



Title	Towards the design of novel boron- and nitrogen-substituted ammonia-borane and bifunctional arene ruthenium catalysts for hydrogen storage
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Publication date	2014-02-05
Publication information	Bandaru, Sateesh, Niall J. English, Andrew D. Phillips, and J. M. Don MacElroy. "Towards the Design of Novel Boron- and Nitrogen-Substituted Ammonia-Borane and Bifunctional Arene Ruthenium Catalysts for Hydrogen Storage." Wiley, February 5, 2014. https://doi.org/10.1002/jcc.23534 .
Publisher	Wiley
Item record/more information	http://hdl.handle.net/10197/5381
Publisher's statement	This is the author's version of the following article: S. Bandaru, N. J. English, D. Andrew, J.M.D. Phillips, J.M.D. MacElroy. (2014) "Towards the design of novel boron- and nitrogen-substituted ammonia-borane and bifunctional arene ruthenium catalysts for hydrogen storage" Journal of Computational Chemistry, 35(12): 891-903 which has been published in final form at http://dx.doi.org/10.1002/jcc.23534
Publisher's version (DOI)	10.1002/jcc.23534

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Towards the design of novel boron- and nitrogen-substituted ammonia-borane and bifunctional arene ruthenium catalysts for hydrogen storage

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Electronic-structure density functional theory (DFT) calculations have been performed to construct the potential energy surface for H₂ release from ammonia-borane, with a novel bifunctional cationic ruthenium catalyst based on the sterically bulky β -diketiminato ligand [D. F. Schreiber et al, ACS Cat. 2012, 2, 2505]. The focus is identifying both a suitable substitution pattern for ammonia-borane optimised for chemical hydrogen storage and allowing for low-energy dehydrogenation. The interaction of ammonia-borane, and related substituted ammonia-boranes, with a bifunctional η^6 -arene ruthenium catalyst and associated variants, are investigated for dehydrogenation. Interestingly, in a number of cases, hydride-proton transfer from the substituted ammonia-borane to the catalyst undergoes a barrier-less process in the gas phase, with rapid formation of hydrogenated catalyst in the gas phase. Amongst the catalysts considered, *N,N*-difluoro ammonia-borane and *N*-phenyl ammonia-borane systems resulted in negative activation energy barriers. However, these types of ammonia-boranes are inherently thermodynamically unstable and undergo barrier-less decay in the gas phase. Apart from *N,N*-difluoro ammonia-borane, the interaction between different types of catalyst and ammonia borane was modelled in the solvent phase, revealing free-energy barriers slightly higher than those in the gas phase. Amongst the various potential candidate Ru-complexes screened, few are found to differ in terms of efficiency for the dehydrogenation (rate-limiting) step. To model dehydrogenation more accurately, a selection of explicit protic solvent molecules was considered, with the goal of lowering energy barriers for the H-H recombination. It was found that primary (1°), 2° and 3° alcohols are the most suitable to enhance reaction rate.

Keywords: Ammonia-borane, density functional theory, dehydrogenation, ruthenium, bifunctional, catalysis.

Introduction

Molecular hydrogen gas has emerged as one of the most promising alternative power fuel sources, both as a transportation medium and for proton-exchange membrane fuel cells, and as a replacement for batteries for portable electric source.^[1] However, a number of difficulties have arisen in regards to small- and large-scale storage. In recent years, ammonia borane (and related amine boranes) has been proposed as one of the most promising materials for the hydrogen storage, due to the combination of high gravimetric (19.6 wt% H₂) and volumetric hydrogen densities. Moreover, this material decomposes at moderate temperatures. Significant efforts are underway to design and optimise materials for efficient chemical hydrogen storage, from both synthetic and computational perspectives. Overall, progress has been made in recent years in the discovery of new materials for this purpose.^[2]

Thermal decomposition of a single ammonia borane molecule yields one H₂ equivalent and a polymeric amino borane product with a corresponding activation energy barrier of ~ 36 kcal.mol⁻¹.^[3] Prolonged thermolysis is known to produce the cyclic and volatile borazene, which is an undesirable by-product in terms of PEM fuel cell poisoning. The activation energy barrier for the first equivalent of H₂ from ammonia borane is higher than that for B-N bond cleavage,^[4] so an efficient catalyst is required for hydrogen transfer at temperatures appropriate for use with fuel cells. Extensive studies published in the literature on the dehydrogenation of ammonia-borane, both in the solid state and in solution have shown that reaction catalysed by transition-metal and s-block metal-centred complexes can enable efficient hydrogen release at lower temperatures.^[5-9] Many experiential studies have considered acid-catalysed^[10] and transition-metal catalysed^[11] dehydrogenation processes from ammonia-borane; interestingly, recent reports show enhanced dehydrogenation in ionic liquid-based media.^[12] Balazs *et al* have explained theoretically and experimentally the differences between ammonia- and phosphine-boranes.^[13]

