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## Enantioselective hydrogenation of cyclic imines catalysed by Noyori–Ikariya half-sandwich complexes and their analogues†

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**A method for enantioselective hydrogenation of cyclic imines with gaseous hydrogen has been developed. Easily accessible Noyori–Ikariya Ru(II) and Rh(III) complexes can be used directly without an inert atmosphere. Substrate activation has been achieved by trifluoroacetic acid. A new hydroxyl-functionalized complex is reported, showing high activity in transfer hydrogenation.**

Efficient methods toward the construction of optically enriched amines are in the forefront of modern synthetic chemistry.<sup>1</sup> One such method is the asymmetric transfer hydrogenation (ATH) of imines catalysed by chiral half-sandwich Ru(II),<sup>2</sup> Rh(III),<sup>3,4</sup> and Ir(III)<sup>3</sup> complexes. Asymmetric hydrogenation (AH) reactions directly using gaseous hydrogen are often preferred, and the existing ATH catalytic systems have thus been modified to be applicable under AH conditions.<sup>5</sup> The first use of complexes [Ru(II)Cl(η<sup>6</sup>-arene)(*N*-R-sulfonyl-DPEN)] (where DPEN = 1,2-diphenylethylene-1,2-diamine and R = aryl or alkyl) in AH was reported by Ohkuma *et al.* in 2006 in the reduction of ketones.<sup>5a</sup> The key difference from ATH was a switch from basic to mildly acidic conditions (*i.e.*, methanol as the solvent). The authors found autodissociation of the Ru–Cl bond to be essential.<sup>5c</sup> To facilitate this, a Ru–triflate complex was used.<sup>5a–e</sup> Wills's<sup>5f</sup> and Ikariya's<sup>5g</sup> tethered complexes proved useful in AH of ketones without modification, *i.e.* as Ru–chloride complexes.

The first AH of cyclic imines using this catalytic system was shown by Li *et al.* on a Cp\*–Rh(III) (Cp\* = 1,2,3,4,5-pentamethylcyclopentadienyl) catalyst.<sup>6a</sup> They generated a [Rh]<sup>+</sup>SbF<sub>6</sub><sup>–</sup>

complex *in situ* by reacting the Rh–chloride complex with AgSbF<sub>6</sub>. For acyclic imines, a Cp\*–Ir(III) catalyst with a chiral phosphate anion was employed.<sup>6b</sup> Ikariya and co-workers developed an alternative strategy for the AH of acyclic imines with an Ir(III) catalyst and AgSbF<sub>6</sub>, proposing that Ag<sup>+</sup> can activate the substrate.<sup>6c</sup> Imine AH was further screened by Chen *et al.* by testing various counteranions.<sup>6d,e</sup> They also synthesized enantio-enriched 1,2,3,4-tetrahydroquinolines *via* AH of quinolines using the Ru–triflate complex under a variety of reaction conditions.<sup>6f–i</sup>

In this work, we present a method for the AH of cyclic imines with the aim of simplifying the reaction conditions: standard metal–chloride complexes are employed and the necessity of an inert atmosphere is avoided.

For the initial experiments, catalyst [RuCl(η<sup>6</sup>-*p*-cymene)(*S,S*)-TsDPEN] (**A**) and substrate 6,7-dimethoxy-1-methyl-3,4-dihydroisoquinoline (6,7-dimethoxy-1-methyl-DHIQ, **1**) were selected because both substances are very often used to benchmark ATH.<sup>7</sup> Screening of solvents (Table S1, ESI†) revealed that the reaction did not proceed in acetonitrile whilst only minimal reactivity was observed in DMSO (< 5% conversion) and methanol (10% conversion). In this catalytic system, it is presumed that imines require activation by polarization of the C=N bond in order to undergo reduction.<sup>8</sup> This activation has been achieved by Brønsted<sup>8a</sup> or Lewis acids,<sup>8a,9</sup> the electron-withdrawing effect of a CF<sub>3</sub> group,<sup>10</sup> or conversion of the imine to a quarternary iminium salt.<sup>11</sup> Therefore, we envisaged that we could activate the C=N bond by adding a suitable acid (Table S2, ESI†). Using methanol as the solvent, tetrafluoroboric acid (48% wt solution in water, 1 equiv.) enhanced the reaction only moderately (19% conversion) and trifluoromethanesulfonic acid (1 equiv.) had no effect (9% conversion). Gratifyingly, trifluoroacetic acid (1 equiv.) increased the conversion to 57%. Smaller amounts were found to be insufficient, probably because the substrate could not be fully protonated.<sup>‡</sup> Excess trifluoroacetic acid gave no improvement, but could be detrimental by causing partial or full protonation of the TsDPEN ligand. The conversion was further improved to 96% by increasing the temperature to 40 °C. At this point, it was found that the reaction was equally feasible in dichloromethane

