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COVER ARTICLE Rosenthal *et al.* Catalytic dehydrogenation of dimethylamine borane by group 4 metallocene alkyne complexes and homoleptic amido compounds

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COMMUNICATION

Catalytic dehydrogenation of dimethylamine borane by group 4 metallocene alkyne complexes and homoleptic amido compounds[†]

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Dehydrogenation of $Me_2NH \cdot BH_3$ (1) by group 4 metallocene alkyne complexes of the type $Cp_2M(L)(\eta^2-Me_3SiC_2SiMe_3)$ [$Cp = \eta^s$ -cyclopentadienyl; M = Ti, no L (2Ti); M = Zr, L = pyridine (2Zr)] and group 4 metal amido complexes of the type $M(NMe_2)_4$ [M = Ti (8Ti), Zr (8Zr)] is presented.

Introduction

Along with the increasing current interest in hydrogen technology, the research on suitable, safe and stable hydrogen storage materials became more and more important. Amine borane adducts are discussed to be promising candidates to meet the requirements for such applications since they possess a high gravimetric hydrogen capacity and release of the energy carrier is easily possible using suitable catalysts.¹ The use of metal hydrides and transition metal complexes for this purpose was demonstrated on several occasions.² However, the most prominent disadvantage so far is the regeneration of the dehydrogenation products. This problem was addressed successfully by Dixon and Gordon and co-workers, who used benzenedithiol and organotin hydrides for the reduction of polyborazylene.³

Very recently, Manners *et al.* reported on the dehydrogenation of Me₂NH·BH₃ (1) using group 4 metallocene complexes.⁴ They found that starting from different Cp₂MCl₂/*n*-BuLi precursors (M = Ti, Zr, Hf) the *in situ* formed [Cp₂M] species can perform catalytic dehydrogenation reactions. It became evident that Cp₂TiCl₂/*n*-BuLi shows the highest activity whereas the corresponding zirconocene system displays no activity at all. The reason for this behavior could be found in the different stabilities of the species formed during the catalytic cycle. This assumption is corroborated by the results of Roesler and co-workers who reported on the isolation and full characterization of the adduct from the reaction of [Cp₂Zr] with H₃N·BH₃.⁵ The mechanism of the overall reaction was studied by Luo and Ohno using DFT calculations,⁶ spectroscopic evidence supporting the theoretical results was provided later by Manners *et al.*⁴

In this context, the use of other group 4 metallocene sources such as the metallocene alkyne complexes of the type

 $Cp'_2M(L)(\eta^2-Me_3SiC_2SiMe_3)$ (Cp' = unsubstituted or substituted η^5 -cyclopentadienyl; **2Ti**: Cp' = Cp, M = Ti, no L, **2Zr**: Cp' = Cp, M = Zr, L = pyridine, **7Ti**: $Cp' = Cp^*$, M = Ti, no L, **7Zr**: $Cp' = Cp^*$, M = Zr, no L)^{7,8} appeared to be interesting to study. These compounds release the alkyne under relatively mild conditions resulting in the formation of the highly reactive 14 electron fragments [Cp'_2M], which can then undergo further stoichiometric and catalytic reactions. Examples for the application of these alkyne complexes include the formation of metallacycles, catalytic hydroaminations and polymerisation reactions.⁹

In this contribution we present studies on the application of group 4 metal complexes, in particular metallocene alkyne complexes and metal amides for the catalytic dehydrogenation of dimethylamine borane.

Results and Discussion

Catalytic dehydrogenation of 1 with 2M

For a direct comparison, all catalytic experiments were performed using a catalyst concentration of 2 mol% (as used before by Manners *et al.*). Solutions of the amine borane 1 were cannulatransferred to stirred solutions of the corresponding metallocene catalyst **2M**, followed by immediate extensive gas evolution. The colour of the reaction mixtures deepened during the reaction to give dark reddish/black solutions in all cases. Analysis of the reaction gases by gas chromatography confirmed the exclusive formation of hydrogen.

