A hydridoirida-β-diketone as an efficient and robust homogeneous catalyst for the hydrolysis of ammonia–borane or amine–borane adducts in air to produce hydrogen†

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The first homogeneous metal-catalysed hydrolysis of ammonia–borane or amine–borane adducts for hydrogen generation, using a stable organometallic complex [$IrHCl\{(PPh_2(o\text{-}C_6H_4CO))_2H\}$], is reported.

The search for new fuels[1–2] has made the safe storage of hydrogen in a chemical compound, and its deliverance upon demand, the subject of recent intensive research. Ammonia–borane is an attractive candidate as a potential hydrogen storage material for transportation applications. It contains 19.6 weight% in hydrogen, and is thermally and water stable at room temperature.[2] Reports on the dehydrogenation reaction or dissociation and hydrolysis of ammonia–borane and amine–borane adducts, promoted by transition-metal catalysts under mild conditions, have appeared in the literature only recently. Growing efforts are being devoted to searching for new metal catalysts, optimising their catalytic activities and recovering the hydrogen storage material in order to reach practical applications, such as hydrogen generation for portable fuel cells.[2–3] The homogeneous dehydrocoupling of ammonia–borane (AB), methylamino–borane (MeAB) or dimethylamino–borane (DMAB), catalysed by Ir,[4] Ti,[5] Rh,[6] or Ru[7] may efficiently afford up to one equivalent of hydrogen gas under an inert atmosphere. A nickel carbene complex is able to release more than two equivalents of H_2 from AB in benzene–diglyme solution under argon.[8] Theoretical studies have suggested that electron delocalisation involving the carbene may be essential for low energy H transfers in this catalytic AB dehydrogenation.[9] Hydrolytic reactions can afford up to three equivalents of hydrogen per mol of starting material. The generation of H_2 from AB by the hydrolysis route is catalysed by first row transition metals, supported or as nanoparticles.[10–12] Efficient water/air-stable Ni nanoparticles have been reported recently.[13] Noble-metal heterogeneous systems, which often require an inert atmosphere, also allow fast H_2 release from AB at room temperature.[14–16] Efficient regeneration methods of AB from the dehydrogenation products or from the borate salts have also been reported.[17]

We describe now the first homogeneous metal-catalysed hydrolysis of ammonia–borane or amino–boranes to efficiently produce up to three equivalents of hydrogen, using a hydridoirida-β-diketone.[18] Metalla-β-diketones can be considered as acylhydroxycarbene complexes stabilised by intramolecular hydrogen bonds between the acyl and the hydroxycarbene moieties.[19]

The hydridoirida-β-diketone [$IrHCl\{(PPh_2(o\text{-}C_6H_4CO))_2H\}$] (**1**)[18] is an efficient homogeneous catalyst for hydrogen generation from hydrolysis of AB in THF–H_2O mixtures, at room temperature in the presence of air, and releases stoichiometric amounts of hydrogen according to eqn (1).

$$H_3N-BH_3+2H_2O\xrightarrow[298K,\,THF-H_2O]{1}NH_4^{\ +}+BO_2^{\ -}+3H_2 \qquad (1)$$

The rate of hydrogen release is strongly dependent on the solvents ratio (Fig. S1, ESI†). The best results were obtained for mixtures THF–H_2O = 1 : 1, so that with an initial AB concentration of 0.46 M and a 0.5 mol% catalyst loading, the hydrolysis of AB and the release of 2.73 equivalents of hydrogen gas, 87% of the maximum hydrogen content that could be produced, was observed within 19 min. At the end of the reaction, mixtures of complex **1**, the related dihydridoirida-β-diketone [$IrH_2\{(PPh_2(o\text{-}C_6H_4CO))_2H\}$] (**2**) and other non-identified species could be recovered from the solution upon evaporation of THF, as confirmed by NMR spectroscopy (Fig. S2, ESI†). The transformation of **1** into **2** promoted by bases has been reported.[20] When using higher amounts of water, initial complete dissolution of **1** and H_2 evolution occurred until the formation of a precipitate prevented hydrogen release after 12 min if THF–H_2O = 4 : 6, or after 9 min if THF–H_2O = 3 : 7. This precipitate was identified as **2** by NMR (Fig. S3, ESI†).