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under the conditions developed for methanol. However, this avenue was not pursued any further as it is not a preferred solvent in the pharmaceutical industry, mainly for environmental reasons. Dried and/or degassed solvents were not necessary since we obtained identical results both with and without paying attention to this aspect.

We still could not achieve full conversion. Neither the addition of acid or catalyst, nor increasing the reaction temperature, nor prolongation of the reaction time led to significant improvement. Eventually, it was discovered that the order of addition of the reaction mixture components played a critical role. The original order was as follows: (1) substrate, (2) methanol, (3) catalyst, and (4) acid – after switching the catalyst and acid, the reaction proceeded to full conversion. Given that the substrate must be protonated, it is advisable for it to react with the acid first. Subsequently, the catalyst can be added with a significantly lower risk of deactivation.

Under optimized conditions, the method was tested on a mini-library containing six catalysts and twelve substrates (Fig. 1). Aside from complex **A**, its derivative, the 16e<sup>-</sup> amido complex **B**, was selected to examine the role of the Ru–Cl bond autodissociation<sup>5c</sup> and capability of **B** to react with hydrogen – e.g. in the AH of quinolines it was reported that **B** was catalytically inactive.<sup>6f</sup> Complex **C** was chosen as an alternative to **A**, bearing a different η<sup>6</sup>-arene. **D** and **E** were studied as representatives of the newer tethered complexes, and Rh(III) analogue **F** was included in order to show the applicability of the method on another metal. As substrates we tested nine DHIQs differing by substitutions in positions 1, 6 and 7 (**1–9**), 3,4-dihydro-β-carbolines harmalane (**10**) and harmaline (**11**), and cyclic *N*-sulfonyl imine **12**.

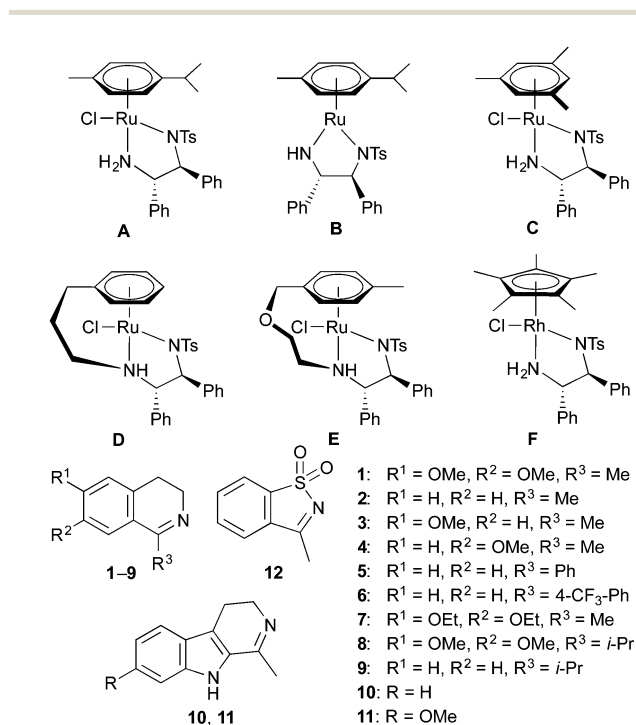


Fig. 1 Complexes **A–F** and substrates **1–12** used in this study.

