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Asymmetric transfer hydrogenation reaction in water: Comparison of chiral proline amide/amine ruthenium(II) complexes

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ABSTRACT

Chiral proline amide/amine ligands (**2**, **3**), synthesized by multi-step reaction starting from L-proline (**1**), were evaluated as catalyst generated *in situ* from $[RuCl_2(p\text{-cymene})]_2$ for asymmetric transfer hydrogenation of aromatic ketones in the presence of sodium formiate and sodium dodecyl sulfate (SDS). The results revealed that efficiencies and enantioselectivities strongly depend on the N-substituents.

Introduction

Transition metal-catalyzed transfer hydrogenation of carbonyl compounds is one of the most important reactions in pharmaceutical and chemical industries [1]. Whereas direct hydrogenation of unsaturated compounds is more widely applied, transfer hydrogenation (TH) is a powerful alternative in view of its easy handling, the ready availability of hydrogen donor, low cost of reducing agents and safety [1,2]. Therefore, the asymmetric transfer hydrogenation (ATH) of prochiral ketones using various chiral ligands is highly efficient method to obtain enantiomerically enriched alcohols. For this purpose, several catalysts such as chiral diamines have been used [1a,b,3]. Over the last two decades, chiral proline amide ligands and their derivatives (**I**–**IV**) have been applied in many asymmetric catalyzes, such as asymmetric aldol, Michael addition reaction and high enantioselectivities have been obtained [4]. Moreover, the catalytic activities of amide ligands in ATH reaction were reported by several groups (*ee*'s up to 95%) (Fig. 1) [5]. Karim and co-workers also published the synthesis of proline-derived chiral diamine ligands (**V**–**VI**) containing phenyl or naphthyl group on nitrogen atom (Fig. 1). Their catalytic activities in ATH revealed that the substitution of phenyl by naphthyl group was increased the activity and enantioselectivity (*ee*'s up to 95%) in isopropyl alcohol (IPA) [6]. In this study, we have evaluated the catalytic efficiency of proline-derived chiral amides/diamines (**2**, **3**) in ATH reaction. To the best of our knowledge, these chiral ligands (**3**) have not been evaluated in ATH, except **2a** [5d], although they are known in the literature [7]. For this purpose, herein, we compared the proline-derived chiral diamine ligands with amide analogs and also investigated the steric effect of aryl ring in the enantioselectivity.

Results and discussion

*Synthesis and characterization of proline-derived chiral amide/diamine ligands (**2**, **3**) and ruthenium complexes (**4b**, **5b**)*

Chiral proline amides/amines (**2**, **3**) were prepared by three/four-step reactions, starting from the commercially available L-proline (Scheme 1).

NMR spectra of the products were in accordance with the literature values [8]. The complex (**5b**) consists of $[RuCl(C_{14}H_{22}N_2)(\eta^6\text{–}C_{10}H_{14})]^+$ cation, the charge being balanced by one interstitial chloride anion (Fig. 2). The structure exhibits a typical three legged piano-stool geometry (a description commonly used for half–sandwich compounds) with Ru^{II} coordinated by two N atoms of the organic ligand, which acts as bidentate and a terminal Cl atom. The coordination geometry around Ru^{II} atom is distorted octahedron with three sites occupied by the *p*-cymene ligand (with an η^6 coordination mode) while the remaining three sites occupied by

