

Dehydrocoupling of dimethylamine-borane catalysed by rhenium complexes and its application in olefin transfer-hydrogenations†

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Re(I) complexes are applied as catalysts for the dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ and the transfer-hydrogenation of olefins.

Recently there has been increasing interest in the development of transition-metal-catalysed reactions which allow the generation of new bonds between main group elements.¹ In particular, the dehydrocoupling of amine-borane adducts catalysed by transition metal complexes have become more and more important with respect to hydrogen storage.² Late transition metal compounds including those with Rh, Pd, Ru, Ir and Ni centers, as well as such with early transition metals, such as Ti, have been employed. For example, the group of Ian Manners has reported the dehydrocoupling of amine-boranes catalysed by Rh colloids³ and an early transition metal Ti complex.⁴ Both, colloidal Rh and the Ti complex, are even active in the tandem dehydrocoupling–hydrogenation reactions.⁵ More active catalysts for hydrogen release from ammonia–borane are an Ir-pincer⁶ complex and a first row transition metal Ni-complex.⁷

Recent research of our group focuses on the development of new catalysts for the dehydrogenation–hydrogenation of amine-boranes. Considerable attention was paid to the non-noble middle transition metal rhenium, which is known to often show “non-catalytic” tendencies obeying the 18-electron rule and possessing a certain reluctance to form coordinatively unsaturated species. This however can in most cases be overcome using special ligand sphere effects. So far, rhenium complexes can catalyse C–H activations⁸ and based on the fact that amine-boranes are isoelectronic with alkanes, we indeed considered their application to the chemistry of amine-boranes.

Herein we report the first example of mono-nitrosyl Re(I) complexes $[\text{ReBr}_2(\text{NO})(\text{PR}_3)_2\text{L}]$ (L = H_2 **1**, CH_3CN **2** and ethylene **3**) to catalyse dehydrocoupling of dimethylamine-borane ($\text{Me}_2\text{NH}\cdot\text{BH}_3$) and its application in transfer-hydrogenation reactions. The organometallic chemistry of mono-nitrosyl Re(I) complexes bearing the phosphines P^iPr_3 (**a**) and PCy_3 (**b**) and dihydrogen, acetonitrile and ethylene as labile ligands was reported by our group.⁹ These species can also serve as precursors for the preparation of rhenium hydride complexes which are catalysts in hydrogenation and hydrosilylation reactions.¹⁰ When a solution of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ in dioxane was treated with a catalytic amount (1 mol%) of the rhenium dihydrogen complex $[\text{ReBr}_2(\text{NO})(\text{P}^i\text{Pr}_3)_2(\eta^2\text{-H}_2)]$ (**1a**) and stirred at 85 °C, evolution of hydrogen gas was

observed. After 4 h a ^{11}B -NMR spectrum indicated that the conversion to the cyclic aminoborane dimer $[\text{Me}_2\text{N}\text{-BH}_2]_2$ (δ 4.50 ppm, t, J_{BH} = 112 Hz) was almost complete with a 92% yield. Significantly, besides the signal of a small amount of starting material, another signal of low intensity is generated in the ^{11}B -NMR spectrum at –44.8 ppm which was identified as $^i\text{Pr}_3\text{P}\cdot\text{BH}_3$.¹¹ This result suggested that $\text{Me}_2\text{NH}\cdot\text{BH}_3$ not only acts as a hydrogen donor, but also as a phosphine abstractor. However, from the NMR data it was not possible to judge whether one or two phosphine ligands were abstracted during the reaction course. Besides **1a**, the analogous Re(I) complexes **1b**, **2a,b**, **3a,b** are all effective for dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ (Table 1). In all cases trace amounts of the corresponding $\text{R}_3\text{P}\cdot\text{BH}_3$ species were detected. For comparison, the thermally induced dehydrogenation of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ can be initiated only at temperatures above 130 °C.¹² A blank reaction carried out at 85 °C for 6 h demonstrated that $\text{Me}_2\text{NH}\cdot\text{BH}_3$ was totally stable at this temperature. It is worth mentioning at this point that in preliminary experiments these rhenium complexes showed also activity for dehydrocoupling of ammonia-borane $\text{NH}_3\cdot\text{BH}_3$ revealing borazine $[\text{NH}\text{-BH}]_3$ as the major product.¹³

Based on the fact that one equivalent of H_2 could be released from $\text{Me}_2\text{NH}\cdot\text{BH}_3$ using the Re(I) complexes as catalysts, we proceeded to investigate $\text{Me}_2\text{NH}\cdot\text{BH}_3$ as a hydrogen source in olefin transfer-hydrogenations. When equal amounts of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ and 1-octene were mixed in dioxane with 1 mol% of the Re(I) species **1a**, integration of the ^1H -NMR signals indicated a 93% conversion of 1-octene to the hydrogenated

Table 1 Dehydrocoupling of Me_2NHBH_3 catalyzed by Re(I) at 85 °C

Entry	Catalyst	L	R	Dehydro (%) ^a	TOF (h ⁻¹)
1	none	none	none	0	0
2	1a	H–H	ⁱ Pr	92	23
3	1b	H–H	Cy	96	24
4	2a	CH_3CN	ⁱ Pr	99	25
5	2b	CH_3CN	Cy	91	23
6	3a	$\text{CH}_2=\text{CH}_2$	ⁱ Pr	88	22
7	3b	$\text{CH}_2=\text{CH}_2$	Cy	91	23

^a On the basis of the integration of ^{11}B -NMR spectrum (96 MHz) of the reaction mixture.

