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The Remarkable Effect of a Simple Ion: Iodide-Promoted Transfer Hydrogenation of Heteroaromatics

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Dedicated to Professor Marty Cowie on the occasion of his 65th birthday

Among a variety of heteroaromatics, 1,2,3,4-tetrahydroquinolines, -isoquinolines and -quinoxalines are three significant substructures in many bioactive compounds and have attracted a great deal of attention in research concerning pharmaceuticals, agrochemicals, dyes and fragrances, as well as hydrogen-storage materials.[1] They can be directly accessed by hydrogenation from commercially available quinolines, isoquinolines and quinoxalines. Traditionally, stoichiometric metal hydrides and reactive metals are used as reducing reagents.[2] Apart from producing copious waste and using often hazardous reagents, these methods suffer from limited substrate scope, incompatibility with functionality and poor chemoselectivity.

A more attractive method is to use catalytic hydrogenation. Over the past several decades, a number of homogeneous and heterogeneous catalysts have been applied to the hydrogenation of heteroaromatics, including the asymmetric version.[3–7] The need for high H_2 pressure, high reaction temperature or high catalyst loading is typical of metal-catalysed hydrogenation. Obviating the need for hydrogen gas, transfer hydrogenation (TH) offers an alternative. However, only a few catalysts have been reported thus far that allow for the TH of heteroaromatics, and in all cases the catalyst loading is relatively high ($\geq$0.5%).[8] Furthermore, in either hydrogenation or TH, there appears to be no catalyst capable of reducing all three classes of heteroaromatics: quinolines, isoquinolines and quinoxalines. Herein, we disclose a highly effective catalyst system, enabled by a simple ion, I^-, which shows unprecedented activity in the reduction of these heteroaromtics under mild conditions.

We recently reported the first example of asymmetric transfer hydrogenation (ATH) of quinolines in water with formate as the hydrogen source.[8f] Excellent enantioselectivities were obtained with a Rh–Ts-dpen catalyst, [Cp*RhCl(Ts-dpen-H)][9] (Ts-dpen = *N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine).[10] Following this success, we attempted the ATH of quaternary quinoline salts, aiming to directly obtain chiral *N*-substituted 1,2,3,4-tetrahydroquinolines. We chose the *N*-methyl-2-methylquinoline iodide salt as a benchmark substrate and Rh–Ts-dpen as the catalyst (1 mol%). There was little reduction using sodium formate as the reductant in water at 40°C in 24 h, under which quinolines were readily reduced.[8f] Somewhat surprisingly, changing the aqueous formate to the azeotropic HCO_2H/NEt_3 mixture led to an excellent isolated yield of 95% but a very low enantiomeric excess (*ee*) value of 5% for the tetrahydro product. Interestingly, similar conversion was also observed under identical conditions with $[(Cp^*RhCl_2)_2]$ as catalyst, without adding the Ts-dpen ligand. Thus, the low *ee* value might result from the diamine ligand in Rh–Ts-dpen being replaced by the iodide anion in the salt during the reaction. Bearing in mind the unusual effects of iodide documented in catalysis[11] and the scarcity of effective catalysts for TH of heteroaromatics,[8] we thought it would be interesting to explore whether $[(Cp^*RhCl_2)_2]$ in combination with the iodide ion would lead to a simple but active catalyst.

Choosing 2-methylquinoline **1a** (pK_a 5.4) as a model substrate, which is expected to be protonated when using formic acid (pK_a 3.6) as the reductant, the TH was first carried out with 0.05 mol% $[(Cp^*RhCl_2)_2]$ in the azeotropic HCO_2H/NEt_3 at 40°C. The reduction was insignificant, with the conversion of **1a** being only 6% (Table 1, entry 2), indicating that iodide might indeed be necessary. To our delight, in the presence of 1 or even 0.1 equivalent of an iodide salt, tetrabutylammonium iodide (TBAI), full conversion was observed (Table 1, entries 3 and 4). In contrast, the analogous bromide salt TBAB is much less effective (Table 1, entry 5) and the chloride TBAC is ineffective (entry 6). The cheaper KI was equally effective, showing that it is the iodide ion that promotes the catalysis (Table 1, entry 7). Remarkably, in the presence of KI, the metal loading could be decreased to 0.01 mol% without affecting the conversion (Table 1, entry 8). At an even a lower loading of 0.001 mol% of rhodium with 0.5 equivalent of KI added, a moderate conversion of 71% was still obtained, albeit in a longer reaction

