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ORIGINAL PAPER

Synthesis and electrochemical characterization of iminophosphine-based ruthenium(II) complexes and application in asymmetric transfer hydrogenation reaction as catalysts

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Abstract
A range of Ru(II) complexes have been prepared with chiral iminophosphine ligands ([(2-PPh_2)C_6H_4CH=NCH(CH_3)C_6H_5(4-R)]; R = –H, *p*-CH_3, *p*-NO_2) and characterized by ^{1}H, ^{13}C, ^{31}P{^{1}H} NMR and FTIR spectroscopy. The electrochemical properties of the [Ru$(PN)_2Cl_2$] complexes were investigated in ACN/TBAP solution with cyclic voltammetry and square wave voltammetry techniques. The use of chiral [Ru$(PN)_2Cl_2$] complexes as catalysts for the asymmetric transfer hydrogenation of aromatic and aliphatic ketones was studied in 2-propanol in an attempt to demonstrate the effect of substituents, which attached to the phenyl ring bonded to the nitrogen donor, on the catalytic activity and enantioselectivity. It was seen that the electronic effects of these substituents did not contribute to the catalytic efficiency of the ruthenium(II) catalysts.

Keywords Iminophosphine · Ruthenium · Electrochemistry · Asymmetric transfer hydrogenation

Introduction

Application of new transition metal complexes in catalytic reactions leading to high activity has increased in academic and industrial areas for the preparation of building blocks of biological interest [1–3]. Asymmetric transfer hydrogenation reaction is one of these catalytic reactions and used to attain secondary alcohols by the reduction of simple ketones via different ligands and transition metal complexes as catalysts [4–6]. The synthesis of many important chiral drugs is accomplished by reducing ketones in basic media and using non-toxic ^{i}PrOH as hydrogen source. During the 1990s, Noyori's studies on asymmetric transfer hydrogenation with C_2-symmetric phosphine ligands, which have showed high catalytic activity, increased the interest of researchers, and researchers have incessantly designed a series of phosphorus- and nitrogen-based ligands and tested their catalytic effects for hydrogenation reactions [7–12].

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It is known that the catalytic efficiency of iminophosphine (PN) ligands increases in the catalytic reactions. Therefore, in complex structures, the ruthenium metal coordinates with the soft phosphorus and the hard nitrogen acts as an efficient catalyst [13–15]. In this paper, we reported the synthesis of PN-based chiral Ru(II) complexes and their characterization. These complexes were used as catalyst for the asymmetric reduction of acetophenone, substituted benzophenones and aliphatic ketones in 2-propanol as a hydrogen source.

Experimental

General methods and materials

All the synthesis and catalytic reactions were carried out under an argon atmosphere using conventional Schlenk glassware. Solvents were dried using established procedures and then immediately distilled under argon prior to use [16]. The (*S*)-(−)-α-methylbenzylamine, (*S*)-(−)-α,4-dimethylbenzylamine and (*S*)-α-methyl-4-nitrobenzylamine hydrochloride were purchased from Sigma-Aldrich Chemie GmbH (Steinheim, Germany) and used without further purification. 2-(Diphenylphosphino)benzaldehyde and [Ru$(dmso)_4Cl_2$] were synthesized as described in literature [17, 18].

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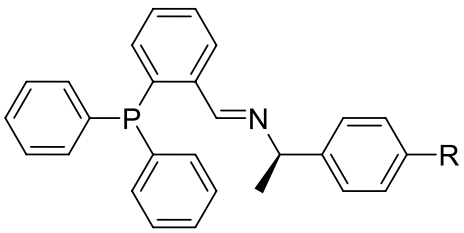
Elemental analysis was performed using a LECO CHNS 932 instrument. Infrared spectra were recorded on Perkin Elmer RX1 Spectrophotometer in the range between 4000 and 650 cm^{-1}. All ^{1}H, ^{13}C NMR and $^{31}P\{^{1}H\}$ spectra were recorded at 25 °C with deuteriated $CDCl_3$ in a Bruker Avance-400 NMR spectrometer. $^{31}P\{^{1}H\}$ NMR spectra were recorded with complete proton decoupling and referenced with 85% H_3PO_4 as external standard. The catalytic products were analyzed with a Perkin Elmer Clarus 500 series gas chromatograph equipped with a flame ionization detector and β-Dex (30 m × 0.25 mm × 0.25 μm) capillary column. Enantiomeric excesses and conversions were also determined by HPLC analysis using a Hitachi L 2300 with a Chiralcel OD-H column. Thin-layer chromatography was performed to monitor the reactions.