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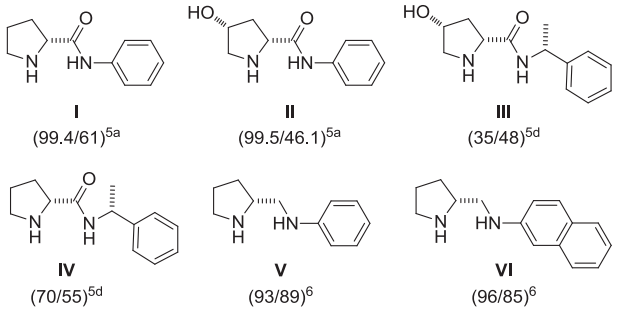
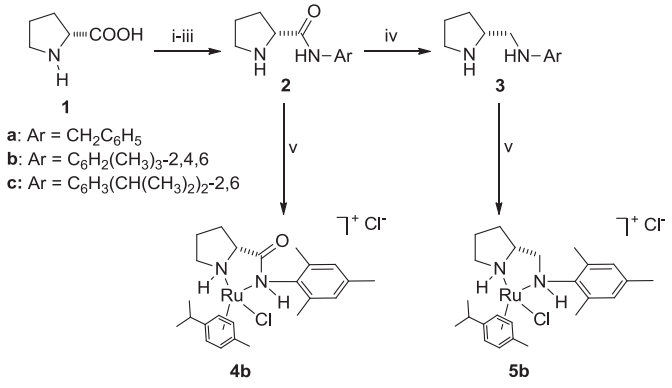


Fig. 1. Chiral proline-derived chiral amide/diamine ligands used for ATH of acetophenone (yield/ee).



Scheme 1. Synthesis of proline-derived chiral amide/diamine ligands (**2**, **3**) and ruthenium complexes (**4b**, **5b**). Reaction conditions: i) $(Boc)_2O$, Et_3N, CH_2Cl_2; ii) EtOCOCl, Et_3N, Ar-NH_2, THF; iii)TFA, CH_2Cl_2; iv) $LiAlH_4$, THF; v) $[RuCl_2(p\text{-cymene})]_2$, toluene.

bidentate ligand to form a five-membered chelate ring and Cl ligand. The distorted octahedral geometry is evident from the bond angles given in Table 1. The coordination environment yields a chiral ruthenium center with *S* configuration, according to the ligand priority sequence η^6–*p*–cymene > Cl > N1 > N2 [9–11]. N1, N2 and C14 atoms are also chiral centers with the absolute configuration of *S*, *R* and *S*, respectively. The five membered chelate ring (Ru1\N1\N2\C14\C15) adopts an envelope conformation with atom C14 displaced by −0.3328 Å from the mean plane of the other ring atoms (Table 2).

Table 1
Selected geometric parameters for **5b** (Å, °).

Ru1–Cl1	2.402(2)	Ru1–C5	2.161(9)
Ru1–N1	2.235(6)	Ru1–C6	2.178(10)
Ru1–N2	2.129(6)		
Ru1–C1	2.231(11)	Cl1–Ru1–N1	83.24(19)
Ru1–C2	2.204(12)	Cl1–Ru1–N2	87.0(2)
Ru1–C3	2.181(12)	N1–Ru1–N2	76.4(2)
Ru1–C4	2.242(8)		

The six-membered ring of the *p*-cymene is almost planar, with a maximum deviation of 0.033 (8) Å (C1) and an overall r.m.s. deviation of 0.0201 Å. The dihedral angle between the *p*-cymene ring (C1–C6) and the isopropyl group (C8–C9) planes is 70.86 (0.82)°. The distance between the Ru^{II} ion and the least-squares plane of the *p*-cymene aromatic ring is 1.684 (4) Å, which is very close to that reported in other Ru^{II} arene complexes [12,13]. Defining X as the centroid of the aromatic ring, the Cl1–Ru1–X, N1–Ru1–X and N2–Ru1–X angles are 125.95 (18), 135.2 (2) and 130.9 (2)°, respectively. The Ru–Cl bond distance is normal and also agrees well with those in related complexes [14,15]. The two Ru–N bond distances are substantially different [2.129 (6) and 2.235 (6) Å], longer than those reported in other complexes, such as in [{RuCl(η^6–cym)}$_2$(μ-1,6,7,12-Tetraazaperylene)](PF$_6$)$_2$ [16] (2.105(2) and 2.105(2) Å) and [(η^6–*p*–Pr^{i}C$_6$H$_4$Me)RuCl(2,2′-bipyrimidine)][PF$_6$] [17] (2.084 (2) and 2.080 (3) Å).