These observations suggest the dehydrogenation reaction being homogeneous. Performing the catalytic reaction in the presence of Hg led to similar results and this is a further indication that the process is homogeneous.[6,16] After completion of the catalytic reaction, the borate products from the hydrolysis were identified by $^{11}B\{^1H\}$ NMR. The disappearance of the starting AB resonance at −23.2 ppm and the presence of a singlet at 16.1 ppm, which we assign to borate formed in the reaction, were observed. It has been reported that the chemical shift of borates can be dependent on the conditions of their preparation and that equilibrium processes and rapid exchange between different borate species may occur.[15] The $^{11}B\{^1H\}$ NMR spectrum of a sample prepared in THF–H_2O = 1 : 1 mixtures by mixing equimolar amounts of boric acid and an aqueous ammonia solution exhibited a single peak at 15.4 ppm (Fig. S4, ESI†). The rate of hydrogen release depends also on the catalyst loading. As shown in Fig. 1, with the same initial AB concentration, a 0.25 mol% catalyst loading increases the time required to afford 2.73 equivalents of hydrogen to at least 50 min,

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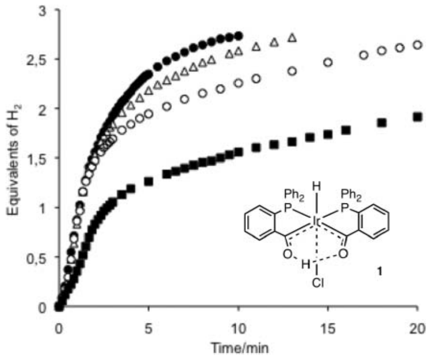


Fig. 1 Hydrogen release from H_3NBH_3 using 0.25 mol% (■), 0.5 mol% (○), 0.75 mol% (△), and 1.0 mol% (●) of **1** as catalyst in THF–H_2O = 1 : 1 mixtures.

while a 0.75 mol% or a 1 mol% catalyst loading reduces the time to *ca.* 13 or 10 min respectively.

Complex **1** is also able to hydrolyse amine–borane adducts in THF–H_2O = 1 : 1 mixtures to produce the quantitative release of three equivalents of hydrogen gas as shown in Fig. 2. In the absence of **1**, AB and also amine–borane adducts in a THF–H_2O = 1 : 1 mixture remain unaltered after 2 h. With initial substrate concentration of 0.46 M, DMAB is hydrolysed completely within 5 min when using a 0.5 mol% loading of **1** or after 4 min when using a 1 mol% catalyst loading. The more encumbered *tert*-butylamino–borane (TBAB) requires an activation period and longer reaction times. With initial substrate concentration of 0.46 M, a 2 min activation period and a further 24 min (0.5 mol% catalyst loading) or 4 min activation period and a further 8 min (1 mol% catalyst loading) are needed to allow the release of all three equivalents of hydrogen gas. The kinetic profile of the hydrogen generation suggests the formation of an intermediate that builds up and later falls.[21] However, no analytical technique was available to follow the concentration of the substrate under atmospheric pressure and intermediates could not be detected. On the other hand complex **1** shows very low activity to hydrolyse the triethylamine–borane (TEAB) adduct. After 120 min the release of only 8% (0.5 mol% catalyst loading) or 19% (1 mol% catalyst loading) of three equivalents of hydrogen gas is observed. This observation suggests that a suitable catalytic activity requires the presence of a NH functionality in the amino–borane substrate. Nevertheless steric hindrance effects could also be responsible for this low activity.