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product octane after 1 h at 85 °C. ^{11}B -NMR provided evidence that $\text{Me}_2\text{NH}\cdot\text{BH}_3$ was completely consumed and that besides the major product $[\text{Me}_2\text{N}\cdot\text{BH}_2]_2$, again trace amounts of $^i\text{Pr}_3\text{P}\cdot\text{BH}_3$ and also $(\text{Me}_2\text{NH})_2\text{BH}$ (δ 28.00 ppm, d, $J_{\text{BH}} = 137$ Hz) were present. In contrast to the colloidal rhodium⁵ catalysed dehydrocoupling–hydrogenation tandem-reaction with free H_2 as an intermediate, the reaction catalysed by Re(I) is homogeneous and the conversions remained quantitative regardless whether the reaction was carried out in open or closed vessels. This suggested that free H_2 does not appear in the reaction course and that it is indeed transfer-hydrogenation in its true sense instead of a tandem-reaction. The other Re(I) complexes **1b**, **2a,b**, **3a,b** were all effective catalysts in such reactions (Table 2). Cyclic substrates like 1,5-cyclooctene, COD and indene could also be hydrogenated with $\text{Me}_2\text{NH}\cdot\text{BH}_3$ as a hydrogen donor. In the case of substituted olefins, like α -methylstyrene and 1-methylcyclohexene, the yields were lower, presumably due to higher steric congestion inhibiting the required close contacts with the Re center. In addition, NMR evidence for hydroboration of the olefin was not found.

Subsequently some other details of the mechanisms of the Re(I)-catalysed processes were studied. The key question was what ligand dissociation (Br^- , L or PR_3) might get crucially involved in the reaction pathway. 1) In the presence of 20 eq. of $[\text{NEt}_4]\text{Br}$, both dehydrocoupling and transfer-hydrogenation were unaffected. This suggested that Br^- dissociation would not occur in both cases of catalysis. 2) Considering the role of the labile ligand L, it is interesting to note that the rhenium complexes of type **1**, **2** and **3** are interchangeable by labile ligand substitution. For example, in the presence of ethylene gas, the dihydrogen complex **1** and the acetonitrile complex **2** could easily be converted at room temperature to the ethylene species **3**. In the same way, the acetonitrile complex **2** and the ethylene complex **3** could be converted to the dihydrogen complex **1** applying a H_2 atmosphere. 3) Based on our previous observation that PR_3 ligand on the Re(I)

center could be abstracted by $\text{Me}_2\text{NH}\cdot\text{BH}_3$ yielding the $\text{R}_3\text{P}\cdot\text{BH}_3$ adducts, we wondered whether the PR_3 group would indeed leave the coordination sphere initiating the catalytic cycle. To investigate the PR_3 effect, the phosphine-free Re(I) complex $[\text{ReBr}_2(\text{NO})(\text{CH}_3\text{CN})_3]$ (**4**) was used as a catalyst in both reactions. Dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ did indeed work in 96% yield in absence of a phosphine after 4 h at 85 °C using **4** as the catalyst. This revealed that the PR_3 group is not a key player in the $\text{Me}_2\text{NH}\cdot\text{BH}_3$ dehydrogenation. In contrast, however, **4** turned out to be incapable of catalysing the transfer-hydrogenation of olefins. A hydrogenated product could not be observed at all and only 38% of the $\text{Me}_2\text{NH}\cdot\text{BH}_3$ was dehydrogenated. This indicated that the presence of rhenium bound phosphine(s) was quite critical in the olefin activation process. However in contrast to this observation when an excess of the corresponding phosphine (10 mmol%) was added, catalytic transfer-hydrogenations of **1**, **2** and **3** became completely blocked, neither a dehydrocoupling nor a hydrogenated product could be detected after 4 h at 85 °C. This indicated that transient dissociations of PR_3 are essential to the transfer-hydrogenation process.

