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Group 4 metallocene catalysed full dehydrogenation of hydrazine borane†

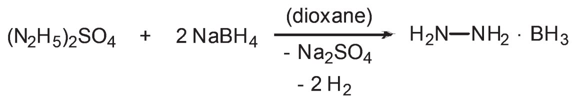
Johannes Thomas, Marcus Klahn, Anke Spannenberg and Torsten Beweries*

A study of the full dehydrogenation of hydrazine borane (H_2N–$NH_2{\cdot}BH_3$) to give H_2 and N_2 as gaseous products catalysed by a variety of group 4 metallocene alkyne complexes of the type $Cp'_2M(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (Cp′ = substituted or unsubstituted η^5-cyclopentadienyl; M = Ti, no L; M = Zr, L = pyridine) and group 4 metallocene hydrides is presented. Volumetric data show that the amount of hydrogen released is strongly dependent on both, the metal and the cyclopentadienyl ligand.

Introduction

The problem of hydrogen storage is one main aspect of current research in connection with the so-called hydrogen economy.[1] Among all the approaches for storing the hydrogen cleanly and efficiently, the use of chemical hydrides for this purpose appears to be promising, mostly due to their high gravimetric hydrogen capacities (*e.g.* 19.6 wt% in ammonia borane (AB) and 15.4 wt% in hydrazine borane (HB)).[2] Methods for the generation of the energy carrier from these compounds include hydrolysis in aqueous solutions, catalytic dehydrocoupling in suitable solvents as well as controlled thermal decomposition of the solid species. Significant efforts regarding regeneration of the spent fuels were made very recently;[3] however, for practical applications of AB and structurally similar chemical hydrides this is still a major problem.[4]

HB and its parent, thermally labile and explosive compound hydrazine bisborane (16.9 wt%, HBB), can easily be synthesised by reacting the corresponding hydrazine sulfates (*i.e.* dihydrazine sulfate and hydrazine sulfate, respectively) with sodium borohydride in dioxane (Scheme 1).[5] A detailed study on the synthesis and full characterisation of HB was published very recently by Demirci *et al.*[6]



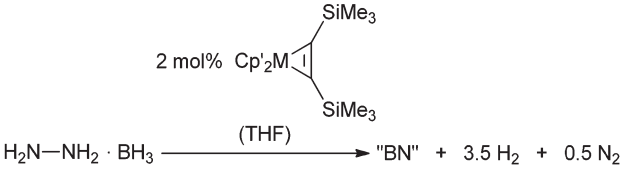
$$(N_2H_5)_2SO_4 \quad + \quad 2\,NaBH_4 \xrightarrow[\substack{-\ Na_2SO_4 \\ -\ 2\,H_2}]{(dioxane)} H_2N{-}NH_2 \cdot BH_3$$

Scheme 1 Synthesis of HB.

The thermal decomposition of hydrazine borane was first reported by Goubeau and Ricker.[5] Recently, Lentz *et al.* have described a method of improving the hydrogen storage capabilities of HB by adding equimolar amounts of LiH.[7] The authors point out that the mechanism of decomposition of this mixture is complicated and rather difficult to investigate since the reaction products are insoluble in common organic solvents. However, theoretical studies by Nguyen and Dixon suggest a dehydrogenation mechanism very similar to that of the well-known AB dehydrogenation with the terminal NH_2 group acting as a substituent for the $[H_2N{\cdot}BH_3]$ unit, making the HB system structurally very similar to AB.[8] Additionally, as another method of hydrogen generation from HB, hydrolysis in the presence of heterogeneous catalysts was reported by Demirci and Xu and co-workers (Ni–Pt nanoparticles).[9] In this report, H_2 selectivities as high as 93% were achieved. Most interestingly, along with hydrolysis of the BH_3 unit in this case also decomposition of the N_2H_4 moiety was observed to yield H_2 and N_2. The nature of the decomposition pathway and thus of the ratio H_2/N_2 in the gas phase was found to be strongly dependent on the composition of the $Ni_{1-x}Pt_x$ nanoparticles. Additionally, Özkar *et al.* presented a study of the hydrolysis of HB catalysed by Rh(0), which was generated from a $RhCl_3$ precursor.[10] However, to the best of our knowledge, a transition metal catalysed homogeneous process for the dehydrogenation of HB has not been described to date. Compared to other methods described before, this would allow for a better understanding of the mechanism of dehydrogenation. Moreover, reaction temperatures should be much lower than in thermolysis studies.

