

Ammonia–Borane Dehydrogenation

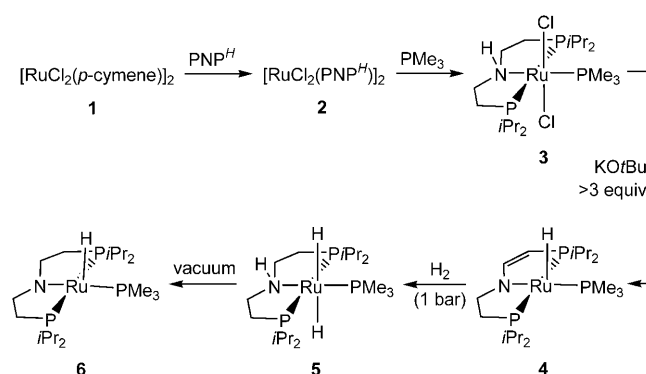
Ruthenium Complexes with Cooperative PNP Ligands: Bifunctional Catalysts for the Dehydrogenation of Ammonia–Borane**

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The quest for alternative energy sources has sparked considerable interest in chemical hydrogen storage.^[1] A promising approach is the reversible hydrogenation and dehydrogenation of small molecules, such as alcohols or ammonia–borane ($\text{H}_3\text{B}-\text{NH}_3$).^[2] In particular, the latter has been proposed because of its high hydrogen to mass ratio.^[3] Although transition-metal-catalyzed homogenous hydrogenations are widespread reactions in synthetic organic chemistry and industrial processes, efficient catalysts for dehydrogenation are surprisingly rare. Only recently, few homogeneous and colloidal transition-metal catalysts were reported for the release of up to 2.8 equivalents of H_2 from ammonia–borane under mild conditions.^[4]

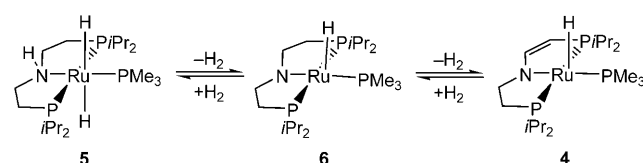
Bifunctional catalysts bearing cooperative amino ligands, which are involved in the catalytic cycle via reversible chemical transformations, were successfully introduced by Noyori et al. for the hydrogenation and transfer hydrogenation (TH) of polar double bonds.^[5,6] According to the principle of microscopic reversibility the dehydrogenation of polar functional groups could be possible with this catalyst class, however such bifunctional catalysts have not been utilized for these reactions to date.^[7] Herein we present new Ru^{II} compounds having PNP amido chelate ligands, which can undergo reversible hydrogenation/dehydrogenation reactions both at the N functionality and the ethylene backbone. The reactivity of the ruthenium complexes is utilized for the homogeneous catalytic dehydrogenation of ammonia–borane with unprecedented activities.^[7]

trans- $[\text{RuCl}_2(\text{PMe}_3)(\text{PNP}^H)]$ (**3**) is prepared almost quantitatively in two steps starting from $[\{\text{RuCl}_2(p\text{-cymene})\}_2]$ (**1**) (Scheme 1).^[8] Upon reaction with 3.3 equivalents of KOtBu , the dark green, highly air sensitive complex **4** was isolated in 95 % yield. The reaction was rapid and no intermediates were detected by using ^{31}P NMR spectroscopy. When less than three equivalents of KOtBu was used, only incomplete conversion of **3** was observed. The formation of **4** can be attributed to deprotonation of the N center of **3** and subsequent β -hydride elimination. Finally, **4** would then



Scheme 1. Synthesis of amido complex **6** ($\text{PNP}^H = \text{HN}(\text{CH}_2\text{CH}_2\text{P}i\text{Pr}_2)_2$).

result from the deprotonation of an intermediate hydrido-chloro-imino complex at the acidic α position relative to the imino group.^[9] The novel ligand of enamido complex **4** represents an aliphatic analog of $[\text{RuH}(\text{CO})\{\text{NC}_5\text{H}_3(\text{CHP}i\text{Pr}_2)(\text{CH}_2\text{P}i\text{Pr}_2)\}]$ which was reported by Milstein et al. to be obtained upon deprotonation of a pyridine-based PNP pincer complex.^[10] The reversibility of the ligand backbone dehydrogenation was demonstrated by the reaction of **4** with H_2 . The resulting amino complex **5** underwent the partial elimination of H_2 during workup, and could therefore not be obtained analytically pure. However, evacuation of the solid crude-product under dynamic vacuum at room temperature gives analytically pure, dark red, and highly air sensitive amido complex **6** in yields around 85 % over five steps. Whereas **6** quantitatively adds hydrogen in solution under H_2 atmosphere, **6** slowly releases H_2 under argon at room temperature over several days, demonstrating that the heterolytic H_2 activation reactions shown in Scheme 2 are



