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β-Amino alcohols as ligands for asymmetric transfer hydrogenation of ketones in water

Xiaofeng Wu, Xiaohong Li, Matthew McConville, Ourida Saidi, Jianliang Xiao *

Liverpool Center for Materials and Catalysis, Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, UK

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Abstract

Chiral β-amino alcohols were used as ligands for ruthenium, rhodium and iridium-catalyzed asymmetric transfer hydrogenation of acetophenones in water with formate as reductant. The catalysts were showed to be capable of asymmetric transfer hydrogenation of ketones in water, but their activities and enantioselectivities varied with the ligands used and with solution pH values, with higher pH favouring higher rates and better enantioselectivities.

Keywords: Asymmetric transfer hydrogenation; β-Amino alcohols; Formate; Water; pH

1. Introduction

Asymmetric transfer hydrogenation (ATH) of prochiral ketones and imines is a pivotal reaction for the synthesis of chiral secondary alcohols and amines due to its versatility and practical simplicity [1–24]. Of all the important developments made in this area in recent years, the most significant is the use of ruthenium complexes containing (*R,R*)-TsDPEN [(1*R*,2*R*)-*N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine] or simple β-amino alcohols, which were developed by Noyori, Ikariya, Hashiguchi and co-workers [25–27]. The well-defined Ru-TsDPEN catalyst enables highly effective reduction of a wide range of ketones with up to 97% ee in 2-propanol or in the azeotropic mixture of formic acid and triethylamine [25].

The β-amino alcohol-based Ru(II) catalysts give rise to some of the best results for the ATH of ketones in terms of enantioselectivities and catalytic activities in 2-propanol [1–8,26,28–46]. Similar Rh(III) and Ir(III) catalysts have been reported as efficient catalysts for the ATH of aromatic ketones in 2-propanol as well [1–8,47–49]. With the ruthenium catalyst, the TOF could reach 8500 mol mol^{-1} h^{-1}, and a high substrate/catalyst (S/C) ratio of 7000 could be employed [26,29,30,32]. Under similar conditions, the rhodium and iridium catalysts finished in up to 95% ee at a S/C ratio of 5000 [47]. However, the β-amino alcohol-coordinated Ru(II), Rh(III) and Ir(III) catalysts appear to be incompatible with the azeotropic HCOOH–NEt_3 reduction system [6,31], which has proved to be efficient for most other ligands.

We recently communicated that the ATH of aromatic ketones with the Noyori-Ikariya Ru-(*R,R*)-TsDPEN catalyst or M-(*R,R*)-TsCYDN [(1*R*,2*R*)-*N*-(*p*-toluenesulfonyl)-1,2-cyclohexyldiamine] (M = Ru, Rh, Ir) can be significantly accelerated by using water as solvent and sodium formate as hydrogen donor [50–54,55–60]. The reaction could complete in a few minutes, furnishing ee's of up to 99%. We now report that the ATH of aromatic ketones, catalyzed by the Ru(II), Rh(III) or Ir(III) complexes of β-amino alcohols, can be carried out smoothly either in an aqueous solution containing HCOOH and NEt_3 or in neat water using HCOONa as hydrogen donor [61].

2. Experimental

$[RuCl_2(p\text{-cymene})]_2$, $[RhCp^*Cl_2]_2$, $[IrCp^*Cl_2]_2$, β-amino alcohol ligands and ketones were obtained from Aldrich, Fluka or Strem and were used as received. The products of the ATH were analyzed by a Varian CP-3380 GC equipped with a Chrompack Chirasil-Dex CB column (25 m × 0.25 mm). The precatalyst was generated in situ by reacting a β-amino alcohol ligand (0.012 mmol) with $[RuCl_2(p\text{-cymene})]_2$, or

* Corresponding author. Tel.: +44 151 7942937; fax: +44 151 7943589.
E-mail address: j.xiao@liv.ac.uk (J. Xiao).

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$[Cp^*RhCl_2]_2$, or $[Cp^*IrCl_2]_2$ (0.005 mmol) in 2 mL of a solvent at 40 °C for 1 h; the suspension was then used for the reduction reaction.

