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Transfer hydrogenation reactions catalyzed by chiral half-sandwich Ruthenium complexes derived from Proline

ARUN KUMAR PANDIA KUMAR and ASHOKA G SAMUELSON*
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India
e-mail: ashoka@ipc.iisc.ernet.in

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Abstract. Chiral ruthenium half-sandwich complexes were prepared using a chelating diamine made from proline with a phenyl, ethyl, or benzyl group, instead of hydrogen on one of the coordinating arms. Three of these complexes were obtained as single diastereoisomers and their configuration identified by X-ray crystallography. The complexes are recyclable catalysts for the reduction of ketones to chiral alcohols in water. A ruthenium hydride species is identified as the active species by NMR spectroscopy and isotopic labelling experiments. Maximum enantio-selectivity was attained when a phenyl group was directly attached to the primary amine on the diamine ligand derived from proline.

Keywords. Asymmetric transfer hydrogenation; Proline diamine ligands; Half-sandwich ruthenium complexes; Chiral alcohols; Ruthenium hydride.

1. Introduction

Asymmetric reduction of carbonyl compounds is an important reaction[1] as it leads to chiral secondary alcohols, a key functional group found in several fine chemicals, agrochemicals[2] and pharmaceuticals.[3–7] In nature, oxidoreductases catalyze transfer hydrogenation of carbonyl compounds to give stereospecific alcohols using alcohol dehydrogenases such as horse liver dehydrogenase with cofactors like NADH or NADPH.[8,9] In the laboratory, transfer hydrogenation reactions are conveniently carried out with a wide range of catalysts which are convenient alternatives to high pressure hydrogenation which demands special vessels and hydrogen gas.[10,11] As early as in 1970, the research groups of Ohkubo and Sinou suggested the use of $[RuCl_2(PPh_3)_3]$ as a catalyst to carry out asymmetric transfer hydrogenation (ATH) in the presence of either a chiral hydrogen donor or a chiral monophosphine ligand.[12,13] But only in 1995, a breakthrough was made by Noyori and coworkers using a half-sandwich ruthenium catalyst containing a chiral N-sulfonylated 1,2-diamine ligand for ATH of ketones and imines.[14–18] The important feature of this catalyst is that the ligand and the metal play an active role in the transfer of two hydrogen atoms, one of which is attached to the N of the ligand and hence protic in nature and the other attached to Ru and hence considered hydridic. The bifunctional nature of the catalyst leads to chiral alcohols with very high enantiomeric excesses under mild conditions. In the case of acetophenone as a substrate, formation of (*S*)-1-phenylethanol in 97% ee and 95% yield was observed.[14] Noyori and co-workers identified the origin of enantioselectivity[19] in Noyori-Ikariya type half-sandwich complexes with C-H$^{\cdots}\pi$ interactions between the arene ring and a wide range of substrates.[20,21] Few studies have tested the hypothesis by comparing very similar ligands with and without C-H$^{\cdots}\pi$ interactions arising from the chiral ligand and substrate for enhancing enantioselectivity.[22]

Although the use of green solvents like water is preferable,[23] solubility problems force one to use isopropanol[14,24] or a mixture of formic acid and triethyl amine ($HCOOH:Et_3N$)[15] for transfer hydrogenation. Several ligands modelled after the Noyori catalyst have been developed for the asymmetric transfer hydrogenation reactions in water based on sulfonated diphenylethylenediamine[25,26] (TsDPEN) and sulfonated-cyclohexyldiamine[27,28] (Ts-CYDN) ligands using sodium formate[29] as a hydrogen source. A recent report by Denizalti and co-workers on the asymmetric transfer hydrogenation of ketones in water, but with added SDS, employing *in situ* generated ruthenium proline amide and diamine complexes[30] prompts us to report in this work, a closely related series of chiral half-sandwich ruthenium(II) complexes containing (*S*)-N-substituted-2-aminomethylpyrrolidine ligands, their synthesis and use as catalysts for the asymmetric transfer hydrogenation of ketones in water. We have characterized the complexes completely through X-ray crystallography

*For correspondence

and shown how silver nitrate can activate sluggish catalysts and how the reaction can be carried out without using sodium dodecyl sulphate (SDS) as an additive which they found detrimental to the enantioselectivity. Further, we have shown the formation of a hydride intermediate through isotopic labelling and spectroscopy. Our systematic study by varying the substituent on the chiral ligand suggests that phenyl groups on the proline ring has a beneficial effect in the enantioselectivity in the reduction of a variety of ketones and supports the earlier hypothesis of Noyori.[21]

2. Experimental

2.1 *Materials and methods*

All reactions and manipulations were routinely performed under a nitrogen atmosphere using standard Schlenk techniques in oven-dried glassware. L-Proline, benzylchloroformate, benzylamine, L-prolinamide, aniline were obtained from Sigma-Aldrich U.S.A. All ketone substrates were obtained from Sigma-Aldrich U.S.A. Ethyl amine was distilled from 70% aqueous solution and stored over potassium hydroxide pellets at −20°C. Tetrahydrofuran was distilled over sodium/benzophenone. Triethylamine was distilled first over KOH and then over $LiAlH_4$. Analytical thin layer chromatography (TLC) was performed using precoated silica gel plates supplied by Merck (60 F254). Subsequent to elution, plates were visualized using UV radiation (254 nm). Preparative TLC was done using ChemLabs Silica gel GF 254. Nuclear magnetic resonance spectra were recorded on a Bruker AMX 400 spectrometer operating at 400 MHz for ^{1}H, 61.3 MHz for ^{2}H NMR, 100 MHz for ^{13}C NMR. ESI-HRMS measurements were performed on an Agilent 6538 UHD accurate-mass Q-TOF LC/MS instrument. Elemental analyses were performed by using a Thermo Finnigan Flash EA 1112 CHNS analyzer. HPLC analysis was performed using a Chiralcel OD column and Chiralcel OJ-H column on a Merck Hitachi Lachrome HPLC device.