Leibniz-Insitut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Str. 29a, 18059 Rostock, Germany. E-mail: torsten.beweries@catalysis.de; Fax: +49 381 1281 104; Tel: +49 381 1281 51104

†Electronic supplementary information (ESI) available: NMR spectra, XRD analysis of the dehydrogenation product, volumetric data and details referring to the regeneration experiments as well as crystallographic details in cif format. CCDC 936330. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt51370j



Scheme 2 Hypothetical full dehydrogenation of HB with group 4 metallocene alkyne complexes as catalysts.

Very recently, our group has reported on the dehydrogenation of dimethylamine borane (3.4 wt% H_2, DMAB) with titanocene and zirconocene alkyne complexes of the type $Cp'_2M(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (Cp′ = substituted or unsubstituted η^5-cyclopentadienyl; M = Ti, Zr; L = pyridine, THF).[11] In these complexes the highly reactive 14 electron metallocene fragment $[Cp'_2M]$ is stabilised by the bis(trimethylsilyl)acetylene ligand which is eliminated under reaction conditions and thus liberates the free reactive metallocene species.[12] Significant differences in catalytic activity were observed when changing the Cp ligand as well as the metal centre. In this contribution, we extend our previous studies to the catalytic dehydrogenation of HB using group 4 metallocene alkyne complexes (Scheme 2) as well as group 4 metallocene hydrides.

Results and discussion

Catalytic experiments

In a typical catalytic experiment, the metallocene catalyst was dissolved in a double-walled thermostatically controlled reaction vessel, followed by the addition of the HB solution to the stirred solution. In this context it should be noted that for our investigations we were restricted to THF as the solvent because HB is only sparingly soluble in non-polar solvents such as toluene or *n*-hexane. More polar solvents than THF or even protic solvents were not suited for dehydrogenation experiments due to the limited stability of the catalyst complexes in these media.[13] Gas evolutions were measured using an automatic gas buret; details of the experimental setup were published by us elsewhere.[11b] An example of a gas evolution curve is shown in Fig. 1. Analysis of the gas phase after the reaction showed the presence of hydrogen along with significant amounts of nitrogen.

Interestingly, in all cases the gas evolution curves show a significant kink, indicating that the release of the gaseous products from HB does not take place in a linear fashion. Instead, the formation of a to some extent stable intermediate is likely. Such non-linear gas evolution curves were also observed by Demirci and co-workers, who assigned this to the stepwise decomposition with release of H_2 from the BH_3 unit in a first stage followed by concomitant formation of H_2 and N_2 by decomposition of the N_2H_4 fragment.[14]

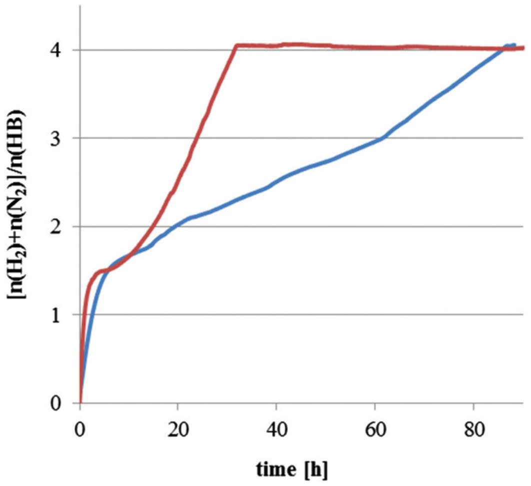


Fig. 1 Gas evolution curve recorded during dehydrogenation of HB in THF with 2 mol% $(iPrC_5H_4)_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**1f**) at 25 °C (blue line) and 50 °C (red line).

Table 1 Group 4 metallocene bis(trimethylsilyl)acetylene complex catalysed dehydrogenation of HB

Catalyst	*T* (°C)	*t* (h)	$[n(H_2) + n(N_2)]/n[HB]$
$Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ **1a**	25	87	3.9
	50	46	4.0
$Cp^*_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ **1b**	25	24	0.0
	50	24	0.0
rac-(ebthi)$Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$[15] **1c**	25	45	0.3
	50	47	3.9
$(MeC_5H_4)_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ **1d**	25	70	4.0
	50	64	3.9
$(EtC_5H_4)_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ **1e**	25	177	3.9
	50	47	4.0
$(iPrC_5H_4)_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ **1f**	25	79	3.9
	50	32	4.0
$Cp_2Zr(py)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ **2a**	25	65	0.9
	50	10	0.5
$Cp^*_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ **2b**	25	93	4.0
	50	30	1.8
rac-(ebthi)$Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ **2c**	25	75	4.0
	50	30	1.8

