Amineborane dehydrogenation promoted by isolable zirconium sandwich, titanium sandwich and N_2 complexes†

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Catalytic dehydrogenation of R_2NHBH_3 (R = Me, H) promoted by a family of bis(cyclopentadienyl)titanium and bis(indenyl)zirconium compounds is reported; structure–reactivity relationships as a function of cyclopentadienyl and indenyl substituents have been examined.

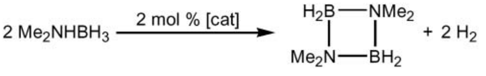
Storing and transporting H_2 in a safe and convenient manner is one of the key challenges to implementing a practical hydrogen economy.[1] Chemical methods whereby H_2 is stored and released in compounds that undergo reversible dehydrogenation and hydrogenation reactions have been identified as a viable strategy. Metal borohydrides,[2] amineboranes[3] and related substrates[4] have emerged as a particularly attractive class of compounds due to their high weight percentages of hydrogen and known ability to undergo H_2 release under hydrolytic conditions,[4] and in the presence of metal catalysts.[5]

In the realm of transition metal catalysis, heterogeneous rhodium supported on alumina[2] and various platinum salts have proven effective. Attempts to use homogeneous rhodium precursors such as $[Rh(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) have also resulted in catalytic amineborane dehydrogenation, although sigmoidal kinetic behavior and mercury poisoning experiments support Rh(0) colloids as the active species.[6] Recently, Heinekey, Goldberg and co-workers reported the application of a thermally robust pincer-ligated iridium precursor that exhibits high activity and maintains solubility throughout turnover.[7]

The high cost of precious metals inspires the search for more inexpensive base metal alternatives. Baker and co-workers reported *N*-heterocyclic carbene nickel complexes that, upon warming to 60 °C, exhibit long catalyst lifetimes and high levels of hydrogen release for amineborane dehydrogenation.[8] Kinetic isotope effects on partially and fully deuterated isotopologues support N–H and B–H bond breaking in the rate determining step. In early metal chemistry, Manners *et al.* have described the catalytic dehydrogenation of Me_2NHBH_3 with 2 mol% of $(\eta^5\text{-}C_5H_5)_2TiCl_2$ activated with two equivalents of ^nBuLi.[9] Unfortunately, the ill-defined nature of the species arising from the interaction of the alkyllithium reagent with titanocene dichloride renders mechanistic studies, establishment of structure–reactivity relationships and identification of the active species difficult.

Inspired by these findings, we reasoned that isolable bis(cyclopentadienyl)titanium compounds and related dinitrogen derivatives would be excellent candidates for amineborane dehydrogenation, possibly allow identification of the active species and result in a systematic study of the catalytic performance as a function of the cyclopentadienyl substituent. The robust titanium–cyclopentadienyl bond also renders the formation of colloids unlikely. Well-defined, isolable and crystallographically characterized bis(cyclopentadienyl)titanium sandwich complexes $(\eta^5\text{-}C_5Me_4R)_2Ti$ (R = $SiMe_2{}^tBu$, $SiMe_3$, ^tBu, ^iPr) were initially independently reported by the groups of Lawless[10] and Mach,[11] and later expanded upon by our laboratory.[12,13] These compounds, along with associated bis(cyclopentadienyl)[13] and *ansa* dinitrogen derivatives[14] form the basis of this study. Related bis(indenyl)zirconium sandwich compounds[15,16] and their hydrogenated variants[17] have also been assayed. This approach has yielded one of the most active catalysts for Me_2NHBH_3 dehydrogenation and established fundamental cyclopentadienyl substituent effects on the catalytic reaction.

Our studies commenced with the dehydrogenation of Me_2NHBH_3 (eqn 1).



