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Asymmetric transfer hydrogenation of aryl-alkyl ketones catalyzed by ruthenium(II) complexes having chiral pyridylmethylamine and phosphine ligands

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Abstract

In the asymmetric transfer hydrogenation of aromatic ketones using propan-2-ol or a formic acid–triethylamine mixture as hydrogen donor, a mixed ligand ruthenium(II) complex generated in situ from pyridylmethylamine ligands and $RuCl_2(PPh_3)_3$ or $RuHCl(PPh_3)_3$ were examined. In propan-2-ol, the direction of the chirality induction was very sensitive to the aryl substituent of chiral amino unit in pyridylmethylamine ligands. Using $HCOOH/NEt_3$ as hydrogen donor, catalytic activities and enantioselectivities were much improved (up to 100% conversion and 86% e.e.) with ruthenium complex generated from $RuHCl(PPh_3)_3$ and 2-pyridylmethyl-1-(*R*)-phenylethylamine. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Transfer hydrogenation; Chiral catalysis; Pyridylmethylamine ligands; Ruthenium complex

1. Introduction

Catalytic transfer hydrogenation with propan-2-ol or $HCOOH/NEt_3$ is a convenient method to reduce ketones since there is no need to employ a high hydrogen pressure or to use hazardous reducing agents. In this process, rhodium, iridium and ruthenium complexes coordinated by diphosphine or dinitrogen ligands have been used as catalysts [1–5]. Recently, with ruthenium(II)-base catalysts bearing specific ligands including NH moiety such as 1,2-diamine [6], aminoalcohol [7,8] and bis(oxazolinyl)amine [9], satisfactory results of catalytic activity and enantioselectivity have been reported in the reaction of simple ketones using propan2-ol as hydrogen donor. With iridium (I)-base catalysts, pyridylimine [1,10] and pyridylmethylamine [1] from 2-pyridinecarboxaldehyde derivatives had shown moderate catalytic activity and enantioselectivity.

For our part, we have examined the various ligands (diphosphine, diamine, phosphine–amine, pyridine–phosphine) for the ruthenium catalysts for the effective transfer hydrogenation of ketones and found that the pyridine–phosphine ligand showed a good activity for the reaction [11]. Based on these results we have examined the ruthenium catalyst having both

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chiral pyridylmethylamine ligand, 2-pyridylmethyl-1-(*R*)-phenylethylamine (**1a**) [12], 2-pyridylmethyl-1-(*R*)-(1-naphthyl)ethylamine (**1b**), or 2-(6-methylpyridylmethyl)-1-(*R*)-phenylethylamine (**1c**) and phosphine ligand to the asymmetric transfer hydrogenation of ketones.

In this paper, we report the effect of chiral pyridylmethylamine and phosphine ligands to the ruthenium(II) catalyzed asymmetric transfer hydrogenation of aryl-alkyl ketones with propan-2-ol or formic acid–triethylamine mixture ($HCOOH/NEt_3$) as hydrogen donor.

2. Experimental

2.1. General procedure

^1H and ^{31}P NMR spectra were recorded on a JEOL EX-270 or JEOL LA-400 spectrometers, with tetramethylsilane (Me_4Si) as an internal standard and 85% H_3PO_4 as an external standard, respectively. *J* values are given in Hz. Mass spectra were obtained with a JEOL LX-1000 instrument with a fast atom bombardment ionization method. Enantiomeric excesses were determined by HPLC. Chiralcel OB-H and OD-H columns (Daicel Chemical Industry) were used at room temperature with *n*-hexane/propan-2-ol as the mobile phase and detection by a UV–VIS spectrophotometric detector. Micro vacuum distillation was performed with a Sibata GTO-350RS Kugelrohr distilling apparatus. Column chromatography was carried out on silica gel (Merck, 230–400 mesh) using ethyl acetate/*n*-hexane as eluent.

2.2. Preparation of pyridylmethylamine ligands *1a–c*

A mixture of (*R*)-phenylethylamine (2.2 g, 18 mmol) and 2-pyridinecarboxaldehyde (1.9 g, 18 mmol) in CH_2Cl_2 was stirred with Al_2O_3 at room temperature for 18 h. The Al_2O_3 was removed by filtration and the filtrate was evaporated. The obtained orange oil (3.7 g, 98%) was reduced by stirring overnight under hydrogen atmosphere with palladium carbon in methanol. The palladium carbon was removed by filtration and the filtrate was evaporated. The residue was distilled by a Kugelrohr to give pyridylmethylamine ligand **1a** (2.8 g, 76%). The ligand **1b** (50%) and **1c** (70%) were also synthesized according to this procedure. By this series of transformations, **1a–c** were obtained as homochiral compounds without racemization and it was confirmed by ^1H NMR analysis of diastereomeric salts of **1a–c** with (*S*)-mandelic acid.

