ChemComm

COMMUNICATION

View Article Online View Journal | View Issue

Cite this: Chem. Commun., 2013, 49, 1005

Received 11th November 2012, Accepted 12th December 2012

DOI: 10.1039/c2cc38145a

www.rsc.org/chemcomm

Tandem ammonia borane dehydrogenation/alkene hydrogenation mediated by [Pd(NHC)(PR₃)] (NHC = *N*-heterocyclic carbene) catalysts[†]

Caroline E. Hartmann,^a Václav Jurčík,^{ab} Olivier Songis^b and Catherine S. J. Cazin*^{ab}

[Pd(NHC)(PR₃)] complexes were shown to be active catalysts in the dehydrogenation of ammonia borane and the subsequent hydrogenation of unsaturated compounds at very low catalyst loadings (0.05 mol% for some substrates).

Catalytic hydrogenation of C–C multiple bonds is one of the most important processes in organic chemistry.¹ Associated with this process is the use of hydrogen gas whose physical properties complicate its safe, efficient and economical storage.² As the need for an easily transportable source of hydrogen has attracted considerable attention in the context of novel environmentally benign energy sources,³ we hypothesised that an opportunity existed to employ one of these "*hydrogen storage materials*"⁴ as a readily available hydrogen source. We reasoned that such a material could be used as a chemical reagent in catalysis.

The level of research activity to identify a material that could deliver hydrogen on demand has been high in recent years.^{2,5,6} In this context and in efforts to look ahead where alternatives to petroleum-based fuels will be required, ammonia borane (H₃N-BH₃, **AB**) appears attractive in view of its high thermal stability and hydrogen content (19.6% by weight).⁷ Recent reports have focused on several aspects of **AB** as a hydrogen source and the means to control its H₂ release.⁸ A small number of studies have reported application of **AB**-congeners in hydrogenation reactions catalyzed by heterogeneous Pd/C and Ra–Ni⁹ and limited homogeneous hydrogenation of ketones using Ru.¹⁰

We have recently described activation of H_2 by [Pd(NHC)(PCy₃)] (NHC = *N*-heterocyclic carbene)¹¹ and applications of these systems in the catalytic hydrogenation of alkenes.^{12,13} This initial reactivity encouraged us to explore whether these



Scheme 1 Formation of the dihydride complex 4

 $[Pd(NHC)(PR_3)]$ complexes could react with NH₃BH₃ to, in a first instance, generate H₂ and subsequently, in a tandem process, use this H₂ to perform hydrogenation of C–C multiple bonds.

In initial reactions, $[Pd(IPr)(PCy_3)]$ **1** (IPr = N,N'-bis-(2,6-diiso-propylphenyl)imidazol-2-ylidene) was mixed with morpholineborane **2** in C₆D₆ and resulted in an immediate gas release. The identity of the gas as H₂ was confirmed by ¹H NMR analysis of the reaction headspace. Hydrogen release was accompanied by the formation of morpholinoborane **3**. When the experiment was performed in a sealed NMR-tube, quantitative formation of the dihydride complex, $[Pd(H)_2(IPr)(PCy_3)]$ **4** was observed after several days (Scheme 1).¹¹

These results encouraged us to test the capability of $[Pd(IPr)(PCy_3)]$ 1 to mediate the catalytic release of dihydrogen from NH₃BH₃. As a negligible amount of gas was released at room temperature, solutions of NH₃BH₃ in various solvents were heated to 50 °C in the presence of 1 (1 mol%). A closed flask equipped with a pressure sensor permitted the monitoring, in a quantitative manner, of the hydrogen volume generated as a function of time and solvent. Reactions in hexane did not result in any gas release while there was slow H₂ release in THF and toluene. Optimum results were obtained when reactions were performed in isopropanol.¹⁴

Since $[Pd(NHC)(PR_3)]$ complexes are known to be highly efficient catalysts for hydrogenation reactions,¹² we reasoned that a tandem reaction could possibly be established if the

^a Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans 16, 43007 Tarragona, Spain

^b EaStCHEM School of Chemistry, University of St Andrews, St Andrews, KY16 9ST, UK. E-mail: cc111@st-andrews.ac.uk; Fax: +44 (0)1334 463808