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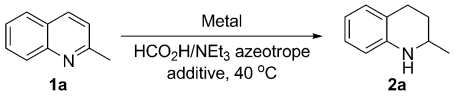
Table 1. Effect of iodide on the TH of **1a**.[a]



Entry	Metal, mol %[b]	t [h]	Additive, equiv	Conv. [%][c]
1	none	12	none	NR[d]
2	Rh, 0.1	12	none	6
3	Rh, 0.1	12	TBAI, 1.0	100
4	Rh, 0.1	15	TBAI, 0.1	100
5	Rh, 0.1	15	TBAB, 0.1	42
6	Rh, 0.1	15	TBAC, 0.1	8
7	Rh, 0.1	15	KI, 0.1	100
8	Rh, 0.01	12	KI, 0.2	100
9	Rh, 0.001	48	KI, 0.5	71
10	Ir, 0.01	12	KI, 0.2	<1
11	Ru, 0.01	12	KI, 0.2	<1
12	$RhCl_3$, 0.01	12	KI, 0.2	NR[d]

[a] Reaction conditions: **1a** (0.5 mmol), HCO_2H/NEt_3 azeotrope (3 mL), 40 °C. [b] Rh = $[(Cp^*RhCl_2)_2]$, Ir = $[(Cp^*IrCl_2)_2]$ and Ru = $[\{RuCl_2(p\text{-cymene})\}_2]$; number refers to Rh content. [c] Determined by ^1H NMR spectroscopy. [d] No reaction observed.

time (Table 1, entry 9). This yields a turnover number (TON) close to 7.1×10^4, which is, to the best of our knowledge, the highest TON value ever reported in catalytic reduction of heteroaromatics. However, under similar conditions, other metal compounds, such as $[(Cp^*IrCl_2)_2]$ and $[\{RuCl_2(p\text{-cymene})\}_2]$, failed to catalyse the reduction (Table 1, entries 10–12).

The beneficial effect of iodide in asymmetric hydrogenation with H_2 has been noted in a number of instances, though the mechanistic details remain to be delineated.[5a,h,11,12] Few examples of an iodide effect in TH are known or have been studied, however.[8d,13] We therefore decided to take a further look into the rate acceleration by iodide. Figure 1 shows the effect of iodide concentration $[I^-]$ on the conversion of **1a** to **2a** at 4.5 h in the HCO_2H/NEt_3 azeotrope. A dramatic increase in the reaction rate was observed when $[I^-]$ was increased, up to 20 mol % with respect

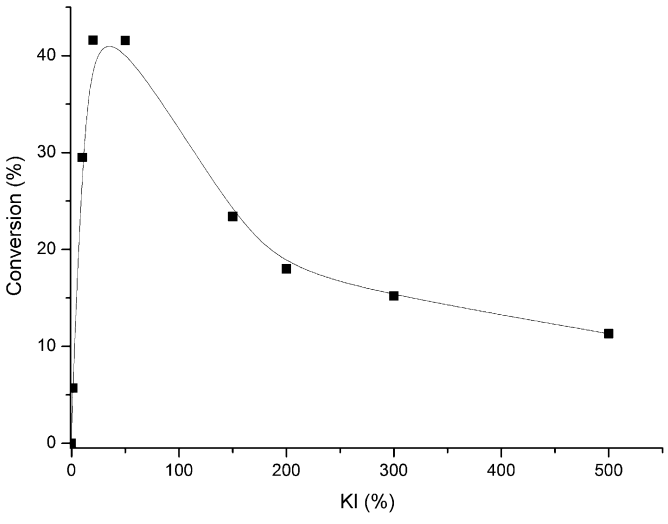


Figure 1. Effect of the concentration of iodide on the TH of **1a** (0.5 mmol) catalysed by $[Cp^*RhCl_2]_2$ (0.005 mol %). Reactions were carried out in the HCO_2H/NEt_3 azeotrope (3 mL) for 4.5 h at 40 °C.