Electrochemical studies of iminophosphine ligands [19] and their Ru(II) complexes were carried out in acetonitrile (ACN) solution under Ar atmosphere. 0.1 M tetrabutylammonium perchlorate (TBAP) was used as the supporting electrolyte and the concentration of the complexes and free ligands was 1 mM. Cyclic voltammetry (CV) and square wave voltammetry (SWV) techniques were utilized using CHI 6094D electrochemical analyzer equipped with three-electrode cell system. A glassy carbon electrode (GCE) with 3.0 mm diameter used as working electrode, a Pt wire auxiliary electrode and all potentials were referred to (Ag/Ag^{+}) reference electrode. The solution was degassed with a continuous flow of Ar gas before and during the scanning.

Cyclic voltammetry measurements were performed in the potential range of − 1.5 and 1.5 V with 100 mV/s scan rate and SWV settings where: step potential 4 mV; amplitude 25 mV at a frequency of 15 Hz.

Ligand **1, 2** and **3** were synthesized according to the methods of Frauenlob and Yılmaz [19, 20] (Scheme 1).



R= -H (**1**), -CH_3 (**2**), -NO_2 (**3**)

Scheme 1 Structure of iminophosphine ligands

Preparation of bis(1-(2-(diphenylphosphino) phenyl)-*N*-(1-phenylethyl)methanimine) dichlororuthenium(II), [Ru((2-PPh_2) $C_6H_4CH{=}NCH(CH_3)C_6H_5)_2Cl_2$] (1b)

A mixture of *cis*-[$Ru(dmso)_4Cl_2$] (0.200 g, 0.420 mmol) and 1-(2-(diphenylphosphino)phenyl)-*N*-(1-phenylethyl) methanimine (**1**) (0.394 g, 1 mmol) in 30 mL of dry THF was heated under reflux for 6 h. The resulting brown solution was then evaporated to dryness, and the resulting solid was dissolved in CH_2Cl_2 (ca. 10 mL). The crude solution was triturated with diethyl ether (ca. 50 mL) to afford a red solid, which was filtered off and dried under high vacuum. Yield: 0.346 g (86%). $[\alpha]_D^{25} = 39.1$ ($c = 0.003$ M $CHCl_3$). ^{1}H NMR (400.2 MHz), $CDCl_3$: δ 8.93 (s, 2H, CH=N, H^{7}), 8.39 (dd, $J = 7.3$, 3.0 Hz, 2H, Ar), 7.63–7.31 (m, 18H, Ar), 7.21 (d, $J = 5.4$ Hz, 14H, Ar), 7.12 (dd, $J = 8.3$, 6.3 Hz, 2H, Ar), 6.99–6.93 (m, 2H, Ar), 4.49 (q, $J = 6.3$ Hz, 2H, H^{8}), 1.00 (d, $J = 6.8$ Hz, 6H, H^{9}). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 172.5 (C^{7}), 144.5 (C^{10}), 143.3, 136.8, 136.6, 133.1, 132.6, 132.0, 131.6 (s), 130.4, 129.4, 128.4, 127.9, 127.3, 126.9, 68.3 (C^{8}), 15.3 (C^{9}). ^{31}P NMR (162.0 MHz, $CDCl_3$): δ (ppm) 45.90 (s). FT-IR, (KBr, cm^{-1}) υ: 1626 (–C=N), 3051 (ArCH). Anal. calcd. for $C_{54}H_{48}Cl_2N_2P_2Ru$: C, 67.64; H, 5.05; N, 2.92%. Found: C, 66.49; H, 5.49; N, 3.12%.