2.2 *General procedure for the synthesis of (S)-N-substituted-2-aminomethylpyrrolidine ligands*

Literature procedures were used for the preparation of **L1**,[38] **L2**,[39] **L3**,[39] and **L4**.[39]

L1: Yield: 66%; ^{1}H NMR ($CDCl_3$): δ 7.17 (t, 2H, $J = 7.44$ Hz), 6.69 (t, 1H, $J = 7.32$ Hz), 6.63 (d, 2H, $J = 7.84$ Hz), 3.38 (m, 1H), 3.16 (dd, 1H, $J = 4.6, 4.64$ Hz), 2.92 (m, 3H), 1.74 (m, 3H), 1.46 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.9, 129.6, 117.7, 113.4, 58.1, 49.1, 46.9, 30.0, 26.2

L2 : Yield: 49%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.15 (m, 1H), 2.84 (m, 2H), 2.62-2.42 (m, 4H), 1.81 (m, 1H), 1.66 (m, 2H), 1.26 (m, 1H), 1.04 (t, 3H, $J = 7.2$ Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) : δ 58.7, 55.7, 46.9, 44.8, 30.2, 26.2, 15.7

L3: Yield: 61%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (m, 1H), 7.31 (m, 4H), 3.79 (s, 2H), 3.22 (m, 1H), 2.88 (m, 2H), 2.49 (m, 2H), 1.87 (m, 1H), 1.69 (m, 2H), 1.31 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 128.8, 128.6, 127.3, 58.8, 55.1, 54.7, 46.9, 30.2, 26.2

L4: Yield: 36%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.06 (m, 1H), 2.88 (m, 2H), 2.56 (m, 2H), 1.77 (m, 3H), 1.31 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 61.5, 47.5, 46.9, 29.6, 26.2.

2.3 *General procedure for the synthesis of chiral half-sandwich ruthenium proline diamine complexes*

To a solution of [Ru(*p*-cymene)Cl_2]$_2$ (0.286 mmol) in dry isopropanol (10 mL) was added (*S*)-N-substituted-2-aminomethylpyrrolidine ligand (0.573 mmol) and triethylamine (1.15 mmol). The resulting reaction mixture was kept at 80°C for 1 h. The solvent was removed under vacuum, and ethanol was then added and kept for crystallization under nitrogen atmosphere. The yellow crystals formed were filtered and dried.

C1: Yield: 80%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.20 (d, 1H, NH, $J = 10.0$ Hz), 7.98 (d, 2H, $J = 7.76$ Hz), 7.59 (q, 1H, NH, $J = 7.84$ Hz), 7.32 (t, 2H, $J = 7.52$ Hz), 7.20 (t, 1H, $J = 7.36$ Hz), 5.70 (d, 1H, $J = 5.76$ Hz), 5.66 (d, 1H, $J = 5.76$ Hz), 5.46 (d, 1H, $J = 5.84$ Hz), 5.44 (d, 1H, $J = 5.8$ Hz), 4.05 (m, 1H), 3.55 (m, 1H), 3.38 (m, 1H), 3.18 (m, 1H), 2.70 (m, 1H), 2.36 (m, 1H), 2.25 (s, 3H), 1.97 (m, 3H), 1.35 (m, 1H), 0.98 (d, 6H, $J = 6.8$ Hz); Anal.Calcd for $C_{21}H_{30}Cl_2N_2Ru$: C 52.28; H 6.27; N 5.81, Found: C 51.85; H 6.02; N 5.62; ESI-HRMS: m/z calculated for $[C_{21}H_{30}N_2RuCl]^+$: 447.1140 $[M\text{-}Cl]^+$; found: 447.1143.

C2: Yield: 75%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (q, 1H, NH, $J = 7.40$ Hz), 6.95 (m, 1H, NH), 6.28 (d, 1H, $J = 5.64$ Hz), 5.86 (d, 1H, $J = 5.68$ Hz), 5.66 (d, 1H, $J = 5.76$ Hz), 5.26 (d, 1H, $J = 5.96$ Hz), 3.79 (m, 1H), 3.29 (m, 3H), 3.03 (m, 2H), 2.72 (m, 1H), 2.45 (s, 3H), 2.08 (q, 1H, $J = 12.12$ Hz), 1.96 (m, 2H), 1.78 (m, 2H), 1.36 (t, 3H, $J = 7.32$ Hz), 1.28 (dd, 6H, $J = 6.88$, 6.92 Hz); Anal. Calcd for $C_{17}H_{30}Cl_2N_2Ru$: C 47.00; H 6.96; N 6.45, Found: C 46.32; H 6.57; N 6.17; ESI-HRMS: m/z calculated for $[C_{17}H_{30}N_2RuCl]^+$: 399.1140 $[M\text{-}Cl]^+$; found: 399.1137.

C3: Yield: 82%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (q, 1H, NH, $J = 7.36$ Hz), 7.75 (d, 2H, $J = 6.92$ Hz), 7.44 (t, 2H, $J = 7.36$ Hz), 7.37 (m, 1H), 7.03 (m, 1H,

NH), 6.08 (d, 1H, $J = 6.0$ Hz), 5.84 (d, 1H, $J = 5.6$ Hz), 5.37 (d, 1H, $J = 6.0$ Hz), 4.50 (d, 1H, $J = 6.0$ Hz), 4.24 (dd, 1H, $J = 6.84$, 6.88 Hz), 4.03 (dd, 1H, $J = 7.2$, 7.28 Hz), 3.75 (m, 1H), 3.33 (m, 1H), 3.03 (m, 2H), 2.44 (m, 1H), 2.34 (s, 3H), 2.14 (q, 1H, $J = 12.28$ Hz), 1.97 (m, 2H), 1.79 (m, 2H), 1.26 (dd, 6H, $J =$ 3.4, 3.6 Hz); Anal.Calcd for $C_{22}H_{32}Cl_2N_2Ru$: C 53.22; H 6.50; N 5.64. Found: C 52.36; H 6.03; N 5.38; ESI-HRMS: m/z calculated for $[C_{22}H_{32}N_2RuCl]^+$: 461.1297 $[M\text{-}Cl]^+$; found: 461.1298.

C4: Yield: 72%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (q, 2H, NH_2, $J = 9.0$ Hz), 7.19 (m, 1H, NH), 6.0 (d, 1H, $J = 5.52$ Hz), 5.82 (d, 1H, $J = 5.6$ Hz), 5.72 (d, 1H, $J = 5.64$ Hz), 5.70 (d, 1H, $J = 5.76$ Hz), 3.56 (m, 1H), 3.23 (m, 1H), 3.12 (m, 2H), 2.73 (m, 2H), 2.44 (s, 3H), 2.34 (m, 1H), 1.79 (m, 3H), 1.30 (dd, 6H, $J =$ 6.8 Hz); Anal.Calcd for $C_{15}H_{26}Cl_2N_2Ru$: C 44.34; H 6.45; N 6.89, Found: C 44.81; H 6.79; N 7.13; ESI-HRMS: m/z calculated for $[C_{15}H_{26}N_2RuCl]^+$: 371.0827 $[M\text{-}Cl]^+$; found: 371.0828.