1a: A yellow oil: δ_H(270 MHz, $CDCl_3$) 1.39 (3 H, d, Me), 2.06 (1 H, br, NH), 3.72 (2 H, s, CH_2), 3.80 (1 H, q, CH), 7.09–7.36 (7 H, m, ArH), 7.57 (1 H, t, $J = 7.6$, ArH), 8.53 (1 H, d, $J = 4.95$, ArH); *m/z* (FAB) 213 [$(M + 1)^+$]; $[\alpha]_D^{20} + 48.1$ (c 4.08 in MeOH).

1a · 2 HCl: A white powder: (Found: C, 58.81; H, 6.11; N, 9.84. Calc. for $C_{14}H_{18}N_2Cl_2$: C, 58.96; H, 6.36; N, 9.82%).

1b: A viscous yellow oil: δ_H(400 MHz, $CDCl_3$) 1.58 (3 H, d, Me), 2.63 (1 H, br, NH), 3.84 (1 H, d, CH_aH_b), 3.90 (1 H, d, CH_aH_b), 4.74 (1 H, q, CH), 7.12 (9 H, m, ArH), 8.15 (1 H, d, ArH), 8.57 (1 H, d, $J = 4.62$, ArH); *m/z* (FAB) 263 [$(M + 1)^+$]; $[\alpha]_D^{20} - 4.77$ (c 3.99 in MeOH).

1b · 2HCl · H_2O: A hygroscopic white powder: (Found: C, 61.2; H, 6.85; N, 7.93. Calc. for $C_{18}H_{24}N_2OCl_2$: C, 61.5; H, 6.67; N, 8.05%).

1c: A yellow oil: δ_H(270 MHz, $CDCl_3$) 1.44 (3 H, d, Me), 2.4 (1 H, br, NH), 2.52 (3 H, s, Me), 3.73 (2 H, s, CH_2), 3.85 (1 H, q, CH), 7.0 (2 H, d, $J = 7.59$, ArH), 7.2–7.42 (5 H, m, ArH), 7.49 (1 H, t, $J = 7.59$, ArH); *m/z* (FAB) 227 [$(M + 1)^+$]; $[\alpha]_D^{20} + 45.6$ (c 3.90 in MeOH).

1c · 2HCl · H_2O: A white hygroscopic powder: (Found: C, 57.1; H, 7.07; N, 8.86. Calc. for $C_{15}H_{22}N_2OCl_2$: C, 56.8; H, 6.99; N, 8.83%).

2.3. General procedure for the ruthenium catalyzed transfer hydrogenation with propan-2-ol

Ruthenium(II) catalyst was prepared from 1 mol% of $RuCl_2(PPh_3)_3$ and 4 mol% of **1** in

propan-2-ol heating at 85°C for 30 min under nitrogen atmosphere. After the introduction of aryl-alkyl ketones to the catalyst solution, the reduction was conducted in the presence of 5 mol% of KOH. After the ruthenium catalyst was removed by filtration over short silica gel column, the conversion was determined by ^{1}H NMR analysis. The enantiomeric excess of the product was determined by chiral HPLC after purifying by column chromatography.

2.4. General procedure for the ruthenium catalyzed transfer hydrogenation with HCOOH/NEt$_3$

Ruthenium(II) catalyst was prepared from 1 mol% of $RuHCl(PPh_3)_3$ or $RuCl_2(PPh_3)_3$ and 5 mol% of **1** in THF heating at 60°C for 30 min under nitrogen atmosphere. Subsequently, aryl-alkyl ketones and $HCOOH/NEt_3$ were added to the solution. The product was treated and analyzed similarly to the reaction in propan-2-ol.