Organometallic-catalysed dehydrocoupling of amine-boranes and -phosphorus have attracted a considerable amount of attention and scrutiny, in particular due the central role in the generation of a new group of binary 13/15 materials, and for possible future use as energy-transport vectors for dehydrogenation to produce H₂.^[14] A wide range of transition-metal-catalysed ammonia-borane reactions are known experimentally, with a handful of these studied in-depth by theoretical methods. Prominent among these systems are those involving middle- and late-transition-metal complexes (*e.g.*, Fe, Ru, Rh, Ir, Ni). In the field of materials development for

hydrogen storage, the design of new catalysts, such as these, is a challenging task for both theorists and experimentalists. Swinnen et al have carried out some DFT modelling of reaction pathways for catalysed chemical hydrogen uptake and release in ammonia boranes, hydrazine and ammonia alane derivatives thereof,^[15,16] and this has been an important step in elucidating the key steps with a view towards improving the overall efficiency and reversibility of such processes. An example of further work in this area lies in the studying the mechanisms involved in the dehydrogenation of AB, mediated by a novel bifunctional η^6 -arene β -diketiminato ruthenium catalyst,^[17] as this is currently under investigation;^[18] in this case, the first step is energetically the most favourable process and the dehydrogenation step is slightly less favourable energetically, while in the overall reaction, the final H₂ recoupling/dehydrogenation step is found to be rate-limiting.^[18] In particular, Swinnen *et al* have reported a catalytic process in ref. 15 which is very similar to those studied in the present study, in which, at its heart, two H atoms of ammonia borane are shifted to two Ru/C centres of the complex, with subsequent elimination of the two H atoms leading to generation of H₂ from a Ru-H₂ complex.

The present study focuses mainly on identifying a suitable substitution pattern for an amine borane, which is optimised with regard to chemical hydrogen storage with the bifunctional η^6 -arene β -diketiminato ruthenium catalyst.^[17] We investigate, through density functional theory (DFT) methods, the nature of the mechanistic pathway for the interaction between AB and related variants and the catalyst, including simple coordination and hydrogen transfer steps. Moreover, we have computationally examined different substituent patterns of the Ru-complex, in an effort to more deeply understand the steps and associated energy barriers associated with the decoupling from the dihydrogen-coordinated intermediate. Finally, we have also considered effects of explicit solvent molecules for the rate-limiting dehydrogenation step. Ammonia borane (AB), substituted amine boranes and η^6 -arene β -diketiminato ruthenium complexes and related transition states are labelled as ‘AB’, ‘sub-AB’ and ‘Ru Catalyst’ and ‘TS’, respectively.

Computational Details

Initially, we optimised structures using four different DFT functionals, M06L^[19], B3LYP^[20], B97D^[21], and M05-2X^[22], on the available X-ray crystal structure geometries of the experimentally-synthesised complex Ru Catalyst **I**^[17] and its derivative **II** (cf. Scheme 1), in combination with the mixed basis set using the ‘Gen’ keyword implemented in Gaussian 09.^[23]

The Ru atom was represented by the Stuttgart/Dresden effective core potential and associated basis set, SDDAll.^[24] A mixed basis set employing the Stuttgart potential was applied to the transition metal (Ru), while the remaining C, N, B, H atoms were modelled using Pople-type basis sets, i.e 6-31+G(d). Following geometry optimisation, frequency calculations were also carried out on the optimised geometries at the same level of theory to assess the nature of stationary points, *i.e.*, whether they are transition states (TS) or higher-order saddle points. Zero-point energy corrections at 298 K have been obtained through frequency analyses obtained at the M06L level of theory with a mixed basis set SDDAll+ 6-31+G(d) level, and are unscaled. The main differences in computed geometrical parameters from the X-ray crystal structure geometries (given in bold) are reported in Table 1 at the four different levels of theory. We also validated the functionals above by comparison with CCSD(T) and MP2 calculations for some of the smaller species in this study, on either M06L- or MP2-optimised geometries, and further information is provided in the Supporting Information (Table S1). It was found that CCSD(T) or MP2 calculations were not necessary across all species (of particular importance for the larger ones, due to lack of computational expedience and tractability) to capture the essence of the geometries and energetics.

(Scheme 1 nearer to here)

For structure **I**, apart from the bond angles (with all DFT functionals overestimating C^{cent}-Ru-N^{cent} by 2°, and Ru-N^{cent}-C11 overestimated by 3.4°), all other bond lengths and angles are close to experimental values. Among the levels of theory, B3LYP and B97D slightly overestimate these values, and M06L and M05-2X parameters are close to the X-ray crystal structure geometries. In case of Ru-cat **2**, aside from a few bond distances, all other geometric parameters are close to the corresponding solid-state metrics determined through single crystal X-ray diffraction studies.

(Table 1 nearer to here)

Amongst these four levels of theory, the optimised geometries obtained using the M06L and M05-2X methods can essentially reproduce the solid-state structure of the Ru-complex **I** and **II**.