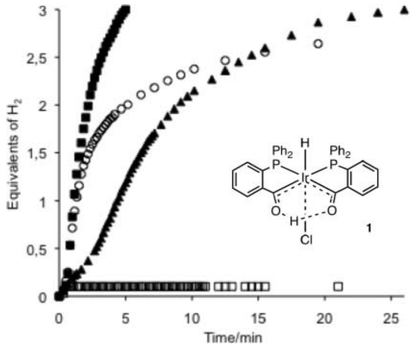
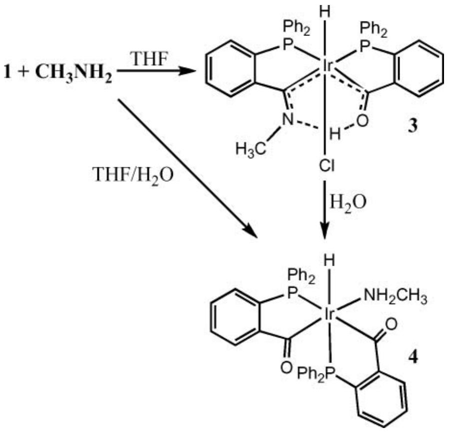


Fig. 2 Hydrogen release using 0.5 mol% of **1** as catalyst in THF–H_2O = 1 : 1 mixtures from: AB (○); DMAB (■); TBAB (▲) or TEAB (□).

Plausible mechanisms considered to account for the heterogeneous catalysed hydrolysis of NH_3BH_3 include the establishment of interactions between the AB molecule and the metal particle surface to form activated complex species, to which attack by a H_2O molecule readily leads to concerted dissociation of the B–N bond and the hydrolysis of the resulting BH_3 intermediate.[10] More recently, the involvement of boron-to-metal hydrogen transfer to form a transient M–H bond, similar to that proposed in the metal-catalysed borohydride hydrolysis, has been suggested.[12,22]

The cleavage of the B–N bond, as a consequence of the interaction of AB with the catalyst, may afford the amine. Metalla-β-diketones are known to react with ammonia or amines to afford metalla-β-ketoimines;[19] therefore we have studied the reaction of **1** with amines. The reaction of **1** with methylamine (see Scheme 1) in dry THF leads to the hydridoirida-β-ketoimine **3**, which reacts with water to afford the hydridoaminodiacyl complex **4**. The reaction of **1** with methylamine in a THF–H_2O = 1 : 1 mixture leads directly to **4**. On the other hand, **1** fails to react with NEt_3 in dry THF. After 24 h reaction, only unreacted **1** could be recovered. The reaction of **1** with NEt_3 in a THF–H_2O = 1 : 1 mixture affords the known dimer acyl-bridged species $[Ir_2H_2(PPh_2(o\text{-}C_6H_4CO))_2(\mu\text{-}PPh_2(o\text{-}C_6H_4CO))_2]$.[20]



Scheme 1 Reaction of **1** with methylamine.

The formation of **3** and **4** was demonstrated spectroscopically and that of **3** also by X-ray diffraction analyses. The $^{31}P\{^1H\}$ NMR spectrum of **3** shows two doublets at 30.8 and 15.0 ppm respectively with $^2J(P,P)$ of 7 Hz, the $^{13}C\{^1H\}$ NMR spectrum shows two doublets at 243.9 and 221.8 ppm respectively due to acyl and imino groups *trans* to phosphorus atoms ($^2J(P,C)$ of 106 and 103 Hz respectively) and the ^1H NMR spectrum shows a hydride resonance in the high field region, at −20.67 ppm, as a triplet due to $^2J(P,H)$ of 15 Hz, which agrees with the hydride being *trans* to chlorine and *cis* to both phosphines, and a low field singlet at 13.2 ppm that supports the presence of fairly strong N···H···O hydrogen bonds[19] and the existence of an irida-β-ketoimine. The $^{31}P\{^1H\}$ NMR spectrum of **4** shows two doublets at 30.5 and 25.7 ppm respectively with $^2J(P,P)$ of 5 Hz, the $^{13}C\{^1H\}$ NMR spectrum shows two doublets at 239.9 ($^2J(P,C)$ of 102 Hz) and 213.9 ($^2J(P,C)$ of 5 Hz) ppm respectively due to acyl groups *trans* or *cis* to phosphorus atoms and the ^1H NMR spectrum shows a hydride resonance in the high field region, at −7.94 ppm, as doublet of doublet due to ${}^{2}J(\mathrm{P,H})_{trans}$ of 130.0 Hz and ${}^{2}J(\mathrm{P,H})_{cis}$ of 20.0 Hz, which agrees with the structure shown in Scheme 1.