3. Result and discussion

3.1. Synthesis of pyridylmethylamine ligands

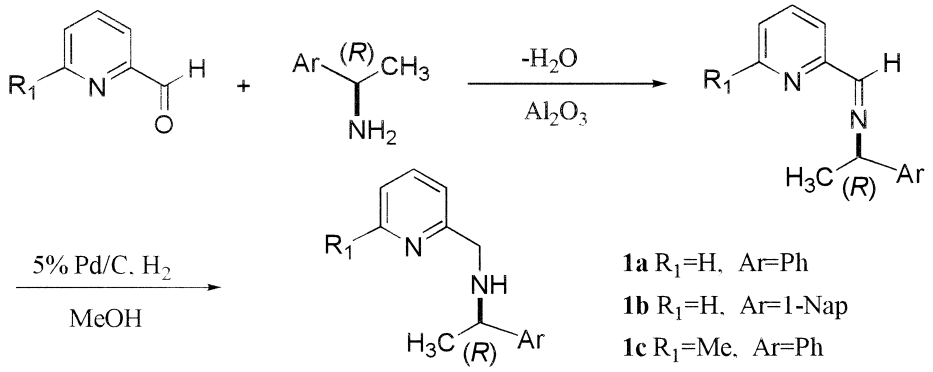
The chiral pyridylmethylamine ligands **1a–c** were readily synthesized as follows: chiral primary amines were converted to the imines by the reaction with 2-pyridinecarboxaldehyde derivatives, and these imines were reduced to the ligands **1a–c** by the hydrogenation using Pd/C in methanol in 50–76% yields (Scheme 1).

3.2. Asymmetric transfer hydrogenation of ketones (hydrogen donor: propan-2-ol)

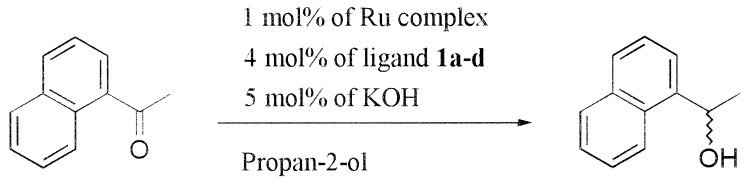
3.2.1. Ligand effect

The transfer hydrogenation was examined with 1 mol% of $RuCl_2(PPh_3)_3$ and 4 mol% of the ligand using propan-2-ol as hydrogen donor. As co-catalyst, 5 mol% of KOH was used and the reduction of 1-acetonaphthone was examined at 25 or 85°C under nitrogen atmosphere (Scheme 2).

In the reaction system derived from $RuCl_2(PPh_3)_3$ and pyridylmethylamine ligand, the mixed ligand complex formation was ascertained by FAB-MS. The peak corresponding to the dimeric ruthenium complex containing **1a** and triphenylphosphine in 1:1 ratio, $[RuCl_2(\mathbf{1a})(PPh_3)]_2$, was observed ($m/z$ 1257 $(M-Cl)^+$). The ratio of **1a** to ruthenium in solution was changed to find the optimum conditions and, in the presence of more than 2 equiv. **1a** to ruthenium, the stereoselectivity became constant. The results were summarized in Table 1,



Scheme 1.



Scheme 2.

generally using 4 equiv. **1** to ruthenium in solution. The ruthenium catalysts bearing pyridylmethylamine ((*R*)-**1a–c**) showed moderate to high catalytic activities while the catalyst with pyridylimine, (*R*)-ppei [10], was not effective under this standard conditions (**1a–c** or ppei/Ru = 4). The enantioselectivities obtained by Ru-**1a** were moderate and Ru-**1b** or Ru-**1c** gave low enantioselectivities. Free triphenylphosphine ligand released during the complexation of chiral ligand with $RuCl_2(PPh_3)_3$ may affect the reactivity and enantioselectivity [9]. Therefore, $RuCl_2(PPh_3)_3$ and **1a–c** or pyridylimine ligand were heated in propan-2-ol at reflux temperature and resulting orange solution was evaporated in vacuo to dryness. The orange residue was washed three times with ether to remove free PPh_3 and excess pyridylmethylamine before adding 1-acetonaphthone and KOH. By removing excess ligands, the catalytic activities of the pyridylmethylamine complexes, Ru-**1a–c**-PPh_3, increased and the reaction proceeded even at 25°C (entries 6 and 10), while the enantioselectivity was decreased using **1a**. Addition of 3 equiv. of **1a** to the complex obtained above, however, suppressed the transfer hydrogenation in propan-2-ol suggesting that the complex without phosphine ligand, formed by the competitive coordination of **1a**, has a low activity. Using ruthenium hydride complexes, $RuHCl(PPh_3)_3$ and $RuH_2(PPh_3)_4$, which are effective catalysts for the transfer hydrogenation of ketones [13] as ruthenium precursor, the reaction proceeded at 25°C though the enantioselectivities were low.