Scheme 2. Hydrogenation/dehydrogenation equilibria between amino (**5**), amido (**6**), and enamido (**4**) complex.

reversible. To the best of our knowledge, the reversible hydrogenation/dehydrogenation of ethylene bridges in amido chelate complexes, which are frequently used as hydrogenation catalysts, has not been directly observed.^[11]

The chemical shifts ($\delta = -8.00$ and $\delta = -8.52$ ppm) and $^2J(\text{H},\text{P})$ coupling constants ($^2J(\text{H},\text{P}) = 16.7\text{--}24.3$ Hz) of the

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two hydride signals of **5** exclude a configuration in which the hydrides are in a *trans* position to the amino or a phosphine ligand.^[11] The meridional coordination of the PNP^H pincer results from the *trans*-dihydride configuration. For enamido complex **4**, the hydride chemical shift ($\delta = -31.68$ ppm) and the $^2J(\text{H,P})$ coupling constant for the PMe₃ ligand ($^2J(\text{H,P}) = 47$ Hz) differ significantly from amido complex **6** ($\delta = -24.18$ ppm; $^2J(\text{H,P}) = 54$ Hz), suggesting considerably different coordination geometries. Because of their high solubility we were unable to grow single crystals of either **4** or **6**, therefore DFT models of the two complexes were generated (Figure 1).^[8] Whereas the ruthenium center of enamide **4**

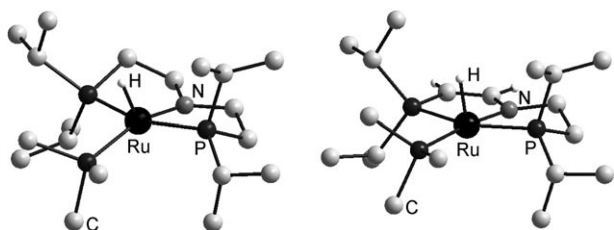
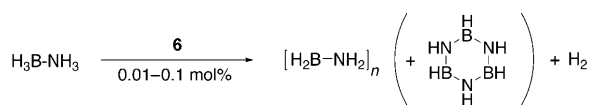


Figure 1. Minimized structures of **6** (left) and **4** (right) from DFT calculations (B3LYP/6-31 + G**); H atoms except hydrides and vinylene protons are omitted). Selected bond angles of **6**: N–Ru–PMe₃ 159.8°; N–Ru–H_{Hydrid} 120.9°; Me₃P–Ru–H_{Hydrid} 79.3°; and **4**: N–Ru–PMe₃ 172.6°; N–Ru–H_{Hydrid} 102.5°; Me₃P–Ru–H_{Hydrid} 84.6°.

exhibits a slightly distorted square-pyramidal coordination polyhedron, amido complex **6** can best be described as a trigonal-bipyramidal having a Y-shaped distortion. The considerably smaller H–Ru–PMe₃ angle in **6** explains the NMR spectroscopic results. Such Y-shaped coordination geometry as that found in **6**, are typically found for five coordinate *d*⁶-complexes having a strong π -donating ligand.^[12] Therefore, the molecular structure of **4** can be an indication of weaker N→Ru π interaction resulting from dehydrogenation of the ligand backbone, indicating the delocalization of the free electron pair of the nitrogen donor into the vinylene group.^[13]

Amido complex **6** was used in the dehydrogenation of ammonia–borane (Scheme 3).^[8] Upon addition of the catalyst to a THF solution of H₃B–NH₃ (0.54 M) at room temperature,



Scheme 3. Catalytic dehydrogenation of ammonia–borane.

vigorous H₂ evolution was instantaneous and the formation of a white precipitate was observed. Even with very small catalyst loadings (0.01 mol% **6**) high catalytic activities were observed (Figure 2). Pseudo first-order rate constants of 0.013 s^{−1} (0.1 mol% **6**) and 0.0021 s^{−1} (0.01 mol% **6**) were obtained from logarithmic plots (turnover frequency = 13–21 s^{−1}). Whereas catalyst loadings of 0.1 mol% **6** produce slightly more than 1 equivalent of H₂, 0.01 mol% of **6** produced 0.83 equivalents of H₂ (turnover number = 8300).