¹¹B NMR investigations revealed the formation of a mixture of dehydrogenation products (Fig. 1). The constitution of the latter is very close to the one observed before,⁴ however, in our case, no product **6** was found. Instead, only the linear intermediate $Me_2NH-BH_2-NMe_2-BH_3$ (**3**, ¹¹B NMR: 2.2 ppm) and the products cyclic dimer [Me_2N-BH_2]₂ (**4**, 5.5 ppm) and dehydrogenated aminoborane $Me_2N=BH_2$ (**5**, 38.2 ppm) were found in solution (Scheme 1).¹⁰



Scheme 1 Catalytic dehydrogenation of 1.

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procedures, NMR spectra and ESI-MS of the dehydrogenation reactions. See DOI: 10.1039/c1dt10366k



Fig. 1 ¹¹B{¹H} NMR spectra (96 MHz, 297 K, toluene, unlocked) of the reaction of **1** with **2Ti** (2 mol%). Last spectrum recorded at t = 26 h.

Thus, the reaction mechanism should be similar as described in literature. Most surprisingly and in contrast to the already published results, the zirconocene alkyne complex shows activity in the catalytic dehydrogenation of dimethylamine borane. Although being significantly less active compared to the titanocene complex (2Ti: 86% conversion after 16 h, 2Zr: 42% conversion after 16 h, Fig. 2), it becomes clear that under these conditions [Cp₂Zr] is a suitable catalyst. Manners et al. used Cp₂ZrCl₂/n-BuLi¹¹ and found no conversion after 20 h. In this context, it should be noted that the authors performed the reaction to give the metallocene $[Cp_2Zr]$ at -15 °C, followed by warming of the solution to room temperature and addition of Me₂NH·BH₃. Dioumaev and Harrod showed that under these conditions, no [Cp₂Zr] is present in solution.¹² Instead, a mixture of zirconocene complexes including butylzirconocene(III), zirconocene(III) hydride, butenylzirconocene(IV) hydride dimer and 1,1-bis(cyclopentadienyl)-2-methyl-3-(zirconocenyl hydride)-1-zirconacyclobutane(IV) dimer is formed upon warming of dibutylzirconocene to room temperature.



Fig. 2 Hydrogen evolution curves of the catalytic dehydrogenation of 1 with 2M (top: M = Ti, bottom: M = Zr). Conditions: toluene, 2 mol% catalyst, 24 °C.

An explanation for the lower activity of **2Zr** compared to **2Ti** could be found in the stronger complexation of the alkyne to the metal in the first case,^{7b} which hinders the generation of the free metallocene, most likely the catalytically active species. ¹¹B{¹H} NMR spectra of this reaction also indicate the lower activity of the zirconocene complex; details referring to this can be found in the Electronic Supplementary Information (ESI[†]).¹³

Catalytic dehydrogenation of 1 with 7M

Under the same conditions as used before for the **2M** catalysed reactions (2 mol% catalyst, toluene, 24 °C), permethylated metallocene alkyne complexes $Cp*_2M(\eta^2-Me_3SiC_2SiMe_3)$ (**7M**) display no activity for the catalytic dehydrogenation of **1**. This behaviour was observed before by Chirik and co-workers, who found that sterically more demanding substituents at the cyclopentadienyl ligand result in a significant decrease of activity in the catalytic dehydrogenation of **1**.¹⁴ Moreover, in the metallocene alkyne complex catalysed dehydrogenative coupling of silanes to polysilanes reduced reactivity was observed when increasing the steric demand of the Cp ligand.¹⁵

Catalytic dehydrogenation of 1 with homoleptic M(IV) complexes

To evaluate the influence of the oxidation state at the titanium center on the performance of the catalyst, we tested homoleptic Ti(IV) complexes. Manners *et al.* showed that Ti(0) and Ti(III) compounds display no activity in dehydrogenation reactions, however, Ti(IV) species were not investigated.