Fig. 3 shows an ORTEP view of complex **3** with the labelling scheme of the asymmetric unit.[23] The geometry about the metal atom is a distorted octahedral with four positions occupied by P–C of two bidentate ligands bonded between them by an enolic hydrogen bond, and the other two positions occupied by one hydride ligand and by a Cl atom mutually *trans*. The Ir–P distances indicate a larger *trans* influence for the acyl group than for the imino group. The Ir–C distances comprising the chelate ligands are equivalent and similar to those in previously reported irida-β-diketones.[18] The C1–O1 distance in **3** agrees with those reported for other metalla-β-diketones.[18,19] The C20–N1 bond length (1.310(7) Å) evidences a substantial double bonding in the $\mathrm{N–C_{carbene}}$ bond,[24] and the angles involving N1 confirm the formation of an imino fragment. The O···N distance, 2.735(7) Å, is in accordance with a strong hydrogen bridge bond, and the O1–H2–N1 angle, 153.3°, is consistent with a nearly linear O···H···N bridge.

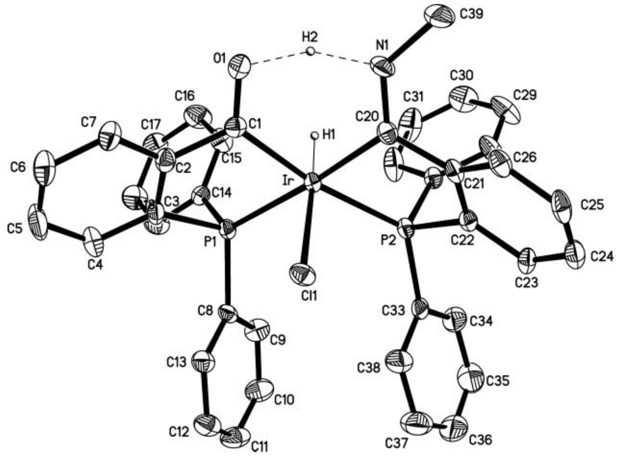
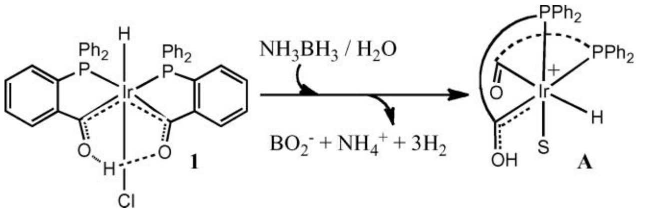


Fig. 3 ORTEP view of complex **3** showing the atomic numbering (25% probability ellipsoids) and the intramolecular hydrogen bond. The hydrogen atoms except two and the label of some C atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ir–P1, 2.307(2); Ir–P2, 2.343(1); Ir–C1, 2.042(6); Ir–C20, 2.043(6); Ir–CL1, 2.512(2); Ir–H1, 1.43; C1–O1, 1.237(7); C20–N1, 1.310(7); O1···N1, 2.735(7); C20–Ir–C1, 92.9(2); C20–Ir–P1, 174.8(2); C1–Ir–P1, 81.9(2); C1–Ir–P2, 171.3(2); C20–Ir–P2, 79.72; P1–Ir–P2, 105.53(5); N1–C20–C21, 119.4(5); C20–N1–C39, 128.6(6); O1–H2–N1, 153.3.