The non-coordinated chloride anions interconnect the $[RuCl(C_{10}H_{14})(C_{14}H_{22}N_2)]^+$ cations via hydrogen bonds into a chain running along [010] (Fig. S3 in ESI). Besides, the compound contains intra-molecular C–H···Cl type weak interaction (C14–H14···Cl1) generating an S(5) ring motif [18].

These ligands were tested in the ATH reaction of aromatic ketones (Table 3). As can be seen from Table 3, the best yield was obtained with the ligand **2a**. However, the amine ligand **3c** did not show activity. The results showed that the amides ligands (**2a**–**c**) had the better yield than the amine counterparts (**3a**–**c**). Besides, the enantioselectivity was improved but the yield was decreased when the bulky chiral ligands were used. In this respect, the chiral

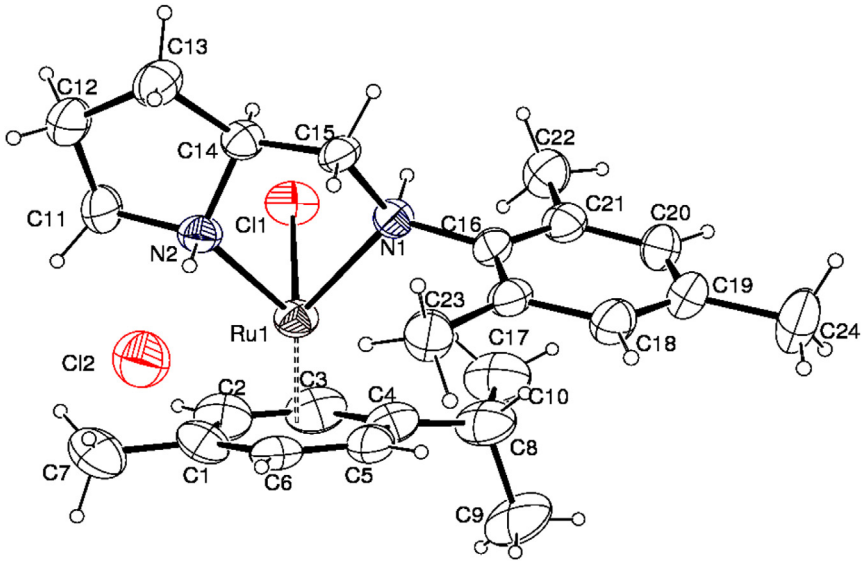


Fig. 2. The molecular structure of **5b**, with the atom labeling. Displacement ellipsoids are shown at the 40% probability level. The CH_2Cl_2 solvent molecules have been omitted for clarity.

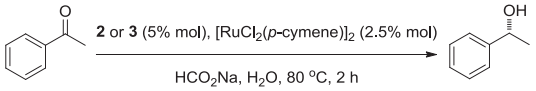
Table 2
Crystallographic data for $C_{25}H_{38}N_2Cl_4Ru$.

Crystal data	
Chemical formula	$C_{25}H_{38}N_2Cl_4Ru$
Formula weight	609.44
Temperature (K)	293(2)
Space group	$P2_1$
Crystal system	Monoclinic
a, b, c (Å)	9.2088(6), 12.1642(6), 12.6561(11)
α, β, γ (°)	90.00, 100.322(6), 90.00
Cell volume (Å^3)	1394.76(17)
Formula unit cell Z	2
ρ_{calc} (g/cm^3)	1.451
F(000)	628.0
Absorption coefficient μ (mm^{-1})	0.961
Crystal size (mm^3)	0.4719 × 0.1871 × 0.1342
Data collection	
Diffractometer	Xcalibur, Eos
Temperature (K)	293(2)
Radiation/wavelength (Å)	MoK_α/0.71070
Reflections measured	6334
Independent/observed reflections	4700/4031
Range of *h*, *k*, *l*	$-11 \le h \le 9$, $-15 \le k \le 14$, $-13 \le l \le 15$
Refinement	
Data/Restraints/Parameters	4700/1/295
Final R indexes [$I \ge 2\sigma$ (I)]	$R_1 = 0.0588$, $wR_2 = 0.1577$
Final R indexes [all data]	$R1 = 0.0703$, $wR_2 = 0.1724$
Goodness-of-fit on F^2	1.047
Largest diff. peak/hole (e Å^{-3})	1.54/−0.73