2.4 *General procedure for the catalytic transfer hydrogenation reaction*

To a solution of a ruthenium catalyst (0.0168 mmol) in degassed water (8 mL) was added a ketone (0.168 mmol) and sodium formate (0.84 mmol). The reaction mixture was kept in a thermostat at 60°C. 1 mL of the solution from the reaction mixture was withdrawn at 1 h, 2 h and 12 h; extracted with 5 mL of ethyl acetate; dried over anhydrous sodium sulphate and analyzed by ^{1}H NMR spectroscopy. Conversion was calculated from the ^{1}H NMR spectrum. Chiral alcohols were purified by preparative thin layer chromatography. Enantiomeric excess (ee) was determined using the chiral HPLC technique employing the Chiralcel OD column, except in the case of 1-(4-Chlorophenyl)ethanol, 1-(2-Chlorophenyl)ethanol, 1-(4-Nitrophenyl)ethanol), for which it was determined using a Chiralcel OJ-H column.

2.4a *1-(4-Methoxyphenyl)ethanol*:[31] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, 2H, $J = 8.8$ Hz), 6.89 (d, 2H, $J = 8.4$ Hz), 4.87 (q, 1H, $J = 6.4$ Hz), 3.80 (s, 3H), 1.81 (1H, bs, OH), 1.48 (d, 3H, $J = 6.4$ Hz); Enantiomeric excess (%) at 12 h (isopropanol/hexane 10/90 0.5 mL/min, $t_1 = 16.9$ min for the *S* enantiomer, $t_2 =$ 15.9 for the *R* enantiomer) **C1** = 50 (*R*), **C2** = 16 (*S*), **C3** = 28 (*S*), **C4** = 2 (*S*).

2.4b *α-Tetralol*:[31] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (m, 1H), 7.20 (m, 2H), 7.09 (m, 1H), 4.79 (q, 1H, $J = 4.8$ Hz), 2.73 (m, 2H), 1.92 (m, 2H), 1.76 (m, 3H). Enantiomeric excess (%) at 12 h (isopropanol/hexane 2/98 0.9 mL/min, $t_1 = 17.4$ min for the *S* enantiomer, $t_2 = 19.8$ for the *R* enantiomer) **C1** = 74 (*S*), **C2** = 36 (*S*), **C3** = 74 (*S*), **C4** = 12 (*S*).

2.4c *1-Phenylpropanol*:[31] ^{1}H NMR(400 MHz, $CDCl_3$): δ 7.34 (m, 5H), 4.60 (t, 1H, $J = 6.4$ Hz), 1.88 (1H, br), 1.72 (m, 2H), 0.94 (t, 3H, $J = 7.2$ Hz); Enantiomeric excess (%) at 12 h (ethanol/hexane 5/95 0.5 mL/min, $t_1 = 16.1$ min for the *S* enantiomer, $t_2 = 14.2$ for the *R* enantiomer) **C1** = 48 (*R*), **C2** = 15 (*S*), **C3** = 15 (*S*), **C4** = 8 (*S*).

2.4d *1-(2-Naphthyl)ethanol*:[31] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (m, 4H), 7.60 (m, 3H), 5.08 (q, 1H, $J =$ 6.4 Hz), 1.98 (bs, 1H, OH), 1.57 (d, 3H, $J = 6.4$ Hz); Enantiomeric excess (%) at 12 h (ethanol/hexane 5/95 0.5 mL/min, $t_1 = 26.4$ min for the *S* enantiomer, $t_2 =$ 29.3 for the *R* enantiomer) **C1** = 28 (*R*), **C2** = 20 (*S*), **C3** = 34 (*S*), **C4** = 4 (*S*).

2.4e *1-(1-Naphthyl)ethanol*:[31] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, 1H, $J = 8.36$ Hz), 7.88 (d, 1H, $J =$ 7.68 Hz), 7.79 (d, 1H, $J = 8.24$ Hz), 7.69 (d, 1H, $J =$ 7.28 Hz), 7.51 (m, 3H), 5.70 (q, 1H, $J = 6.4$ Hz), 2.08 (bs, 1H, OH) 1.68 (d, 3H, $J = 6.4$ Hz); Enantiomeric excess (%) at 12 h (ethanol/hexane 5/95 0.5 mL/min, $t_1 = 29.2$ min for the *S* enantiomer, $t_2 = 41.0$ for the *R* enantiomer) **C1** = 56 (*R*), **C2** = 68 (*S*), **C3** = 22 (*S*), **C4** = 2(*S*).

2.4f *1-Indanol*:[31] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (m, 1H), 7.27 (m, 3H), 5.26 (t, 1H, $J = 6.0$ Hz), 3.03(m, 1H), 2.82 (m, 1H), 2.51 (m, 1H), 1.96 (m, 2H); Enantiomeric excess (%) at 12 h (isopropanol/hexane 2/98 0.9 mL/min, $t_1 = 19.8$ min for the *S* enantiomer, $t_2 =$ 23.0 for the *R* enantiomer) **C1** = 54 (*S*), **C2** = 30 (*S*), **C3** = 22 (*S*), **C4** = 2 (*S*).

2.4g *1-(4-Chlorophenyl)ethanol*:[32–34] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (m, 4H), 4.88 (q, 1H, $J = 6.4$ Hz), 1.90 (bs, 1H, OH), 1.47 (d, 3H, $J = 6.4$ Hz); Enantiomeric excess (%) at 12 h (isopropanol/hexane 10/90 0.5 mL/min, $t_1 = 13.6$ min for the *S* enantiomer, $t_2 =$ 14.5 for the *R* enantiomer) **C1** = 22 (*R*), **C2** = 28 (*S*), **C3** = 45 (*S*), **C4** = 10 (*S*).

2.4h *1-(4-Bromophenyl)ethanol*:[32–34] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, 2H, $J = 1.6$ Hz), 7.28 (d, 2H, $J = 1.2$ Hz), 4.89 (q, 1H, $J = 6.4$ Hz), 1.85 (bs, 1H, OH), 1.49 (d, 3H, $J = 6.8$ Hz); Enantiomeric excess (%) at 12 h (isopropanol/hexane 5/95 0.5 mL/min, $t_1 = 8.3$ min for the *S* enantiomer, $t_2 = 9.4$ for the *R* enantiomer) **C1** = 28 (*R*), **C2** = 12 (*R*), **C3** = 38 (*S*), **C4** = 2 (*S*).

2.4i *1-(2-Chlorophenyl)ethanol*:[32–34] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (m, 1H), 7.31 (m, 2H), 7.20 (m, 1H), 5.30 (q, 1H, $J = 6.32$ Hz), 2.02 (bs, 1H, OH), 1.49 (d, 3H, $J = 6.44$ Hz); Enantiomeric excess (%) at 12 h (isopropanol/hexane 10/90 0.5 mL/min, $t_1 = 10.9$ min for the *S* enantiomer, $t_2 = 11.5$ for the *R* enantiomer) **C1** = 38 (*R*), **C2** = 18 (*S*), **C3** = 24 (*S*), **C4** = 10 (*S*).