HB dehydrogenation experiments were performed at 25 °C and at 50 °C (Fig. S4–S7†). In order to evaluate the influence of cyclopentadienyl substituents and metal centres, different group 4 metallocene alkyne complexes of the type $Cp'_2M(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ were tested. The results of the catalytic tests are compiled in Table 1. In all cases, reaction times of more than 24 hours were required for full consumption of the substrate. It became evident that the iPr substituted complex **1f** is the most active catalyst for HB dehydrogenation. The higher activity of this catalyst compared to other metallocene bis(trimethylsilyl)acetylene complexes was reported by us earlier;[11b] however, a rationalisation for this reaction behavior is still very difficult. Most surprisingly, the permethylated titanocene complex **1b** was found to be totally inactive. It should be noted that control experiments without any catalyst in THF gave no gas evolution at all, thus indicating that HB is stable under reaction conditions and the described dehydrogenation reactions are solely catalysed by the metallocene complexes.

The reactivity of zirconocene complexes **2a**–**2c** turned out to be more diverse. Whereas **2a** did not show full consumption of HB, most surprisingly the fully methylated complex **2b** as well as the bridged complex **2c** gave almost quantitative conversion at 25 °C. A rationalisation for this behaviour can be found in the interaction of the solvent THF with the metallocene fragments in **2a**, which was described earlier.[16] Due to the increased steric demand of Cp* ligands and the bridged *rac*-(ebthi) ligand, respectively, this coordination is not preferred in **2b** and **2c**.

As mentioned above, in all experiments using group 4 metallocene alkyne complexes as dehydrogenation catalysts, a kink was observed in the hydrogen evolution curves. This motivated us to investigate whether this is also present if other metallocene complexes are used as catalysts. In previous studies of the dehydrogenation of other amine borane compounds, metal hydrides were assumed to be present as intermediates in the catalytic cycle.[17] Mechanistic studies using computational methods as well as the synthesis of well-defined intermediate complexes further supported the role of metal hydride fragments.[18] This prompted us to evaluate if group 4 metal hydride complexes can also be employed for the catalytic dehydrogenation of HB. Thus, we used an *in situ* system consisting of Cp'_2TiF_2 and iBu_2AlH [Cp'_2 = Cp_2 (**3a**), Cp^*_2 (**3b**), *rac*-(ebthi) (**3c**)] to generate titanocene hydrides as well as the literature-known dimeric zirconocene dihydride complex [*rac*-(ebthi)ZrH-(μ-H)]$_2$ (**4**) (Table 2),[19a] which can also be obtained by reaction of the corresponding zirconocene difluoride with iBu_2AlH.[19b]

Titanocene(III) hydrides are well precedented in the literature; however, almost no monomeric species with isolated hydride functionalities are known. To the best of our knowledge, Cp^*_2TiH (**5**), which was first described by Andersen and co-workers,[20] is the only example for this class of compounds. In order to evaluate the role of this structural motif in the dehydrogenation of HB, we synthesised the mononuclear hydride complex **5** *via* hydrogenolysis of the corresponding methyl complex Cp^*_2TiMe. Catalytic tests revealed that this complex is also moderately active for the dehydrogenation of HB.

It should be noted that many titanocene hydrides are stabilised by interaction with other metal centres, thus yielding dinuclear complexes such as $Cp^*_2Ti(\mu\text{-H})_2Mg(\mu\text{-H})_2TiCp^*_2$[21] or the dimeric titanocene μ-(η^5:η^5-fulvalene)-di-(μ-hydride)-bis-(η^5-cyclopentadienyltitanium).[22] The application of the dimeric zirconocene dihydride complex **4** gave smooth and complete dehydrogenation of HB; interestingly, in this case the gas evolution curve did not show the above mentioned kink. Unfortunately, the reaction behaviour of *in situ* generated titanocene hydrides was found to be very different. Volumetric curves recorded clearly differ in shape, and catalytic activity is strongly dependent on the nature of the Cp′ ligand (Fig. 2). Whereas the mixture of $Cp^*_2TiF_2$ and iBu_2AlH (**3b**) fully converts the HB, dehydrogenation ceases at a conversion of 65 and 55% for Cp_2TiF_2/iBu_2AlH (**3a**) and *rac*-(ebthi)TiF_2/iBu_2AlH (**3c**), respectively (T = 50 °C). A reason for this behaviour is assumed to be the limited stability of the corresponding titanocene hydrides. It should be noted that both, iBu_2AlH and the titanocene fluoride complexes, alone only produce trace amounts of H_2. The synergistic effect of both species generates an active and stable titanocene(III) hydride complex.