To obtain information on the course of the catalytic reaction, a multinuclear NMR study of the catalytic hydrolysis of NH_3BH_3 in a THF-d_8–D_2O mixture was carried out (Fig. S5, ESI†). After 7 min the ${}^{11}\mathrm{B}\{{}^{1}\mathrm{H}\}$ NMR spectrum presents a singlet at $\delta = -25.2$ ppm due to unreacted AB along with a single peak at $\delta = 17.2$ ppm due to the formation of B–O bonds. As the reaction progresses the amount of AB decreases and that of borate increases. On completion of the reaction (*ca.* 100 min) the resonance due to AB disappears, revealing its complete consumption. Borane intermediates could not be observed. The ^{1}H NMR spectra indicate the gradual disappearance of the quartet centred at $\delta = 1.37$ ppm (${}^{1}J_{\mathrm{B-H}} = 92$ Hz) due to AB and the formation of HD at $\delta = 4.52$ (t) ppm (${}^{1}J_{\mathrm{D-H}} = 43$ Hz) and of H_2 at $\delta = 4.55$ (s) ppm. The appearance of H_2 is due to the unavoidable presence of light water vapor in heavy water in contact with air, and to the isotopic effect making the reaction with H_2O faster than with D_2O.[22] The amount of H_2 decreases relative to HD while the reaction progresses. Signals for complex **1** were not observed, instead the appearance of a triplet at $\delta = -9.07$ ppm (${}^{2}J_{\mathrm{P-H}} = 13$ Hz) occurs, due to coupling to two phosphorus atoms as indicated by ${}^{1}\mathrm{H}\{{}^{31}\mathrm{P}\}$ NMR. This suggests the presence of an iridium species (**A**) containing a hydride *trans* to the carbon atom of an acyl group and *cis* to two phosphorus atoms. The intensity of this resonance decreases upon progression of the catalytic reaction, most likely due to H/D exchange. In accordance with this observation the ${}^{31}\mathrm{P}\{{}^{1}\mathrm{H}\}$ NMR spectra show two resonances at $\delta = 7.2$ (s) and 6.4 (s) ppm, which remain unaltered during the hydrolysis and correspond to the two phosphorus atoms mutually *cis* of **A**, as confirmed by selective phosphorus decoupled ^{1}H NMR experiments (Fig. S6, ESI†). These resonances appear as singlets due to unobservable coupling constants. On completion of the reaction the appearance of another species **B** is observed. In the absence of AB the complete transformation of **A** into **B** occurs and this transformation may be accelerated by opening the tube, whereupon hydrogen is lost. Species **B** is most likely to be closely related to **1**; its spectroscopic features ($\delta{}^{1}$H −21.31 ppm; $\delta{}^{31}\mathrm{P}\{{}^{1}\mathrm{H}\}$, 18.7 ppm) are quite alike to those of **1**, and we believe that it can afford **1** and **2** upon evaporation of THF.

As shown in Scheme 2, the formation of **A** can be rationalised taking into account that in protic solvents the displacement of chloride from **1** is easier. This may allow the interaction of AB with **1**, with cleavage of the B–N bond favoured by the formation of an irida-β-ketoimine, whose hydrolysis could afford species **A**, containing a hydroxycarbene moiety, and able to get involved in the cleavage of another AB molecule. The cleavage of the B–N bond would allow the hydrolysis of the borane to afford H_2 and borate. This proposal is consistent with the more encumbered TBAB requiring an activation period. As indicated previously, NEt_3 fails to undergo ketoimine formation. According to this, Et_3NBH_3 would not allow the formation of species **A**.



Scheme 2 Formation of **A** from **1** during the catalytic hydrolysis of AB.

In conclusion, we have reported on the first homogeneous metal-catalysed hydrolysis of ammonia–borane or amino–boranes to efficiently produce hydrogen. Further studies to clarify mechanistic details of these reactions are under way.

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23 Crystal data for **3**: M = 821.25, monoclinic, space group $P2_1/n$, a = 12.815(1) Å, b = 19.381(1) Å, c = 14.364(1) Å, β = 108.180(1)°, V = 3389.5(4) Å^3, Z = 4, D_c = 1.609 Mg m^{-3}, μ(Mo-Kα) = 0.71073, no. of independent reflections 5956, R_1 = 0.033 for $I > 2\sigma(I)$ reflections, wR_2 (all data) = 0.079. Software for the Smart System V5.04 and SHELXTL V 5.1, Bruker-Siemens Analytical X-ray Instrument Inc., Madison, WI, 1998. CCDC 776710.

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