Full conversion was achieved with substrates **1–4** in 6 hours with complexes **A–D** and **F** (Table 1). **A** and **B** showed comparable activity and enantioselectivity, implying that the Ru–Cl autodissociation is not rate limiting and that **B** can react with molecular hydrogen under such conditions. Interesting differences emerged with **E** – the 6-methoxy substituted substrates **1** and **3** showed lower reactivity than **2** and **4**, which agrees with our previous ATH study on this set of substrates.<sup>13</sup>

1-Aryl-DHIQs **5** and **6** were poorly reactive with the exception of Rh(III) complex **F**, delivering nearly racemic products, which is in agreement with previously reported findings from ATH.<sup>3</sup> Otherwise, maximum conversions (26% and 24%) were achieved with combinations **6-A** and **5-D**, respectively. 1-Aryl-substituted DHIQs thus require different reaction conditions and most likely different, more reactive catalysts. Experiments towards the efficient extension of our methodology to these substrates are currently underway.

6,7-Diethoxy-substituted imine **7** performed similarly to those described above, except that with **D** and **E** we observed lower reactivity. Imines **8** and **9**, bearing an isopropyl group in position 1, showed quite dissimilar performance: just like **7**, the 6,7-dimethoxy derivative **8** gave very high conversions with all complexes apart from **D** and **E**. On the contrary, **9** exhibited sluggish reactivity and surprisingly, only the tethered complex **D** afforded full conversion out of the **A–E** Ru(II) series. β-Carbolines **10** and **11** behaved in line with the previously described substrates. Apparently, the structurally more complex imines (containing bulkier substituents in positions 1, 6 or 7, or having the β-carboline scaffold) are less reactive when using tethered catalysts **D** and **E**. Eventually we attempted the AH of *N*-sulfonyl imine **12** – unfortunately, it was not soluble under the reaction conditions in methanol, and did not react in dichloromethane.

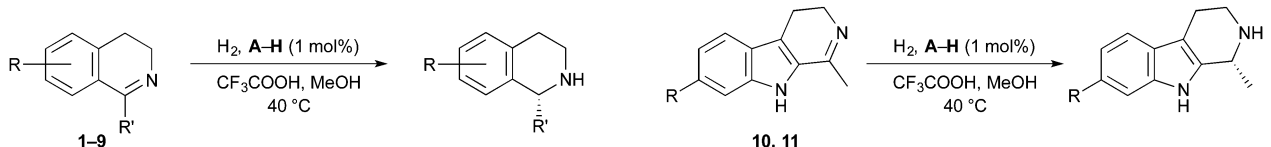
Good-to-excellent enantioselectivity was achieved in most cases (Table 1). Lower ee values were typically obtained with complexes **D** and **F**, and imine **9** gave only moderate enantioselectivity.

One reaction was performed on a ten-fold scale with complex **A** and substrate **1** (0.44 mmol of **1**; all other components scaled up accordingly) to show the synthetic utility of these reactions. The product was obtained at 92% yield, 97% ee and >95% purity.

In the course of this project, we also synthesized a complex bearing a 4-hydroxybutyl group at the η<sup>6</sup>-arene (**G**, see Fig. 2). Such a functionalization offers the possibility of its immobilization – unlike heterogenization *via* the DPEN ligand, which has been shown on many examples,<sup>7</sup> the arene ligand has been utilized much less often.<sup>14</sup>

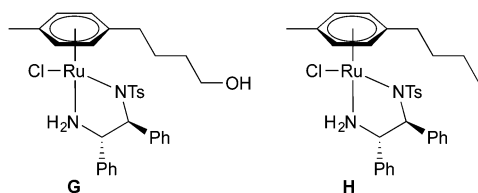
We employed the [4+2] cycloaddition reaction<sup>5g,15,16</sup> of a terminal alkyne (5-hexyn-1-ol) with a 1,3-diene (isoprene) to conveniently synthesize cyclohexadiene **13** (Scheme S1, ESI<sup>†</sup>). In the original procedure,<sup>5g</sup> the authors suggested that along with 1,4-substituted cyclohexa-1,4-diene (**13a**), only analogous 1,3-substituted cyclohexa-1,4-diene (**13c**) was formed (>80:20 ratio). However, with the aid of 2D NMR spectroscopy (Fig. S2, ESI<sup>†</sup>), we identified that three regioisomers **13a**, **13b** (being a 1,4-substituted cyclohexa-1,3-diene) and **13c** were formed in a ratio of 74:19:7. As these could not be separated, the mixture served