2.4j *1-(4-Nitrophenyl)ethanol*:[32–34] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, 2H, $J = 8.8$ Hz), 7.55 (d, 2H, $J = 8.4$ Hz), 5.03 (q, 1H, $J = 3.6$ Hz), 2.10 (bs, 1H, OH), 1.52 (d, 3H, $J = 6.4$ Hz); Enantiomeric excess (%) at 12 h (ethanol/hexane 5/95 0.8 mL/min, $t_1 = 39.5$ min for the *S* enantiomer, $t_2 = 43.9$ for the *R* enantiomer) **C1** = 20 (*R*), **C2** = 20 (*S*), **C3** = 46 (*S*), **C4** = 6 (*S*).

2.4k *4-Phenyl-2-butanol*:[32–34] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (m, 3H), 7.20 (m, 2H), 3.83 (m, 1H), 2.7 (m, 2H), 1.78 (m, 2H), 1.24 (d, 3H, $J = 6.2$ Hz); Enantiomeric excess (%) at 12 h (isopropanol/hexane 10/90 1.0 mL/min, $t_1 = 12.2$ min for the *S* enantiomer, $t_2 = 8.6$ for the *R* enantiomer) **C1** = 84 (*S*), **C2** = 84 (*S*), **C3** = 23 (*S*), **C4** = 4 (*S*).

2.4l *2-Bromo-1-phenyl ethanol*:[32–34] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (m, 5H), 4.80 (dd, 1H, $J = 3.2$, 3.6 Hz), 2.68 (bs, 1H, OH), 3.63 (m, 2H); Enantiomeric excess (%) at 12 h (isopropanol/hexane 2/98 1.0 mL/min, $t_1 = 22.1$ min for the *S* enantiomer, $t_2 = 26.5$ for the *R* enantiomer) **C1** = 96 (*S*), **C2** = 30 (*R*), **C3** = 35 (*S*), **C4** = 2 (*S*).

2.4m *1-(Furan-2-yl)ethanol*:[32–34] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, 1H, $J = 1.94$ Hz), 6.33 (d, 1H, $J = 1.4$ Hz), 6.24 (d, 1H, $J = 2.8$ Hz), 4.90 (q, 1H, $J = 6.56$ Hz), 2.24 (bs, 1H, OH), 1.56 (d, 3H, $J = 6.6$ Hz); Enantiomeric excess (%) at 12 h (ethanol/hexane 1/99 1.0 mL/min, $t_1 = 31.5$ min for the *S* enantiomer, $t_2 = 28.3$ for the *R* enantiomer) **C1** = 86 (*S*), **C2** = 36 (*S*), **C3** = 32 (*S*), **C4** = 4 (*S*).

2.5 *Crystal Data*

Crystals of ruthenium diamine complexes **C2**, **C3** and **C4** suitable for X-ray diffraction study were carefully picked and mounted on the goniometer head. The unit cell parameters and intensity data were collected at room temperature employing a Bruker SMART APEX CCD diffractometer equipped with a MoK_α X-ray source (50 kV, 40 mA). Data acquisition was carried out using SMART software and the data reduction was carried out using SAINT software.[35] The empirical absorption corrections were carried out using the SADABS program.[36] The structure was solved and refined using the SHELXL-97 program.[37] Hydrogen atoms were fixed in idealized positions and refined using a riding model. The crystallographic details of **C2**, **C3** and **C4** have been summarized in Table 1. Crystallographic data for **C2**, **C3** and **C4** have been deposited with the Cambridge Crystallographic Data Centre in the cif files

Table 1. Crystal data and refinement details for **C2**, **C3** and **C4**.

	C2	**C3**	**C4**
Formula	$C_{17}H_{30}Cl_2N_2Ru$	$C_{22}H_{32}Cl_2N_2Ru$	$C_{15}H_{26}Cl_2N_2Ru$
Formula weight	434.40	496.47	406.05
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	P212121	P212121	P212121
T (K)	293 (2)	293 (2)	293 (2)
a, Å	9.1526 (6)	8.5597 (16)	8.3272 (4)
b, Å	10.3465 (6)	9.354 (2)	9.6615 (5)
c, Å	20.2390 (12)	28.647 (6)	22.0185 (9)
α, deg	90.00	90.00	90.00
β	90.00	90.00	90.00
γ	90.00	90.00	90.00
V, Å	1916.6 (2)	2293.8 (8)	1771.46 (14)
Z	4	4	4
d_{calc}, g cm^{-3}	1.505	1.438	1.524
μ(mm^{-1})	1.096	0.926	1.180
λ(Å)	0.71073	0.71073	0.71073
R[a]	0.0475	0.0345	0.0272
R_w	0.0696	0.0785	0.0741

[a] $R = \sum(|F_o| - |Fc|)/\sum|F_o|$, $Rw = [\sum w(|F_o| - |Fc|)^2/\sum w|F_o|^2]^{1/2}$ (based on reflections with $I > 2\sigma(I)$).

CCDC 880005, 880004 and 885471 respectively. Data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3. Results and Discussion

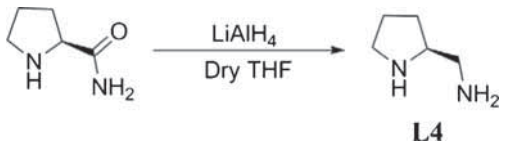
Ligands were synthesized from the naturally occurring chiral amino acid L-proline. (*S*)-N-phenyl-2-aminomethylpyrrolidine **L1** was prepared from L-proline by reacting it with phosphorous pentachloride to give the acid chloride. The resultant acid chloride was treated with aniline in THF to yield N-phenyl-proline amide. Finally, the amide was reduced with $LiAlH_4$ to yield **L1** (Scheme 1).[38]

The synthesis of (*S*)-N-ethyl **L2** and (*S*)-N-benzyl-2-aminomethylpyrrolidine **L3** was however more cumbersome and involved the conversion of L-proline to N-carbobenzoxy proline by reacting it with benzyl chloroformate in the presence of a base. The resultant N-carbobenzoxy proline was converted into N-carbobenzoxy-proline-*p*-nitrophenol ester using *p*-nitrophenol and N,N′-Dicyclohexylcarbodiimide. To this ester suitable amines (ethyl or benzyl amine) were added to get the corresponding amides (ethyl or benzyl). The amides thus obtained were subjected to hydrogenation in the presence of Pd/C catalyst and molecular hydrogen followed by lithium aluminium hydride to give diamine ligands as shown in Scheme 2 (ethyl **L2** or benzyl **L3**).[39]

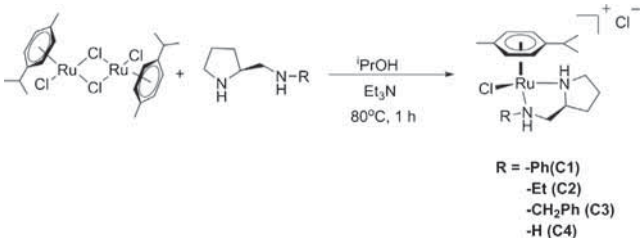
The 2-aminomethylpyrrolidine **L4** ligand was prepared from the L-proline amide which on reduction with lithium aluminium hydride afforded the 2-aminomethylpyrrolidine **L4** ligand (Scheme 3).[39] Formation of ligands was confirmed by ^1H and ^{13}C NMR spectroscopy.

