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A readily accessible ruthenium catalyst for the solvolytic dehydrogenation of amine–borane adducts†

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The use of the readily available complex [Ru(*p*-Cym)(bipy)Cl]Cl as an efficient and robust precatalyst for homogeneously catalysed solvolysis of amine–borane adducts to liberate the hydrogen content of the borane almost quantitatively is being presented. The reactions can be carried out in tap water, and in aqueous mixtures with non-deoxygenated solvents. The system is also efficient for the dehydrocoupling of dimethylamine–borane under solvent-free conditions.

Introduction

Nowadays, hydrogen is considered as a competent energy vector capable of replacing fossil fuels in the near future. Its safe storage and controlled liberation are some of the most challenging problems that need to be solved for its consolidation. Several materials are being considered for solid hydrogen storage. Among them B–N based compounds are the most promising ones due to their high gravimetric hydrogen storage capacity. Ammonia–borane ($H_3N{\cdot}BH_3$, AB), with a hydrogen content of 19.6 wt% and high stability, is one of the most plausible candidates for this purpose.[1–5]

The use of catalytic amounts of metals to induce a controlled release of H_2 from AB is an appealing strategy, and it is being intensively pursued in recent years. Two different catalytic pathways are known for a controlled hydrogen release from AB: dehydrogenation and solvolysis. The former, promoted by several metallic nanoparticles or clusters[6–8] and organometallic complexes (*i.e.* based on Rh,[9,10] Ru,[11–13] Ir,[14,15] Os,[16] Fe[8] or Pd[17]), generates one equivalent of H_2 per mole of substrate and the AB ends up in the form of $[H_2B{-}NH_2]_n$ oligomeric or polymeric materials (eqn (1)). Only some Ru nanoclusters[13] and two homogeneous catalysts based on Ru[18–20] and Ni[21] are able to further dehydrogenate the formed polyaminoboranes generating up to 2.8 equiv. of H_2. The solvolytic route is generally accepted to proceed by a fast hydrolysis/alcoholysis of the BH_3 liberated in the aqueous or alcoholic media after catalytic cleavage of the adduct.[22] Consequently, it renders up to 3 equivalents of H_2 per mole of AB, half of it coming from the H_2O or alcohols present in the solvent mixture (eqn (2)).

$$nH_3N{\cdot}BH_3 \rightarrow [NH_2BH_2]_n + nH_2 \tag{1}$$

$$H_3N{\cdot}BH_3 + 2H_2O \rightarrow NH_4^{\ +} + BO_2^{\ -} + 3H_2 \tag{2}$$

Several metallic nanoparticles efficiently catalyse this reaction.[4,5,22–24] To the best of our knowledge there are only four reported homogeneous catalytic systems for the hydrolytic cleavage of AB, intended for H_2 production. In 2010 Garralda and coworkers reported on the use of an Ir(III) hydrido-β-diketone complex able to generate up to three equivalents of H_2 per mole of the substrate operating in mixtures of THF–H_2O.[25,26] Nearly concomitant was the publication of an *in situ* formed ruthenium catalyst species generated from dicarbonylruthenacyclic complexes under catalytic conditions.[27] More recently two other very effective systems based on iridium(III) have been reported: a bis-*ortho*-metalated Ir(III) NHC[28,29] and an Ir(III) P–N–P pincer,[30] which showed exceptional activities and robustness. Based on these few examples it seems that iridium complexes modified with sophisticated ligands (P–N–P pincers, cyclometalated-NHC or phosphane-β-diketones) are the most effective catalysts for this reaction. Lower price of ruthenium compared to iridium would make it *a priori* a more adequate metal of choice, nevertheless its low activity (Ru loading ~10% reported for Djukic's system)[27] does not compensate for this advantage.