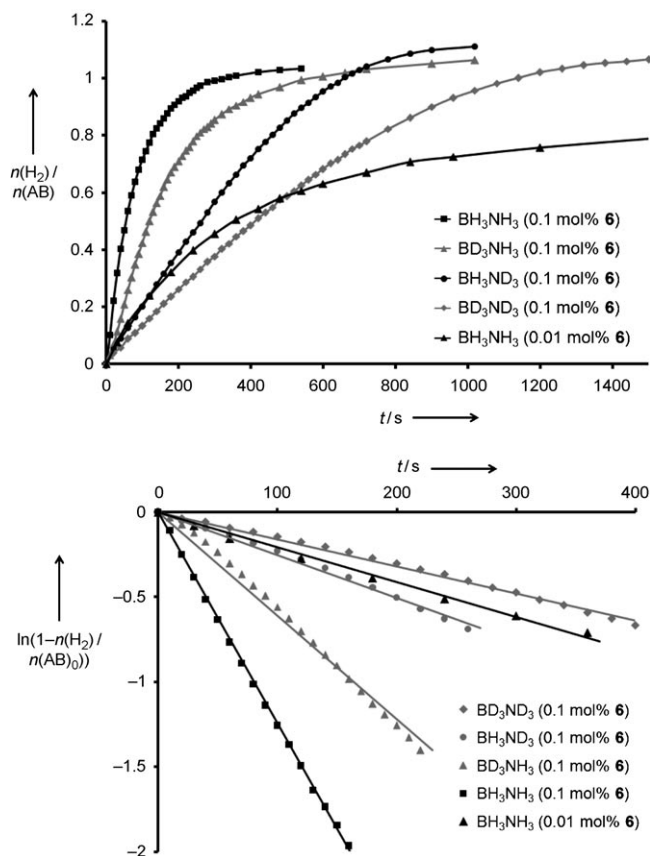


Figure 2. Time course (above) and logarithmic plot (below) for ammonia–borane (AB) dehydrogenation catalyzed by **6** in THF at room temperature. Straight lines were obtained by linear regression analysis of the data points.

The addition of Hg to the reaction affected neither the activity nor the H₂ yield. To the best of our knowledge complex **6** marks the most active known homogeneous catalyst for ammonia–borane dehydrogenation.^[7] A powder diffractogram, and MAS-¹¹B NMR and IR spectra of the precipitate are in agreement with the formation of a polymer dehydrocoupling product (BH₂NH₂)_n.^[4d] The small amounts of borazine detected in the reaction solution by using ¹¹B NMR methods explains the H₂ yield of slightly over 1 equivalent.

Additional information about the mechanism was obtained by running the reaction with deuterated substrates. By using 0.1 mol% catalyst loadings large kinetic isotope effects (KIE) of 2.1 (D₃B–NH₃), 5.2 (H₃B–ND₃), and 8.1 (D₃B–ND₃) were found relative to H₃B–NH₃ dehydrogenation.^[8] In comparison, KIEs of 1.7 (D₃B–NH₃), 2.3 (H₃B–ND₃), and 3.0 (D₃B–ND₃) were reported for ammonia–borane dehydrogenation using a nickel carbene complex.^[4e] The KIEs are in agreement with a concerted mechanism in which the N–H and B–H bond cleavages are in the rate-determining step, as was found for TH using Noyori's bifunctional ruthenium catalysts.^[14,15] At an early stage of the reaction (20 mol% **6**) only amino complex **5** was found by ³¹P NMR methods.^[16] However, the slow H₂ elimination from complex **5** indicates that the spontaneous loss of H₂ to regenerate **6** cannot be of relevance for the catalytic cycle.

In conclusion we presented ruthenium(II) complexes having PNP-pincer ligands, which can participate in the reversible, heterolytic H₂ activation with the nitrogen atom and the ligand backbone. NMR spectroscopic results and DFT calculations show that the novel cooperative enamido ligand of **4** exhibits significantly different donor properties, compared to amido analog **6**. Therefore, π donation by the amido nitrogen atom can be controlled by the reversible chemical transformations within the pincer backbone. Amido complex **6** shows unprecedented activity and turnover numbers in the dehydrogenation of ammonia–borane under mild conditions with low catalyst loadings. The present results are in agreement with a bifunctional Noyori–Morris-type mechanism, having a concerted transfer of a hydride (B–H) and a proton (N–H) from the substrate to a catalyst species.^[5,14] Therefore, our results suggest that bifunctional catalysts could be suitable for efficient hydrogen production from other small molecules with polar E–H bonds. Initial results also show that **6** exhibits good activities in the acceptor-less dehydrogenation of alcohols.