Table 2 Group 4 metallocene hydride catalysed dehydrogenation of HB

Catalyst	T (°C)	t (h)	$[n(H_2) + n(N_2)]/n[HB]$
Cp_2TiF_2/iBu_2AlH **3a**	25	110	1.1
	50	110	2.6
$Cp^*_2TiF_2/iBu_2AlH$ **3b**	25	110	1.1
	50	108	4.0
rac-(ebthi)TiF_2/iBu_2AlH **3c**	25	110	1.6
	50	110	2.2
[*rac*-(ebthi)ZrH(μ-H)]$_2$ **4**	25	43	3.9
	50	44	4.0
Cp^*_2TiH **5**	25	132	1.1
	50	120	1.5

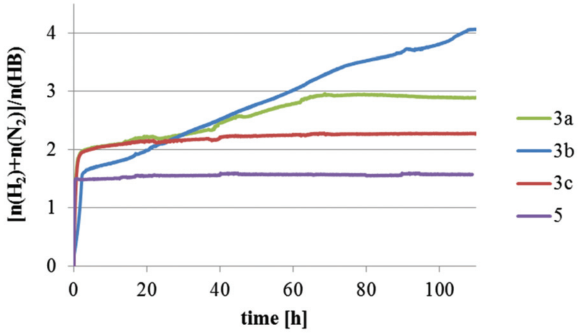


Fig. 2 Gas evolution curve recorded during dehydrogenation of HB with *in situ* generated titanocene hydride systems **3a–c** and the isolated titanocene(III) hydride **5** at 50 °C in THF.

Thus, we assume that formation of a catalytically active hydride intermediate takes place during dehydrogenation of HB with metallocene alkyne complexes. Also, it became evident that titanocene(III) species play an important role in the catalytic dehydrogenation of HB, an assumption that was made before for other dehydrocoupling reactions using group 4 metallocenes.[17d,23]

Fortunately, we were able to isolate crystals from the reaction of $Cp^*_2TiF_2$ and iBu_2AlH in toluene, which were suitable for X-ray analysis. The molecular structure (Fig. 3) of the formed hitherto unknown complex **6** shows the decamethyltitanocene fragment and the aluminium dialkyl unit bridged by two hydrides.

Bond lengths of the central Ti–H–Al–H unit of Ti1–H1 1.88(2) and Al1–H1 1.66(2) Å were obtained, thus reflecting the overlap of the resonance forms shown in Fig. 4. Hence, compound **6** is best referred to as an adduct between decamethyltitanocene(III) monohydride and the alane iBu_2AlH. Similar complexes were described earlier, *e.g.* Bulychev and co-workers reported on the parent compound $Cp_2Ti(\mu\text{-H})_2AlCl_2\cdot OEt_2$.[24] It should be noted that catalytic experiments using the isolated complex **6** gave similar results compared to the *in situ* system **3b**.

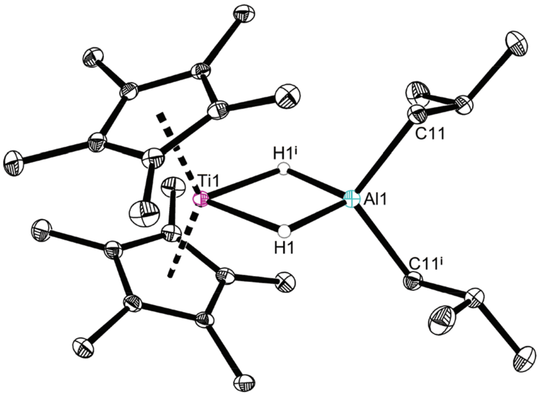


Fig. 3 Molecular structure of **6**. Thermal ellipsoids correspond to 30% probability. Hydrogen atoms (except bridging hydrides) are omitted for clarity. ^{i}Symmetry operator used to generate equivalent atoms: $-x + 2, y, -z + 0.5$.

Analysis of the dehydrogenation products

In order to evaluate the mechanism of HB dehydrogenation, we aimed to perform *in situ* NMR experiments. However, in ^{11}B NMR only a decrease of the starting material was detected (Fig. S2†). Resonances due to the dehydrogenation product or intermediates were not observed, owing to the complete insolubility of the formed polyaminoborane polymers.