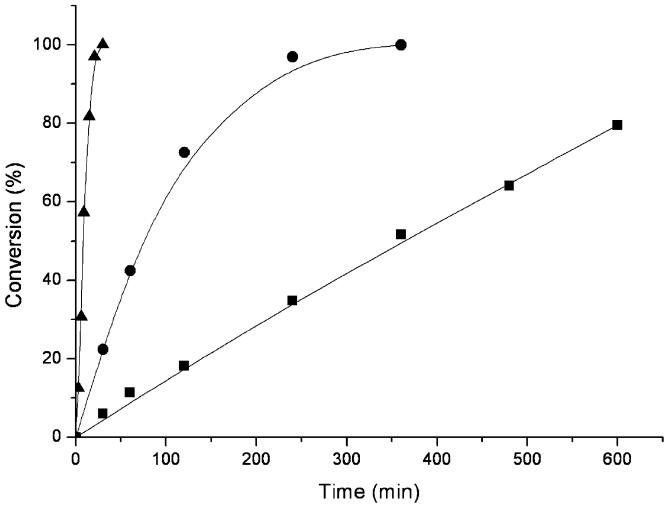
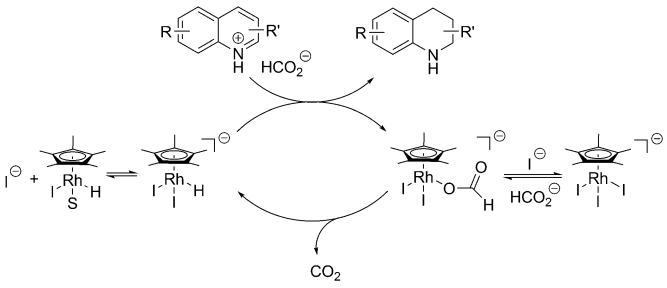


Figure 2. Effect of I^- on the TH of **1a** (0.8 mmol) catalysed by $[(Cp^*RhX_2)_2]$ (0.5 mol %) (■ X = Cl, ● X = I, ▲ X = Cl plus 20 mol % KI). Reactions were carried out in the HCO_2H/NEt_3 azeotrope (5 mL) at 40 °C.

to **1a**; thereafter the rate decreased with more iodide added, suggesting that the iodide is involved in the turnover-limiting step or steps prior to this step. This finds support in the conversion-time profiles shown in Figure 2, obtained using as catalysts $[(Cp^*RhCl_2)_2]$, $[(Cp^*RhI_2)_2]$ and $[(Cp^*RhCl_2)_2]$ in the presence of 20 mol % KI (1 mol % rhodium in each case). Clearly, the iodo dimer catalysed significantly faster hydrogenation than its chloro analogue. More interestingly, the kinetics for these two catalysts appears to be distinctively different. With the chloro catalyst, the reduction appears to be zero order in [**1a**], whereas in the case of the iodo catalyst, the profile suggests rate dependence on [**1a**]. In the presence of excess I^- (20 mol % KI), the reduction became still faster, with the initial rate being approximately 7 times that obtained with $[(Cp^*RhI_2)_2]$ and approximately 40 times that with $[(Cp^*RhCl_2)_2]$ alone. These results suggests that in the presence of excess I^-, an active Cp*Rh-iodo catalyst is generated from $[(Cp^*RhCl_2)_2]$ and its presence alters the hydrogenation kinetics, with the turnover rate limited by hydride formation with $[(Cp^*RhCl_2)_2]$ but more likely by hydride transfer when iodide is added.

A plausible mechanism is shown in Scheme 1. The key feature is that the substrate, which is most likely to be pro-

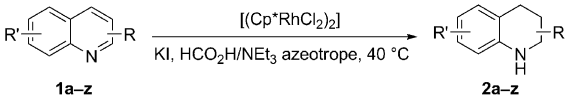


Scheme 1. Suggested mechanism for the Cp^*Rh^{III}-I catalysed TH of quinoline.