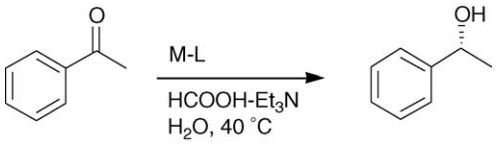
A typical procedure is given for acetophenone reduction in neat water: after preparing the precatalyst, HCOONa (340 mg, 5.0 mmol) and acetophenone (120 mg, 1.0 mmol) were added to the solution. Following quickly degassing three times, the solution was allowed to react at 40 °C for a certain period of time. After cooling to room temperature, the organic phase was extracted with Et_2O (3 mL × 2 mL) and passed through a short silica gel column before being subjected to chiral GC analysis.

We also examined the ATH of acetophenone to (*R*)-1-phenylethanol in a mixture of HCOOH and NEt_3 in the presence of water. The precatalyst was prepared in situ by reacting a β-amino alcohol ligand (0.012 mmol) with $[RuCl_2(p\text{-cymene})]_2$, or $[Cp^*RhCl_2]_2$, or $[Cp^*IrCl_2]_2$ (0.005 mmol) in 1 mL of water at 40 °C for 1 h followed by adding HCOOH (5.3–3.8 mmol) and NEt_3 (5.7–6.1 mmol). The ATH started with introduction of 1 mmol acetophenone to the suspension of the precatalyst. After reacting for a certain period of time, the reaction mixture was worked up as above.

3. Results and discussion

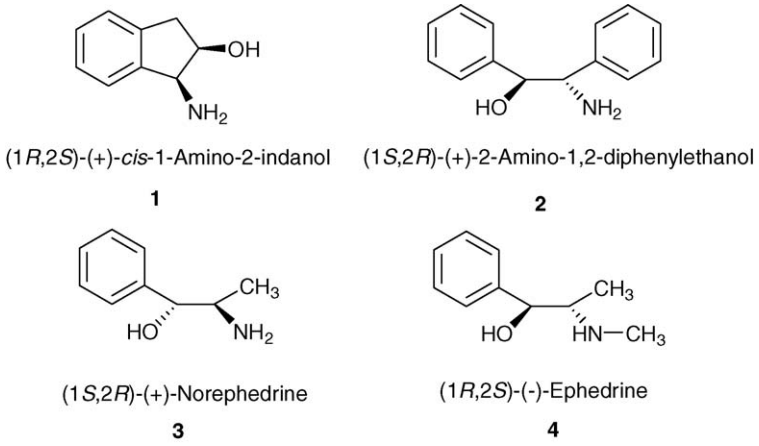
Following on from the study into aqueous-phase ATH by catalysts containing diamine ligands [50–54], we examined the same reactions with catalysts made of the amino alcohol ligands **1**–**4** in an attempt to determine the scope of catalysts applicable in water (Scheme 1). We initially studied the ATH of acetophenone with Ru-**1** derived in situ from $[RuCl_2(p\text{-cymene})]_2$ and (1*R*,2*S*)-(+)-*cis*-1-amino-2-indanol **1**. While this catalyst is active in 2-propanol, it showed no activity in the azeotropic HCOOH–NEt_3 (2.5/1 HCOOH/NEt_3 molar ratio). This confirms what Wills observed earlier [6,31]. However, when a 1:1 mixture of the azeotrope and water was used instead, a reaction was observed although both the conversion and ee were low (<10% in 48 h). This is somehow reminiscent of the ATH by HCOOH–NEt_3 with a Peg-supported Ru-TsDPEN catalyst, which was active in recycle runs only when some water was present [62]. The low rates and ee's could stem from the solution

Table 1
ATH of acetophenone with metal–amino alcohol complexes in HCOOH–Et_3N–H_2O[a]



Entry	Catalysts	F/T ratio[b]	Time (h)	Con (%)[c]	ee (%)[c]
1	Ru-**1**[d]	1.8/1	42	33	45
2		1/1.7	40	58	45
3	Rh-**1**[d]	1.8/1	48	60	14
4		1/1.7	150	90	87
5	Ir-**1**[d]	1.8/1	48	5	3
6		1/1.7	48	17	55
7	Ru-**2**[e]	1.8/1	72	11	23
8		1/1.7	40	33	52
9	Rh-**2**[e]	1.8/1	20	3	37
10		1/1.7	20	51	56
11	Ir-**2**[e]	1.8/1	48	11	23
12		1/1.7	1.5	100	55
13	Ru-**3**[d]	1.8/1	48	6	2
14		1/1.7	48	71	61
15	Rh-**3**[d]	1.8/1	48	65	4
16		1/1.7	48	24	17
17	Ir-**3**[d]	1.8/1	48	7	3
18		1/1.7	48	48	4
19	Ru-**4**[e]	1.8/1	42	75	72
20		1/1.7	40	81	75
21	Rh-**4**[e]	1.8/1	20	5	53
22		1/1.7	20	40	52
23	Ir-**4**[e]	1.8/1	48	12	9
24		1/1.7	48	99	32