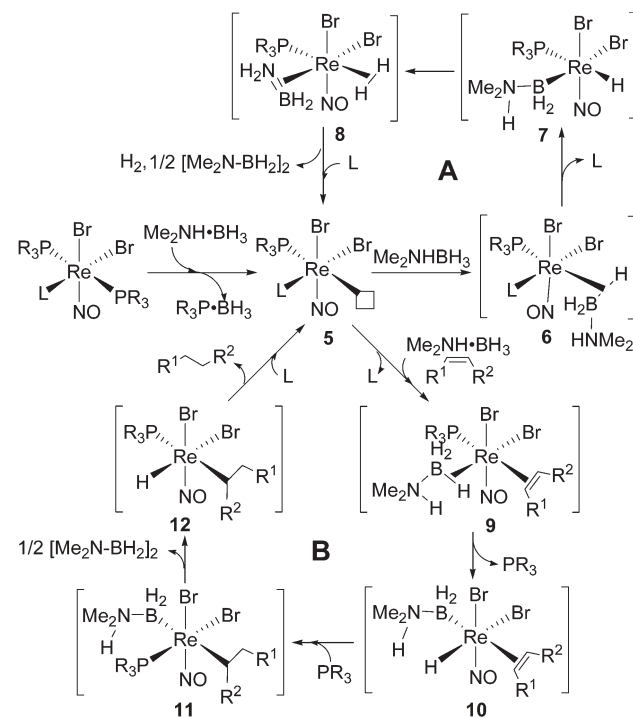
A mechanism for the dehydrocoupling and the transfer-hydrogenation was thus established and is sketched in Scheme 1.

In cycle **B** first a phosphine ligand is abstracted by BH_3 generated by $\text{Me}_2\text{NH}\cdot\text{BH}_3$ dissociation creating a vacant site for occupancy by the olefinic substrate. Secondly, the labile ligand L is substituted by $\text{Me}_2\text{NH}\cdot\text{BH}_3$ leading to the B–H σ -complex **9**, which subsequently oxidatively adds to form the Re(III) hydride **10**. During this process the other phosphine ligand may also dissociate. In a relatively fast step the coordinated olefin inserts into a Re–H bond to generate a Re-alkyl species, thus preventing H_2 complex formation of type **8** of cycle **A**. The alkyl species is then stabilized by re-coordination of free phosphine resulting in the

Table 2 Rhenium-catalyzed transfer-hydrogenation reaction of olefins applying $\text{Me}_2\text{NH}\cdot\text{BH}_3$ as a H_2 source^a

Entry	Substrate	Catalyst	Time (h)	Dehydro (%) ^b	Hydro (%) ^c
1	1-Octene	none	4	0	0
2	1-Octene	1a	1	99	93
3	1-Octene	1b	1	99	94
4	1-Octene	2a	1	99	95
5	1-Octene	2b	1	99	84
6	1-Octene	3a	2	99	99
7	1-Octene	3b	2	99	99
8	<i>cis</i> -Cyclooctene	1a	4	99	99
9	1,5-Cyclooctadiene	1a	4	99	99
10	α -Methylstyrene	1a	4	99	76
11	4-Methoxystyrene	1a	4	99	99
12	Indene	1a	4	99	99
13	1-Methylcyclohexene	1a	4	99	47
14	4-Methylcyclohexene	1a	4	99	99

^a Reactions were performed using 0.01 mmol of catalyst, 1.0 mmol of Me_2NHBH_3 and appropriated amount of alkene in dioxane (0.5 mL). ^b On the basis of the integration of ^{11}B -NMR spectrum. ^c On the basis of the integration of ^1H -NMR spectrum.



Scheme 1

six-coordinated complex **11**. Then a β -H shift occurs presumably accompanied by phosphine elimination and readdition giving the dehydrogenated borazene and **12**. Finally, the alkane is formed via reductive-elimination, the generated vacant site is re-occupied by an olefin molecule and $\text{Me}_2\text{NH}\cdot\text{BH}_3$ leading to the σ -complex **9** and closing of the catalytic cycle. In the case of the catalytic dehydrocoupling reaction (cycle **A**), the presence of three potential vacant sites of **5** enable B–H coordination and subsequent oxidative addition (conversion of **6** into **7**). Proton transfer from the acidic ammonium type function to the hydride ligand furnishes the dihydrogen–borazene complex **8**, from which H_2 gas and borazene are liberated. A reaction path involving primary N–H activation cannot be excluded. N–H reactivity seems however less preferred for thermodynamic and kinetic reasons, since N–H bonds are generally stronger (bond dissociation energies: B–H 83 kcal mol⁻¹, N–H 104 kcal mol⁻¹)¹⁴ and show less propensity for H-coordination. For transfer hydrogenations cycle **B** is expected to be faster than cycle **A**.

In conclusion, complexes of the middle-transition element rhenium catalysed the dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ and the transfer-hydrogenation of olefins. A plausible mechanism has been put forward, which is based on the availability of three potential vacant sites and a facile Re(I)/Re(III) redox change so that primary interaction between the rhenium center, the amine-borane and the olefins can take place. Essential for the generation of vacant sites is the permanent presence of the two non-dissociating π -donor bromide ligands acting as powerful *cis*-labilizers in the course of the catalytic reactions. Extension of these studies will target development of still more active rhenium complexes by ligand sphere tuning and their applications in related amine-borane chemistry for hydrogen storage.

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