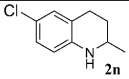
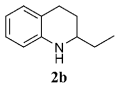
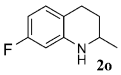
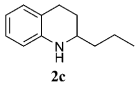
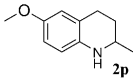
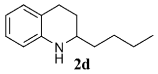
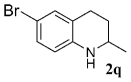
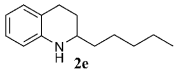
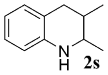
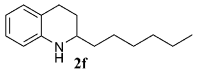
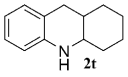
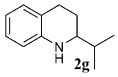
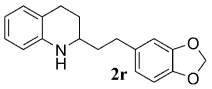
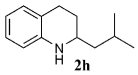
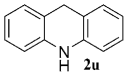
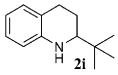
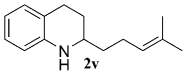
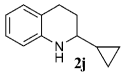
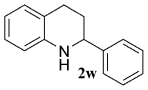
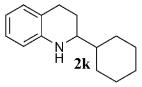
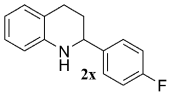
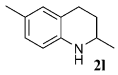
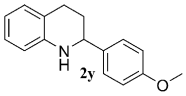
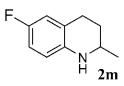
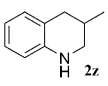
tonated under the reaction conditions, is reduced by an anionic diiodo Rh–H hydride, probably via a 1,4-addition pathway as indicated by deuterium labelling (see the Supporting Information).[14] The anionic charge is likely to make the hydride more hydridic, and this would be reinforced by the stronger bonding of the soft iodide to Rh^{III} and its stronger "trans" effect than the hard chloride,[15] facilitating hydride transfer to the substrate. Increasing $[I^-]$ increases the concentration of the hydride and hence the rate; however, when $[I^-]$ becomes too high, the equilibrium shown in Scheme 1 will favour the triiodo species, decreasing the concentration of active catalyst and so the rate. Therefore, a maximum is expected in the conversion–$[I^-]$ profile seen in Figure 1.

Having identified the optimised conditions, we subjected a variety of quinoline derivatives to the TH. As can be seen from Table 2, the reduction affords good to excellent yields at 40 °C with 0.01–0.1 mol % catalyst. Notably, the reaction can be carried out in air; degassing did not show any detectable difference. Quinolines bearing various alkyl substituents at the 2-position (**1a–f**) proceeded successfully to give the corresponding hydrogenated products in excellent yields (Table 2, entries 1–6). Pleasingly, good to excellent yields were obtained for quinolines with bulky substituents at the 2-position (**1g–k**; Table 2, entries 7–11), and in particular, 1,2,3,4-tetrahydro-2-tert-butylquinoline (**2i**) was obtained with 99 % yield. In homogeneous hydrogenation, the best result reported previously for this substrate was 43 % con-

Table 2. TH of quinolines with $[(Cp^*RhCl_2)_2]$–KI in the HCO_2H/NEt_3 azeotrope.[a]



1a–z 2a–z

Entry	Product	S/C[b]	*t* [h]	Yield [%][c]	Entry	Product	S/C[b]	*t* [h]	Yield [%][c]
1	 **2a**	10000	12	91	14	 **2n**	10000	24	92
2	 **2b**	10000	15	93	15	 **2o**	10000	12	83
3	 **2c**	10000	12	93	16	 **2p**	10000	24	73
4	 **2d**	10000	15	96	17	 **2q**	10000	48	83
5	 **2e**	10000	15	84	18	 **2s**	10000	15	89
6	 **2f**	10000	10	72	19	 **2t**	10000	20	69
7	 **2g**	10000	15	91	20	 **2r**	10000	12	95
8	 **2h**	10000	12	93	21	 **2u**	5000	12	98
9	 **2i**	10000	15	99	22	 **2v**	10000	24	71
10	 **2j**	10000	15	85	23	 **2w**	1000	48	98
11	 **2k**	10000	11	96	24	 **2x**	1000	48	98
12	 **2l**	10000	12	76	25	 **2y**	1000	26	94
13	 **2m**	10000	12	74	26	 **2z**	5000	12	88

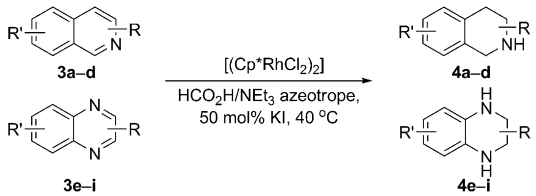
[a] Reaction conditions: **1** (0.5 mmol), $[(Cp^*RhCl_2)_2]$ (0.025–0.25 μmol), KI (0.1–0.8 mmol), HCO_2H/NEt_3 azeotrope solution (3 mL), 40 °C, 12–48 h. [b] Substrate/rhodium molar ratio. [c] Yields of isolated products.