[a] The reaction was carried out at 40 °C, using 1 mmol of acetophenone and a S/C ratio of 100 in 2 mL solvent.
[b] Molar ratio of HCOOH/NEt_3; $V_{HCOOH/Et_3N} = V_{H_2O} = 1$ mL.
[c] Determined by GC equipped with a chiral column.
[d] The configuration of alcohol product was *S*.
[e] The configuration of alcohol product was *R*.



(1*R*,2*S*)-(+)-*cis*-1-Amino-2-indanol **1**

(1*S*,2*R*)-(+)-2-Amino-1,2-diphenylethanol **2**

(1*S*,2*R*)-(+)-Norephedrine **3**

(1*R*,2*S*)-(-)-Ephedrine **4**

Scheme 1. β-Amino alcohol ligands used in this study.

being too acidic, as is demonstrated for the Ru-TsDPEN catalyst [50].

With the observations in mind, we investigated the aqueous ATH of acetophenone by HCOOH–NEt_3 with the HCOOH/NEt_3 ratios lowered. Under such conditions, the ATH reaction becomes feasible indeed. Thus, as shown in Table 1, the ATH of acetophenone by HCOOH–NEt_3 (1.8/1) with Ru-**1** gave a 33% conversion with 45% ee in 42 h in water (entry 1, Table 1); the conversion improved when the HCOOH/NEt_3 ratio was further lowered to 1/1.7 (entry 2, Table 1). The same reaction was also examined with the catalysts Rh-**1** and Ir-**1**, and again a lower HCOOH/NEt_3 ratio favors better conversions and ee's (entries 3–6, Table 1). The ee value of 87% is the best enantioselectivity we have thus far obtained with β-amino alcohol ligands in aqueous HCOOH–NEt_3 (entry 4, Table 1). Faster reduction has also been observed in the azeotropic HCOOH–NEt_3 when the HCOOH/NEt_3 ratio is lowered [3,63–65].

The easily available β-amino alcohols **2**–**4** were also tested. Using (1*S*,2*R*)-(+)-2-amino-1,2-diphenylethanol **2**, the reduction of acetophenone appears to be slower than using **1** in most cases, along with slightly decreased ee's (entries 7–12, Table 1). However, it is worthy noting that Ir-**2** afforded a complete conversion in a short time of 1.5 h, albeit with a moderate ee of 55% (entry 12, Table 1). A comparison of **2** with norephedrine **3** shows that replacing the phenyl group is detrimental to both the rates and ee's (entries 13–18, Table 1). This may be partly due to the amino group in **3** being easier to be protonated and hence easier to dissociate from the metal [50]. Placing a methyl group at the amino nitrogen led to significantly improved conversions and ee's in the case of ruthenium, but ephedrine **4** did not work well with rhodium and iridium (entries 21–24, Table 1). The ee values from the reduction with Ru-**4** decreased with time, consistent with reduction possibly involving ruthenium species containing no amino ligand. Whilst it is difficult to draw conclusions regarding the influence of ligands and metals on the catalytic activity and enantioselectivity, it is clear that a more basic reducing medium favors higher conversions and ee's. The effects of substituents in related ligands on reduction rates and stereoselectivities have previously been investigated by the groups of Blacker and Martin [3], van Leeuwen [41,43], Carpentier [2,38] and Wills and co-workers [66].

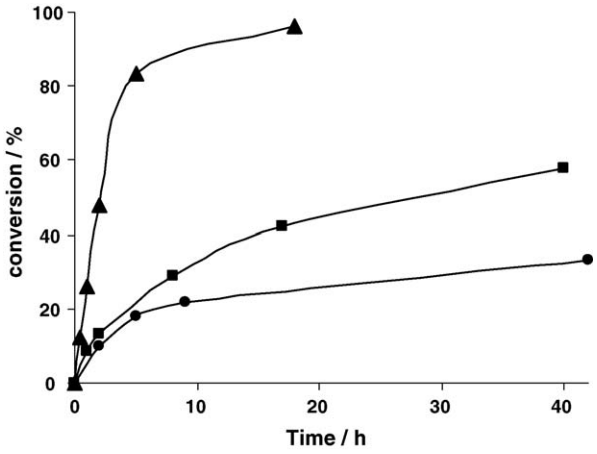
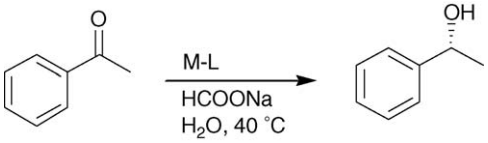