Table 1 AH of imines **1–11** catalysed by complexes **A–H**. Conversion and ee values are given in %<sup>a</sup>


Imine	Complex <b>A</b>		Complex <b>B</b>		Complex <b>C</b>		Complex <b>D</b>		Complex <b>E</b>		Complex <b>F</b>		Complex <b>G</b>		Complex <b>H</b>	
	cnv	ee	cnv	ee	cnv	ee	cnv	ee	cnv	ee	cnv	ee	cnv	ee	cnv	ee
<b>1</b>	>99	96	>99	96	>99	96	>99	78	44	94	>99	89	98	95	95	96
<b>2</b>	>99	87	>99	85	>99	81	>99	59	>99	84	>99	76	>99	87	>99	87
<b>3</b>	>99	92	>99	92	>99	89	>99	68	84	90	>99	90	>99	92	90	91
<b>4</b>	>99	93	>99	92	>99	90	>99	74	>99	91	>99	75	>99	91	>99	91
<b>5</b>	1	n.d.	4	n.d.	3	n.d.	24	11	0	n.d.	>99	7	2	n.d.	6	n.d.
<b>6</b>	26	5	2	n.d.	1	n.d.	12	n.d.	0	n.d.	>99	9	2	n.d.	3	n.d.
<b>7</b>	>99	97	>99	96	98	97	70	83	31	95	98	96	98	97	99	97
<b>8</b>	>99	98	>99	98	98	98	90	96	27	98	>99	99	99	98	99	96
<b>9</b>	39	72	35	70	38	39	>99	66	23	61	>99	84	88	82	>99	81
<b>10</b>	>99	97	>99	97	>99	97	70	93	69	95	>99	95	99	96	99	96
<b>11</b>	>99	95	>99	95	98	92	71	88	90	91	>99	93	99	93	98	90

<sup>a</sup> Amount of substrate  $n = 44 \mu\text{mol}$ , concentration of substrate  $c = 88 \text{ mM}$ , catalyst loading 1 mol%, TFA-to-substrate molar ratio A/S = 1,  $p(\text{H}_2) = 15 \text{ bar}$ ,  $40 \text{ }^\circ\text{C}$ , 6 h. Order of addition: imine-solvent-acid-catalyst.

Fig. 2 Complexes **G** and **H**.

for the synthesis of Ru(II) dimer (**14a**),<sup>17</sup> which further afforded **G** by complexation with the (*S,S*)-TsDPEN ligand (Scheme S1, ESI<sup>†</sup>). As expected, dimer **14a** contained around 7% of the *meta*-substituted analogue (**14b**) originating from **13c**. In the spectra of **G** this could no longer be resolved due to signal broadening. Complex **G** was further characterized by single-crystal X-ray diffraction (Fig. S3 and S4, ESI).<sup>†</sup>

In the context of this study, we were interested in both AH and ATH with **G** to evaluate its eligibility for its use as a modular substitute for **A**. Monitoring the ATH of imines **1–4**, **8–10** and **12** by <sup>1</sup>H NMR,<sup>18</sup> we observed enhanced reactivity in comparison to complex **A** (Table 2, Fig. S1, ESI<sup>†</sup>). To probe whether the hydroxyl group of **G** was responsible for this, we synthesized complex **H** (Fig. 2, Scheme S1, ESI<sup>†</sup>), which does not contain any heteroatom on the η<sup>6</sup>-arene. Surprisingly, ATH using **H** revealed similar or only slightly lower performance compared to **G**, except for *N*-sulfonyl imine **12**, which can form an O–H...O=S hydrogen bond with **G** that may increase the reactivity. Therefore, the hydroxyl group was not the key parameter responsible for the enhanced reactivity of **G**. The reaction kinetics (one example in Fig. 3, complete set of results in Fig. S1, ESI<sup>†</sup>) suggest the hydrogenations with **A** to be first order, while **G** and **H** are closer to zero-order kinetics. Systematic studies to clarify this phenomenon are currently underway in our laboratories.