Metal complexes were synthesized by carrying out the reaction of ruthenium cymene dimer with chiral (*S*)-N-substituted 2-aminomethylpyrrolidine ligands (Scheme 4).[40] The corresponding chiral ruthenium complexes **C1**, **C2**, **C3** and **C4** were obtained as yellow crystalline complexes whose structures were confirmed by NMR, ESI-HRMS and X-ray crystallography.

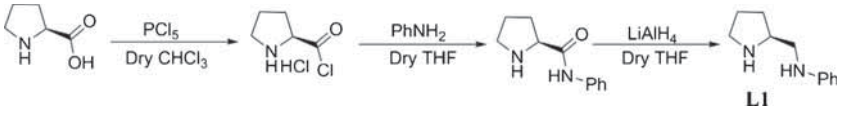
The crystal structure of the ruthenium complex **C1** is already available in the literature[40] while that of **C2**, **C3** and **C4** are reported in this paper. The molecular structures of three complexes are depicted in Figure 1. The complexes were obtained as single diastereoisomers crystallizing in the orthorhombic, chiral $P2_12_12_1$ space group. The configuration around the ruthenium center



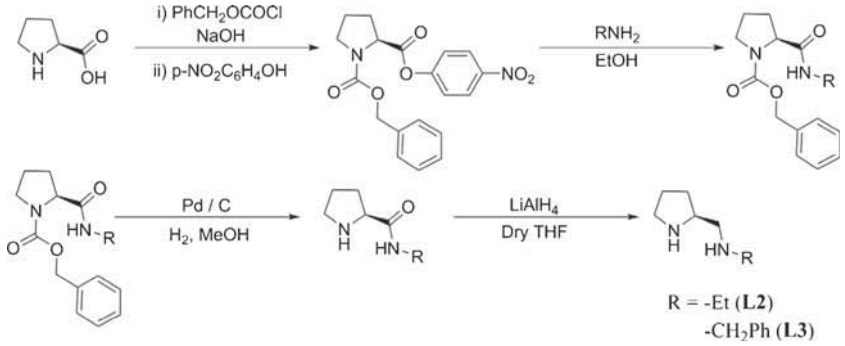
Scheme 3. Synthesis of (*S*)-2-aminomethylpyrrolidine **L4**.



Scheme 4. Synthesis of chiral half-sandwich ruthenium proline diamine complexes.



Scheme 1. Synthesis of (*S*)-N-phenyl-2-aminomethylpyrrolidine **L1**.



Scheme 2. Synthesis of (*S*)-N-ethyl (**L2**) or benzyl-2-aminomethylpyrrolidine (**L3**).

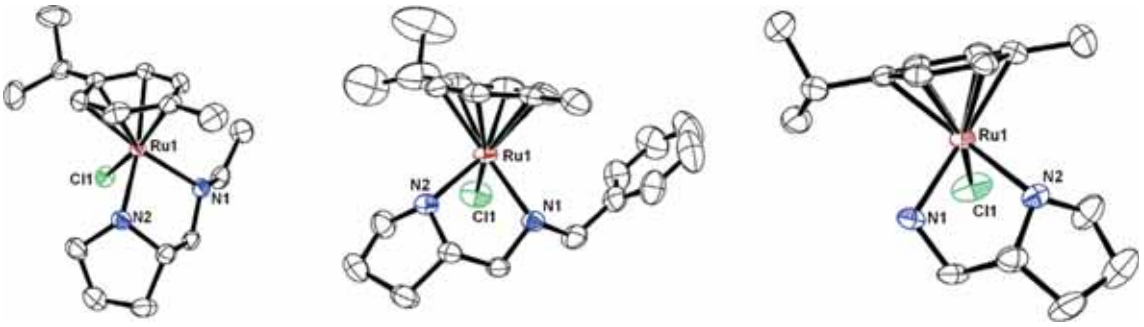
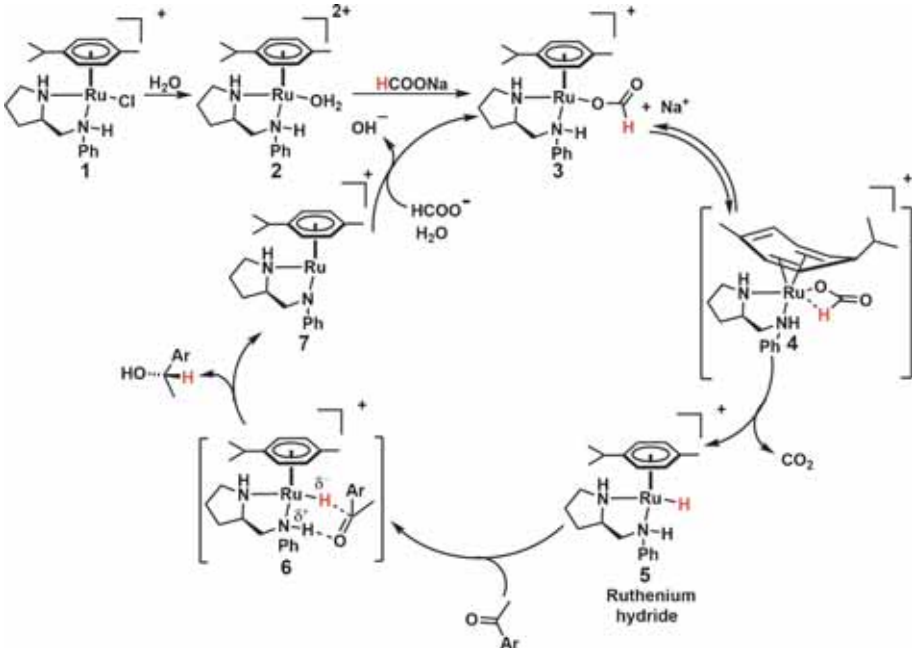


Figure 1. ORTEP view of **C2**, **C3** and **C4** at the 40% probability level showing selected atom labeling. Hydrogen atoms are omitted for clarity.