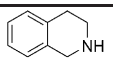
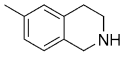
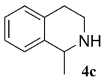
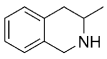
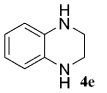
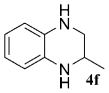
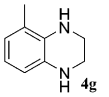
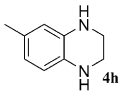
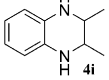
version with 2 mol% of a rhodium catalyst in 48 h.[8g] The isolated C=C bond in **1v**, which is challenging in hydrogenation with molecular hydrogen, was tolerated (Table 2, entry 22). Also interestingly, 2,3-disubstituted and 3-substituted quinolines (**1s**, **1t** and **1z**; Table 2, entries 18, 19 and 26) and an example of fused quinolines (**1u**; entry 21) can be smoothly reduced. A problem was encountered with the less basic 2-arylquinolines (**1w**–**y**), where good yields were obtained with a higher metal and iodide loading and a longer reaction time (Table 2, entries 23–25). To showcase the practicability of this methodology, we tried the TH of 5.0 g of **1a** with 0.01 mol% rhodium (1.0 mg). The reduction afforded **2a** in 97% isolated yield in 24 h at 40°C.

The more challenging quinoxalines and particularly isoquinolines were next attempted (Table 3). The latter structures have not been reduced, until now, to tetrahydroisoquinolines under TH due to their stable aromaticity. Higher catalyst loading was necessary for some of these substrates, however. Thus, using 0.2 mol% rhodium loading, good to excellent yields were obtained for a range of tetrahydroisoquinolines (**4a**–**d**; Table 3, entries 1–4). This represents the lowest metal loading reported in metal-catalysed hydrogenation of this class of substrates. Excellent yields were also observed in the reduction of several quinoxalines (**3e**–**i**; Table 3, entries 5–9) with as low as 0.02 mol% rhodium loading. The accelerating effect of iodide was again noted. Thus, no reaction was observed in the TH of **3a** and **3e** when the iodide salt was omitted.

In conclusion, we have developed a new protocol for the reduction of quinolines, isoquinolines and quinoxalines. Enabled by the simple iodide ion, which accelerates the hydrogenation presumably by altering the reaction mechanism, the protocol is efficient, practical and operationally simple, providing a valuable alternative to currently used methods for heterocycle reduction.

Table 3. TH of isoquinolines and quinoxalines with $[(Cp^*RhCl_2)_2]$–KI in HCO_2H/NEt_3.[a]



Entry	Product	S/C[b]	t [h]	Yield [%][c]
1	 4a	500	24	83
2	 4b	500	24	95
3	 4c	500	24	92[d]
4	 4d	500	24	91
5	 4e	5000	12	99
6	 4f	5000	12	86
7	 4g	5000	12	92
8	 4h	5000	12	90
9	 4i	500	24	91

[a] Reaction conditions: **3** (0.5 mmol), $[(Cp^*RhCl_2)_2]$ (0.05–0.5 μmol), KI (0.25 mmol), HCO_2H/NEt_3 azeotrope solution (3 mL), 40°C, 12–24 h. [b] Substrate/rhodium molar ratio. [c] Yields of isolated products. [d] HCO_2H/NEt_3 3.5:1.0.

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Keywords: formic acid · heterocycles · hydrogenation · iodine · rhodium

[1] a) A. R. Katritzky, S. Rachwal, B. Rachwal, *Tetrahedron* **1996**, *52*, 15031; b) J. D. Scott, R. M. Williams, *Chem. Rev.* **2002**, *102*, 1669; c) K. W. Bentley, *Nat. Prod. Rep.* **2006**, *23*, 444; d) R. H. Crabtree, *Energy Environ. Sci.* **2008**, *1*, 134; e) V. Sridharan, P. A. Suryavanshi, J. C. Menendez, *Chem. Rev.* **2011**, *111*, 7157.

[2] a) G. W. Gribble, *Chem. Soc. Rev.* **1998**, *27*, 395; b) M. R. Pitts, J. R. Harrison, C. J. Moody, *J. Chem. Soc. Perkin Trans. 1* **2001**, 955.