We present here a readily accessible [Ru(*p*-Cym)(bipy)Cl]Cl (*p*-Cym = *para*-cymene, bipy = 2,2′-bipyridine) water-soluble complex as an efficient catalyst precursor for solvolytic dehydrogenation of amine–boranes. It operates in air, tap water and aqueous mixtures with non-deoxygenated solvents,

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with high activities and stability. This catalytic system is also active for an unprecedented dehydrocoupling of dimethylammonia–borane in the absence of a solvent, forming the cyclic $[Me_2NBH_2]_2$ as the only reaction product.

Results and discussion

Catalytic experiments

In a standard experiment the precatalyst, [Ru(*p*-Cym)(bipy)Cl]Cl (0.5 mol%), was mixed with the substrate for 30 min. This pretreatment guarantees the reproducibility of the results. After this period, the solvent was added and the gas evolution was measured in a water-filled inverted gas burette.

Several solvent mixtures have been assayed to optimise the reaction conditions (see Table 1, and Fig. S1†). These results showed that the hydrogen generation is moderate in pure alcohols and undetectable in freshly distilled dry THF. This observation points to a hydrolytic mechanism rather than a dehydrogenation being responsible for the hydrogen liberation. Accordingly, increasing the H_2O proportion in the solvent mixture has a beneficial effect on the activity of the system. Surprisingly, in pure water, in spite of the complete solubility of both the catalyst and substrate, the overall activities are similar to those observed for the mixture THF–H_2O = 1/1. For this reason THF–H_2O = 1/3 and iPrOH–H_2O = 1/1 were selected as standard reaction conditions.

Using these solvent mixtures ~2.8 equivalents of H_2 per AB have been released within 18 minutes at room temperature (2 eq. were evolved in ~10 min). When these reactions were conducted at 40 °C, 2.8 equivalents of H_2 were evolved in less than 10 minutes. ^{11}B-NMR analysis at the end of the reaction (using an internal D_2O capillary) showed only a broad singlet between 8 and 19 ppm attributed to the different borates in equilibrium in solution.[24,27,29,31] After evaporation of the solvent, ^{11}B-NMR of the reaction residue in DMSO-d_6 showed a sharp singlet at 1.54 ppm as the only boron-containing species, which is consistent with a tetrahedral, negatively charged boron centre with four B–O sigma bonds.[29,32] Two blank experiments (one without the catalyst and the other with 0.5% (Ru) of the dimeric complex $[Ru(p\text{-Cym})Cl_2]_2$ used to synthesize the catalyst precursor) showed only residual H_2 production (less than 0.1 equivalents for the former and 0.4 equivalents for the latter) when the reactions were conducted for 2 hours in THF–H_2O = 1/3 at rt. To test the homogeneous nature of the active catalyst, ~1000 equivalents of metallic Hg have been added at 33% conversion, which did not affect the reaction profile, supporting the hypothesis of a homogeneously catalysed reaction.[6]

Table 1 The measured TOF (h^{-1}) for the solvolytic dehydrogenation of AB using different solvents

	TOF^a (h^{-1})			Total H_2 ^{b} time (min)
	1.0 eq. H_2	1.5 eq. H_2	2.0 eq. H_2	
THF	0	0	0	0
THF–H_2O = 3/1	277	225	182	2.7(100)
THF–H_2O = 1/1	538	451	383	2.7(45)
THF–H_2O = 1/3	766	775	774	2.8(18)
H_2O	530	455	342	2.7(50)
iPrOH–H_2O = 1/1	909	856	830	2.9(17)
iPrOH	66	69	68	2.7(235)
MeOH–H_2O = 1/1	323	288	232	2.7(85)
MeOH	211	122^c	—	1.4(40)

Reaction conditions: 1.38 mmol AB, 0.5 mol% [Ru(*p*-Cym)(bipy)Cl]Cl, 3 mL solvent, rt. ^{a} TOF reported at 1.0, 1.5 and 2.0 equivalents of H_2 liberated with respect to AB. Calculated based on the consumption of AB. ^{b} The total number of equivalents of H_2 liberated with respect to AB at the end of the reaction. ^{c} 1.4 eq.