ligand **2c** gave the best enantioselectivity (90%) for acetophenone although the yield of the product was moderate (Table 3, Entry 3). Additionally, it was known that the surfactants give advantages in terms of yield and enantioselectivity in ATH [5,19]. Therefore, in order to increase the reaction yield, sodium dodecyl sulfate (SDS) used as phase transfer catalyst (PTC) for ATH reaction of acetophenone in the presence of ligand **2c** (Table 3, Entries 6–8). When 2 mol% of SDS was used, the yield was considerably improved. Increasing the amount of SDS led to higher yield but the lower *ee* (Table 3, Entries 6–8). The ruthenium complexes **4b** and **5b** were also synthesized and tested in ATH. The results are comparable to those obtained by *in situ*, so no isolation and purification of the ruthenium complexes was required.

Under the optimized reaction conditions, we extended the scope of the reaction using a variety of ketones with the ligand **2c** (Table 4). The electron-withdrawing substituents on acetophenone gave better yield than donating groups (Table 4, Entry 2–7). When

Table 3
ATH of acetophenone.



Entry	Ligands/complexes	Yield (%)	ee (%)
1	**2a**(**3a**)	99(60)	28(14)
2	**2b**(**3b**)	69(30)	80(71)
3	**2c**(**3c**)	30(<5)	90(n.d.)
4[a]	**2b**	94	82
5[a]	**3b**	50	62
6[a]	**2c**	50	94
7[b]	**2c**	54	94
8[c]	**2c**	86	89
9[a]	**4b**	95	81
10[a]	**5b**	55	64

[a] 2% mol SDS.
[b] 5% mol SDS.
[c] 10% mol SDS was used.

Table 4
ATH of ketones using ligand **2c**.

Entry	Ketone	T (°C)	t (h)	Yield (%)	ee (%)
1	$PhCOCH_2CH_3$	80	2	68	99
2	2′Cl-$PhCOCH_3$	80	0.5	99	91
3	2′Cl-$PhCOCH_3$	40	4	92	96
4	4′Cl-$PhCOCH_3$	80	0.5	93	92
5	4′Cl-$PhCOCH_3$	40	4	83	97
6	4′MeO-$PhCOCH_3$	80	0.5	60	91
7	4′MeO-$PhCOCH_3$	80	2	96	90
8	4′MeO-$PhCOCH_3$	40	4	35	99
9	4′MeO-$PhCOCH_3$	40	12	47	98
10	3′,4′–$(CH_3)_2$–$PhCOCH_3$	80	2	92	94
11	2-Acetylnaphthone	80	2	87	99
12	$PhCOCH_2Cl$	80	0.5	99	91
13	$PhCOCH_2Cl$	40	4	63	94

Reactions conditions: 5% mol ligand, 2.5% mol $[RuCl_2(p\text{-cymene})]_2$, 0.5 mmol ketone, 5 mmol HCO_2Na, SDS (2% mol), H_2O.

chloroacetophenone derivatives were used, the yield was >90% after 0.5 h at 80 °C. The decrease of the reaction temperature from 80 to 40 led to extend the reaction time and to slightly increase the enantioselectivity (Table 4, Entry 2–4). We also used 2-acetylnaphthalene and 2-chloroacetophenone as substrate for the transfer hydrogenation reaction, affording excellent enantioselectivities. Although the ligand **2a** showed better yield than the others, chiral ligand **2c** gave the excellent enantioselectivity (99%). The enantioselectivity increased changing the phenyl group by 2,6-diisopropylphenyl (Table 4).