Previous studies have shown that the full characterisation of HB dehydrogenation products is very challenging, mainly due to their insolubility in common polar solvents.[7] Thus, we performed XRD studies on the isolated material (Fig. S3†). Different samples were obtained by filtration of the reaction solution, washing with cold THF and drying under vacuum. However, despite repeated XRD runs, no accurate information on the composition of the dehydrogenated material could be obtained. Broad signals at 2θ = 26 and 43° suggest the formation of polyborazylenes and different boron nitride species.[25,26] The very intense reflection at approximately 2θ = 16° was tentatively assigned to higher boranes (*e.g.* $B_{13}H_{19}$, ICDD 00-085-0336).

Results from elemental analysis (ICP-OES) of a material that showed the release of 4 equivalents of (H_2 + N_2) gave a B/N ratio of 1 : 1.03, thus suggesting that half a mole of dinitrogen was present in the evolved gas mixture.

A comparison of the IR spectra of pure HB and the solid dehydrogenation product is depicted in Fig. 5. Whereas the IR spectrum of the starting material shows very intense bands in the N–H as well as in the B–H stretch regions at 2650–3350 cm^{-1} and 2250–2400 cm^{-1}, respectively, these signals were not found in the spectrum of the dehydrogenation product. Moreover, strong bands in the N–H asymmetric bending region (1588 and 1620 cm^{-1}) were absent in the spectrum of the dehydrogenated material. Instead, a sharp signal at 3214 cm^{-1} indicates the presence of NH groups. A broad signal at 2450 cm^{-1} most likely indicates the presence of BH or BH_2 groups in a polymeric regime.

Our results from XRD and IR spectroscopy are well in line with data reported very recently by Demirci and co-workers.[6]

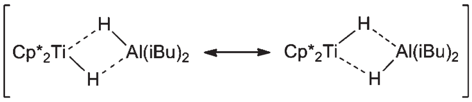


Fig. 4 Resonance forms for complex **6**.

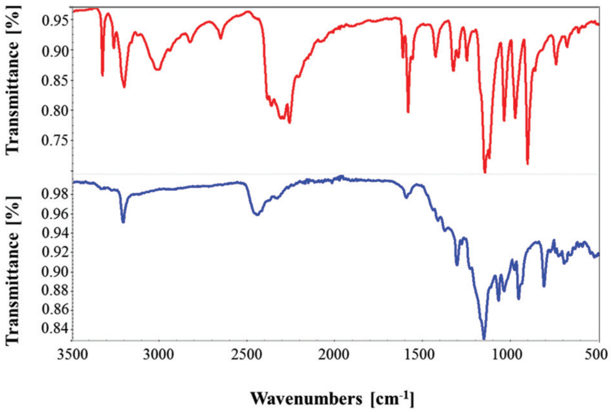


Fig. 5 Comparison of the IR spectra of HB (red) and the dehydrogenation product (blue).

Thermal decomposition of HB gave a polymeric structure which – from IR spectroscopy and XRD – appears to be very similar to the material isolated from the herein described metallocene catalysed dehydrogenation reaction. As for the constitution of the solid decomposition product, the authors suggest several likely structural units, most of them involving cyclic [H_2N–NH–BH_2] units.[6]

Additionally, we attempted to regenerate the spent HB fuel by reaction of the latter with a hydrogen-rich reducing agent. We chose hydrazine, an approach which was reported earlier by Sutton and Gordon and co-workers for the regeneration of a spent AB material.[3b] Indeed, addition of an excess of hydrazine to the HB dehydrogenation product dispersed in THF resulted in the highly selective formation of HB as evidenced by ^{11}B NMR (quartet at −17.65 ppm, Fig. S8†) after heating at 50 °C for 24 h. Further optimisations of the regeneration protocol are currently under investigation in our group.

Conclusions

We have demonstrated the group 4 metallocene alkyne complex catalysed dehydrogenation of hydrazine borane. Significant differences in the catalytic performance of the catalyst complexes became evident with the iPr substituted complex **1f** being the most active. Additionally, isolated and *in situ* generated group 4 metallocene hydride complexes were tested for the dehydrogenation reaction. Most interestingly, in this case the dinuclear bridged zirconocene complex [*rac*-(ebthi)ZrH-(μ-H)]$_2$ was the most active catalyst. Analysis of the insoluble reaction products showed that most likely a mixture of cyclic [H_2N–NH–BH_2] structures and boron nitride species is present after the dehydrogenation reaction. To the best of our knowledge, this is the first example for a transition metal catalysed homogeneous process for the dehydrogenation of hydrazine borane. Significant improvements in catalytic activity are still needed; however, the potential of hydrazine borane and related compounds as a chemical hydrogen storage material appears to be considerable.

Acknowledgements

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