Similarly as for the dehydrogenation of 1 with 2M, in the reactions with metal amides $M(NMe_2)_4$ (8M, M = Ti, Zr) immediate and extensive hydrogen evolution was observed. The solutions of the reaction mixtures turned dark red for 8Ti but remained yellow for 8Zr. This might indicate subtle differences in the reaction pathways.

One possible reaction mechanism includes the initial formation of a metallaaziridine species from a metal amido complex as suggested earlier by Nugent et al. (Scheme 2).¹⁶ This assumption finds experimental support in the results of Schafer and co-workers who isolated such metallacycles and highlighted their role in catalytic reactions involving metal amido complexes.¹⁷ Another possibility which was also mentioned very recently by Wright et al. for the Al(NMe₂)₃ catalysed dehydrogenation of Me₂NH·BH₃ is the initial deprotonation of the substrate along with formation of Me₂NH and β -hydride elimination to give a four-membered M-N–B–N ring, which could then eliminate H_2 or $(Me_2N)_2BH$ (6), respectively.¹⁸ This mechanism might explain the formation of a relatively large amount of the latter compound, as indicated by the signal at 29.1 ppm in ${}^{11}B{}^{1}H{}$ NMR spectra (Fig. 3^{19}). Studies on the reaction mechanism and the fate of the catalyst are still ongoing and will be published in due course. However, from NMR investigations it becomes clear that the composition of the mixture of dehydrogenation products – although containing the same species - is different compared to the 2M catalysed reactions. Volumetric analysis of the hydrogen evolution in the reactions using 8M revealed that both metal amides display the same catalytic activity (Fig. 4), indicating that in this case the influence of the metal can be neglected. Most likely, this is due to the similarities in M-N(alkyl) bond energies (e.g. Ti-NEt₂ 307 kJ mol⁻¹, Zr–NEt₂ 337 kJ mol⁻¹).²⁰



Scheme 2 Metallaaziridines from metal amido complexes.¹⁶



Fig. 3 ¹¹B{¹H} NMR spectra (96 MHz, 297 K, toluene, unlocked) of the reaction of **1** with **8Ti** (2 mol%). Last spectrum recorded at t = 30 h.



Fig. 4 Hydrogen evolution curves of the catalytic dehydrogenation of 1 with 8M (top: M = Ti, bottom: M = Zr). Conditions: toluene, 2 mol% catalyst, 24 °C.

We also performed catalytic tests with other homoleptic Ti(IV) compounds such as $Ti(O'Pr)_4$ (9) and $TiCl_4$ (10) to find out whether the amido functionality plays a crucial role for the performance of the catalyst. We found that both, 9 and 10 show no activity at all; this indicates that the presence of a group which can undergo insertion reactions to start a catalytic cycle is necessary.

Conclusions

We have demonstrated the homogeneous catalytic dehydrogenation of $Me_2NH \cdot BH_3$ by group 4 metallocene(II) alkyne complexes and group 4 metal(IV) amides (Table 1). It became evident that

Table 1Catalytic dehydrogenation of $Me_2NH \cdot BH_3$. Conditions: toluene,24 °C, 2 mol% catalyst. Yields were determined by volumetric analysis

Catalyst	Time/h	Yield (H_2) (%)
2Ti	16	86
2Zr	16	42
7Ti	16	0
7Zr	16	0
8Ti	22	86
8Zr	22	87
9	16	0
10	16	0

the $[Cp_2Zr]$ fragment is active for such reactions, however being significantly less active than the corresponding titanocene species. Moreover, metal(IV) amide complexes have proved to be suitable for dehydrogenation of Me₂NH·BH₃ as well. In contrast to the $[Cp_2M]$ catalysed reactions, in this case no influence of the metal was observed. It should be noted that in all cases exclusively hydrogen was released from the reaction mixtures.

Acknowledgements

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