[†] Electronic supplementary information (ESI) available: Experimental details, kinetic profiles, dehydrogenation experiments and NMR spectra. See DOI: 10.1039/c2cc38145a

	Ph	Pd catalyst	Ph /	
Ph NH ₃ BH ₃ , 16 h, 50 °C Ph Ph				
Entry	Catalyst	Loading (mol%)	Solvent	Conv. ^b (%)
1	$[Pd(IPr)(PCy_3)]$ 1	1	THF	<5
2	$\left[Pd(IPr)(PCy_3) \right] 1$	1	Toluene	<5
3	$\left[Pd(IPr)(PCy_3) \right] 1$	1	CH_2Cl_2	$< 5^{c}$
4	$\left[Pd(IPr)(PCy_3) \right] 1$	1	ⁱ PrOH	95
5	$[Pd(IPr)(PCy_3)]$ 1	0.05	ⁱ PrOH	88^d
6	[Pd(SIPr)(PCy ₃)] 5	0.05	ⁱ PrOH	99
7	Without Pd	—	ⁱ PrOH	N.R.
8	[Pd(IPr)(PPh ₃)] 6	0.05	ⁱ PrOH	<5
9	[Pd(SIPr)(PPh ₃)] 7	0.05	ⁱ PrOH	<5
10	$\left[Pd(IPr)_2 \right] 8$	0.05	ⁱ PrOH	25
11	$[Pd(IPr)(PAd_2^nBu)]$ 9	0.05	ⁱ PrOH	60
12	Pd/C 10	0.05	ⁱ PrOH	N.R.

1

2

3

4

5

6

7

8

9

10

^{*a*} Reaction conditions: *trans*-stilbene (0.5 mmol), catalyst, NH₃BH₃ (1 eq.), solvent (1 mL), 50 °C, 16 h. ^{*b*} Conversion, determined by GC, average of at least two runs. ^{*c*} Reaction carried out at 40 °C. ^{*d*} No ^d No reaction occurred at rt.

reaction medium contained an alkene. The hydrogenation of trans-stilbene was selected as a model reaction. Table 1 presents some of the most salient results of this model tandem NH₃BH₃ dehydrogenation/alkene hydrogenation sequence.¹⁵ As was observed for the NH₃BH₃ dehydrogenation reaction, alcohol solvents lead to highest conversions (Table 1, entries 1-4). Control reactions (Table 1, entries 7 and 12) without palladium and with palladium on charcoal led to no conversion. A series of mixed NHC/phosphine were then tested (Table 1, entries 5, 6 and 8-11). The complex [Pd(SIPr)(PCy₃)] 5 (SIPr = N, N'-bis(2, 6-diisopropylphenyl)imidazolidin-2-ylidene),was proven to be the most effective at lower catalyst loadings (Table 1, entries 5 and 6). Although [Pd(SIPr)(PCy₃)] 5 performs best, the trend emerging from Table 1 clearly shows that bulky electron-rich mixed systems are capable of achieving significant conversions (Table 1, entries 10 and 11) while less electron-rich complexes (Table 1, entries 8 and 9) fail in the tandem transformation.

As NH₃BH₃ can liberate up to 3 equivalent of H₂, the amount of NH₃BH₃ necessary for an efficient transformation was varied to gauge the effectiveness of the NH₃BH₃ dehydrogenation reaction. When the reaction was performed with 1 equivalent of ammonia-borane and 6-fold excess of 4-allylanisole, a 53% yield of the hydrogenated product was obtained which corresponds to 3 equivalents of H₂ from one molecule of ammonium borane. This is in agreement with the expected transformation of NH₃BH₃ to the corresponding ammonium tetraalkoxyborate and 3 equivalent of dihydrogen.^{2b} Further NMR experiments aiming to clarify the fate of AB indicate that NH₃BH₃ is directly converted to borate.^{2b} Kinetic profiling of the oxidation of borane to borate corresponds to the conversion of 4-allylanisole to 4-propylanisole.¹²

To examine the substrate scope of this tandem reaction, a number of alkenes were subjected to the optimised reaction conditions. A range of olefins could be hydrogenated efficiently at 0.05 mol% catalyst loading (Table 2, entries 1-5), whereas with less reactive substrates 0.25-1 mol% of 5 was used. In the View Article Online

