)): δ 23.1 (s) ppm.

Methanolysis of $H_3N–BH_3$ with Complexes 1–2. A solution of 1.16 mmol of the desired amine-borane adduct in 2 mL of methanol was prepared in a round bottom 40 mL flask fitted with a gas outlet and with a side arm sealed with a tight-fitting septum cap. The flask was connected via the gas outlet to a gas burette filled with water. The amine-borane adduct solution was immersed in a thermostated water bath to reach the desired temperature under atmospheric pressure (1 atm) and in the presence of air. A solution of the selected precatalyst, 3.75 mg, 4.64x10$^{−3}$ mmol of **1** or 3.87 mg, 2.32x10$^{−3}$ mmol of **2**, in 0.5 mL of methanol was syringed through the septum into the reaction flask, magnetic stirring connected and timing started. Gas evolution began immediately and the released gas was measured by determining periodically the volume of water displaced in the burette.

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KEYWORDS

Ammoniaborane, hydrogen release, irida-β-diketones, methanolysis

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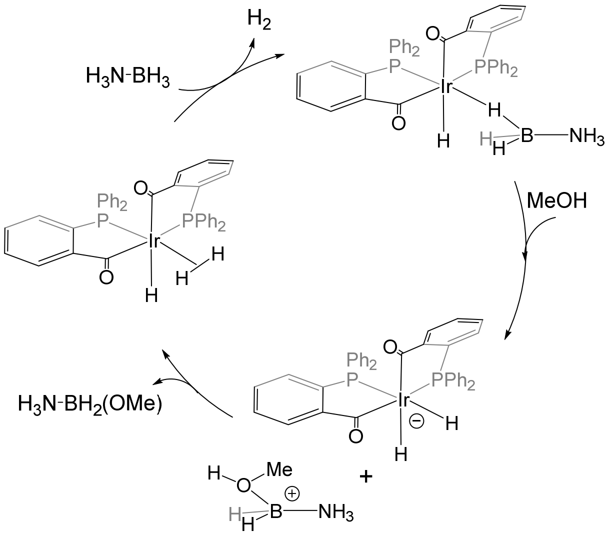
Table of Contents Graphic



Hydridoirida-β-diketones promote methanolysis of ammonia-borane by end-on η^1-fashion borane coordination of H_3NBH_3 (see graph) and of intermediates $H_3NBH_{3-x}(OMe)_x$ (X = 1, 2) in a similar manner, followed by nucleophilic attack of MeOH to boron, and release of hydrogen.