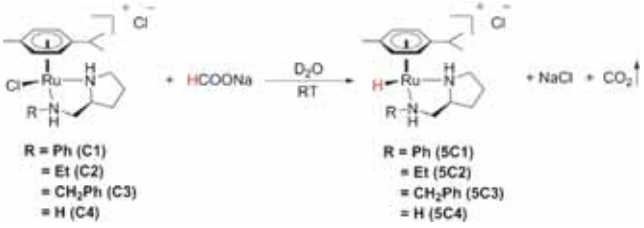
based on the Cahn-Ingold-Prelog nomenclature gave *S* configuration in **C2** and **C4** wheras in **C3** ruthenium adopts the *R* configuration[41–44] Details of the molecular structure are given in the supporting information. Because the complexes are soluble in water, the transfer hydrogenation reaction was carried out using sodium formate as a reducing agent in water making the reaction eco-friendly, benign, and convenient. The use of **C1** has only been reported as a catalyst in isopropanol and it was reported to be inactive in a mixture of triethyl amine-formic acid.[45]

In the proposed mechanism of transfer hydrogenation of ketones in water, the first step is the formation of an aqua complex **2** from the chloro complex **1**, which reacts with sodium formate to form the ruthenium-formate complex **3**. The η^4-mode of binding in **4** is suggested to avoid the formation of a 20 electron complex en-route to the ruthenium hydride species **5** by extrusion of carbon dioxide. The substrate will then coordinate to ruthenium and both H^- and H^+ will be transferred simultaneously to the ketone to yield the chiral alcohol in an intermediate such as **6**. The resultant ruthenium amido complex **7** is a $16e^-$ species that on reaction with sodium formate and water will regenerate the ruthenium sodium formate complex **3** and the catalytic cycle continues as shown in Scheme 5.[46]

To probe the formation of an intermediate like **5**, a stoichiometric reaction was carried out with sodium formate and ruthenium diamine catalysts **C1**, **C2**, **C3**, and **C4** as depicted in Scheme 6. The reaction was carried out in a NMR tube where the ruthenium proline diamine catalyst was dissolved in 0.4 mL of D_2O containing sodium formate. The hydride formation was monitored by ^{1}H NMR spectroscopy. Formation of the ruthenium hydride species was ascertained by ^{1}H NMR spectrum where in all cases, hydride peaks were observed



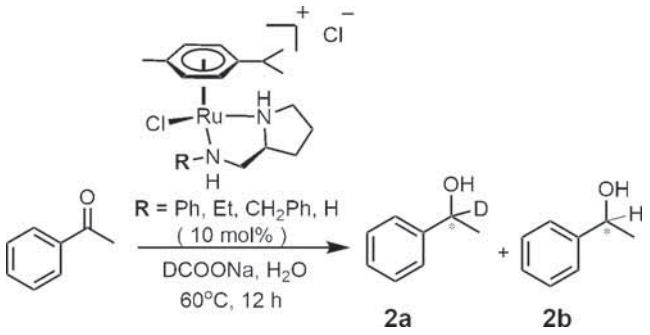
Scheme 5. Proposed mechanism of transfer hydrogenation reaction of ketones in water.



Scheme 6. Stoichiometric reaction of ruthenium proline diamine complexes with HCOONa.

in the up-field region of the ^{1}H NMR spectrum. The hydride chemical shift values for **5C1**: $\delta -6.93$ ppm, **5C2**: $\delta -7.63$ ppm, **5C3**: $\delta -7.43$ ppm and **5C4**: $\delta -7.46$ ppm are shown in Figure 2. Formation of ruthenium hydride species of complex **C1** was further confirmed by the mass spectrometry. HRMS (ESI) m/z calculated for $[C_{21}H_{31}N_2Ru]^+$: 413.1530; found 413.1506. This study suggested that ruthenium catalysts **C1**, **C2**, **C3** and **C4** are forming the hydride which is probably the active species in the reduction of ketones to form chiral alcohols.

The transfer hydrogenation reaction was then attempted with deuterated sodium formate (DCOONa). DCOONa on reaction with ruthenium proline diamine complex will lead to the formation of ruthenium deuteride species and subsequently the deuteride will be transferred to the acetophenone to form **2a**. If the deuteride attached to the Ru exchanges its deuterium with hydrogen in the solvent, it may lead to the formation of the ruthenium hydride species which will transfer the hydride to the acetophenone to give **2b**. The reaction was carried out employing ruthenium catalysts **C1**, **C2**, **C3**, and **C4** with acetophenone as a substrate



Scheme 7. Transfer hydrogenation of acetophenone employing deuterated sodium formate (DCOONa).

in water (Scheme 7). It led to the formation of both **2a** and **2b**.

Formation of **2a** and **2b** was confirmed by ^{1}H, ^{2}H and ^{13}C NMR spectroscopy. **2a** showed a singlet in the ^{2}H NMR spectrum at δ 4.88 ppm corresponding to the deuterium and in the ^{1}H decoupled ^{13}C NMR spectrum a triplet at δ 70.45 ppm corresponding to the α carbon attached to the deuterium atom. The C-D coupling constant is found to be 22.8 Hz. Ratio of **2a** and **2b** was calculated from the ^{1}H NMR spectrum. Table 2 lists the ratio of **2a** and **2b** and the enantiomeric excess. In the case of ruthenium catalyst **C1** more of **2a** was observed compared to what was observed in the reaction with catalysts **C2–C4**.

Ruthenium diamine catalysts were optimized with acetophenone as a model substrate. The catalyst, base, and substrate were taken in 1:50:10 ratio and the reaction was carried out at 60°C. The reaction was monitored by ^{1}H NMR spectroscopy and the enantiomeric excess was determined using a Chiralcel OD column.