B3LYP and B97D functions generally slightly overestimate bond lengths and bond angles; although in some cases underestimate slightly. The overall performance of M06L is in good agreement as compared to the geometries obtained from X-ray diffraction studies^[14] and from available literature reports.^[25] For a few transition states, intrinsic reaction coordinate (IRC) calculations were performed to elucidate reaction pathways, which connect the TS and higher-order stationary points to local minima of the reactants and the corresponding products. Following the relatively good performance of M06L for prediction of geometrical properties, we have utilised this level of theory for the remaining calculations, and results have been analysed, explained and rationalised at the same level of theory. The CCSD(T) and MP2 results in Table S1 of Supporting Information do not change the complexion of this conclusion about the basic suitability of M06L. Indeed, from a comparison of functionals in ref. 25, it is concluded that M06L has the best overall performance for a combination of thermochemistry, thermochemical kinetics, metallochemical and non-covalent interactions, bond lengths, and vibrational frequencies. The (comparative) worst performance area for M06L was of barrier heights, although these were predicted more accurately than for any other local functional, and with about the same accuracy as the popular B3LYP functional.

Charge analysis was carried out by using the ‘Natural Population Analysis’ (NPA)^[26] keyword implemented in G09 at the M06L level of theory. Tetrahydrofuran (THF) solvent effects were modelled *via* the PCM continuum model^[27] (with a static dielectric constant of 7.58 debye) by single-point energy calculations on gas-phase-optimised geometries.

Results and discussion

This study provides an energetic assessment for the viability of dehydrogenation from ammonia borane and related substituted amine boranes mediated catalytically by η^6 -arene β -diketiminato ruthenium complexes. Each step of the reaction cycle is examined separately, in specific detail. Importantly, since these particular catalysts are known only to eliminate one equivalent H₂ from AB, we have only examined theoretically a single removal of H₂. The nature of the resulting AB by-product, which is normally cyclic or polymeric, shall not be considered in the present work. However, first it is important to understand the energetics of self-dehydrogenation of AB and sub-AB substrates without the aid of a catalyst, so as to provide a kinetic and thermodynamic reference for the catalysed cycle.

Self-dehydrogenation of Ammonia Borane and Substituted Analogues

Ammonia borane (AB), **a** and the substituted ammonia boranes, **b-l**, were divided into two different categories: structures **a-j**, which are substituted at the nitrogen centre, while **k-l** feature boron-substitution. All of these optimised structures **a-l** are shown in Fig. 1.

(Fig 1 nearer to here)

Our treatment of the thermal self-dehydrogenation of ammonia borane (**a**) and substituted AB (**b-l**) involves the formation of H₂ and the iminoborane (H₂N=BH₂, **IB**) or substituted iminoboranes, whereby a N-B π -bond is formed. Experimentally, IBs are only isolated when large bulky groups, such as 2,4,6-(CH₃)₃C₆H₃ aryls are employed.^[28] This mechanism is well established^[29-30], so for comparison of the activation energy barriers, we carried out calculations to locate the corresponding TS without the catalyst, at the M06L level of theory. The reaction is depicted in figure S1. The gas phase activation energy barrier of the intra-molecular dehydrogenation of AB in vacuo is 41.79 kcal mol⁻¹ (AB→AB-TS) and the corresponding B-N bond rotation barrier of AB from staggered to eclipsed conformation is 2.2 kcal mol⁻¹ (cf. Supporting Information, Fig. S1). According to the report of Nguyen *et al.*,^{30c} the intermolecular activation energy barrier of AB is 36.4 kcal/mol. In our case, one H₂ molecule is released *via* intramolecular dehydrogenation AB-TS (cf. Supporting Information, Fig. S1). The AB-TS is 41.7 kcal/mol in magnitude in the gas phase, whilst after zero-point energy-correction (M06L/Gen + ZPE), it is 37.4 kcal/mol. This is consistent with the reported value of 36.4 kcal/mol at the CCSD(T)/CBS level of theory.^{30c}

This energy would be incorporated during the dehydrogenation process, as the eclipsed conformation is necessary for H-H coupling and H₂ release sequence. When a solvation model is employed, specifically the polarizable continuum (PCM) model with THF as the solvent, the activation free-energy barrier is surprisingly higher, 48.96 kcal mol⁻¹. Consistent with other studies, the gas-phase reaction energy is endothermic at 4.3 kcal mol⁻¹.^[31]

In Figure S1, the corresponding total energy of the optimised structures (staggered conformation) of AB (**a**) and related substituted AB in atomic units are listed. The thermally induced self-dehydrogenation activation energy barriers are given in parenthesis. Energies with