ChemComm



 80^{c} 11 0.5 69⁰ 12 13 0.05 88 $75^{c,e}$ 140.25

^a Reaction conditions: substrate (0.5 mmol), [Pd(SIPr)(PCy₃)] 5, NH₃-BH₃ (0.5 eq.), ¹PrOH (1 mL), 50 °C, 16 h. ^b Isolated yield, average of two reactions. ^c Yield determined by ¹H NMR using 1,3,5-trimethoxybenzene or 4-bromoanisole as internal standard. ^d Using MeOD as solvent. Using 0.33 eq. NH₃BH₃.

case of methylcinnamate, the C=C bond was selectively reduced (Table 2, entry 6), while with chalcone and cyclohexenone quantitative yields of completely hydrogenated products were obtained (Table 2, entries 7 and 8). Selective reduction of 1,4-cyclooctadiene to cyclooctene was achieved in 79% yield in isopropanol (Table 2, entry 9), while in methanol complete reduction of the diene to cyclooctane was achieved (Table 2, entry 10). Finally, we were interested to test our system for the semi-reduction of internal alkynes. Diphenylethyne was semireduced to cis-stilbene in high yield using a catalyst loading of only 0.05 mol% (Table 2, entry 13) while dimethylhexynediol was semi-reduced using 0.33 eq. of NH₃BH₃ (Table 2, entry 14).

A highly efficient $[Pd(NHC)(PR_3)]$ catalytic system for the tandem dehydrogenation of **AB** coupled with the hydrogenation of alkenes and alkynes has been developed which proves effective for a wide array of alkenes. The optimised protocol makes use of alcohol solvents and very low catalyst loadings (0.05–0.25 mol%). The efficient hydrogenation of alkene/alkyne substrates using solid NH₃BH₃ in place of H₂ presents an improvement in terms of safety and logistics with the removal of the risks inherent to the transport and manipulation of an explosive compressed gas. Further studies aimed at testing the generality of this tandem reaction and demonstrating the usefulness of **AB** as a convenient H₂ delivery agent in chemical transformations are presently ongoing in our laboratories.

We thank the EPSRC and the Royal Society (University Research Fellowship to CSJC), the German Federal Excellence Initiative (FYS grant to C.H.), the Karlsruhe House of Young Scientists (KHYS) from the Karlsruhe Institute of Technology (grant to C.H.) and the Deutscher Akademischer Austauschdienst (German Academic Exchange Service, grant to C.H.) for support.

Notes and references

- 1 J. G. de Vries and C. J. Elsevier, Handbook of Homogeneous Hydrogenation, Wiley-VCH, Weinheim, 2007.
- 2 For recent reviews on hydrogen storage materials for automotive applications, see: (a) J. Yang, A. Sudik, C. Wolverton and D. J. Siegel, *Chem. Soc. Rev.*, 2010, 39, 656; (b) C. W. Hamilton, R. T. Baker, A. Staubitz and I. Manners, *Chem. Soc. Rev.*, 2009, 38, 279; (c) A. W. C. van der Berg and C. O. Areán, *Chem. Commun.*, 2008, 668; (d) T. B. Marder, *Angew. Chem., Int. Ed.*, 2007, 46, 8116.
- 3 For a recent discussion on this topic see: T. W. Graham, C.-W. Tsang, X. Chen, R. Guo, W. Jia, S.-M. Lu, C. Sui-Seng, C. B. Ewart, A. Lough, D. Amoroso and K. Abdur-Rashid, *Angew. Chem.*, *Int. Ed.*, 2010, **49**, 8708.
- 4 (a) R. Coontz and B. Hanson, Science, 2004, 305, 957; (b) G. W. Crabtree and M. S. Dresselhaus, MRS Bull., 2008, 33, 421;
 (c) I. P. Jain, P. Jain and A. Jain, J. Alloys Compd., 2010, 503, 303.
- 5 (a) M. Chandra and Q. J. Xu, J. Power Sources, 2006, 156, 190;
 (b) M. Chandra and Q. J. Xu, J. Power Sources, 2006, 159, 855;
 (c) Q. J. Xu and M. Chandra, J. Power Sources, 2006, 163, 364;

(d) C. W. Yoon and L. G. Sneddon, J. Am. Chem. Soc., 2006, 128, 13992; (e) F. Cheng, H. Ma, Y. Li and J. Chen, Inorg. Chem., 2007, 46, 788; (f) M. T. Nguyen, V. S. Nguyen, M. H. Matus, G. Gopakumar and D. A. Dixon, J. Phys. Chem. A, 2007, 111, 679; (g) P. V. Ramachandran and P. D. Gagare, Inorg. Chem., 2007, 46, 7810.