Preparation of complex 2b and 3b

(Bis(1-(2-(diphenylphosphino)phenyl)-*N*-(1-(*p*-tolyl) ethyl)methanimine)dichloro) ruthenium(II), [Ru((2-PPh_2) $C_6H_4CH{=}NCH(CH_3)C_6H_4(4\text{-}CH_3))_2Cl_2$] (**2b**) and bis(1-(2-(diphenylphosphino)phenyl)-*N*-(1-(4-nitrophenyl) ethyl)methanimine)dichloro ruthenium(II), [Ru((2-PPh_2) $C_6H_4CH{=}NCH(CH_3)(4\text{-}NO_2)C_6H_4(4\text{-}NO_2)_2Cl_2$] (**3b**) were prepared by a procedure similar to that used for the preparation of **1b**.

[Ru((2-PPh_2)$C_6H_4CH{=}NCH(CH_3)C_6H_4(4\text{-}CH_3))_2Cl_2$] (**2b**). Yield 302 mg (73%). $[\alpha]_D^{25} = 22.0$ ($c = 0.003$ M $CHCl_3$). ^{1}H NMR (400.2 MHz, $CDCl_3$): δ 8.99 (s, $2H^{7}$), 8.47 (s, 2H, H), 7.72–7.58 (m, 16H), 7.45–7.23 (m, 14H), 7.10 (d, $J = 7.9$ Hz, 4H), 3.48 (q, $J = 7.0$ Hz, 2H, H^{8}), 2.31 (s, 6H, H^{14}), 1.08 (d, $J = 6.6$ Hz, 6H, H^{9}). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.6 (C^{7}), 142.8, 140.9, 136.2 (C^{10}), 134.6, 131.1, 129.0, 129.9, 128.9, 128.1, 128.0, 127.6, 126.9, 126.3, 67.7 (C^{8}), 24.1 (C^{9}), 18.1 (C^{14}). ^{31}P NMR (162.0 MHz, $CDCl_3$): δ (ppm) 46.02 (s). FT-IR, (KBr, cm^{-1}) υ: 1688 (-CH=N), 3055 (ArCH). Anal. calcd. for $C_{56}H_{52}Cl_2N_2P_2Ru$: C, 68.15; H, 5.31; N, 2.84%. Found: C, 68.31; H, 5.59; N, 2.89.

[Ru((2-PPh_2)$C_6H_4CH{=}NCH(CH_3)(4\text{-}NO_2)C_6H_4(4\text{-}NO_2)_2Cl_2$] (**3b**). Yield 302 mg (73%). $[\alpha]_D^{25} = 5.0$

($c = 0.003$ M $CHCl_3$). ^{1}H NMR (400.2 MHz, $CDCl_3$): δ 9.00 (s, 2H, H^7), 8.40–8.32 (m, 2H, Ar), 8.06 (d, $J = 8.6$ Hz, 4H, Ar), 7.65–7.34 (m, 16H, Ar), 7.32–7.20 (m, 12H, Ar),7.01 (dd, $J = 10.1$, 8.2 Hz, 2H, Ar), 4.58 (q, $J = 6.5$ Hz, 2H, H^8), 1.23 (d, $J = 6.4$ Hz, 6H, H^9). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 167.2 (C^7), 141.4 (C^{10}), 131.9, 130.3, 129.5, 129.3, 129.0, 128.6, 128.5, 127.4, 126.1, 123.9, 123.7, 123.5, 65.2 (C^8), 27.0 (C^9). ^{31}P NMR (162.0 MHz, $CDCl_3$): δ (ppm) 45.15 (s). FT-IR, (KBr, cm^{-1}) υ: 1630 (–CH=N), 3049 (ArCH). Anal. calcd. for $C_{54}H_{46}Cl_2N_4O_4P_2Ru$: C, 61.84; H, 4.42; N, 5.34%. Found: C, 62.31; H, 4.76; N, 4.91.

General procedure for asymmetric transfer hydrogenation reactions

Under an argon atmosphere, the $[Ru(PN)_2Cl_2]$ complexes (0.1 mmol%), ^{i}PrOH (3.0 mL), base (1.2 mmol), and the substrate (1.0 mmol) were introduced into a Schlenk tube, respectively. The reaction mixture was stirred at appropriate temperature for 24 h. Next, the mixture was cooled and diluted with Et_2O and chromatographed on silica gel. Conversions and enantiomeric excesses were determined by GC and HPLC analysis.