zero-point vibration corrections are highlighted in bold text. Moreover, the B-N bond distance and NBO-calculated charges are shown on B and N atoms determined at the M06L/6-31+G(d) level of theory. From inspection of Figure 1, it is clearly observed that mono-fluoro *N*-substitution, i.e., structure “**b**” increases the activation energy barrier by ~1.43 kcal mol⁻¹ with respect to AB. Di-fluoro substitution on nitrogen, i.e. structures “**c**” further enhances the activation energy barrier by ~2.27 kcal mol⁻¹. Mono-fluoro substitution on the nitrogen atom reduces the B-N bond distance to 1.585 Å, whereas di-fluoro substitution on nitrogen only reduces the B-N bond to 1.625 Å, in comparison the distance of 1.659 Å in AB. Experimentally, crystallisation of AB in the solid state results in a marked shrinkage of the B-N bond from 1.657 Å^[32] to 1.564 Å vis-à-vis the gas-phase,^[33] but also in the development of short N-H···H-B intermolecular contacts (2.02 Å).^[34] Hence any external interaction with the hydrogen atoms will strongly influence the length of the N-B bond. The NPA charges of mono- and di-fluoro-*N*-substituted AB systems shift from -0.989e for AB to -0.368e and +0.205e, respectively. There is a shift towards higher positive charge on the N atom, with slightly higher negative charge developing on the boron atom vis-à-vis AB as a result of the HOMO and LUMO energy values being slightly lower in energy, along with an increase in the HOMO-LUMO separation, (*i.e.*, the hardness “ η ” of the molecules is greater). Thus, these fluoro-substituted AB species can be considered more stable than AB. This increasing stability relative to AB means that the corresponding gas phase dehydrogenation barriers are also slightly higher than AB itself. Substitution of electron-donating groups such as methyl, allyl and di-methyl on the nitrogen atom results in sub-AB thermal-dehydrogenation barriers being slightly higher than the putative AB. Interestingly, cyclic systems resulting from cyclopropyl and phenyl *N*-substitution results in these particular sub-ABs having reduced activation barriers by ~1 to 6 kcal mol⁻¹, respectively. Further methyl *B*-substitution results in a thermal dehydrogenation barrier, ~6.3 kcal mol⁻¹ lower than that of AB, whereas fluoro-substitution on the *B* centre only slightly increases the barrier. Among all of these sub-AB systems, 2-chloro ethyl (**g**), cyclo-propyl (**h**) and phenyl substituted on the nitrogen atom (**i**), and structures featuring methyl substituted on the *B* atom (**k**), were found to affect lower dehydrogenation energy barriers.

(Scheme 2 nearer to here)

Catalytically Mediated Dehydrogenation of Ammonia Borane

To gain further insight into the catalytic dehydrogenation of AB and related substituted AB substrates, we modelled the interactions with the bi-functional η^6 -arene β -diketiminato ruthenium catalyst **1**. In 2007, Phillips et al^[35] reported the first example of an organo-ruthenium complex bearing the β -diketiminato ligand, **I**. In this case, the enhanced electron donating capability of this N,N' -ligand combined with steric bulkiness enables facile isolation of a cationic coordinative unsaturated system. This strong anionic N,N' -coordinated ligand imparts significant charge to the chelated metal. To determine initially the energies involved in catalytically assisted dehydrogenation of AB, we first choose to study the phenyl-substituted Ru Catalyst, instead of 2,6-dimethylphenyl-substituted ($2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3$) version which was employed in the experimental studies^[17], to reduce and minimise any possible additional steric interactions.

The first step of the catalytic mechanism is the AB coordination with the bifunctional complex **1**, and then subsequent transfer of two hydrogen atoms from AB to the metal and β -carbon positions as shown in Scheme 2. Specifically, H from the B atom transfers to the Ru centre, affording a metal hydride, while simultaneously a proton (H^+) from N is added to the nucleophilic β -C site, transforming the anionic β -diketiminato ligand into a neutral chelating β -diimine. In contrast to single site catalysts, during the dihydrogen addition from AB, there is no change in the metal oxidation state, which suggests that extensive ligand reorganization around the metal coordination sphere is not required.

Firstly, the Ru-complex **1** associates with AB “**a**” to form an association complex “**2**”. The formation of **2** is an energetically downhill process shown in Fig. 2. The structure of complex **2** is shown in Fig. 3 and reveals the closest distance, 1.99 Å, between AB and the catalyst **1** occurs through the primary (B)H-Ru interaction. Experimentally, Whittlesey and co-workers observed a similar (B)H-Ru interaction of distance 2.107(14) Å in a cationic Ru-xantphos hydride complex.^[36] In contrast, the calculated model **2** shows an additional, but substantially weaker, N(H)-C(β) interaction of 2.57 Å. Importantly, the coordinated AB molecule maintains the lower energy staggered conformation, but the interaction causes a shortening of the B-N bond from 1.66 Å to 1.62 Å, which is consistent with removal of electron density from AB. The catalyst component of **2** shows almost no structural changes, except for a bending of the β -diketiminato ligand along the N,N' -axis. Energetically, in this first step, formation of the reaction complex “**2**” results in a corresponding change in the free energy of $-0.6 \text{ kcal mol}^{-1}$, where the enthalpy component is $-11.64 \text{ kcal mol}^{-1}$, and is lower in energy than “**1+AB**” (cf. Fig. 3), suggesting a

favourable interaction between **1** and AB, which reasonably, is not entropically favourable due partly to association of two molecules. However, on closer inspection of the individual components of the entropy, specifically ΔS_{rot} and ΔS_{vib} , a significantly increased overall entropy is encountered due to loss of rotation and vibrational degrees of freedom upon going from **1+AB**→**2**. To provide more realistic energy values, solvation effects are also considered by using THF. Interestingly, the calculations predict that the ΔH for the formation of **2** from combination of **1+AB** in solvent is significantly less energetic with a value of $-4.50 \text{ kcal mol}^{-1}$.