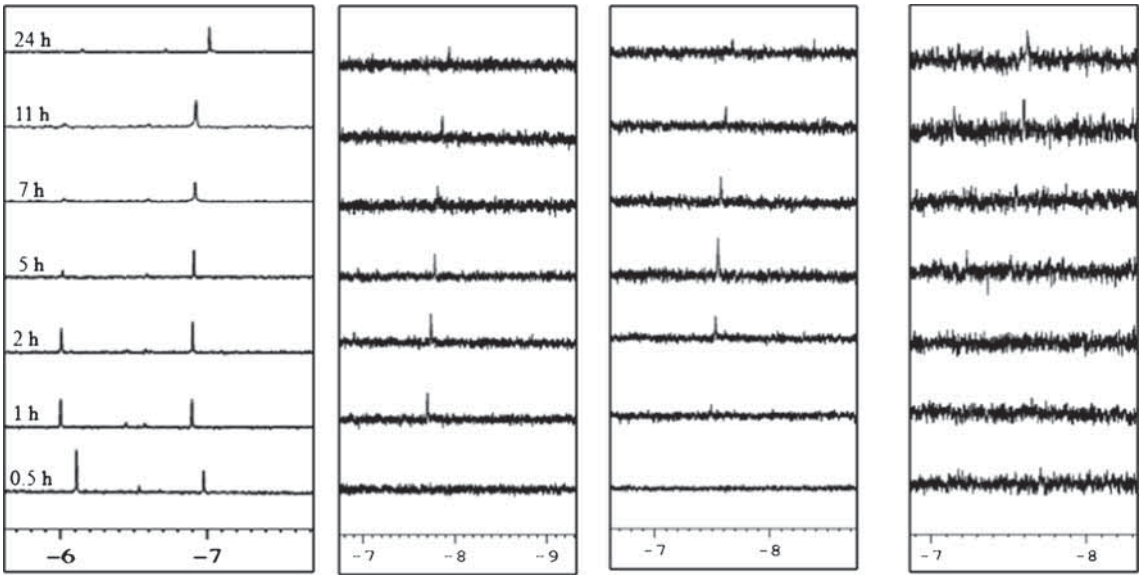


Figure 2. ^{1}H NMR spectra of hydrides of ruthenium diamine complexes **C1**, **C2**, **C3** and **C4** respectively.

Table 2. Ratio of **2a** and **2b** in the transfer hydrogenation reaction of acetophenone with DCOONa.

Entry	R	Conversion (%)	Ratio of Products[a] (%) 2a	2b	ee[b] (%)
1	-Ph	96	89	11	22 (*R*)
2	-Et	82	79	21	20 (*S*)
3	$-CH_2Ph$	82	78	22	24 (*S*)
4	$-NH_2$	82	73	27	8 (*S*)

[a]Ratio of products are determined by ^{1}H NMR and are an average of two runs. [b]Enantiomeric excess is determined by chiral HPLC analysis using Chiralcel OD column.

C1 afforded 93% of 1-phenyl ethanol with an enantiomeric excess of 10% (*R*) at 12 h (Table 3, entry 1) but the maximum enantiomeric excess of 31% (*R*) was obtained at 4h. Since the mechanism of transfer hydrogenation reaction required generation of a vacant site at ruthenium, the effect of silver ions to aid the formation of an aqua complex was probed. Reactions carried out with 10 mol% and 20 mol% of $AgNO_3$ showed almost quantitative conversion at 12 h (Table 3, entry 2 and 3). A catalyst loading of 10% appeared to be optimum (Table 3, entry 4).

With **C2**, 85% conversion was observed after 12 h and addition of $AgNO_3$ provided little advantage. The formation of *S* isomer of 1-phenylethanol was observed (Table 3, entry 5 and 6). The same trend was observed with catalyst **C3** (Table 3, entry 7 and 8) and **C4** (Table 3, entry 9 and 10). In both cases, conversion was not enhanced in the presence of silver nitrate and the formation of *S* isomer of 1-phenylethanol was observed. Only with catalyst **C1**, silver nitrate was found to enhance the yields. The transfer hydrogenation reaction was then carried out with ketones having different electronic and steric demands. It was deemed necessary to use silver nitrate only in the case of catalyst **C1** and so reactions with catalysts **C2**, **C3** and **C4** were carried out without silver nitrate.

C1 resulted in good yields of chiral alcohols with moderate to good enantioselectivities. Maximum enantiomeric excess of 96% (*S*) was obtained for 2-bromo-1-phenyl ethanol (entry 10, Table 4). An electron withdrawing substituent on the ketone resulted in good yields of the chiral alcohol compared to yields with an electron donating substituent. With difficult substrates such as α-tetralone (entry 12, Table 4) and indanone (entry 13, Table 4), good enantioselectivities were observed with **C1**. The importance of using silver nitrate as an additive appears to be more important for sluggish substrates such as indanone. Formation of 1-indanol was observed with 50% conversion in the presence of $AgNO_3$, whereas reduced conversion was observed in the absence of an additive (entry 13, Table 4).

Compared to **C1**, less conversion was observed with **C2** for most of the ketones. In the case of two substrates, the enantiomeric excess was higher with **C2** than with **C1** (entries 7 and 8, Table 4) although the yields were lower. The presence of $AgNO_3$ was not enhancing the rate of the reaction, presumably because catalysts

Table 3. Transfer hydrogenation of acetophenone with catalysts **C1**, **C2**, **C3** and **C4**[a].

Entry	Catalyst amount	Catalyst	Additive	Conversion[b] (%) 4 h	12 h	ee[c] (%) 4 h	12 h	Isolated Yield (%)
1	10 mol %	C1	–	81	93	31 (*R*)	10 (*R*)	79
2	10 mol %	C1	$AgNO_3$ (10 mol %)	88	99	18 (*R*)	16 (*R*)	87
3	10 mol %	C1	$AgNO_3$ (20 mol %)	91	99	26 (*R*)	8 (*R*)	87
4	5 mol %	C1	–	51	64	20 (*R*)	24 (*R*)	56
5	10 mol %	C2	–	78	85	12 (*S*)	10 (*S*)	73
6	10 mol %	C2	$AgNO_3$ (20 mol %)	79	86	14 (*S*)	10 (*S*)	75
7	10 mol %	C3	–	64	87	22 (*S*)	8 (*S*)	75
8	10 mol %	C3	$AgNO_3$ (20 mol %)	65	89	25 (*S*)	10 (*S*)	78
9	10 mol %	C4	–	69	77	8 (*S*)	6 (*S*)	69
10	10 mol %	C4	$AgNO_3$ (20 mol %)	75	77	8 (*S*)	6 (*S*)	70

[a]Reactions were carried out at 60°C, the ratio of catalyst/ substrate/formate was 1:10:50. [b]The conversion was determined by ^{1}H NMR spectroscopy. [c]Enantiomeric excess was determined by chiral HPLC analysis using chiralcel OD column.