(1)

This particular substrate was chosen due to its commercial availability and high solubility in non-polar hydrocarbon solvents. The series of bis(cyclopentadienyl)titanium sandwich and dinitrogen complexes presented in Fig. 1 were assayed for catalytic dehydrogenation, and the turnover frequencies are reported in Table 1. In a typical experiment, 2 mol% of the catalyst precursor

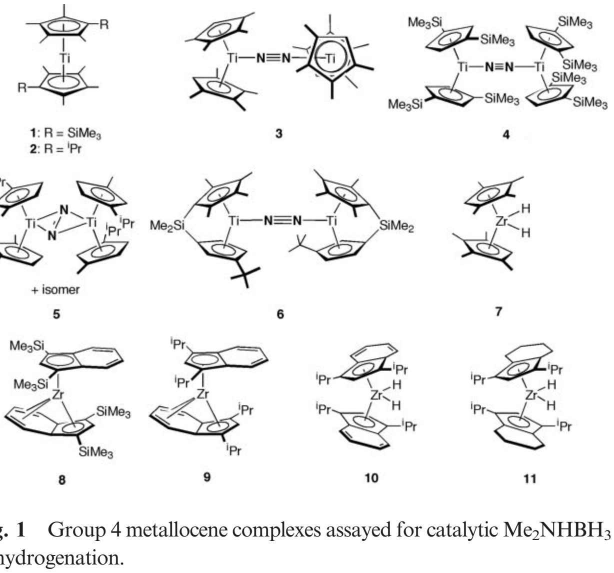


Fig. 1 Group 4 metallocene complexes assayed for catalytic Me_2NHBH_3 dehydrogenation.

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was dissolved in a benzene-d_6 solution containing 0.610 M Me_2NHBH_3. The progress of the catalytic reaction was monitored by ^1H and ^{11}B NMR spectroscopy. The latter has proven particularly useful as Me_2NHBH_3 appears at −13.4 ppm (q, $J_{B–H}$ = 95 Hz), distinct from the peak centered at 5.0 ppm (t, $J_{B–H}$ = 112 Hz) for the cyclic product. Notably, dihydrogen gas was detected by ^1H NMR spectroscopy during the catalytic runs and in preparative scale experiments by Toepler pump analysis. Combustion in the presence of CuO routinely yielded 80% of the expected H_2 gas. Control experiments conducted at 65 °C at the same concentration of substrate in the absence of metal complex produced no conversion to the product after five days.

Sandwiches **1** and **2**, which contain highly substituted cyclopentadienyl rings, are relatively poor catalyst precursors, requiring higher temperatures (65 °C) to achieve only modest rates of turnover. Notably, sandwich **2**, bearing the less substituted and more electron donating rings, exhibits a faster rate of dehydrogenation. Based on data presented below, we believe that for these two compounds, steric effects dominate and account for the observed activity difference.

The dimeric bis(cyclopentadienyl)titanium dinitrogen complexes **3**, **4**, **5** and **6** are also active for Me_2NHBH_3 dehydrogenation. The turnover frequencies reported in Table 1 are corrected for the amount of titanium from dimeric species. Particularly noteworthy is the activity of precatalyst **4**,[13] which produced complete dehydrogenation within minutes at 23 °C. Unfortunately, the *ansa*-titanocene **6**[14] is a poor precatalyst for the dehydrogenation reaction. In general, it appears that relatively electron withdrawing silyl substituents[18] increase the rate of catalytic turnover unless steric contributions are dominant, as in the case of **1** and **2**.

Several zirconium complexes were also studied for the catalytic dehydrogenation of Me_2HNBH_3. The zirconocene dihydride **7**[15] along with the bis(indenyl)zirconium sandwich complexes **8** and **9**[16] were evaluated. The isolable bis(indenyl) and bis(tetrahydroindenyl)zirconium dihydride compounds **10** and **11**[17] were also studied. Each zirconium derivative exhibited poor turnover frequencies (Table 1) and required heating to 65 °C for even modest rates. Comparing the turnover frequencies for **8** and **9** are again consistent with electron withdrawing substituents[19] increasing the rate of dehydrogenation. The [$SiMe_3$] complex is more sterically crowded (perhaps favouring reductive elimination) yet undergoes more facile turnover.