- 6 (a) T. J. Clark, C. A. Russell and I. Manners, J. Am. Chem. Soc., 2006, 128, 9582; (b) M. C. Denney, V. Pons, T. J. Hebden, D. M. Heinekey and K. L. Goldberg, J. Am. Chem. Soc., 2006, 128, 12048; (c) R. J. Keaton, J. M. Blacquiere and R. T. Baker, J. Am. Chem. Soc., 2007, 129, 1844; (d) T. J. Clark, G. R. Whittell and I. Manners, Inorg. Chem., 2007, 46, 7522; (e) P. M. Zimmerman, A. Paul, Z. Zhang and C. B. Musgrave, Angew. Chem., Int. Ed., 2009, 48, 2201; (f) G. Alcaraz, L. Vendier and S. Sabo-Etienne, Angew. Chem., Int. Ed., 2010, 49, 918.
- 7 (*a*) US DOE "Basic Research Needs for the Hydrogen Economy" (http://www.sc.doe.gov/bes/reports/files/NHE_rpt.pdf);
- (b) D. A. Dixon and M. Gutowski, J. Phys. Chem. A, 2005, 109, 5129.
 8 (a) J. S. Wang and R. A. Geanangel, Inorg. Chim. Acta, 1988, 148, 185;
 (b) M. E. Blumh, M. G. Bradley, R. Butterick, U. Kusari and L. G. Sneddon, J. Am. Chem. Soc., 2006, 128, 7748; (c) G. Wolf, J. Baumann, F. Baitalow and F. P. Hoffmann, Thermochim. Acta, 2000, 343, 19; (d) F. Baitalow, J. Baumann, G. Wolf, K. Jaenicke-Rossler and G. Leitner, Thermochim. Acta, 2002, 391, 159; (e) C. A. Jaska, K. Temple, A. J. Lough and I. Manners, J. Am. Chem. Soc., 2003, 125, 9424; (f) F. H. Stephens, R. T. Baker, M. H. Matus, D. J. Grant and D. A. Dixon, Angew. Chem., Int. Ed., 2007, 46, 746.
- 9 (a) M. Couturier, J. L. Tucker, B. M. Andresen, P. Dubé and J. T. Negri, Org. Lett., 2001, 3, 465; (b) M. Couturier, B. M. Andresen, J. L. Tucker, P. Dubé, S. J. Brenek and J. T. Negri, Tetrahedron Lett., 2001, 42, 2763; (c) M. Couturier, B. M. Andresen, J. L. Tucker, P. Dubé, S. Breneck and J. T. Negri, Tetrahedron Lett., 2001, 42, 2285.
- 10 N. Blaquiere, S. Diallo-Garcia, S. I. Gorelsky, D. A. Black and K. Fagnou, J. Am. Chem. Soc., 2008, 130, 14034.
- 11 S. Fantasia, J. D. Egbert, V. Jurčík, C. S. J. Cazin, H. Jacobsen, L. Cavallo, D. M. Heinekey and S. P. Nolan, *Angew. Chem., Int. Ed.*, 2009, 48, 5182.
- 12 V. Jurčík, S. P. Nolan and C. S. J. Cazin, Chem.-Eur. J., 2009, 15, 2509.
- 13 For a recent review on NHC-based catalysts in hydrogenation and transfer hydrogenation, see *N*-Heterocyclic Carbene Complexes in Additions to Multiple bonds, A. A. Danopoulos, in *N*-Heterocyclic Carbenes in Transition Metal Catalysis and Organocatalysis, ed. C. S. J. Cazin, Springer, London, 2011, vol. 32, p. 24.
- 14 For details on the dehydrogenation of NH_3BH_3 using 1, see ESI,[†] section 2.
- 15 For the full optimization study, see ESI⁺.