In general, 97% pure AB has been used for these experiments, but the use of technical grade AB or tap water did not affect the activity of the system.

To extend the scope of this system, the same catalytic conditions were assayed on different substrates (see Fig. 1). The lack of reactivity of trisubstituted amine–boranes (triethylamine–borane TEAB and trimethylamine–borane TMAB), already observed by Garralda and coworkers[25] for iridium-based catalysts, suggests the need for at least one N–H functionality on the substrate for the reaction to proceed. It is often claimed that a loosely bound coordination of the ammonia–borane to the metal centre is responsible for the activation of AB for either dehydrocoupling or hydrolytic dehydrogenations. Except for bifunctional catalysts,[33] the initial interaction of the AB with the metal centre is commonly accepted to proceed through the hydric hydrogens of the borane or the B–H bonds.[8,27,34–40] In fact, an Ir(III) complex containing coordinated BH_3 through an elongated B–H σ bond is postulated as dormant state species in AB dehydrogenation reactions

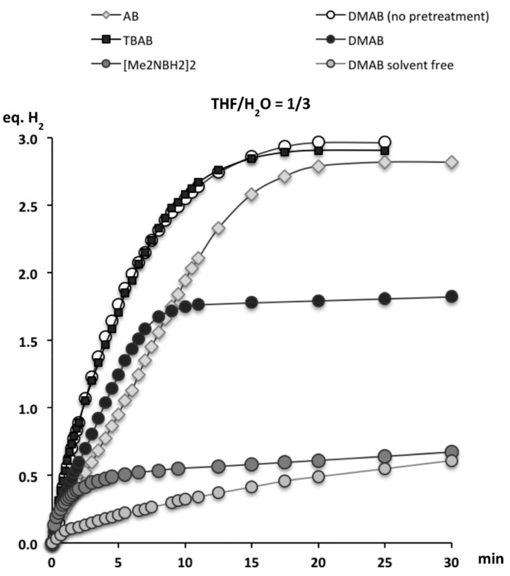

Fig. 1 Reaction profile (gas evolution) using different substrates. Unreactive substrates (TEAB and TMAB have not been represented since no gas evolution was detected). Reaction conditions: 1.38 mmol substrate, 0.5 mol% [Ru(*p*-Cym)(bipy)Cl]Cl, 3 mL THF–H_2O 1/3, rt (iPrOH–H_2O 1/1 in ESI†).

when using Ir(*t*BuPOCOP)H_2 as a catalyst.[41] According to our observations, it could be suggested that the presence of a N–H bond in the substrate, obviously necessary for dehydrocoupling reactions, also played an important role in solvolytic dehydrogenations, lowering the energetic barrier that prevents the cleavage of the amine–borane adduct and subsequent borane solvolysis.