Results and discussion

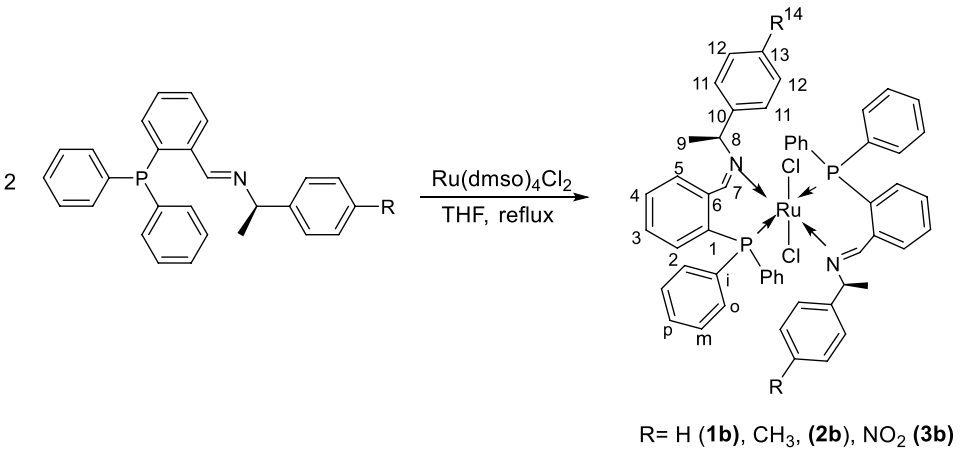
The reaction of chiral iminophosphine ligands (**1–3**) with $[Ru(dmso)_4Cl_2]$ resulted in the formation of PN bidentate chelate complexes, $[Ru(PN)_2Cl_2]$ (**1b–3b**), as shown in Scheme 2. The $[Ru(PN)_2Cl_2]$ complexes were fully characterized by elemental analysis, NMR and FTIR spectroscopy. The ^{1}H NMR spectra showed that the signal due to azomethine protons (N=C<u>H</u>) appeared at 8.93 (**1b**), 8.99 (**2b**) and 9.00 (**3b**) ppm as a singlet after coordination to the Ru(II) center [21, 22]. In addition, from ^{13}C-NMR spectra, displacement of imine carbon signal from upfield in non-coordinated ligands (**1**: 158.0, **2**: 158.0, and **3**: 159.4 ppm) to the downfield in the ruthenium(II) complexes (**1b**: 172.5, **2b**: 171.6, and **3b**: 167.2 ppm) also suggested the coordination of imine nitrogen to the ruthenium(II) center. The chemical shift and coupling constant of H^8 were split into quartet [23] [4.49 ppm, $J = 6.3$ Hz (**1b**), 3.48 ppm, $J = 7.0$ Hz (**2b**), 4.58 ppm, $J = 6.5$ Hz (**3b**)] due to the coupling of H^9 proton. The ^{1}H-NMR spectrum showed that a doublet signal was observed at $\delta = 1.00$ ppm ($J = 6.6$ Hz, **1b**), 1.08 ppm ($J = 6.6$ Hz; **2b**), and 1.23 ppm ($J = 6.4$ Hz, **3b**) which was assigned to protons of the CH group bonded to the methyl group. Meanwhile, the signal of aromatic protons of the complexes appeared between 8.39 and 6.93 ppm.

In the ^{31}P NMR spectra, the signals from phosphorus atom in the ruthenium complexes (**1**: − 15.92; **2**: − 12.46; **3**: − 12.36 ppm), which show only one singlet, have shifted from upfield to the downfield after complexation (**1b**: 45.90; **2b**: 46.02; **3b**: 45.15 ppm). Besides, In the FTIR spectrum, displacement of C=N stretching frequencies from 1634 to 1645 cm^{-1} in the free iminophosphine ligands to lower values of 1607–1619 cm^{-1} in the $[Ru(PN)_2Cl_2]$ complexes indicates the coordination of imine nitrogen to the ruthenium center [24, 25]. Also, micro analyses for C, H, and N of the complexes proved that the iminophosphine–Ru complexes were formed with 2:1 ratio. It was found that **1b, 2b** and **3b** were very soluble in dichloromethane, chloroform, ethanol and acetone; however, they were insoluble in *n*-hexane and diethyl ether.