[3] For reviews on catalytic hydrogenation of heteroaromatics, see: a) C. Bianchini, P. Barbaro, M. Macchi, A. Meli, F. Vizza, *Helvetica Chimica Acta* **2001**, *84*, 2895; b) F. Glorius, *Org. Biomol. Chem.* **2005**, *3*, 4171; c) R. Kuwano, *Heterocycles* **2008**, *76*, 909; d) D. S. Wang, Q. A. Chen, S. M. Lu, Y. G. Zhou, *Chem. Rev.* **2012**, *112*, 2557.

[4] For examples of non-asymmetric organometallic hydrogenation of heteroaromatics, see: a) Y. Watanabe, T. Ohta, Y. Tsuji, T. Hiyoshi, Y. Tsuji, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2440; b) A. Alvanipour, L. D. Kispert, *J. Mol. Catal.* **1988**, *48*, 277; c) S. I. Murahashi, Y. Imada, Y. Hirai, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2968; d) P. Baiczewski, J. A. Joule, *Synth. Commun.* **1990**, *20*, 2815; e) E. Baralt, S. J. Smith, J. Hurwitz, I. T. Horvath, R. H. Fish, *J. Am. Chem. Soc.* **1992**, *114*, 5187; f) S. M. Lu, X. W. Han, Y. G. Zhou, *J. Organomet. Chem.* **2007**, *692*, 3065; g) G. Zhu, K. Pang, G. Parkin, *J. Am. Chem. Soc.* **2008**, *130*, 1564; h) N. Hashimoto, Y. Takahashi, T. Hara, S. Shimazu, T. Mitsudome, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Chem. Lett.* **2010**, *39*, 832; i) G. E. Dobereiner, A. Nova, N. D. Schley, N. Hazari, S. J. Miller, O. Eisenstein, R. H. Crabtree, *J. Am. Chem. Soc.* **2011**, *133*, 7547.

[5] For examples of asymmetric organometallic hydrogenation of heteroaromatics, see: quinolines: a) W. B. Wang, S. M. Lu, P. Y. Yang, X. W. Han, Y. G. Zhou, *J. Am. Chem. Soc.* **2003**, *125*, 10536; b) M. T. Reetz, X. G. Li, *Chem. Commun.* **2006**, 2159; c) N. Mrsic, L. Lefort, J. A. F. Boogers, A. J. Minnaard, B. L. Feringa, J. G. de Vries, *Adv. Synth. Catal.* **2008**, *350*, 1081; d) H. Tadaoka, D. Cartigny,

T. Nagano, T. Gosavi, T. Ayad, J. P. Genet, T. Ohshima, V. Ratovelomanana-Vidal, K. Mashima, *Chem. Eur. J.* **2009**, *15*, 9990; e) T. L. Wang, L. G. Zhuo, Z. W. Li, F. Chen, Z. Y. Ding, Y. M. He, Q. H. Fan, J. F. Xiang, Z. X. Yu, A. S. C. Chan, *J. Am. Chem. Soc.* **2011**, *133*, 9878–9891; isoquinolines: f) S. M. Lu, Y. Q. Wang, X. W. Han, Y. G. Zhou, *Angew. Chem.* **2006**, *118*, 2318; *Angew. Chem. Int. Ed.* **2006**, *45*, 2260; quinoxalines: g) N. Mrsic, T. Jerphagnon, A. J. Minnaard, B. L. Feringa, J. G. de Vries, *Adv. Synth. Catal.* **2009**, *351*, 2549; h) W. Tang, L. Xu, Q. H. Fan, J. Wang, B. Fan, Z. Zhou, K. H. Lam, A. S. C. Chan, *Angew. Chem.* **2009**, *121*, 9299; *Angew. Chem. Int. Ed.* **2009**, *48*, 9135; i) Q. A. Chen, D. S. Wang, Y. G. Zhou, Y. Duan, H. J. Fan, Y. Yang, Z. Zhang, *J. Am. Chem. Soc.* **2011**, *133*, 6126; j) S. Urban, N. Ortega, F. Glorius, *Angew. Chem.* **2011**, *123*, 3887; *Angew. Chem. Int. Ed.* **2011**, *50*, 3803.