Additional studies were conducted in order to determine the origins of catalyst performance, establish structure–activity relationships and to identify the nature of the active species. For the titanium sandwich compounds **1** and **2**, only the paramagnetic titanocene was observed during turnover and it was recovered following conversion to the products. For the dinitrogen compound **3**, a new paramagnetic species (most likely the sandwich derivative)[13] was observed by ^1H NMR spectroscopy during the catalytic reaction. At the completion of catalysis, exposure to an N_2 atmosphere regenerated **3**. Monitoring the conversion rate of Me_2NHBH_3 in the presence of 1 mol% **3** produced clean first order kinetics with an observed rate constant of 2.9(1) × 10^{-4} s^{-1} at 23 °C. Performing the dehydrogenation of Me_2NHBH_3 under one atmosphere of D_2 gas with 1 mol% **3** resulted in incorporation of the isotopic label into the amineborane starting material and the B–H positions of the cyclic product. HD gas was also detected by ^1H NMR spectroscopy. Deuterium incorporation into the N–H position of Me_2NHBH_3 was also possible but could not be detected by multinuclear NMR or IR spectroscopy due to peak overlap with the protio isotopologue.

Table 1 Results of catalytic Me_2NHBH_3 dehydrogenation

Compound	T/°C	TOF/h^{-1}
1	65	0.05
2	65	100
3	23	35
4	23	>420
5	23	92
6	65	0.20
7	65	0.04
8	65	0.34
9	65	0.08
10	65	0.17
11	65	0.02

Based on these observations, a mechanism for amineborane dehydrogenation with the titanium catalysts is presented in Fig. 2 and is similar to that previously proposed by Baker *et al.* for nickel catalysts.[8] Reversible oxidative addition of a B–H bond to the bis(cyclopentadienyl)titanium or zirconium sandwich initiates the cycle, which is followed by β-hydrogen elimination to liberate $Me_2N{=}BH_2$. This material has been detected by ^{11}B spectroscopy and most likely undergoes dimerization in the presence of the metallocene[6] to furnish the observed cyclic product. Reductive elimination of dihydrogen liberates H_2 gas and regenerates the titanium or zirconium sandwich.

Similar studies were conducted with the bis(cyclopentadienyl), bis(indenyl) and bis(tetrahydroindenyl)zirconium compounds with the goal of determining the origin of the poor catalytic performance. Recovering the zirconium species following catalytic dehydrogenation of Me_2NHBH_3 with **7**, **9**, **10** or **11** yielded white crystalline solids identified as the zirconocene borohydride hydride compounds, **12–14**, respectively (Fig. 3). One specific compound, **13**, will be discussed in detail as a representative example. The benzene-d_6 ^1H NMR spectrum of **13** exhibits a number of resonances consistent with a C_1 symmetric zirconocene compound. Notably, upfield resonances diagnostic of a tetrahydroindenyl ring arising from benzo hydrogenation were observed.[15,17] In addition, a Zr–H peak was located at 2.72 ppm, along with a broad resonance at −0.03 ppm assigned to a $[BH_4]^-$ anion.[20,21] Appropriate IR bands for the Zr–H and $[BH_4]^-$ ligand were also observed.

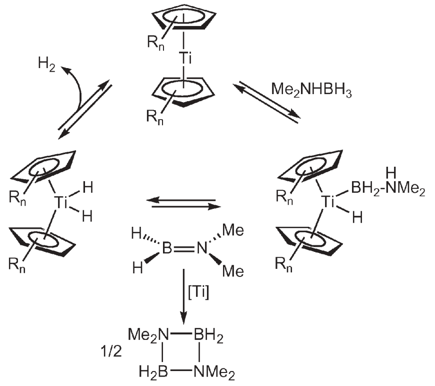
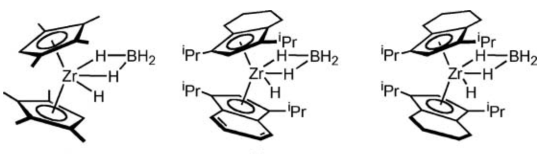


Fig. 2 Proposed mechanism for Me_2NHBH_3 dehydrogenation with titanium sandwich and dinitrogen complexes.