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- [1] J. J. Romm, *Der Wasserstoff-Boom*, Wiley-VCH, Weinheim, **2006**.
- [2] H. Junge, B. Loges, M. Beller, *Chem. Commun.* **2007**, 522–524.
- [3] a) US Department of Energy Report, “Basic Research Needs for the Hydrogen Economy”, zu finden unter http://www.sc.doe.gov/bes/reports/files/NHE_rpt.pdf, **2004**; b) T. B. Marder, *Angew. Chem.* **2007**, *119*, 8262–8264; *Angew. Chem. Int. Ed.* **2007**, *46*, 8116–8118.
- [4] a) C. A. Jaska, K. Temple, A. J. Lough, I. Manners, *Chem. Commun.* **2001**, 962–963; b) C. A. Jaska, K. Temple, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **2003**, *125*, 9424–9434; c) T. J. Clark, C. A. Russell, I. Manners, *J. Am. Chem. Soc.* **2006**, *128*, 9582–9583; d) M. C. Denney, V. Pons, T. J. Hebdon, D. M. Heinekey, K. I. Goldberg, *J. Am. Chem. Soc.* **2006**, *128*, 12048–12049; e) R. J. Keaton, J. M. Blacquiere, R. T. Baker, *J. Am. Chem. Soc.* **2007**, *129*, 1844–1845; f) F. Cheng, H. Ma, Y. Li, J. Chen, *Inorg. Chem.* **2007**, *46*, 788–794; g) J. F. Fulton, J. C. Linehan, T. Autrey, M. Balasubramanian, Y. Chen, N. K. Szymczak, *J. Am. Chem. Soc.* **2007**, *129*, 11936–11949; h) D. Pun, E. Lobkovsky, P. J. Chirik, *Chem. Commun.* **2007**, 3297–3299; i) A. Staubitz, A. Presa Soto, I. Manners, *Angew. Chem.* **2008**, *120*, 6308–6311; *Angew. Chem. Int. Ed.* **2008**, *47*, 6212–6215.
- [5] Reviews: a) R. Noyori, T. Ohkuma, *Angew. Chem.* **2001**, *113*, 40; *Angew. Chem. Int. Ed.* **2001**, *40*, 40–73; b) S. E. Clapham, A. Hadzovic, R. H. Morris, *Coord. Chem. Rev.* **2004**, *248*, 2201–2237; c) K. Muñiz, *Angew. Chem.* **2005**, *117*, 6780–6785; *Angew. Chem. Int. Ed.* **2005**, *44*, 6622–6627.
- [6] H. Grützmacher, *Angew. Chem.* **2008**, *120*, 1838–1842; *Angew. Chem. Int. Ed.* **2008**, *47*, 1814–1818.
- [7] During the preparation of this manuscript a paper has been published which follows the same approach. The TH catalyst [RuCl₂(R₂PCH₂CH₂NH₂)₂]/KOtBu (R = *i*Pr, *t*Bu) exhibits comparable activities in the dehydrogenation of H₃B–NH₃ as complex **6**. Based on the analogy to TH and DFT calculations a bifunctional (Noyori–Morris) mechanism was proposed: N. Blaquiere, S. Diallo-Garcia, S. I. Gorelsky, D. A. Black, K. Fagnou, *J. Am. Chem. Soc.* **2008**, *130*, 14034–14035.
- [8] For syntheses, characterization, catalytic protocols, and quantum chemical details see the Supporting Information.
- [9] V. F. Kuznetsov, K. Abdur-Rashid, A. J. Lough, D. G. Gusev, *J. Am. Chem. Soc.* **2006**, *128*, 14388–14396.
- [10] J. Zhang, G. Leitun, Y. Ben-David, D. Milstein, *Angew. Chem.* **2006**, *118*, 1131–1133; *Angew. Chem. Int. Ed.* **2006**, *45*, 1113–1115.
- [11] R. Abbel, K. Abdur-Rashid, M. Fraatz, A. Hadzovic, A. J. Lough, R. H. Morris, *J. Am. Chem. Soc.* **2005**, *127*, 1870–1882.
- [12] Y. Jean, *Molecular Orbitals of Transition Metal Complexes*, Oxford University Press, Oxford, **2005**.
- [13] The strong contribution of the vinylene carbon *p*-orbitals to the Ru–N π bond (HOMO, HOMO–2), confirm this interpretation: see the Supporting Information.
- [14] K. Abdur-Rashid, S. E. Clapham, A. Hadzovic, J. N. Harvey, A. J. Lough, R. H. Morris, *J. Am. Chem. Soc.* **2002**, *124*, 15104–15118.
- [15] a) C. P. Casey, J. B. Johnson, *J. Org. Chem.* **2003**, *68*, 1998–2001; b) J. B. Johnson, J.-E. Bäckvall, *J. Org. Chem.* **2003**, *68*, 7681–7684.
- [16] **5** could alternatively be formed by heterolytic addition of released H₂ to **6** and is therefore not necessarily involved in the catalytic cycle.