[6] For examples of non-asymmetric organocatalytic hydrogenation of heteroaromatics, see: a) M. Rueping, T. Theissmann, A. P. Antonchick, *Synlett* **2006**, *7*, 1071; b) A. Bruckmann, M. A. Pena, C. Bolm, *Synlett* **2008**, *6*, 900; c) S. J. Geier, P. A. Chase, D. W. Stephan, *Chem. Commun.* **2010**, *46*, 4884.

[7] For examples of asymmetric organocatalytic hydrogenation of heteroaromatics, see: a) M. Rueping, A. R. Antonchick, T. Theissmann, *Angew. Chem.* **2006**, *118*, 3765; *Angew. Chem. Int. Ed.* **2006**, *45*, 3683; b) Q. S. Guo, D. M. Du, J. Xu, *Angew. Chem.* **2008**, *120*, 771; *Angew. Chem. Int. Ed.* **2008**, *47*, 759.

[8] For examples of organometallic transfer hydrogenation of heteroaromatics, see: a) K. Fujita, C. Kitatsuji, S. Furukawa, R. Yamaguchi, *Tetrahedron Lett.* **2004**, *45*, 3215; b) P. Frediani, L. Rosi, L. Cetarini, M. Frediani, *Inorg. Chim. Acta* **2006**, *359*, 2650; c) J. S. Wu, J. Liao, J. Zhu, J. G. Deng, *Synlett* **2006**, *13*, 2059; d) D. W. Wang, W. Zeng, Y. G. Zhou, *Tetrahedron: Asymmetry* **2007**, *18*, 1103; e) A. M. Voutchkova, D. Gnanamgari, C. E. Jakobsche, C. Butler, S. J. Miller, J. Parr, R. H. Crabtree, *J. Organomet. Chem.* **2008**, *693*, 1815; f) C. Wang, C. Q. Li, X. F. Wu, A. Pettman, J. L. Xiao, *Angew. Chem.* **2009**, *121*, 6646; *Angew. Chem. Int. Ed.* **2009**, *48*, 6524; g) V. Parekh, J. A. Ramsden, M. Wills, *Tetrahedron: Asymmetry* **2010**, *21*, 1549; h) J. Tan, W. J. Tang, Y. W. Sun, Z. Jiang, F. Chen, L. J. Xu, Q. H. Fan, J. L. Xiao, *Tetrahedron* **2011**, *67*, 6206.

[9] K. Mashima, T. Abe, K. Tani, *Chem. Lett.* **1998**, *27*, 1199.

[10] S. Hashiguchi, A. Fujii, J. Takehara, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1995**, *117*, 7562.

[11] a) K. Fagnou, M. Lautens, *Angew. Chem.* **2002**, *114*, 26; *Angew. Chem. Int. Ed.* **2002**, *41*, 26; b) P. M. Maitlis, A. Haynes, B. R. James, M. Catellani, G. P. Chiusoli, *Dalton Trans.* **2004**, 3409.

[12] a) F. Spindler, B. Pugin, H. U. Blaser, *Angew. Chem.* **1990**, *102*, 561; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 558; b) Y. Ng Cheong Chan, J. A. Osborn, *J. Am. Chem. Soc.* **1990**, *112*, 9400.

[13] a) O. Saidi, A. J. Blacker, M. M. Farah, S. P. Marsden, J. M. J. Williams, *Chem. Commun.* **2010**, *46*, 1541; b) R. Kawahara, K. Fujita, R. Yamaguchi, *J. Am. Chem. Soc.* **2010**, *132*, 15108.

[14] When using $DCOOH/NEt_3$, full deuteration at the C2 and C4 position of 2-methylquinoline took place. This is consistent with a 1,4-addition pathway, in which the hydride/deutride is first added to the C4 position of protonated 2-methylquinoline, affording an enamine that isomerises into an iminium species under the acidic condition. Finally, addition of a second hydride/deutride at the C2 position leads to the product observed. In support of this, 4-methyl quinoline was much more difficult to reduce, showing a 23% conversion at S/C = 50 and 50 mol% KI after 24 h reaction time.

[15] E. Peris, J. C. Lee, Jr., J. R. Rambo, O. Eisenstein, R. H. Crabtree, *J. Am. Chem. Soc.* **1995**, *117*, 3485. We note, however, that the iodide and hydride are unlikely to be strictly *trans* when the hydride is delivered.

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