(Fig 2 nearer to here)

Once complex **2** is formed, the reaction coordinate proceeds along with a tightening of the interaction between AB and **1**, leading to the first transition state **TS1** (Fig. 2). Importantly, the reaction pathway involves a rotation of the NH_3 group along the N-B axis, imparting the higher energy eclipsed conformation to the now doubly-bound AB; it is important to note that ‘bound’ here does not refer to a covalent bond, but rather the intimate contact between two of the AB’s hydrogen atoms and the Ru centre and the β -carbon atom (cf. the TS1 in Fig. 3). In **TS1** (the structure shown in figure 3) the two shared hydrogen atoms exhibit shortened distances of (B)H-Ru: 1.34 \AA and (N)H-C(β): 1.32 \AA . Correspondingly, the B-N bond is significantly shortened to 1.53 \AA . The catalyst component of **TS1** shows significant structural changes, including a folding down of the flanking aryl groups, with lengthened N-C(α) bonds. The simultaneously dual-type interaction of **1** with **AB** implies that the protic and hydride transfer from “**AB**” to “**3**” must be a concerted pathway. The gas-phase formation of “**3**” from “**1+AB**” has a $5.8 \text{ kcal mol}^{-1}$ activation energy barrier ($2 \rightarrow \text{TS1}$), and a corresponding reaction energy ($\text{TS1} \rightarrow 3$) of $-6.51 \text{ kcal mol}^{-1}$.

In the gas phase, the overall relative energy to form a hydrogenated β -diimine complex “**3**” from “**1**” and “**AB**” is an energetically favourable process ($-12.38 \text{ kcal mol}^{-1}$), but in the solvated model, the formation of “**3+4 (IB)**” is an endothermic process ($11.38 \text{ kcal mol}^{-1}$). These findings suggest that the nature of the solvent is of particular importance in the AB dehydrogenation process mediated by these β -diketiminato-ruthenium complexes.

(Fig 3 nearer to here)

In the second dehydrogenation step, which no longer involves AB or the resulting imino borane by-product, a H₂ molecule is released from “**3**” via **TS2** (cf. Fig. 3). Of interest, experimentally, complex **3** has been characterized through both solution NMR, IR and X-ray diffraction methods (see reference 31 for full details). In the mono-hydride β-diimine complex **3**, the distance between two hydrogen atoms is 1.885 Å, suggesting that there is already an interaction between the two hydrogen atoms (H^{δ+} and H^{δ-}). As complex **3** collapses into **TS2**, the Ru-H and C(β)-H distances are extended from 1.618 to 1.881 Å and from 1.105 to 1.567 Å, respectively. Dehydrogenation of complex “**3**” has a high activation energy barrier, while calculations predict that the dehydrogenation of “**3**” in THF is endothermic by 20.11 kcal mol⁻¹, and the corresponding reaction energy, i.e., **TS2**→**1**+H₂ is 10.75 kcal mol⁻¹.

Interestingly, there was relatively minor change in the energy barriers between the gas phase and solvent. This may be as a result of the solvent-stabilising effects for complex “**3**”. In comparison of AB addition to **1**, and dehydrogenation from “**3**”, a high activation energy barrier was predicted in the latter case. For AB addition to catalyst, the resulting **TS1** features a six-membered structure, whereas the dehydrogenation **TS2** exhibits a four-membered structure (cf. Fig.3). In principle, the four-membered TS feature higher barriers than those of the corresponding six-membered ones. Therefore, we propose a solvent assisted H₂ decoupling mechanism as will be discussed below. The overall activation energy barrier in the gas phase for dehydrogenation step from ammonia borane is 25.78 kcal mol⁻¹, and in THF solvent, the energy of activation is 35.12 kcal mol⁻¹.

The interaction between different substituted amine boranes with catalyst

As previously mentioned, the first step of the reaction involves proton and hydride transfer from AB to the catalyst. Therefore, to understand which substrate would best facilitate this process to the greatest extent, all of the optimised structures of the transition states for the addition of AB (**a**) and B,N-substituted AB variants (**b-l**) to the Ru-complex (**1**) are depicted in Fig. 6, and the corresponding activation energy barriers in both the gas phase and in solvent are shown in parenthesis. The interaction between AB (**a**) and sub-AB (**b-l**) variants with the ruthenium catalyst leads to a six-membered transition state. We hypothesise that in cases which

feature a lower activation barrier connected with **TS1**, a correlation with greater charge separation is observed, thus the NPA charges of the relevant atomic centres within the TS are specified in Table 2.