Fig. 1. Conversion-time diagram for the ATH of acetophenone (1 mmol) with Ru-**1** in aqueous HCOONa and HCOOH–NEt_3 at 40 °C. HCOONa–H_2O (pH 7.3) (-▲-), HCOOH–NEt_3–H_2O (HCOOH/NEt_3 = 1/1.7, pH 5.7) (-■-), HCOOH–NEt_3–H_2O (HCOOH/NEt_3 = 0.9/1, pH 4.8) (-●-).

As aforementioned, the ATH with Ru-TsDPEN is a pH-controlled reaction [50]. To further probe whether similar relation exists in ATH with the amino ligands, we studied the ATH of acetophenone with Ru-**1** under several initial pH values. As shown in Fig. 1, pH indeed plays a critical role in affecting the reaction rates, with the initial rate being much faster in the case of aqueous HCOONa (initial pH 7.3). Intriguingly all there reactions became slower after the initial ca 5 h reaction. This could result from product inhibition, which is made more significant at low pH presumably due to easier ligand dissociation. Product inhibition has previously been suggested by Wills and co-workers to explain the sluggish reduction observed with ketones capable of chelation to ruthenium [67].

A correlation of the initial pH with turnover frequency (TOF) is shown in Fig. 2. The pH values were set by adjusting the

Table 2
ATH of acetophenone with M–L by HCOONa in H_2O[a]



Entry	Ligand	Ru–L			Rh–L			Ir–L		
		Time (h)	Con (%)[b]	Ee (%)[b]	Time (h)	Con (%)[b]	Ee (%)[b]	Time (h)	Con (%)[b]	Ee (%)[b]
1	**1**[c]	12	84	71	20	92	54	5	>99	27
2	**2**	10	95	50	20	85	41	1.5	100	27
3	**3**[c]	5	97	60	5	63	31	5	61	7
4	**4**	3.5	>99	73	22	77	68	2.5	100	54

[a] The reaction was carried out at 40 °C, using 1 mmol of acetophenone and a S/C ratio of 100 in 2 mL of water.
[b] Determined by GC equipped with a chiral column. The configuration of alcohol was *R*, which was determined by comparison of GC retention time with literature data.
[c] The configuration of alcohol was *S*.

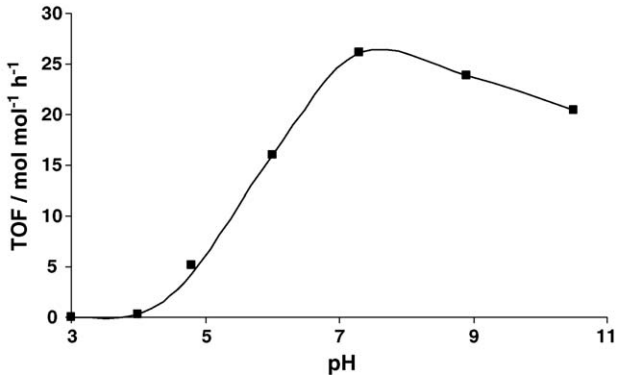


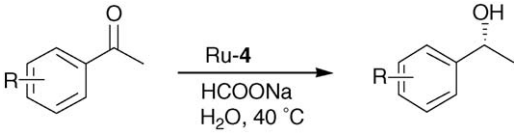
Fig. 2. TOF-pH diagram for the ATH of acetophenone (1 mmol) with Ru-**1** at 40 °C. TOF was based on the conversion of 1 h reaction. The HCOOH–NEt_3–H_2O mixture was used as hydrogen source and solvent when the reaction was performed at pH less than 7, while HCOONa–H_2O was used when the reaction was run at pH greater than 7.