Electrochemical behavior of compounds

The electrochemical properties of the synthesized Schiff base ligands (**1, 2, 3**) and their ruthenium(II) complexes (**1b, 2b, 3b**) were studied by the CV and SWV techniques. The obtained potential data are summarized in Table 1.

Scheme 2 Synthesis of chiral $[Ru(PN)_2Cl_2]$ complexes



R= H (**1b**), CH_3, (**2b**), NO_2 (**3b**)

Table 1 Electrochemical parameters for Ru(II) complexes in 0.1 M TBAP/ACN solution

Compound	Redox couple	E_{pc} (V)	E_{pa} (V)	[a]ΔE_p (mV)	[b]$E_{1/2}$ (V)
1b	Ru^{+2}/Ru^{+1}	−1.311	–	–	–
2b	Ru^{+2}/Ru^{+1}	−1.304	−1.292	12	−1.298
	Ru^{+3}/Ru^{+2}	−0.358	−0.264	94	−0.311
3b	Ru^{+2}/Ru^{+1}	−1.244	−1.157	87	−1.201
	Ru^{+3}/Ru^{+2}	0.128	0.088	40	0.108

[a]$\Delta E_p = E_{pa} - E_{pc}$

[b]$E_{1/2} = (E_{pa} + E_{pc})/2$, $\nu = 100$ mV/s

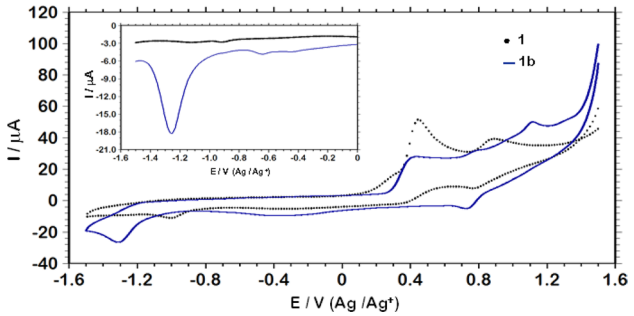


Fig. 1 Cyclic voltammograms of 1 mM of Schiff base ligand **1** (dotted line) and Ru(II) complex **1b** (blue line) in 0.1 M TBAP/ ACN on GC electrode with 0.1 V s^{-1} scan rate (inset: SWV of **1** and **1b**, amplitude = 25 mV; frequency = 15 Hz; step potential = 4 mV)

All the Schiff base ligands exhibited several oxidation peaks at anodic potentials, when the potential scanned from the positive to negative direction (starting from 1.5 to 0.0 V). These peaks are also observed in the CV responses of the synthesized Ru(II) complexes and were not interpreted further. We have focused on the metal-based responses of the Ru(II) complexes at negative potentials of the voltammograms.

Figure 1 shows the cyclic voltammogram responses of ligand (**1**) and its Ru (II) complex (**1b**) on GCE. The cyclic voltammogram of **1b** exhibited one irreversible metal-based reduction peak at $E_{pc} = -1.311$ V due to Ru(II)/Ru(I) redox couple. The reduction of Ru(II) → Ru(I) is clearly observed on the square wave voltammogram at the inset diagram in Fig. 1. **1b** did not show any oxidation response in the positive direction of the scan; however, the E_{pc} value of the Ru(II)/Ru(I) reduction is comparable with the values reported earlier [26, 27]. The reason for irreversible reduction of the complex may be due to short-lived reduced state of the metal or oxidative degradation of the ligands [28].