(Table 2 nearer to here)

(Fig 4 nearer to here)

It is clear that the positively-charged Ru centre accepts the hydride (H^-) from the boron centre. For the addition of AB to the catalyst, the corresponding activation energy barrier is $5.80 \text{ kcal mol}^{-1}$, whereas in the solvent, the barrier is found to be slightly higher, i.e., $15.01 \text{ kcal mol}^{-1}$. For the addition of AB to **1**, the nitrogen centre of AB involved in the TS has a greater negative charge ($-1.092e$) and boron has a slightly positive charge. This charge accumulation on the nitrogen atom may be as a result of charge transfer from β -C site of the Ru-complex to AB of “N”, whereas on the “B” atom, the charge is decreased slightly due to transfer of charge from “B” to the metal atom through the connecting hydrogen atom (cf. Table 2).

In the case of difluoro and phenyl substitution on “N” and “mono-F” substitution on “B”, this resulted in a more favourable sub-AB addition to the **1** than the standard AB addition. The present study’s calculations reveal that these types of substituted AB additions to the catalyst undergo a barrier-less decay to products in the gas phase; in the case of difluoro (**1c**), $-0.05 \text{ kcal mol}^{-1}$ and phenyl-substituted AB (**1i**), $-1.33 \text{ kcal mol}^{-1}$. In these two cases, formation of mono-hydride β -diimine product structures in the gas phase would be instantaneous, by-passing the formation of complexes of the type 2. The corresponding activation energy barrier for addition of difluoro substituted-AB to the catalyst was found to be negative, with the anomalous behaviour of this TS arising due to shortening of the B-N bond distance. Observed in the transition-state geometry, the B-N bond distance decreases from 1.675 \AA in AB to 1.535 \AA , and the nature of B-N bond becomes both shorter and stronger. This is clearly observed from the NPA charge separation on “B” ($0.734 e$) and “N” ($-1.130 e$) atoms. In a corresponding manner, the B-N bond develops greater ionic character in the TS geometry, but also exhibits enhanced π -bonding. The increasing strength of the latter leads to the corresponding substituted-AB molecules being able to release H_2 more readily. In the case of mono-fluoro substitution, the substitution of allyl- ($-C_3H_5$), 2-chloroethyl- or cyclopropyl- for addition of “N” sub-AB to the catalyst **1**, results in

computed activation energy barriers which are slightly better than those of addition to AB. Mono- and di-methyl substitution on the N atom results in computed activation energy barriers for addition of sub-AB which are slightly higher than that of AB. If we considered zero-point energy corrections to the computed activation energy barriers, the barriers for the AB substrate with methyl substitution on the N atom are slightly lower than those of AB, whereas di-methyl substitution on the N atom results in barriers closer to those found for AB.

The addition of AB and sub-AB to the catalyst in THF solvent, results in higher computed energy barriers than in the gas-phase. Comparing the solvent total energies of AB and **1** with the gas-phase energies, the solvent energies are positioned approximately 40 kcal/mol below the gas-phase energies. In a solvent, the reactants are stabilised by approximately 40 kcal/mol vis-à-vis the gas phase, whereas in the TS, the solvent energies lie 31 kcal/mol below the gas-phase energies. This difference of 9 kcal/mol shows a higher barrier value in the case of AB. The observation of a higher activation energy barrier of 9 kcal/mol in the solvent relative to the gas phase may be due to charge transfer from AB to the Ru Catalyst.

The Effect of Catalyst Substitution on Complex Dehydrogenation

Generally, one typical strategy employed to enhance reaction rate is to increase the concentration of the catalyst or raising temperature or some cases, pressure. Alternatively, this may be achieved through providing a secondary pathway for the reaction to proceed, which must include steps with overall net lower activation energy. The function of the catalyst is to provide a means to stabilize and assist the transformation of transition states. A catalyst provides an alternative route for the reaction, which has a lower activation energy barrier.

In the mechanism of hydrogen transfer involving ammonia borane, the H-H recoupling step, which involves complex dehydrogenation is proposed generally to be the rate-limiting process for generating hydrogen gas. This is supported through our calculations, which demonstrate that the dehydrogenation reaction step is rate-limiting step due to having a higher activation energy barrier. At this point in the reaction, the ammonia borane substrate or imino borane by-product is not thought to play a central role in the dehydrogenation process and, in a situation featuring a bifunctional metal-ligand complex, is completely dependent on the catalyst.

In previous work on catalytic processes mediated by Ru- β -diketiminato complexes, understanding the precise electronic nature imparted through the attachment of electron donating or withdrawing substituents to the N'N-cheating ligand has been found to be exceedingly important.^[37-38] To verify this statement in terms of AB dehydrogenation, twelve differently substituted catalysts were considered and the associated efficacies are estimated by considering the rate limiting step namely the dehydrogenation process (cf. Fig 3, Scheme 2).