3.2.2. Variation of substrate

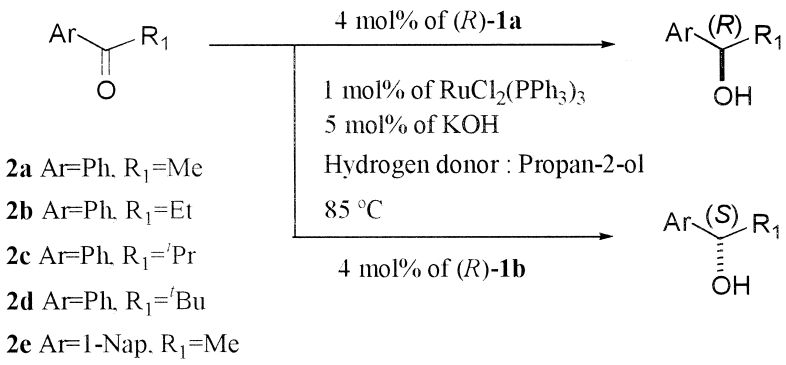
Using standard conditions (in the presence of free PPh_3), a variety of aryl-alkyl ketones have been reduced to the corresponding secondary alcohols (Scheme 3).

As shown in Table 2, moderate enantioselectivities were observed and the highest enantiomeric excess was about 60% e.e. with

Table 1
Asymmetric transfer hydrogenation of 1-acetonaphthone using Ru(II)-**1a–c** catalysts

Entry	Ligand	Ru precursor	**1**/Ru	Temperature (°C)	Time (h)	Yield (%)	% e.e. (configuration)
1	**1a**	$RuCl_2(PPh_3)_3$	2	85	3	64	45 (*R*)
2	**1a**	$RuCl_2(PPh_3)_3$	4	85	5 min	7	49 (*R*)
3	**1a**	$RuCl_2(PPh_3)_3$	4	85	3	77	45 (*R*)
4	**1a**	$RuCl_2(PPh_3)_3$	8	85	3	75	47 (*R*)
5[a]	**1a**	$RuCl_2(PPh_3)_3$	1	85	0.25	79	27 (*R*)
6[a]	**1a**	$RuCl_2(PPh_3)_3$	1	25	24	44	44 (*R*)
7	**1a**	$RuHCl(PPh_3)_3$	4	25	24	33	rac.
8[b]	**1a**	$RuH_2(PPh_3)_4$	4	25	24	23	10 (*S*)
9	**1b**	$RuCl_2(PPh_3)_3$	4	85	3	99	2 (*S*)
10[a]	**1b**	$RuCl_2(PPh_3)_3$	1	25	24	24	13 (*S*)
11	**1c**	$RuCl_2(PPh_3)_3$	4	85	3	99	5 (*R*)
12	(*R*)-ppei	$RuCl_2(PPh_3)_3$	4[c]	85	3	10	31 (*R*)

[a]After catalyst was formed, free PPh_3 and **1** were washed out with ether before adding **1**-acetonaphthone and KOH.
[b]The reaction was carried out in the absence of KOH (see Ref. [13]).
[c](*R*)-ppei/Ru = 4.



Scheme 3.

$RuCl_2(PPh_3)_3$-**1a** catalyst. However, it is noteworthy that *R*-enantiomers of carbinols were generated with Ru-{(*R*)-**1a**} catalyst while Ru-{(*R*)-**1b**} catalyst gave *S*-enantiomers of carbinols under the same conditions. In this reaction conditions, the direction of the chirality induction was much affected by the aryl unit of the ligand **1**. The effect of increasing the bulkiness of alkyl groups of ketones was studied. The steric effect is apparent from the results for methyl-(**2a**), ethyl-(**2b**), isopropyl-(**2c**) phenyl ketones (entries 1, 2, 3) and the highest % e.e. was obtained with **2c** having a bulky isopropyl unit.