Both **G** and **H** were also tested in AH under optimised conditions (Table 1), and their activity was comparable to or

Table 2 ATH of imines **1–4**, **8–10** and **12** catalysed by complexes **A**, **G** and **H**<sup>a</sup>

	ee (%)			TON <sup>b</sup>			TOF <sup>c</sup> (h <sup>-1</sup> )		
	<b>A</b>	<b>G</b>	<b>H</b>	<b>A</b>	<b>G</b>	<b>H</b>	<b>A</b>	<b>G</b>	<b>H</b>
<b>1</b>	93	94	92	142	174	154	178	195	175
<b>2</b>	85	86	85	108	138	135	136	155	157
<b>3</b>	90	91	90	110	138	126	146	163	162
<b>4</b>	87	88	87	125	134	114	160	153	145
<b>8</b>	93	95	95	78	160	150	111	207	198
<b>9</b>	50	70	68	29	82	68	32	102	83
<b>10</b>	92	93	93	148	200	146	183	209	187
<b>12</b>	92	92	92	37	76	39	45	97	46

<sup>a</sup> Amount of substrate  $n = 55 \mu\text{mol}$ , concentration of substrate  $c = 75 \text{ mM}$ , catalyst loading 0.5 mol%, hydrogen source HCOOH/Et<sub>3</sub>N (5:2),  $30 \text{ }^\circ\text{C}$ . <sup>b</sup> Turnover number calculated after 50 min. <sup>c</sup> Turnover frequency calculated at 20% conversion.

higher than that of Ru(II) complexes **A–E**. In particular, the poorly reactive imine **9** was hydrogenated with high conversion. The AH method was thus extended to a complex containing a hydroxyl, and has the potential to be operable with heterogenized catalysts derived from **G**, which are being developed in our laboratories.

The ees delivered by **G** and **H** were very similar to those obtained with **A–F** in both AH (Table 1) and ATH (Table 2) for all substrates, again with the exception of **9**, in which case we observed a significant increase. This means that replacing the isopropyl group of *p*-cymene with butyl or hydroxybutyl had no negative effect on the ee. A similar observation was made earlier for a complex bearing a 2-hydroxyethoxy group on the η<sup>6</sup>-arene.<sup>19</sup>

In conclusion, we present a simple method for the AH of cyclic imines catalysed by Ru(II) and Rh(III) half-sandwich complexes using trifluoroacetic acid for substrate activation. The catalysts were used in the standard Ru–chloride forms, which are easily accessible and non-air sensitive. In contrast to other



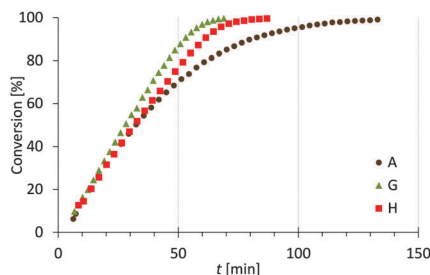


Fig. 3 ATH of imine **1** catalysed by complexes **A**, **G** and **H** using HCOOH/Et<sub>3</sub>N (5:2) in CD<sub>3</sub>CN at 0.5 mol% catalyst loading and a temperature of 30 °C.

reported approaches to imine AH with hydrogen gas, this method does not require air-sensitive additives or an inert atmosphere. New hydroxybutyl-arene-functionalized Ru(II) catalyst was synthesized – such functionalization gives the possibility of modular heterogenization. This complex (and its congener lacking the hydroxyl group) showed enhanced reactivity in imine ATH and performed similarly to the existing catalysts under the newly-developed AH conditions. Asymmetric hydrogenation of imines is still a discussed topic. By this work, we wish to add one more option to the highly versatile collection of possibilities offered by the Noyori–Ikariya class of catalysts.

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## Notes and references

‡ Fan *et al.*<sup>12</sup> found that the addition of trifluoroacetic acid promoted the AH of quinolines with Ir(III)–triflate complexes. However, Ir(III) complexes are much more reactive and their activity is further enhanced by the triflate counteranion. Therefore, we could not employ these reaction conditions in our work.

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