When dimethylamine–borane (DMAB) was used as the substrate, during the pre-catalysis mixing period some gas release was observed. To gain some insight into the nature of the process responsible for this gas evolution, DMAB was mixed with 0.5 mol% of [Ru(*p*-Cym)(bipy)Cl]Cl and the generation of gas was measured in a water-filled inverted gas burette (see Fig. 1, series DMAB solvent free). After 25–30 min the volume corresponding to a half equivalent of hydrogen per mol of DMAB was detected. The gas production stopped after liberation of 1 equivalent of gas (3 h) per mole of substrate. During the course of the reaction, the mixture of solids turned dark and liquefied, and a colourless crystalline material sublimed and condensed on the inner wall of the reaction vial. ^{11}B-NMR analysis results of this crystalline sublimed material and of the reaction residue in DMSO-d_6 were identical.‡ They showed the complete consumption of the substrate, DMAB (δ −13.8 ppm, quartet, J_{H-B} = 114 Hz) and the appearance of a clean triplet at 5.3 ppm, J_{H-B} = 112 Hz. This chemical shift is in agreement with the one reported for the cyclic $[Me_2NBH_2]_2$.[17,42,43] The molecular structure of this compound was confirmed by X-ray diffraction of the sublimed crystals (Fig. S12†), and it is isostructural to the ones previously published by Manners for the same compound.[7,42] These results suggest that the system also acts as an effective catalyst for the dehydrocoupling of DMAB in the absence of a solvent. This dehydrocoupling reaction occurring during the mixing period in the case of DMAB generates a mixture of substrates (DMAB and $[Me_2NBH_2]_2$) that creates an artefact in the reaction profile for this substrate (see Fig. 1, series DMAB), which eventually liberates less than 2 eq. of H_2. To avoid this, this reaction was also conducted without a premixing period to ensure that all the substrate was in the form of DMAB (Fig. 1, series DMAB no pretreatment) and also after liberation of 1 equivalent of H_2, when it was in fact fully converted to $[Me_2NBH_2]_2$ (Fig. 1, series $[Me_2NBH_2]_2$). The results obtained showed that the cyclic $[Me_2NBH_2]_2$ was a rather bad substrate liberating only 0.5 equivalents of H_2 (1 hour). In contrast, when DMAB§ or *tert*-butylamine-borane (TBAB) was employed as the substrate a total hydrogen volume corresponding to more than 2.8 equivalents of hydrogen per mol of substrate was measured at the end of the reaction (5–15 min), which has been considered as evidence that the reaction proceeded through a solvolytic pathway.[25,26,29] When these substrates were used, a much faster hydrogen liberation was observed compared to AB. Previous reports on hydrolytic dehydrogenation of these substrates with iridium-based catalysts showed a faster reaction rate for DMAB compared to TBAB.[25,26] In contrast, with our system similar reaction rates have been measured for both substrates. In fact, the best activities were measured for TBAB in iPrOH–H_2O 1/1, for which a TOF of 4152 h^{-1} was measured at 33% conversion.

To test the recyclability and robustness of the catalyst, several successive additions of 200 equivalents of AB in 0.5 mL of the reaction solvent per mole of the catalyst have been conducted (Fig. 2 and S5 in ESI†). The system showed that, although there is a gradual reduction of the reaction rate (which can be partially attributed to the change in the reaction medium: incremental dilution and precipitation of large quantities of borates which hamper the homogeneity of the solution), the catalyst remained active for at least 6 consecutive cycles, liberating a total of 3360 equivalents of H_2 per mole of Ru.

To gain some insight into the nature of the active species, we performed ^{1}H-NMR analysis of the precatalyst, [Ru(*p*-Cym)(bipy)Cl]Cl, in D_2O. As stated before for related compounds the spectrum showed that in aqueous solutions it exists as an equilibrium mixture of $[Ru(p\text{-Cym})(bipy)Cl]^+$ and the biscationic aqua complex $[Ru(p\text{-Cym})(bipy)(H_2O)]^{2+}$.[44,45] This equilibrium can be shifted back and forth by addition of chloride salts (NaCl) or chloride abstractors (AgOTf) respectively (see S9, ESI†). To test whether the aquo complex was a better suited precatalyst compared to the $[Ru(p\text{-Cym})(bipy)Cl]^+$, we performed catalytic experiments in which an excess of NaCl or AgOTf was added to the catalytic mixture. The results obtained showed that, as expected, the addition of NaCl produces a slight decrease in the catalytic activity. Surprisingly, addition of silver salts caused a dramatic deactivation of the catalytic system. To corroborate whether it was due to some interference from the silver salt in the process, we synthesized the $[Ru(p\text{-Cym})(bipy)(H_2O)](OTf)_2$ complex and tested it as a precatalyst. This compound showed identical activities compared to the parent chloride compound in the mixture THF–H_2O = 1/3.