(Fig 5 nearer to here)

Various different configurations of the catalysts (cf. Fig. S2) were optimised as the four-membered transition state (**C1** to **C9**) which involve the recoupling of the H-H atoms to form hydrogen gas. In Fig. 7, structures of all optimised TS structures are shown. The different substituent patterns include: attachment of electron-withdrawing groups to α -C positions ($-\text{CF}_3$, for structure **C1**, $-\text{F}$ atoms for structure **C2**), N-flanking aryl groups (*p*-Br substitution for structure **C3**, $-\text{CF}_3$ at phenyl *o*-positions for structure **C4**, $-\text{CH}_3$ groups at *o*-positions for structure **C5**), β -position ($-\text{CF}_3$ for **C6** and $-\text{F}$ for structure **C7**), and incorporation of the more basic nitrogen in place of the β -C atom (N atom at β -C atom for structure **C8**). Finally, structure **C9**, featuring an all-hydrogen backbone, *i.e.*, α, α' , β -H, was optimised to examine the effects of reducing the steric profile of the β -diketiminato ligand. In the Supporting Information, we have specified all of the corresponding catalyst optimised structures (cf. Supporting information, Fig. S2). We have computed the activation energy barriers in the gas phase and also in the presence of solvent (THF). All of the activation barriers for the various catalysts are shown in parenthesis. It is clear from Fig. 2 that, amongst all of the different substituted complexes apart from “**C2**”, “**C3**” and “**C8**”, E_{act} is lower by 0.35 to 2.9 kcal mol⁻¹, hence these catalysts would be theoretically more efficient in the recoupling process. Complex **C8** featuring the tri-aza analogue of the β -diketiminato ligand features a higher H₂ release barrier, which can be attributed to greater basicity of N and a generally stronger N-H bond. This is opposite to **C1**, where the α, α' - CF_3 substituent, involving the attachment of a high EWG group, weakens the C(β)-H bond.

Complete Mechanism involving Different Substituted Ru Catalysts

The overall complete catalytic cycle involving three different bifunctional η^6 -arene ruthenium complexes was studied using the M06L level of theory in the gas phase, where both the ammonia borane dehydrogenation and hydrogen release phases were combined. The computed enthalpy profiles of H₂ extraction and release from ammonia borane by three different electronically substituted Ru catalysts are presented in Figure 6, with corresponding free-energy results shown in Figure S3. An explanation from a Gibbs free-energy perspective is featured in the Supporting Information, and Figure S3 therein). Firstly, the Ru complex (**C**) associates with AB to form a lower-energy reaction complex (**2**) *via* (B)H-Ru and (N)H-C(β) weak interactions with the Ru-centre. The subsequent step from **2** to **TS1**, involves a tighter dual interaction between the catalysts and AB, whereby the B-H-Ru interaction is strengthened, while the second (N)H-C(β) interaction is enhanced. Collapse of the first transition state (**TS1**) results in simultaneous hydride transfer from B atom to Ru, and proton transfer from the N atom of AB to the β -carbanion site, yielding a mono-hydride Ru- β -dimine product (**3**). Finally, H₂ is released from the hydrogenated complex **3** *via* **TS2** and the original Ru Catalyst is regenerated and ready for the next reaction cycle. Importantly, the nature of the complex is an important consideration in the overall catalytic efficiencies. The order of computed reaction enthalpies for the AB-complex transition-state energy barriers, i.e. **2**→**TS1**, are α -CF₃ > α -H > α -CH₃, whereby the most electronic withdrawing complex (α -CF₃) has the greatest activation barrier. This can be directly attributed to the decreased nucleophilicity of the β -C site, as suggested by the NPA charges, Table 3. In comparison for the second phase, hydrogen release, **3**→**TS2**, the order from highest to lowest energy barrier is α -CH₃ > α -H > α -CF₃, where again reactivity is strongly collated with basicity of the β -C site, whereby complex **3** with α -CH₃ has stronger C(β)-H bonds. In this case, the strongly electron-withdrawing α -CF₃ substituted complex affords a lower energy barrier (-2.8 kcal mol⁻¹) than the electron-donating α -CH₃ substituted species. Therefore, the effects of incorporating electron-withdrawing substituents work oppositely for the two phases of the catalytic cycle. Hence in a bifunctional system, from a purely enthalpic point of view, it is not possible to formulate a complex that is both efficient at hydrogen extraction from AB, and H₂ release. From the consideration of the entire reaction cycle as shown in figure 6, it is noted that the overall process is slightly endothermic, thus the process is efficient in that the bond enthalpy of the single B-H and N-H bonds of ammonia borane are directly converted to a single H-H bond in H₂ without external loss of energy.

(Figures 6 nearer to here)

The Role of Various Types of Protic Solvent Molecules in the H-H Recoupling Stage

Generally, it is well known that solvent molecules are not always spectators in reaction pathways. For example, the nature of the solvent, in terms of polarity or even hydrogen bonding, is able to stabilise transition states and lower the energy of activation barriers. However, in recent years, for protic solvents, a more intimate and involved role has been discovered.^[39] Recently, H₂O as a solvent, was found to participate in the heterolytic H₂ activation in Cp*Ru(η^2 -H₂)PTA₂ and conversion to the trans-bis-hydride species, Cp*Ru(H)₂PTA₂ *via* an extended proton shuttling process.^[40] In the present study, an alternative reaction mechanism is considered for the role of the protic solvent (one equivalent protic solvent molecule), including the possibility that it could accelerate dehydrogenation from the mono-hydride β -diimine intermediate (**3**) (Fig 2, cf. Scheme 2) to facilitate the liberation of the hydrogen molecule and regeneration of the original catalytic species **1** (cf. Scheme 3).