3.2.3. Dependence of the catalytic activity on phosphine ligand

In the present transfer hydrogenation in propan-2-ol, the active species is generated from Ru-**1**-PPh_3 mixed-ligand complex. As described above, the presence of free PPh_3 lowered the reaction rate, however, addition of diphosphine ligands to the $RuCl_2(PPh_3)_3$-**1a,b** catalyst solution enhanced the catalytic activity drastically. [1] The effect of added diphosphine (1.1 equiv. to Ru atom) was summarized in Table 3 for the reduction of 1-acetonaphthone.

Table 2
Direction of the chirality induction using Ru-{(*R*)-**1a**} and Ru-{(*R*)-**1b**} catalysts

Entry	Ligand	Substrate	Time (h)	Yield (%)	% e.e. (configuration)
1	**1a**	**2a**	6	98	31 (*R*)
2	**1a**	**2b**	6	99	42 (*R*)
3	**1a**	**2c**	6	91	58 (*R*)
4	**1a**	**2d**	3	74	51 (*R*)
5	**1a**	**2e**	3	77	45 (*R*)
6	**1b**	**2a**	3	99	3 (*S*)
7	**1b**	**2c**	6	99	6 (*S*)
8	**1b**	**2d**	3	60	28 (*S*)
9	**1b**	**2e**	3	99	2 (*S*)

The activity of the Ru-**1a** catalyst was much enhanced by diphosphine addition in contrast to the effect of excess PPh_3 to lower the reaction rate (entry 2). Corresponding carbinol was generated in about 90% yields at 25°C in all cases while enantioselectivities were low (entries 3–5). In the case of dppb ligand, an inversion of the chirality was observed (entry 5). The same diphosphine effect was observed using Ru-**1b**-diphosphine catalyst system. The Ru-**1a**-dppp complex was identified by FAB-MS ([RuCl-(**1a**)(dppp)]$^+$(m/z 761)) and ^{31}P NMR ($\delta =$ 34.8 (d, $J_{P-P} = 45.5$ Hz), $\delta = 42.3$ (d, $J_{P-P} =$ 45.5 Hz)) analysis. The complexes, $RuCl_2$-$(PPh_3)_3$–dppp without **1** and $RuCl_2(PPh_3)_3$ -pyridylimine-dppp, have very low activities under present conditions.

[1] Noyori et al. reported that ruthenium(II) complex with a diphosphine–diamine tetradentate ligand acts as a good catalyst precursor in asymmetric transfer hydrogenation of acetophenone (see Ref. [14]).

Table 3
Effect of added diphosphine to the Ru-**1a,1b** catalyst[a]

Entry	Ligand	Additive	Yield (%)	% e.e. (configuration)
1[b]	**1a**	–	44	44 (*R*)
2	**1a**	PPh_3	11	–[c]
3	**1a**	dppe	99	15 (*R*)
4	**1a**	dppp	88	23 (*R*)
5	**1a**	dppb	87	35 (*S*)
6	**1b**	dppp	51	rac.
7	**1b**	dppb	70	14 (*S*)

[a]The reaction was carried out using propan-2-ol as hydrogen donor at 25°C for 24 h ($RuCl_2(PPh_3)_3$/**1a,b**/phosphine/KOH/1-acetonaphthone = 1/4/1.1/5/100).
[b]See Section 3.2.1.
[c]The solution became heterogeneous during the reaction.

3.3. Asymmetric transfer hydrogenation of ketones (hydrogen donor: HCOOH / NEt_3)

The reversibility of the asymmetric transfer hydrogenation of ketones to secondary alcohols with propan-2-ol frequently deteriorates the enantiomeric purity of the chiral products. A decrease of the enantiomeric excess was observed during the reaction time in the reaction in propan-2-ol (Table 1, entries 2 and 3). The reaction using formic acid–triethylamine mixture instead of propan-2-ol could be released from this problem. With this hydrogen donor in asymmetric ketone reduction, only a few examples using 1,2-diamine ligands [15–17] are reported because of the lack of suitable transition metal catalysts.