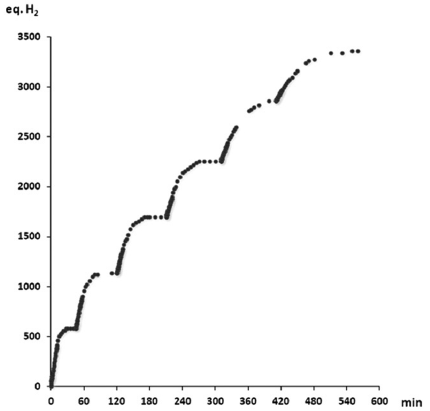

Fig. 2 Reaction profile (equivalents of H_2 per mole of Ru evolved *vs.* time) in 6 successive cycles. Reaction conditions (first cycle): 1.38 mmol AB, 0.5 mol% [Ru(*p*-Cym)(bipy)Cl]Cl, 3 mL THF–H_2O 1/3, rt. Successive additions of 1.38 mmol AB dissolved in 0.5 mL of THF–H_2O 1/3.

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‡ DMSO-d_6 was used as a solvent for solubility reasons, and to avoid further hydrolysis in aqueous solvents.

§ Without a pre-mixing period.

In situ NMR studies

In situ ^{1}H-NMR and ^{11}B-NMR experiments were performed using THF-d_8–H_2O = 3/1 to observe the process at different stages. This solvent mixture was chosen due to the relatively slow reaction rate in this media. ^{11}B-NMR spectra have been recorded at 5 minutes intervals using the exact catalytic conditions. These spectra showed the progressive consumption of AB (quartet at −22.8 ppm, J_{H-B} = 93.8 Hz) and the formation of a species that presents a broad singlet at 19.7 ppm (Fig. S6, ESI†). This singlet was assigned to the borates formed in solution in comparison with the data published elsewhere for other AB hydrolysis catalytic systems.[25,27,29] ^{11}B-NMR in DMSO-d_6 of the residue after evaporation of this reaction mixture showed a singlet at 1.54 ppm, as already observed formerly in catalytic runs. The low catalyst loadings prevented a direct observation of the catalyst resting state under these catalytic conditions. Additional NMR experiments have been performed using 10 times higher catalyst concentrations and a 10/1 AB/Ru ratio in THF-d_8–H_2O 3/1 at 15 °C. ^{11}B-NMR (Fig. 3) and ^{1}H-NMR (Fig. S7 in ESI†) spectra were acquired at 5 min intervals. ^{11}B-NMR spectra show that more than 60% of the AB was already hydrolyzed in the first spectrum (in the delay necessary to introduce the sample into the spectrometer), and it was fully consumed within the first 45 minutes.

^{1}H-NMR spectra showed that in the presence of AB, there is one main set of signals in the aromatic region that corresponds to coordinated *p*-cymene and bipyridine ligands. A clear hydride singlet is observed at −5.71 ppm. This spectroscopic pattern indicates that most of the Ru present under catalytic conditions is in the form of [Ru(*p*-Cym)(bipy)H]$^+$, in comparison with the reported spectroscopic data for this ruthenium hydride.[46] Whether this Ru(II)-hydride is the resting state of the catalyst or a dormant state formed in the presence of H_2 (observed as a singlet at 4.5 ppm) is uncertain. When the NMR tube was vented, a new set of signals appeared in the ^{1}H-NMR spectra (Fig. 4, and Fig. S7 in ESI†). It shows the characteristic pattern of a Ru(II) complex of the type [Ru(*p*-Cym)(bipy)L]$^{n+}$. The aromatic signals of this new species are downfield shifted compared to [Ru(*p*-Cym)(bipy)H]$^+$ and [Ru(*p*-Cym)(bipy)Cl]$^+$ (which was confirmed by adding more precatalysts into the vented NMR tube).