Ru(II) complex **2b** showed a reversible reduction wave with $E_{1/2} = -1.298$ V (Fig. 2). The Schiff base ligand, **2**, is not reversibly reduced within the negative potential limit (0.0 to −1.5 V). Consequently, it is considered that the reduction

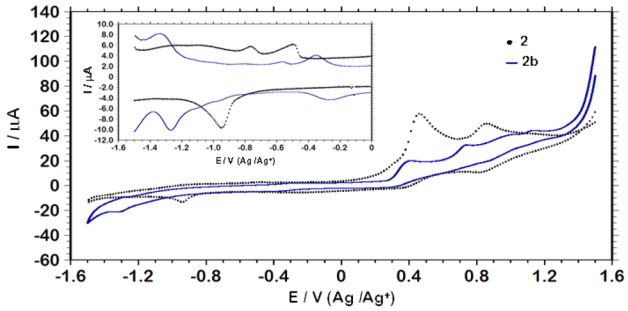


Fig. 2 Cyclic voltammograms of 1 mM of Schiff base ligand **2** (dotted line) and Ru(II) complex **2b** (blue line) in 0.1 M TBAP/ ACN on GC electrode with 0.1 V s^{-1} scan rate (inset: SWV of **2** and **2b**, amplitude = 25 mV; frequency = 15 Hz; step potential = 4 mV)

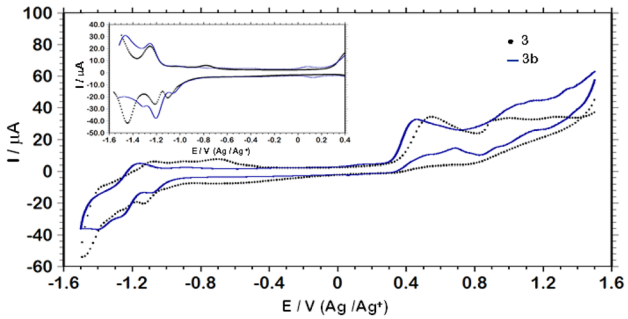


Fig. 3 Cyclic voltammograms of 1 mM of Schiff base ligand **3** (dotted line) and Ru(II) complex **3b** (blue line) in TBAP/ACN on GC electrode with 0.1 V s^{-1} scan rate (inset: SWV of **3** and **3b**, amplitude = 25 mV; frequency = 15 Hz; step potential = 4 mV)

process observed for **2b** complex is metal centered. The inset diagram in Fig. 2 shows the square wave voltammograms of **2** and **2b**. A couple of reduction and oxidation peaks at $E_{pc} = -0.358$ V and $E_{pa} = -0.264$ V in **2b** differently from SWV of **2** were observed. This reductive response indicates that the reduction is metal centered and assigned as Ru(III) to Ru(II). Ru(III) formation can be explained as the result of applying + 1.5 V potential in the beginning of the potential scanning. Ru(III)/Ru(II) reduction response is comparable to previously reported CV studies of ruthenium complex [29].

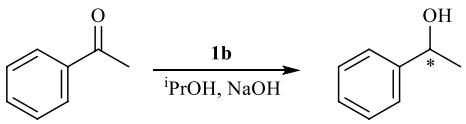
Figure 3 represents the voltammetric responses of **3** and **3b**. In the case of Schiff base ligand **3**, several reductive peaks at the negative potential region differ from the other two ligands. The complex **3b** also showed reversible redox processes during scan of the negative potential range. One of the reduction peaks belonging to the ligand **3** overlapped with the peaks of **3b** and this overlapping did not permit easy evaluation. However, a metal-centered reduction peak is observable in CV with $E_{1/2} = -1.201$ V, which corresponds to Ru(II) to Ru(I) conversion with reductive and oxidative peak potentials at $E_{pc} = -1.244$ V and

$E_{pa} = -1.157$ V. A redox couple is better noticeable in the inset diagram of Fig. 3. These peaks correspond to Ru(III/II) redox couple. The peak at $E_{1/2} = 0.108$ V with $E_{pc} = 0.128$ V and $E_{pa} = 0.088$ V couple was attributed to Ru(III) → Ru(II) conversion [30]. The reasons for the changes in the oxidation and reduction potential of the ruthenium(II) complexes are generally attributed to the stabilizing effect of the ligand by a combination of σ and π effects [31].

Asymmetric transfer hydrogenation

The catalytic activity of the **1b, 2b**, and **3b** complexes were evaluated in ^{i}PrOH, which was used as a hydrogen source, for the asymmetric reduction of aromatic and aliphatic ketones to the corresponding alcohols as shown in Scheme 3 and the data were presented in the Tables 2 and 3.