Table 4. Transfer hydrogenation of various ketones with ruthenium catalysts **C1**, **C2**, **C3** and **C4**.[a]

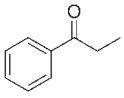
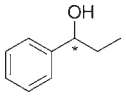
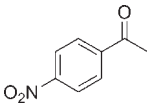
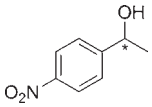
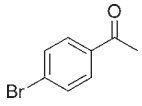
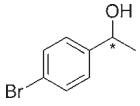
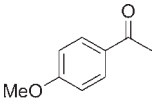
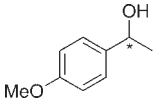
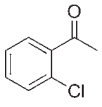
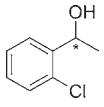
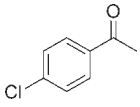
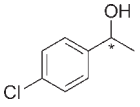
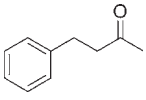
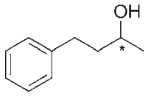
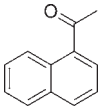
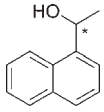
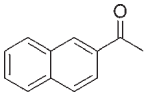
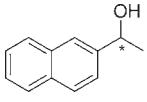
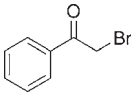
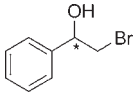
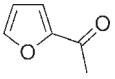
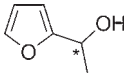
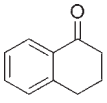
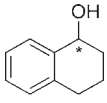
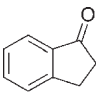
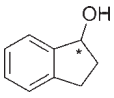
Entry	Catalysts	Substrate	Product	Conversion[b] (%) 1 h	2h	12 h	% ee[c] (*R*/*S*)	Isolated Yield (%)
1	C1			71	78	92	48 (*R*)	81
	C2			72	78	88	15 (*S*)	76
	C3			50	62	71	15 (*S*)	63
	C4			58	63	79	8 (*S*)	71
2	C1			50	62	91	20 (*R*)	81
	C2			30	38	66	20 (*S*)	56
	C3			44	57	65	46 (*S*)	56
	C4			76	78	92	6 (*S*)	80
3	C1			63	78	90	28 (*R*)	78
	C2			67	70	73	12 (*R*)	67
	C3			84	86	92	38 (*S*)	88
	C4			38	65	84	2 (*S*)	75
4	C1			22	35	81	50 (*R*)	72
	C2			14	17	30	16 (*S*)	19
	C3			12	17	26	28 (*S*)	18
	C4			51	52	55	2 (*S*)	49
5	C1			86	92	93	38 (*R*)	80
	C2			71	71	76	18 (*S*)	68
	C3			78	84	85	24 (*S*)	80
	C4			49	57	78	10 (*S*)	72
6	C1			71	77	84	22 (*R*)	71
	C2			81	89	90	28 (*S*)	82
	C3			78	83	88	45 (*S*)	86
	C4			38	48	74	10 (*S*)	69
7	C1			68	71	82	84 (*S*)	73
	C2			24	28	37	84 (*S*)	28
	C3			45	52	68	23 (*S*)	61
	C4			38	55	57	4 (*S*)	52
8	C1			44	62	75	56 (*R*)	67
	C2			30	44	49	68 (*S*)	40
	C3			33	50	64	22 (*S*)	54
	C4			29	56	64	2 (*S*)	57
9	C1			65	71	78	28 (*R*)	69
	C2 C3			35 35	66 52	72 61	20 (*S*) 34 (*S*)	62 53
	C4			24	34	54	4 (*S*)	48
10	C1			71	Quanti-tative	–	96 (*S*)	86
	C2			48	81	Quanti-tative	30 (*R*)	87
	C3			71	86	Quanti-tative	35 (*S*)	92
	C4			63	Quanti-tative	–	2 (*S*)	85
11	C1			70	85	88	86 (*S*)	76
	C2			36	42	43	36 (*S*)	33
	C3			42	48	51	32 (*S*)	45
	C4			34	71	78	4 (*S*)	70
12	C1			17	26	74	74 (*S*)	68
	C2			11	16	26	36 (*S*)	18
	C3			20	24	32	74 (*S*)	26
	C4			17	21	26	12 (*S*)	20

Table 4. (continued)

Entry	Catalysts	Substrate	Product	Conversion[b] (%) 1 h	2h	12 h	% ee[c] (*R*/*S*)	Isolated Yield (%)
13	C1			28	38	50	54 (*S*)	35
	C1			16[d]	28	30	48 (*S*)	19
	C2			15	17	27	30 (*S*)	19
	C2			16[e]	20	34	30 (*S*)	28
	C3			14	16	23	22 (*S*)	17
	C3			20[e]	20	25	24 (*S*)	20
	C4			13	17	32	2 (*S*)	27
	C4			16[e]	25	36	3 (*S*)	29

[a]Reactions were carried out at 60°C, the ratio of catalyst/ substrate/formate was 1:10:50. Conversion was determined by ^{1}H NMR spectroscopy. [c]Enantiomeric excess was determined by chiral HPLC analysis of the reaction mixture after 12 hrs using a Chiralcel OD column excluding substrates in entries 2, 5 and 6 where chiral OJ-H column was used. [d]Without $AgNO_3$. [e]With $AgNO_3$.

C2–C4 were readily hydrolyzed. This can be understood in the reaction with indanone as a substrate (entry 13, Table 4) where the rates were limited by subsequent slow steps. Although very good enantiomeric excess is observed in the formation of α-tetralol 74% (*S*) (entry 12, Table 4) with **C3**, the better yield obtained with **C1** makes it a clear winner. Lower enantioselectivities were obtained for all ketones with **C4** compared to **C1**. Interestingly, the best enantiomeric excess obtained with catalyst **C4** was in the case of α-tetralol (12% (*S*) (entry 12, Table 4).

Recycling the catalyst is an added advantage while working with precious metals. After 12 h of reaction with acetophenone and **C1** (10 mol%) in the presence of HCOONa, formation of 1-phenylethanol was observed with 92% conversion (an average of two runs). The product and the residual starting material were removed by extraction with ethyl acetate and a fresh batch of the substrate was added to initiate the next cycle. Three cycles could be run in this fashion after removal of the organic reactants and products without significant loss in the conversion in the subsequent batch.

4. Conclusions

Chiral half-sandwich ruthenium proline diamine complexes **C1**, **C2**, **C3** and **C4** are readily prepared from the proline-derived diamine ligands **L1**, **L2**, **L3** and **L4**. These complexes are excellent catalysts for the transfer hydrogenation of ketones in water. Stoichiometric reaction of **C1**, **C2**, **C3** and **C4** with sodium formate showed the formation of a ruthenium-hydride as the most probable species involved in the reduction of ketones. **C1** was successfully recycled without affecting the conversion during the transfer hydrogenation of acetophenone. The yield in this reaction was enhanced in the presence of silver nitrate when **C1** was the catalyst whereas other catalysts exhibited no change with addition of silver nitrate. The catalyst **C1** with the phenyl group delivers the best yield and induces higher enantioselectivity compared to the other catalysts that are studied in most cases. This suggests that the observations made by Noyori on the influence of C-H$^{\cdots}\pi$ interactions between the catalyst and the substrate leading to better enantioselectivity might be a general phenomenon worthy of systematic exploitation.

Supplementary Information (SI)

Mass spectra of complexes (S2–S6), ^{1}H NMR spectrum of ligands and complexes (S7–S19), ^{1}H NMR spectrum of deuterated and undeuterated 1-phenylethanol (S20–S27) and HPLC chromatogram of chiral alcohols (Figures S28–S42) are given in the Supporting Information, available at www.ias.ac.in/chemsci.

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