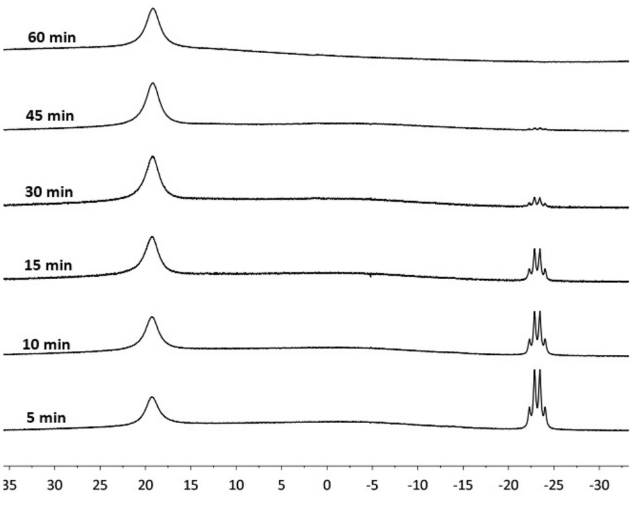

Fig. 3 ^{11}B-NMR spectra at different reaction times. Reaction conditions: 0.14 mmol AB, 0.014 mmol [Ru(*p*-Cym)(bipy)Cl]Cl, 1 mL THF-d_8–H_2O 3/1, 15 °C.

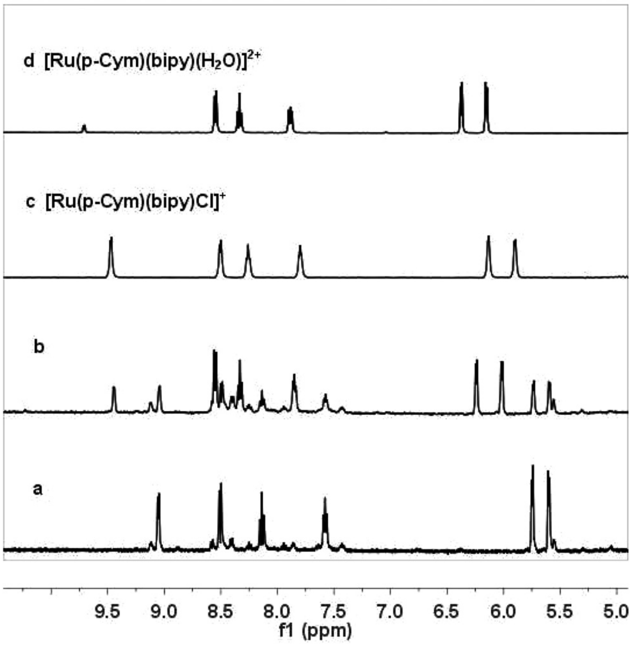

Fig. 4 ^{1}H-NMR spectra, aromatic region, (500 MHz) in THF-d_8–H_2O = 3/1. (a) *In situ* NMR experiment with 60 min of reaction at 15 °C. (b) *In situ* NMR experiment after venting the tube. (c) Ru(*p*-Cym)(bipy)Cl]Cl. (d) Ru(*p*-Cym)(bipy)Cl]Cl + excess of AgOTf.

In an effort to identify this species, we studied by NMR spectroscopy the reaction of [Ru(*p*-Cym)(bipy)Cl]Cl with one equivalent of AB in THF-d_8–H_2O 3/1. The ^{1}H-NMR spectrum showed 3 sets of signals, corresponding to [Ru(*p*-Cym)(bipy)-Cl]$^+$, the putative hydride [Ru(*p*-Cym)(bipy)H]$^+$, and the new species observed at the end of the catalytic runs (see Fig. S11, ESI†). The exact nature of this compound is still uncertain. It might be either an ammonia or a borane complex which would trap the catalyst in the absence of hydrogen, which reverts into the active species when a new batch of substrates is added.

Conclusions

The use of the readily available complex [Ru(*p*-Cym)(bipy)Cl]Cl as an efficient and versatile precatalyst for the homogeneously catalysed solvolytic dehydrogenation of ammonia–borane and amine–borane adducts has been presented. It is shown to be a robust catalyst even in tap water and in aqueous mixtures with non-deoxygenated solvents. *In situ* NMR experiments showed that the [Ru(*p*-Cym)(bipy)H]$^+$ species is the main ruthenium component present under catalytic conditions, though an unidentified compound of the type [Ru(*p*-Cym)(bipy)L]$^{n+}$ seems to act as a dormant state of the catalyst after venting the reaction solutions. [Ru(*p*-Cym)(bipy)Cl]Cl also catalyses the unprecedented dehydrogenation of DMAB in the solid-state, forming the cyclic $[Me_2NBH_2]_2$ as the only reaction product.