Conclusion

In conclusion, chiral proline-derived chiral amide/diamine ligands **2** and **3** used as *in situ* prepared catalysts with $[RuCl_2(p\text{-cymene})]_2$. The complexes **4b**, **5b** were also synthesized. The crystal structure of **5b** was solved by X-ray analysis. According to the X-ray data, the ruthenium center with *R* configuration was confirmed. The catalytic activities of the ligands were evaluated for ATH. Chiral proline amide ligands having more acidic N–H gave better yields as compared with the corresponding amine derivatives. Moreover, it was found that the bulk of the aryl substituents on the ligand increased the enantioselectivity. The ligand **2c** with 2,6-diisopropyl groups on the phenyl provided the excellent yield and enantioselectivity. The protocol with the facile synthesis of the ligand represents a practical and green approach to various functionalized aromatic ketones in water in high yield and *ee* values.

Experimental

General considerations

All reactions were performed in air unless otherwise stated. Reactions involving air-sensitive components were performed by using Schlenk-type flasks under argon atmosphere and high vacuum-line techniques. The solvents were analytical grade and distilled under argon atmosphere from sodium (diethyl ether, tetrahydrofuran, toluene, hexane), P_2O_5 (dichloromethane). Reagents were purchased from Aldrich, Merck, Acros Organics, Alfa Aesar, Fluka, and were used as received. Chiral proline amides/amines (**2**, **3**) were synthesized according to the literature [4a,d,8]. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured on Varian AS 400 Mercury spectrometers and tetramethylsilane (TMS) was used as the internal standard. All coupling constants (*J* values) were reported in Hertz (Hz). Elemental analyses were performed on a Perkin–Elmer PE 2400 elemental analyzer. Optical rotations were taken on a Rudolph Research Analytical Autopol I

automatic polarimeter with a wavelength of 589 nm; the concentration 'c' has units of g/100 mL. The conversion and enantiomeric excess (*ee*) were determined by a chiral GC column Supelco β-Dex 225.

*General procedure for the synthesis of Ru(II) complex (**4b, 5b**)*

$[RuCl_2(p\text{-cymene})]_2$ (0.23 mmol) was added to the solution of **2b**/**3b** (0.46 mmol) in dry toulene under argon. The mixture was stirred at room temperature for 24 h. The orange precipitate was filtered and then recrystallized from CH_2Cl_2/hexane.

4b: Yield: 69%; mp177–180 °C. Anal. Cal. For $C_{24}H_{34}Cl_2N_2ORu$: C, 53.53; H, 6.36; N, 13.17. Found: C, 53.47; H, 6.33; N, 13.14. $[\alpha]_D^{27.4}$ −44.78 (c.0.134 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): 1.10 (d, $J = 7.2$ Hz, 3H, $CH(CH_3)_2$); 1.17 (d, $J = 7.2$ Hz, 3H, $CH(CH_3)_2$); 1.85–2.13 (m, 4H, CH_2); 2.02, 2.20, 2.23 (s, 9H, CH_3; $C_6H_2(CH_3)_3$); 2.59–2.68 (m, 1H, $CH(CH_3)_2$); 2.77–2.81 (bs, 1H, NH); 3.40–3.48 (m, 2H, NCH_2); 4.41–4.43 (m, 1H, CH); 5.62 (m, 3H, *p*-cymene-Ar-H); 5.74 (d, J = 6.0 Hz, 1H, *p*-cymene-Ar-H); 6.79 (s, 2H, $C_6H_2(CH_3)_3$); 9.51 (bs, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25 °C, ppm): 17.9 ($CH(CH_3)_2$); 18.3, 21.0 ($C_6H_2(CH_3)_3$); 21.7 ($CH(CH_3)_2$); 22.5 (CH_3); 28.0 ($CH(CH_3)_2$); 30.9, 31.6, 52.3 65.9 (pro-C); 78.7, 81.1, 81.9, 84.5, 92.7, 101.9 (*p*-cymene-Ar-C); 128.7; 129.9; 135.9; 137.3 (Ar-C); 181.1 (CO).