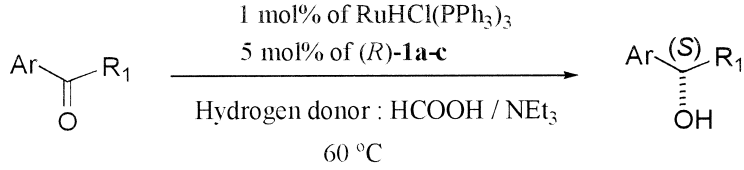
Table 4
Asymmetric transfer hydrogenation using HCOOH/NEt_3 as hydrogen donor

Entry	Ligand	Substrate	Time (h)	Yield (%)	% e.e. (configuration)
1	**1a**	**2a**	48	93	59 (*S*)
2[a]	**1a**	**2a**	120	23	11 (*S*)
3	**1a**	**2b**	66	83	73 (*S*)
4[a]	**1a**	**2b**	66	68	60 (*S*)
5	**1a**	**2c**	120	100	86 (*S*)
6[a]	**1a**	**2c**	141	45	57 (*S*)
7	**1b**	**2c**	76	100	75 (*S*)
8	**1a**	**2d**	72	100	74 (*S*)
9	**1b**	**2d**	90	100	76 (*S*)
10	**1a**	**2e**	70	100	57 (*S*)
11[a]	**1a**	**2e**	44	82	43 (*S*)
12	**1b**	**2e**	63	100	49 (*S*)
13	**1c**	**2e**	65	26	33 (*S*)
14	**1a**	**2f**	120	31	67 (*S*)
15	**1b**	**2f**	61	100	64 (*S*)
16	**1a**	**2g**	40	78	81 (*S*)
17	**1b**	**2g**	89	100	80 (*S*)
18	**1c**	**2g**	85	37	50 (*S*)

[a]$RuCl_2(PPh_3)_3$ complex was used as ruthenium precursor.

We had reported that the ruthenium monohydride species, $RuHCl(PPh_3)_3$, accelerated the transfer hydrogenation of ketones and imines in propan-2-ol [13]. We applied this ruthenium monohydride complex and $RuCl_2(PPh_3)_3$ in the presence of ligand **1** to the asymmetric transfer hydrogenation of ketones with HCOOH/NEt_3 (Scheme 4).

The results were summarized in Table 4. The reaction proceeded more smoothly and stereoselectively with $RuHCl(PPh_3)_3$-**1** catalyst than that



2a Ar=Ph, R_1=Me
2b Ar=Ph, R_1=Et
2c Ar=Ph, R_1=^{i}Pr
2d Ar=Ph, R_1=^{t}Bu
2e Ar=1-Nap, R_1=Me
2f Ar=Ph, R_1=Bn
2g Ar=Ph, R_1=Cy

Scheme 4.

with $RuCl_2(PPh_3)_3$-**1** system while RuHCl-$(PPh_3)_3$-**1a** catalyst was not effective using propan-2-ol as hydrogen donor. Using HCOOH/NEt_3 as hydrogen donor, carbinols of *S*-configuration were generated in higher % e.e. with these catalysts than in propan-2-ol. The enantioselectivity was dependent on the structure of ketones and % e.e. increased gradually up to 86% e.e. (entry 5) by increasing the bulkiness of the alkyl groups of ketones (methyl-(**2a**) < ethyl-(**2b**) < isopropyl-(**2c**), cyclohexyl-(**2g**)), except for two examples (*tert*-butyl (**2d**) and benzyl (**2f**)). Both **1a** and **1b** showed almost the same level of enantioselectivities for the reduction of phenyl–alkyl ketones. On the other hand, with **1c** having 6-methyl substituent on pyridine ring, the reaction rate and enantioselectivities were much lowered (entries 13 and 18).

In the reaction using propan-2-ol, the addition of diphosphine to ruthenium(II) catalyst having **1** and triphenylphosphine ligands much accelerated the reaction rate. In the reaction with HCOOH/NEt_3 hydrogen donor, addition of diphosphine totally suppressed the transfer hydrogenation indicating the apparent difference of the structure of intermediary ruthenium complexes for the present two hydrogen donor systems.

4. Conclusion

We have described the use of ruthenium complex having both pyridylmethylamine and phosphine ligands for the asymmetric transfer hydrogenation of aryl-alkyl ketones with propan-2-ol and HCOOH/NEt_3 as the hydrogen donor. The presence of diphosphine (1.1 equiv. to Ru) in Ru-**1** system much accelerated the reaction rate and the reaction proceeded sufficiently at 25°C in propan-2-ol though the enantioselectivities were low. Using HCOOH/NEt_3 as the hydrogen donor, enantioselectivities were much improved and isobutyrophenone was converted to corresponding alcohol in 100% conversion and 86% e.e. with $RuHCl(PPh_3)_3$-**1a** catalyst.

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