Further studies to unravel the exact nature of the catalyst and to extend the scope of this catalytic system are currently under progress in our laboratories.

Experimental

Materials and methods

Substrates were obtained from commercial sources and were used without further purification. The precatalysts, [Ru(*p*-Cym)(bipy)Cl]Cl and [Ru(*p*-Cym)(bipy)(H_2O)]$(OTf)_2$, were prepared according to published methodologies.[46] Unless otherwise stated, NMR spectra were recorded on a Bruker 500 AVANCE spectrometer equipped with a z gradient BBO probe.

When aqueous solvent mixtures were used, ^{1}H-NMR spectra were recorded using a watergate methodology[47] for solvent suppression using a time domain of 32k, and a spectral width of 20 kHz; the number of scans is 4, the interpulse delay is 1 s, and the acquisition time is 3 s.

^{11}B-NMR spectra were recorded at 160.46 MHz, using a time domain of 32k, and a spectral width of 16 kHz. The number of scans is 128. The interpulse delay is 0.2 s. The acquisition time is 0.3 s.

Catalytic experiments

Solvolytic dehydrogenation of ammonia–borane and amine–boranes. Catalytic reactions were carried out in a septum-closed vial connected to a water-filled inverted gas-burette used to follow the hydrogen release. 1.38 mmol of the substrate (42.5 mg of ammonia–borane) and 0.0069 mmol of the precatalyst (3.2 mg of [Ru(*p*-Cym)(bipy)Cl]Cl, 0.5%) were mixed in the vial and stirred for 30 minutes. After that premixing period, 3 mL of the solvent was added and the progression of the reaction was followed until no further gas liberation was observed. All these procedures were carried out under air. For the reaction at 40 °C the reaction vial was immersed in a thermostated water bath.

Consecutive solvolytic dehydrogenation of AB. After an initial run (performed following the afore-mentioned procedure and quantities), the water in the burette was reset to zero by disconnecting it from the reaction vial. Then, a solution of 1.38 mmol of substrate in 0.5 mL of the solvent was added to the former reaction residue and the gas evolution was measured in the burette.

Solvent-free dehydrocoupling of DMAB. Solvent free dehydrogenation of DMAB was carried out using the same experimental setup as for solvolytic dehydrogenations. In the vial, the same amount of precatalyst (3.2 mg of [Ru(*p*-Cym)(bipy)Cl]Cl, 0.0069 mmol) was mixed with 200 equivalents of DMAB (1.38 mmol, 81.3 mg). Time zero was considered when both solids were mixed.

In situ NMR experiments

Catalytic conditions. 14.2 mg of ammonia–borane (0.46 mmol) and 1.1 mg of [Ru(*p*-Cym)(bipy)Cl]Cl (0.0023 mmol) were stirred for 30 minutes and dissolved in 1 mL of THF–H_2O mixture (3 : 1) using an internal D_2O capillary. After addition of the solvent, the release of hydrogen was immediate. The NMR tube was introduced as fast as possible into the spectrometer and ^{11}B-NMR spectra were acquired at regular time intervals.

Ru concentrated conditions. 4.2 mg of ammonia–borane (0.14 mmol) and 6.3 mg of [Ru(*p*-Cym)(bipy)Cl]Cl (0.014 mmol) were stirred for 30 minutes and dissolved in 1 mL of THF-d_8–H_2O mixture (3 : 1). After addition of the solvent, the release of hydrogen was immediate. The NMR tube was introduced as fast as possible into the spectrometer and ^{1}H-NMR and ^{11}B-NMR spectra were acquired at regular time intervals.

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