5b: Yield: 73%; mp 105–108 °C. Anal. Calc. for $C_{24}H_{36}Cl_2N_2Ru$: C, 54.96; H, 6.92; N, 13.52. Found: C, 54.85; H, 6.88; N, 13.49. $[\alpha]_D^{21.3}$ −69.23 (c.0.26 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): 1.00 (d, $J = 6.8$ Hz, 3H, $CH(CH_3)_2$); 1.23 (d, $J = 6.8$ Hz, 3H, $CH(CH_3)_2$); 1.71–2.09 (m, 4H, CH_2); 2.17, 2.25, 2.33 (s, 9H, $C_6H_2(CH_3)_3$); 2.21–3.40 (m, 5H, NCH_2CH; NCH_2;$CH(CH_3)_2$); 2.64 (s, 3H, CH_3); 3.65–3.68 (m, 1H, CH); 4.78 (d, $J = 5.6$ Hz, 1H, *p*-cymene-Ar-H); 4.90 (d, $J = 5.6$ Hz, 1H, *p*-cymene-Ar-H); 5.46 (bs, 1H, NH); 5.89 (d, $J = 5.2$ Hz, 1H, *p*-cymene-Ar-H); 5.95 (d, $J = 5.2$ Hz, 1H, *p*-cymene-Ar-H); 6.86 (s, Hz, 1H, $C_6H_2(CH_3)_3$); 6.96 (s, Hz, 1H, $C_6H_2(CH_3)_3$); 9.21 (bs, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25 °C, ppm): 18.6 ($CH(CH_3)_2$); 19.2 ($C_6H_2(CH_3)_3$); 20.5 ($CH(CH_3)_2$); 21.8 ($C_6H_2(CH_3)_3$); 21.9 ($C_6H_2(CH_3)_3$); 23.6 (CH_3); 23.9 ($CH(CH_3)_2$); 24.9; 29.3; 48.4; 50.8 (pro-C); 62.7 (NCH_2); 76.5, 79.5, 84.9, 85.4, 102.1, 103.4 (*p*-cymene-Ar-C); 128.9, 129.5, 130.8, 132.3, 136.2, 145.8 (Ar-C).

General procedure for the asymmetric transfer hydrogenation reaction

The solution of $[RuCl_2(p\text{-cymene})]_2$ and chiral piroline ligand in H_2O was stirred at 80 °C for 1 h. Subsequently, ketone, HCO_2Na and SDS were added to the solution. After the desired reaction time, petroleum ether was added to extract the product. The organic phase dried over $MgSO_4$. The yield and enantioselectivity were determined by GC.

X-ray diffraction study

The molecular structure of **5b** is determined by single crystal X-ray diffraction. Single-crystal data were collected at 293(2) K by ω-scan technique, on an Agilent Diffraction Xcalibur diffractometer with an Eos CCD area detector using graphite-monochromated radiation MoKα (λ = 0.71073 Å) from a enhance X-ray source. The data collection, cell refinement and data reduction were performed using the CrysAlisPro program [20]. Solution, refinement and analysis of the structure were done using the OLEX2 system [21]. The crystal structure was solved by the direct method using the SHELXS-97 [22] and refined by full-matrix least squares method based on F^2 against all reflections using the SHELXL-97 [22] The refinement converged to R = 0.0589; wR_2 = 0.1579 for all 6334 reflections and 295 parameters. All non-hydrogen atoms were refined anisotropically. The crystal structure positions of hydrogen atoms were treated as riding atoms. Geometrical calculations were performed using PLATON [23] The figures were made using ORTEP [24] and PLATON [23] The summary of the crystal data, experimental details and refinement results are listed in Table 3.

Acknowledgments

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Appendix A. Supplementary material

CCDC 1008774 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix. BSupplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2014.12.023.

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