(Scheme 3 nearer to here)

In the mechanism for hydrogen storage in ammonia-borane, the rate-limiting step is proposed to be the dehydrogenation/coupling of H₂, which has a higher activation energy barrier than the hydrogen transfer from AB. Seven different protic solvents (ROH, R = H, F, Me, Et, ⁱPr, ^tBu, allyl) were considered explicitly and the corresponding activation energy barriers were calculated by considering this rate-limiting step. The optimised structures (**D1** to **D7**) and selected parameters involved in this step are depicted in Figure 7. In the solvent assisted mechanism, the concerted dehydrogenation occurs *via* a six-membered transition state (cf. Scheme 3). In this case, the C(β)-H bond is broken, and the proton extracted by the lone pair of the O atom on the solvent. However, in this concerted mechanism the original solvent proton is completely transferred to the hydride (H⁻), which is released from the Ru centre. The proton (H⁺), and the hydride (H⁻) couple together and release as a hydrogen molecule. It is clear that this type of transition state where the solvent molecule bridges both the H(C β) and H(Ru) centres, reduces the amount of atomic displacement within the catalyst to enable H₂ coupling, thereby the system is more energy efficient. Such proton-shuttling mechanisms are known to be operative for enzymes in biological systems.^[41]

Amongst all of these protic solvents, *tert*-butyl (HOC₄H₉, pK_a = 19) and *iso*-propyl (HOC₃H₇, pK_a = 16.5) alcohols as solvents enable more facile proton transfer for dehydrogenation, which is correlated with a lower dehydrogenation activation energy barrier. Despite the increased steric bulk of these alcohols, the reduced activation energy is related to increased basicity of the OH oxygen, to stabilise and lower the energy of the TS. In the case of water (**D1**) and hypofluorous acid (**D2**) the computed barriers are found to be higher than the dehydrogenation process without solvent. Moreover, we attempted to use another ammonia borane molecule to see if this would facilitate loss of H₂ in a manner identical to that found for the alcohols, however, a stable six-member transition state could not be located on the potential energy surface.

(Fig 7 nearer to here)

Conclusions

We have studied four different density functionals, *i.e.*, B3LYP, B97D, M06 and M05-2X, on the experimentally synthesised complex **I** and related derivatives **II** and **III** and found that the M06L level of theory is essentially in quantitative agreement with experimental geometries. We have studied the addition of ammonia- and amine-borane to a novel bifunctional η^6 -arene ruthenium (**Ru**⁺¹) catalyst,^[14] whilst H₂ release from hydrogenated product iminoborane, **4** tends to be the rate-limiting step on the reaction-energy coordinate. Computational studies reveal that, amongst all of the substituted ammonia boranes considered, the additions of mono-, *di*-F- and phenyl- N-substituted amine borane systems to the Ru-catalyst are found to lower the activation energy barrier vis-à-vis AB, and they undergo an essentially barrier-less decay to products in the gas phase. This leads to the rapid formation of the di-hydrogenate intermediate in the gas phase. Employing a technique for accounting for solvent (THF) effects, namely the polarisable continuum method (PCM), the computed free energy ΔG barriers for AB addition to the Ru Catalyst were generally found to be slightly higher than the gas phase values. Furthermore, a number of various substituted catalysts have been examined with respect to the rate-limiting step, hydrogen recoupling. However, amongst these catalysts, very small energy variations are observed for hydrogen release from the mono-hydride Ru β -diimine intermediate. The computed reaction pathways are endothermic in nature, and, amongst the three pathways, the α -CF₃-substituted Ru- catalyst can release the H₂ in the most favourable manner. However, several

protic solvents have been evaluated to assist the catalyst with the rate-limiting step to assist dehydrogenation. More basic solvents such as methanol, *iso*-propyl alcohol and *tert*-butanol have been found to enhance the dehydrogenation process compared to water.

It is perhaps appropriate to discuss briefly experimental analogues of substitution, and similarity to other (DFT) mechanistic studies. The fluoro-substitution on amines proposed in the present study is related to those described synthetically by Furrin and Fainzil'berg.^[42] In terms of the mechanistic (DFT) study of Swinnen *et al.*,^[15] which has a very similar mechanism to that studied here (*i.e.*, as mentioned previously, shifting two H atoms of ammonia borane to two Ru/C centres, with their subsequent elimination to generate H₂ from the complex), the findings of the possibility of negligible activation-energy barriers in some cases in the present study echoes some of the conclusions of ref. 15, which found in particular that a second ammonia borane molecules' involvement in the process helps to reduce activation-energy barriers substantially.

Acknowledgements

This material is based upon works supported by Science Foundation Ireland (SFI) under Grant No. [07/SRC/B1160]. We thank SFI and the Irish Centre for High-End Computing for the provision of high-performance computing facilities. ADP thanks SFI for his Stokes Lectureship.

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