12 **13** **14**

Fig. 3 Zirconocene borohydride hydride compounds recovered following Me_2NHBH_3 dehydrogenation.

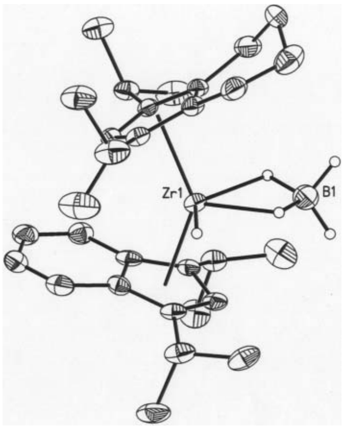


Fig. 4 Molecular structure of **13** at 30% probability ellipsoids.

The solution dynamics of **13** were probed by EXSY NMR spectroscopy. While the $[BH_4]^-$ ligand undergoes rapid exchange of terminal and bridging hydride positions at 23 °C, no exchange was detected between the Zr–H and borohydride positions up to temperatures of 90 °C with a mixing time of 500 ms.

The molecular structure of **13** was also established by X-ray diffraction (Fig. 4) and confirmed the formation of a tetrahydroindenyl ligand from benzo group hydrogenation.‡ The two rings are in a near ideal *anti* configuration with a rotational angle of 169.1°. The other metrical parameters are as expected for a bent zirconocene borohydride complex.[20,21] Zirconocene borohydride hydride **13** most likely arises from N–B cleavage and capture of the BH_3 by zirconocene dihydride. Confirmation of Me_2NH formation was provided by collecting the volatiles and treatment with PhC(O)Cl to yield $PhC(O)NMe_2$. Similar N–B bond cleavage has been identified as a catalyst deactivation pathway in iridium pincer chemistry.[7] However, unlike the iridium compound, warming **12**, **13** or **14** to 65 °C in the presence of excess Me_2NHBH_3 produced modest turnover, slightly slower (**12** and **13**) or similar (**14**) to the parent compounds. Presumably, catalyst activation occurs *via* BH_3 loss, possibly assisted by amineborane.

The most active precatalyst in the series, **4**, was also assayed for the dehydrogenation of H_3NBH_3. In benzene solution, a modest turnover frequency of 0.23 h^{-1} was observed at 65 °C. Most of the substrate and resulting dehydrogenated products were insoluble under these conditions. As a result, the reaction was also carried out in THF at 65 °C. A slightly higher turnover frequency of 0.31 h^{-1} was measured by monitoring the reaction by ^{11}B NMR spectroscopy. $[H_2NBH_2]_3$ was observed as the initial dehydrogenation product, which eventually converted to borazine over time. To determine if THF was deleterious to turnover, dehydrogenation of Me_2NHBH_3 with **4** was also performed in THF. Unlike in benzene-d_6, where rapid catalysis occurs, a modest turnover frequency of 0.29 h^{-1} was measured at 23 °C, suggesting catalyst inhibition from THF coordination to titanium.

In summary, a family of organometallic titanium and zirconium complexes have been evaluated for the catalytic dehydrogenation of Me_2NHBH_3. In general, the titanium compounds are more active than their zirconium counterparts, with the silyl-substituted titanocene dinitrogen complex **4** being one of the most active for Me_2NHBH_3 dehydrogenation. This compound is also effective for parent NH_3BH_3 dehydrogenation, although lower activity is observed in THF solution. These studies highlight the impact of cyclopentadienyl substitution on the rate of amineborane dehydrogenation and demonstrate the ability to tune the rate of H_2 loss by substituent manipulation.