Initially, in order to explore the catalytic activity of the ruthenium(II) catalysts for the asymmetric transfer hydrogenation reactions, the reduction of acetophenone to 1-phenylethanol was chosen as the model reaction to study the efficiency of different bases such as K^{t}OBu, NaOH, K_2CO_3, and Et_3N with catalyst **1b** at 82 °C, as shown in Table 2. The results show that, no product was detected in the absence of base (entry 5). Also the use of Et_3N as base gave no conversion (Table 2, entry 4). However, 1-phenylethanol was obtained in 79% conversion and 39% enantioselectivity with NaOH whilst K^{t}OBu gives 77% conversion and lower enantioselectivity (<5) (Table 2, entries 1 and 2). On the other hand, good product conversion (67%) but very low enantioselectivity (<5) was observed with the using of K_2CO_3 as base (Table 2, entry 4). Thus, NaOH was identified as the most effective base for our catalyst system. The effect of temperature on the performance of the reduction reaction using catalyst **1b** was then examined. The relevant data (Table 2, entry 3) show that on lowering the temperature to 25 °C, the catalyst activity decreases sharply (24%) and no significant beneficial effect on enantioselectivity (40%) is observed. I also added Table 3 to the system.



Scheme 3 The catalytic transfer hydrogenation of acetophenone

Table 2 The effect of base and temperature on the asymmetric transfer hydrogenation of acetophenone with catalyst **1b** in 2-propanol

Entry	Base	Conversion (%)[a]	ee (%)
1	K^{t}OBu	77	< 5
2	NaOH	79 (24)[b]	38 (40)[b]
3	K_2CO_3	67	< 5
4	Et_3N	–	–
5	–	–	–

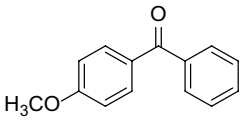
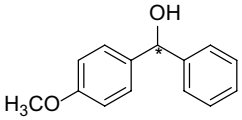
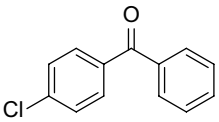
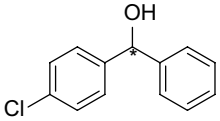
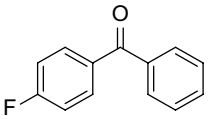
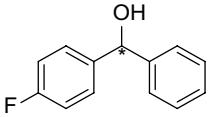
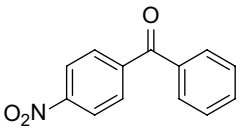
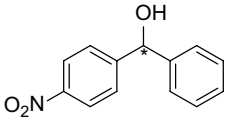
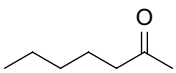
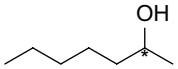
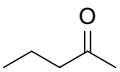
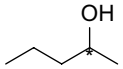
Reaction conditions: acetophenone (1.0 mmol), **1b** (0.1 mmol %), base (1.2 mmol), ^{i}PrOH, 3.0 mL, 82 °C, 24 h and substrate to metal ratio (S/C) was 1000:1

[a]Conversions and enantiomeric excesses (ee) were determined by gas chromatography

[b]25 °C

Next, we aimed to investigate the catalytic activity of **1b–3b** catalysts for the reduction of substituted benzophenones which have electron-donating and electron-withdrawing groups and aliphatic ketones as substrate under the optimized conditions determined in the preliminary studies for **1b** (0.1 mmol% catalyst, NaOH, 82 °C). According to the results in Table 3, the best product conversion (87%) was achieved with catalyst **1b** using 3-chlorobenzophenone as a substrate but in relatively low ee (27%) (entry 2). Under the same reaction conditions, 65% conversion and 22% ee were reached within 24 h with the complex **3b**, while only 7% conversion and very poor enantioselectivity were achieved with the complex **2b** after 24 h (entry 2). On the other hand, with catalyst **3b**, the asymmetric reduction of 3-fluorobenzophenone can be carried out with good conversion (83%) with only 46% ee in 24 h (entry 3). All of the results indicate that the selected substituted benzophenones could only be catalyzed with 46% ee by our catalyst system. So, we thought that the lower enantioselectivity is related to the high reaction temperature. Therefore, we tried to decrease the temperature of the reaction to 50 and 25 °C to see the influence of the temperature on the enantioselectivity, but decreasing the temperature from 82 °C to room temperature dramatically reduced the catalyst conversion and did not affect the catalyst enantioselectivity. The catalytic results show that generally moderate to good conversions were achieved with substituted benzophenones having chloro, fluoro and nitro groups. This suggests that, the electron-withdrawing effect of these substituents reduce the electron density on the carbonyl group and so accelerate the reduction of benzophenone to the corresponding secondary alcohols [32–34]. Besides that, poor enantioselectivities were obtained with our catalyst systems and the lower ees were not significantly affected by the reaction temperature. Next, the performance of the Ru(II) catalysts on the enantioselective reduction of aliphatic ketones was further investigated for 2-heptanone and 2-pentanone under the optimized conditions. Fortunately, as seen from entries 5 and 6, conversion was 88% at 82 °C for 24 h of the reaction when 2-pentanone was used as substrate, whereas it reached 94% with 2-heptanone under the same conditions. However, comparing the results obtained from our catalysts, only 52% enantioselectivity was achieved with the use of aliphatic ketones.