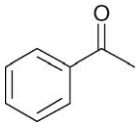
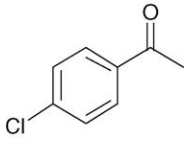
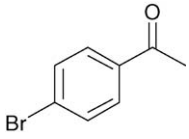
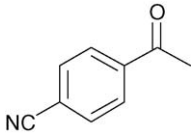
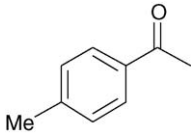
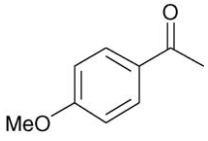
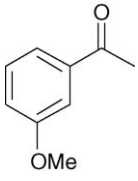
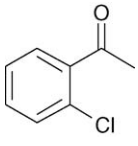
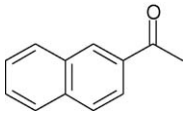
quantity of HCOOH and NEt_3 or HCOONa and NaOH. As can be seen, the reaction barely took place at a pH value less than 4, accelerated until about pH being neutral and slowed down thereafter. The enantioselectivity varied as well, with low ee's observed at low pH values. The $[(\eta^6\text{-}C_6Me_6)Ru^{II}(bpy)(H_2O)]^{2+}$ complex displayed a maximum rate at pH 4 in the ATH of acetophenone by aqueous HCOONa, as reported by Ogo et al. [68].

Since neutral pH leads to better rates and ee's, we examined the ATH of acetophenone with all the ligands and metals in aqueous HCOONa, which has a pH ca. 7. As shown in Table 2, most of the reactions gave good conversions and enantioselectivities in the aqueous medium. Compared with the reactions using aqueous HCOOH–NEt_3, the reaction gave much better conversions and enantioselectivities. Table 2 also shows that among the four β-amino alcohols, ephedrine **4** in combination with ruthenium offers the best choice for activity and enantioselectivity. With Ru-**4**, the reaction proceeded to give (*R*)-1-phenylethanol with >99% conversion in 73% ee within 3.5 h (entry 3, Table 2). It is interesting to note that in 2-propanol Ru-**2** generally gives the best performance [2–8].

Encouraged by the results obtained with Ru-**4**, we extended the reduction to a series of aryl ketones. The reaction was carried out in neat water containing HCOONa without using any cosolvent. As shown in Table 3, the reduction with HCOONa by Ru-**4** delivered almost 100% conversions for most ketones in a few hours. This is comparable with results obtained in the azeotropic HCOOH–NEt_3 using other catalysts [1–7,25–47]. In most cases, the enantioselectivities with Ru-**4** were good. For instance 4′-bromoacetophenone was cleanly reduced in >99% conversion and 74% ee within 2 h (entry 3, Table 3). The reduction of 4′-methylacetophenone gave >99% conversion with 87% ee within 6 h (entry 5, Table 3). The low ee in the case of 2′-chloroacetophenone is probably a result of steric hindrance that affects access of the carbonyl carbon to the Rh(II)-H hydride in the catalytic cycle. These results are comparable with those obtained at a slightly lower S/C ratio and ambient temperature in air [61].

Table 3
ATH of aryl ketones by HCOONa with Ru-**4** in H_2O[a]



Entry	Ketones	Time (h)	Con (%)	Ee (%)
1		3.5	>99	73
2		4.5	>99	72
3		2	>99	74
4		4.5	98	62
5		6	>99	87
6		2	>99	67
7		5	>99	70
8		5	>99	35
9		8	>99	71

[a] See Table 2 for conditions.

4. Conclusions

This paper presents results on ATH of aryl ketones by formate in water with catalysts derived from Ru(II), Rh(III) and Ir(III) complexes of commercially available simple β-amino alcohols, showing that ATH by formate is feasible in water. Compared with reduction by M-TsDPEN in aqueous formate, the enantioselectivities were lower, however. The performance of the amino alcohol catalysts was significantly influenced by the choice of reduction system. The reaction was sluggish when aqueous HCOOH–NEt_3 of low pH was employed; but when performed in water using HCOONa as a hydrogen donor, it gave much better conversions and enantioselectivities. Indeed the reaction rates correlate with the solution pH values and there appears to be a pH window for optimal rates. Among the three metals, Ir(I) catalysts exhibited a higher activity than either Ru(II) or Rh(III) but furnished a lower enantioselectivity, while the Ru(II) catalysts led to better enantioselectivities. The performance of the amino alcohol ligands may be related to their dissociation from the metal centers in aqueous solution, and could be further improved using other amino alcohols, which are readily available.

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