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Notes and references

‡ Crystal data for **13**. $C_{30}H_{47}BZr$, M = 509.71, monoclinic, a = 9.226(3), b = 19.364(4), c = 15.896(4) Å, β = 99.197(9)°, U = 3082.9(2) Å^3, T = 173(2) K, space group $P2(1)/n$, Z = 4, μ(Mo-Kα) = 0.71073 mm^{-1}, 14059 reflections measured, 2963 unique (R_{int} = 0.0854) which were used in all calculations. $R1$ = 0.0495. The final w$R(F^2)$ was 0.0873 (all data). CCDC 642675. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b704941b

1 R. Coontz and B. Hanson, *Science*, 2004, **305**, 957.
2 P. Krishinan, T.-H. Yang, W.-Y. Lee and C.-S. Kim, *J. Power Sources*, 2005, **143**, 17.
3 M. T. Nguyen, V. S. Nguyen, M. H. Matus, G. Gopakumar and D. A. Dixon, *J. Phys. Chem. A*, 2007, **111**, 679.
4 C. W. Yoon and L. G. Sneddon, *J. Am. Chem. Soc.*, 2006, **128**, 13992.
5 T. D. Tilley, *Acc. Chem. Res.*, 2003, **26**, 22.
6 C. A. Jaska and I. Manners, *J. Am. Chem. Soc.*, 2004, **126**, 9776.
7 M. C. Denney, V. Pons, T. J. Hebden, D. M. Heinekey and K. I. Goldberg, *J. Am. Chem. Soc.*, 2006, **128**, 12048.
8 R. J. Keaton, M. Blacquiere and R. T. Baker, *J. Am. Chem. Soc.*, 2007, **129**, 1844.
9 T. J. Clark, C. A. Russell and I. Manners, *J. Am. Chem. Soc.*, 2006, **128**, 9582.
10 P. B. Hitchcock, F. Kerton and G. A. Lawless, *J. Am. Chem. Soc.*, 1998, **120**, 10264.
11 L. Lukesová, M. Horácek, P. Stepnicka, K. Fejfarová, R. Gyepes, I. Cisorová, J. Kubista and K. Mach, *J. Organomet. Chem.*, 2002, **663**, 134.
12 T. E. Hanna, E. Lobkovsky and P. J. Chirik, *J. Am. Chem. Soc.*, 2004, **126**, 14688.
13 T. E. Hanna, I. Keresztes, W. H. Bernskoetter, E. Lobkovsky and P. J. Chirik, *Organometallics*, 2004, **23**, 3448.
14 T. E. Hanna, W. H. Bernskoetter, M. W. Bouwkamp, E. Lobkovsky and P. J. Chirik, *Organometallics*, 2007, **27**, 2431.
15 P. J. Chirik, M. W. Day and J. E. Bercaw, *Organometallics*, 1999, **18**, 1873.
16 C. A. Bradley, I. Keresztes, E. Lobkovsky, V. G. Young and P. J. Chirik, *J. Am. Chem. Soc.*, 2004, **126**, 16937.
17 C. A. Bradley, E. Lobkovsky, I. Keresztes and P. J. Chirik, *J. Am. Chem. Soc.*, 2006, **128**, 6464.
18 J. A. Pool, E. Lobkovsky and P. J. Chirik, *J. Am. Chem. Soc.*, 2003, **125**, 2241.
19 C. A. Bradley, S. Flores-Torres, E. Lobkovsky, H. D. Abruña and P. J. Chirik, *Organometallics*, 2004, **23**, 5332.
20 F.-C. Liu, S.-C. Chen, K.-Y. Lee and S.-M. Peng, *J. Organomet. Chem.*, 2005, **690**, 291.
21 (*a*) T. J. Marks and J. R. Kolb, *J. Am. Chem. Soc.*, 1975, **97**, 3397; (*b*) B. N. James, R. K. Nanda and M. G. H. Wallbridge, *Inorg. Chem.*, 1967, **6**, 1979.