Table 3 Asymmetric transfer hydrogenation of substituted ketones with catalyst **1b**–**3b**[a]

Entry	Substrate	Product	1b		2b		3b	
			Conv. (%)	ee (%)	Conv. (%)	ee (%)	Conv. (%)	ee (%)
1			18 (16)[c] (7)[d]	13 (36)[c] (40)[d]	nd	nd	20 (18)[c] (9)[d]	28 (22)[c] (6)[d]
2			87 (40)[c] (6)[d]	27 (27)[c] (25)[d]	7 (nd)[c] (nd)[d]	<5 (nd)[c] (nd)[d]	65 (48)[c] (15)[d]	22 (26)[c] (18)[d]
3			59 (37)[c] (16)[d]	18 (17)[c] (11)[d]	18 (nd)[c] (nd)[d]	17 (nd)[c] (nd)[d]	83 (62)[c] (24)[d]	46 (38)[c] (9)[d]
4			60 (40)[c] (6)[d]	8 (nd)[c] (nd)[d]	<5 (nd)[c] (nd)[d]	<5 (nd)[c] (nd)[d]	61 (37)[c] (22)[d]	36 (29)[c] (16)[d]
5			94 (58)[c] (28)[d]	52 (46)[c] (43)[d]	46 (18)[c] (nd)[d]	42 (39)[c] (nd)[d]	86 (46)[c] (28)[d]	47 (44)[c] (43)[d]
6			88 (54)[c] (32)[d]	48 (44)[c] (35)[d]	28 (16)[c] (nd)[d]	18 (16)[c] (nd)[d]	66 (46)[c] (18)[d]	34 (34)[c] (32)[d]

nd not detected

[a]Reaction conditions: substrate (1.0 mmol), $[RuL_2Cl_2]$ (0.1 mmol %), NaOH (1.2 mmol), ^{i}PrOH (3.0 mL), 82 °C, 24 h. and substrate to metal ratio (S/C) was 1000:1

[b]Conversions and enantiomeric excesses (ee) were determined by HPLC analyses

[c]50 °C

[d]25 °C

Conclusions

We have successfully synthesized a series of new chiral iminophosphines–Ru(II) complexes and characterized with spectroscopic, optical and electrochemical techniques. To determine their catalytic activities for asymmetric transfer hydrogenation reactions, complex **1b** was applied in the reduction of acetophenone to detect the optimal ATH conditions. Then, all complexes were applied as catalyst for the asymmetric reduction of aliphatic ketones and substituted benzophenones having electron-withdrawing (-fluoro, -bromo and -nitro) and -donating groups (-methoxy). Under our experimental ATH conditions, these Ru(II) complexes efficiently catalyzed the asymmetric transfer hydrogenation of electron-withdrawing substituted benzophenones with relatively low ees. Additionally, with the use of a variety of ligands with different substituents (R: –H, $–CH_3$, $–NO_2$) for the Ru(II)-catalyzed asymmetric transfer hydrogenation of ketones, the catalytic activities and enantioselectivity were not significantly affected. Probably, the electronic effects of these substituents which are quite far away from nitrogen donor did not contribute to the catalytic performance effectively.

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